CO_2 capture from Pre-combustion Processes - Strategies for membrane gas separation.

Colin A. Scholes, Kathryn H. Smith, Sandra E. Kentish, Geoff W. Stevens.

Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC)
Department of Chemical and Biomolecular Engineering, University of Melbourne, Parkville,
VIC, 3010, Australia

Abstract

The application of membrane gas separation to CO_2 capture from a coal gasification process is one potential solution to reduce greenhouse gas emissions. This review considers the potential for either H_2- or CO_2-selective membranes in an integrated gasification combined cycle (IGCC) process. In particular, the advantages and disadvantages of metallic, porous inorganic and polymeric membranes are considered. This analysis is extended to consider membrane technology as an enhancement to the water gas shift reaction, to drive the production of hydrogen above the thermodynamic limit. The review concludes with a brief overview of the economics of incorporating membrane gas separation into the IGCC process and gives an indication of the potential economic use of membrane gas separation technology in the IGCC process.

Keywords: Membrane, gas separation, carbon dioxide, hydrogen, water gas shift, membrane reactors, pre-combustion capture design.

1. Introduction

Anthropogenic induced climate change is very likely driven by increasing atmospheric carbon dioxide levels (IPCC, 2007), caused by the world's dependence on fossil fuels. Currently, the capture of carbon dioxide from large point sources, such as power plants, is considered a viable option to reduce emissions, since it allows storage opportunities such as geo-sequestration. There are three main strategies for CO_2 capture from fossil fuel based power plants (Steeneveldt et al. 2006; Thambimuthu et al. 2005). In post-combustion, CO_2 is captured from the exiting flue gas, while in oxy-fuel combustion air is replaced by oxygen in the combustion process producing mainly H_2O and CO_2 which are readily separated. The third strategy, the focus of this article, is pre-combustion capture, where fossil fuels are reformed into synthesis gas (syngas) comprised mainly of hydrogen and carbon monoxide. This is then further converted to more hydrogen through the water-gas shift reaction, resulting in high pressure CO_2 and H_2. Separation of these two components allows for the storage of CO_2, while H_2 can be used for a number of processes, such as power generation. Pre-combustion capture has a number of advantages, such as the production of a carbon-free fuel and capture of CO_2 at high pressure (Audus et al. 1998; Thambimuthu et al. 2005).

Membrane technology holds great potential for both CO_2 and H_2 separation within such gasification processes for a number of reasons. The simplicity of the approach, the removal of gas through a selective film, ensures it has high-energy efficiencies, small equipment footprint and therefore low capital cost compared to conventional separation processes (Bracht et al. 1997; Shelly 2009). Gas separation membranes have been commercially proven in the sweetening of natural gas (removal of CO_2 and H_2S) and are commonly used for H_2 recovery in refineries. This review focuses on the inclusion of membrane gas separation in pre-combustion carbon capture as part of the integrated gasification combined cycle (IGCC) from a technical and design perspective. Initially, an overview of the IGCC process is provided, highlighting where membranes can be of most advantage. This is followed by a brief review of membranes for H_2 and CO_2 separation, as well as their potential to drive the water-gas shift as membrane reactors. The review then explores potential improvements to the IGCC process as a result of incorporation of membrane gas separation. This is supported by an examination into the economics of membrane technology in IGCC. The review finishes with a discussion on the future direction of this field.

2. Integrated Gasification Combined Cycle (IGCC)

Gasification is a method of generating synthesis gas (syngas) from heating carbonaceous fuels, primarily coal, with reactive gases, such as air or oxygen, often in the presence of steam (Thambimuthu et al. 2005). The syngas components, hydrogen and carbon monoxide, can be used to generate power (combined cycle) or as a feed source for the synthesis of a range of chemicals, such as Fischer-Tropsch reactions and ammonia. If hydrogen is the desired component, the syngas can be further reformed into more hydrogen by undergoing a water-gas shift (WGS) reaction, which converts carbon monoxide into carbon dioxide.

$$\mathrm{CO} + \mathrm{H_2O} \Leftrightarrow \mathrm{CO_2} + \mathrm{H_2} \qquad (1)$$

This reaction is in equilibrium, with the forward conversion exothermic (-40.6 kJ/mol) (Xue et al. 1996), hence the conversion of CO decreases with increase in temperature. To maximize hydrogen production, the WGS reaction is typically undertaken at a lower temperature than gasification, often using metallic catalysts. The syngas upon leaving the gasifier is usually subjected to cooling (heat recovery) and scrubbing (addition of water) or is quenched (addition of water and subsequent cooling) before undergoing the WGS reaction (Lorenzo et al. 2008; Wallace et al. 2002). The purpose of this treatment is to both reduce the temperature and increase the H_2O to CO ratio, required to drive the WGS reaction to produce more hydrogen. Trace components are also generated in the gasification process; examples include H_2S, NH_3, HCN as well as heavy metals and particulates (Scholes et al. 2009). Hence, desulfurization, ammonia scrubbing and often water sprays (to remove particulates and ionic constituents) are needed to further treat the product gas. A typical process design of a coal IGCC undergoing standard WGS with possible CO_2 capture is shown in Figure 1 (Wallace et al. 2002). The addition of the steam cycle to the Quench/Syngas cooler, shift reactors and heat recovery processes are to maximize the energy efficiency of the process.

Figure 1

At this point, the shifted syngas is a high pressure binary mixture of CO_2 and H_2. It is usually preferable to remove the CO_2 prior to turbine combustion of the hydrogen, as the high concentration and pressure assists the separation. While a solvent absorption process would be the current separation approach of choice, membrane gas separation offers many advantages in the separation of CO_2 and H_2, either as a stand-alone operation after the WGS reaction, or by incorporating membrane reactors into the WGS reaction to drive the production of hydrogen. If the membrane separation process retains the H_2 at high pressure the turbine efficiency is maximized. Alternatively, if CO_2 is retained at high pressure, the need for compression involved in the transport and storage of CO_2 is eliminated, which is believed to make pre-combustion capture a much more efficient carbon capture strategy than other large coal-based combined cycles (Bracht et al. 1997).

3. Membrane Types

There are a number of comprehensive reviews that investigate the types of membranes generally available for gas separation (Adhikari and Fernando 2006; Armor 1998; Baker 2002; Maier 1998; Paglieri and Way 2002; Powell and Qiao 2006; Shao et al. 2009; Stern 1994). In this section, only a brief overview of H_2 and CO_2 selective membranes is presented to familiarize the reader with the membrane options available for use in the IGCC process. This overview considers first membranes that permeate H_2 as these are most common, followed by a discussion of membranes that permeate CO_2 but retain H_2.

3.1 H_2 Selective Membranes

3.1.1 Metallic

Metallic membranes can produce hydrogen of up to 99.99% purity (Adhikari and Fernando 2006). These are generally based on palladium, though it is possible to use a range of metals (see Figure 2 and Table 1). In all cases, the process of hydrogen separation is achieved by the dissociative chemisorption of hydrogen on the surface producing atomic hydrogen (Phair and

Donelson 2006); this diffuses through the metal lattice driven by the partial pressure drop to the opposite side of the membrane. Here, atomic hydrogen is recombined into molecular hydrogen and diffuses away from the metallic surface. The rate of this process, and therefore permeability, is influenced by the metal surface roughness, purity and importantly the metallic lattice (Andrew and Haasz 1992; Gryaznov 1999). The rate is also a function of temperature (Figure 2) with palladium showing improved performance at higher temperatures. This process makes metallic membranes almost 100% selective for H_2, since no other gas will undergo dissociation upon the surface. Flux (J) is proportional to the square root of the partial pressure difference across the membrane (Paglieri and Way 2002):

$$J_{H2} = \frac{P_{H2}}{t}\left(\sqrt{f_{feed}} - \sqrt{f_{permeate}}\right) \qquad (2)$$

Where f is the fugacity on the feed and permeate side of the membrane, and P_{H2} the permeability of H_2 across the membrane. Therefore to obtain high flux the feed pressure must be substantially compressed. More commonly the membranes are made as an ultra-thin metallic layer coated on a porous inorganic support, to reduce the amount of precious metals required. In this case, micro-holes within the membrane surface created during fabrication often allow other gases to permeate which leads to a reduction in selectivity (Li et al. 1998).

Figure 2

For ultra-thin membranes, the rate-controlling step becomes the adsorption dissociation of hydrogen on the surface, with Pd being the most efficient (Paglieri and Way 2002), though permeability through the lattice is an order of magnitude less than other metals. This is because of the difference in metallic lattice packing (Adhikari and Fernando 2006). To improve permeability, binary and complex alloys of Pd have been produced; examples are Pd-Cu, Pd-Ag and Pd-Ni, with the permeability of a range of such alloys given in Table 1. All quoted permeabilities are measured at temperatures similar to that found within the gasification process, with the highest permeability reported for a $Hf_{34}Ni_{61}Cu_5$ alloy. Less exotic alloys of Pd with metals such as Cu, Ni and Ag have permeabilities three orders of magnitude lower than this, but still three orders of magnitude greater than pure Pd. For non-Pd based membranes, good permeabilities are reported for Niobium and Vanadium alloys, reflecting the performance of the pure metals, as shown in Figure 2.

Table 1

Pd membranes have a number of problems, which reduce their attractiveness for large scale H_2 separation. Firstly, they can undergo phase changes at low temperature (<300°C), causing catastrophic failure due to hydrogen embrittlement (Adhikari and Fernando 2006). The presence of contaminants in the feed gas can also inhibit hydrogen dissociation and recombination reactions due to surface fouling (Paglieri and Way 2002). In particular, Pd is susceptible to sulfur compounds, CO, NH_3 and chlorine, all of which exist in pre-combustion syngas streams (Scholes et al. 2009). For example, sulfur compounds destroy Pd membranes due to large lattice expansions when Pd-S is produced. Some of these issues have been overcome through the use of Pd alloys. For example the presence of Pt dramatically reduces the effect of sulfur degradation. However, the biggest issue for Pd membranes are their limited lifespan, often months (Lu et al. 2007), and the subsequent cost in replacing the membrane. Given that Pd is a precious metal, there are substantial operating costs associated with Pd-metallic membrane separation. Indeed, commercial application of these membranes has been limited to small volume processes (Steward 1983). To counter this, other metallic membranes have been suggested (Table 1), though there have been no reports on their commercial success.

3.1.2 Porous Inorganic

Porous inorganic membranes have also been applied to the separation of hydrogen from carbon dioxide (see Table 2). A range of inorganic materials have been used, including silica, zeolites, alumina, nitrides, and oxides (Brinker et al. 1993; Coronas et al. 1997; Gavalas et al. 1989; Ha et al. 1993; Jansen and Coker 1996; Li and Hwang 1992; Lu et al. 2007; Megiris and Glezer 1992; Suda et al. 2006; Uhlhorn et al. 1992; Yan et al. 1997). These materials have carefully controlled pore structures and generally separate on the basis of molecular size; the smaller hydrogen molecule passes through while larger species are retained. Alternatively, if the pore sizes are larger, Knudsen diffusion can occur; in this case separation is based on the difference in the mean path of gas molecules due to collisions with pore walls. Surface treatment to improve the sorption of H_2 to the pore walls can improve selectivity by increasing the migration rate of this species along the pore walls – this is known as surface diffusion.

As shown in Table 2, the highest permeabilities are reported for hydrophobic silica based membranes, though with relatively poor selectivities against CO_2, dependent on fabrication technique. Also of benefit to silica systems are their low cost and their thermal and chemical stability, allowing them to be used with corrosive feeds and at high temperatures (conditions of up to 20 atm and 500^{o}C can be tolerated) (Neoff, 2006, Lu et al. 2007). However, low H_2 /CO_2 selectivity is often observed. Exposure to high water vapour concentrations can also lead to performance decline (Galuszka, 2001). For example, Asaeda and Yamasaki (2001) observe a steady decrease in permeance for a silica membrane exposed to humid gases over four months, with the H_2 permeance decreasing by an order of magnitude.

Carbon membranes (Lee and Tsai 2001; Linkov et al. 1994; Petersen et al. 1997; Rao and Sircar 1993) are different from other inorganic membranes, in that they are prepared by pyrolysis of organic polymers at high temperatures (700-1200 K) in an inert atmosphere (carbonization). This generates a microporous membrane, acting as a molecular sieve as well as allowing surface diffusion. They are most commonly used in a non-oxidizing environment at temperature, such as conditions found in pre-combustion carbon capture. Carbon membranes can be prepared either unsupported or they can exist on porous supports. The former suffer from brittleness while the latter are often difficult to prepare. Like silica membranes, they can also suffer performance decline in the presence of high levels of water vapor (Lagorsse et al., 2005). Carbon nanotubes have also been suggested as possible H_2 membranes (Neoff et al. 2006) but these would not currently be cost-competitive.

Table 2

3.1.3 Polymeric

Non-porous polymeric membranes operate by the solution-diffusion mechanism. In this case the permeating gas dissolves into the polymer at one face of the membrane, diffuses across the membrane and then is desorbed at the downstream face. Permeability is thus a function of both gas diffusivity and solubility (Petropoulos 1994). The small size of the hydrogen molecule gives it a large diffusivity compared to other gases. However, the significantly lower critical temperature (Scholes et al. 2009) implies that condensability and therefore solubility of hydrogen within the polymeric membrane will be much lower. In H_2-selective polymeric membranes, the high diffusivity is thus exploited while the effect of low solubility is limited. Such membranes are currently in application for H_2 recovery in the refining and chemical industry (Koros 1991).

Polymeric membranes can be provided as either intrinsically skinned hollow fibres or as asymmetric flat sheets. While it is generally much easier to provide an ultrathin polymer skin layer in these arrangements, they are much less thermally stable with operating temperatures typically restricted to less than 100^oC. In general, glassy polymeric membranes, which operate below the glass transition temperature (Petropoulos 1994) provide high H_2/CO_2 selectivity due to a larger void fraction within the polymeric matrix. Hence, there are a wide range of polymeric membranes available for H_2 separation from CO_2; the performances of some are provided in Table 3. Good permeabilities are observed for polyimides such as 6FDA-Durene, which have high fractional free volume allowing significant amounts of hydrogen to easily diffuse (Powell and Qiao 2006). However, the selectivity against CO_2 is poor because of this high free volume. Greater selectivities are reported for polybenzimidazole and poly(vinyl chloride), but at the expensive of H_2 permeability. A novel and highly effective approach to improving both permeabilility and selectivity is a cross-linking of the membrane surface using a vapor or liquid phase diamine cross-linking agent (PDA or EDA) (Shao et al. 2009, Chung et al. 2006). Generation of mixed matrix membranes through the addition of inorganic particles (Chung et al. 2007, Choi et al. 2008) is another approach which appears to produce less dramatic effects for the H_2/CO_2 gas pair. A further recent development has been the use of thermally re-arranged polymeric membranes, which have been heat treated, but to a lesser extent than carbon membranes (Park et al. 2007, Choi et al. 2010). These membranes display the high permeability and selectivity of carbon membranes but retain flexibility and malleability (see Table 3).

Only one polymer, polybenzimidazole, is studied at the temperatures typical for syngas purification. For this membrane, a peak in H_2 permeability and H_2/CO_2 selectivity is observed between 200 and 270°C (Pesiri et al. 2003). This peak in performance can be related to the increasing diffusivity of the smaller H_2 molecule as temperature increases.

Importantly, polymeric membrane choice is strongly dependent on the ability of the membrane to maintain its separation performance in the process environment. In particular, exposure to condensing gases such as CO_2, water and H_2S can cause plasticization and subsequent mechanical failure (Kesting and Fritzche 1993). The extent of such plasticization is a function of the cohesiveness of the membrane structure and can be reduced by cross-linking of the membrane chains. Such cross-linking tends to concurrently increase selectivity but reduce permeability (Duthie et al., 2007a, Low et al. 2009).

Table 3

3.1.4 Comparison of H_2 Selective Membranes

Metallic and porous inorganic membranes would appear to represent the most practical approach to a H_2 selective membrane within an IGCC process. This is because they are able to undertake high temperature separation, while polymeric membranes, operating at low temperature, force a cooling liability on the process. While Pd-based membranes offer the highest H_2 selectivity, the minor components present in syngas, especially sulfur, present a significant disadvantage. Porous inorganic membranes such as those based on silica or zeolites, are cheaper and offer greater chemical resilience (Bredesen and Peters 2008). However, high water vapor loads can affect performance. The more recently developed thermally re-arranged polymeric membranes may yet offer a third viable alternative. To date, there are no clear winners amongst this group and none have been brought to commercial reality at large scale. More research is required into the development of such materials to bring them to a point where they can seriously challenge the more traditional solvent based approach.

3.2 CO_2 Selective Membranes

The development of a membrane that will retain the small molecular size of H_2 but permeate the larger CO_2 is a significant challenge (Perry et al. 2006). Porous inorganic membranes can only become CO_2 selective by either surface diffusion or capillary condensation. Capillary condensation is an extension of surface diffusion, where low vapor pressures cause partial condensation of the gas within the pores, resulting in more rapid diffusion. For the few CO_2-selective membranes that have been reported, substantial surface modifications have been undertaken to maximize surface diffusion (Luebke and Pennline 2003; Osada et al. 1999; Yazawa et al. 2007). This is generally achieved through the addition of a polymer with CO_2 affinity chemisorbed onto the walls of the pores. An example is porous alumina coated with 2-carbonmethoxyethyl-trichlorosilane, providing a CO_2 permeance of 4.2×10^{-5} $cm^3(STP)/cm^2$ s cmHg, with a CO_2/He selectivity of 2.1 at room temperature (Luebke et al. 2006). The CO_2/H_2 selectivity should be higher given the smaller kinetic diameter of He (Scholes et al. 2009). However, for surface diffusion to be effective, the pore diameter must be less than 3-4 times the diameter of CO_2 (Lee and Hwang 1986). Otherwise, the diffusion of H_2 through the void space in the membrane would eliminate any selectivity. Similarly, surface diffusion will tend to be most effective at low temperatures, where sorption is enhanced but selectivity will fall as WGS temperatures are approached. Further, the pores need to be continuous across the thickness of the membrane, to ensure the surface transport carries CO_2 through the entire membrane; hence membranes must be thin. Interestingly, carbon membranes have been shown to be CO_2-selective (Roa et al. 2003; Yamamoto et al. 1997), by surface diffusion, without the need for any surface modification. In this case it is the association between CO_2 and molecular carbon that provides the sorption.

3.2.1 Polymeric

A range of polymeric membrane performance data for CO_2/H_2 separation is provided in Table 4. For polymeric membranes to be CO_2-selective it is important that the solubility selectivity strongly favors CO_2 and that diffusivity selectivity (which favors H_2) be minimized (Perry et al.

2006). Rubbery polymeric membranes typically have these capabilities. The high mobility of the polymer chains increases the diffusivity of all gases through the polymer matrix (Perry et al. 2006). Solubility selectivity favors condensable gases such as CO_2, organic vapors and hydrocarbons. Rubbery polymers such as poly dimethyl siloxane (PDMS) (Merkel et al. 2001; Pinnau and He 2004) and poly(amide-b-ethylene oxide) (PEBAX) are often cited in this regard (Kim et al. 2001). To improve sorption selectivity further, it is necessary to design the membrane for the target gas, because properties such as molecular size and shape, as well as chemistry, play a major role (Lin and Freeman 2005). Improved CO_2 selectivity can be achieved through the use of polymers with polar groups, such as poly (ether oxide) and poly (propylene oxide), because CO_2 has a strong interaction with these polymers compared to the non-polar H_2 (Hirayama et al. 1999; Nagai et al. 2000; Suzuki et al. 1998). Lin et al. (2006) have designed CO_2-membranes based on crosslinked poly(ethylene glycol) diacrylate (PEGDA) and poly(ethylene glycol) methyl ether acrylate(PEGMEA) polymers. These membranes show high CO_2/H_2 separation performance in the presence of H_2O, while being resilient to H_2S (a significant component in pre-combustion feed gas). However, even for such materials, relatively low CO_2/H_2 selectivities are observed, the highest being 12 for a cross-linked poly(ethylene glycol) acrylate containing branches with methoxy end groups(Lin and Freeman 2005). Conversely, very high permeabilities are readily reported for polymers such as PDMS and PTMSP.

Table 4

It should be noted that the CO_2 permeability and selectivity data reported in both Tables 3 and 4 is a strong function of the measurement temperature and pressure. Increasing partial pressures of CO_2 cause the membrane to plasticize, leading to higher permeabilities of all gases. Conversely, reducing temperature aids the solubility of CO_2 (Duthie et al. 2007b). This has the benefit of selectivity improving CO_2 permeability and hence selectivity. Thus for example, Lin and Freeman(2005) show that the CO_2/H_2 selectivity of a PEGMEA/PEGDA membrane increases from 11 to 40 as temperature is decreased from 35^{o}C to -40^{o}C. While this enhanced selectivity appears attractive, it must be balanced against the energy and cost penalty associated with the use of a refrigeration cycle.

Further, most of the data presented in these Tables is for exposure to pure component gas streams for short periods of time. Performance of polymeric membranes in a gas mixture generally declines relative to the pure gas case, due to competitive sorption and plasticization effects. Similarly, the ability of the polymeric membrane to retain separation performance over long periods time in the process is of importance (Xiao et al. 2009).

3.2.2 Facilitated Transport

Facilitated transport membranes (Table 5) are an extension of polymeric membranes that include a facilitator species that undergoes a reversible complexation reaction with CO_2 within the membrane (Cussler 1994; Noble and Koval 2006) dramatically enhancing the solubility. This process has an analogy with solvent absorption, and adds another separation mechanism to the solution-diffusion process. Generally, the polymeric matrix is a water-soluble polymer, such as polyvinyl alcohol, that forms a hydrogel in the presence of a wet feed gas (Laciak et al. 1990; Meldon et al. 1982). The facilitator can be either fixed-sited within the membrane or mobile and transports CO_2 across the membrane. Examples of facilitators are amino species, polar polymers and ionic liquids (Noble and Koval 2006). The selectivity and reversibility of the CO_2 complexation is critical to the performance of the membrane, however the partial pressure difference across the membrane remains the driving force. Facilitated transport membranes provide large CO_2 permeabilities with very good selectivities at low partial pressures and from this perspective, have a strong potential for CO_2 separation from H_2. Comparison to the rubbery polymeric membranes in Table 4, clearly highlights the improvement in CO_2 selectivity; in general an order of magnitude greater. However, it should be noted that selectivity in these materials decreases strongly as CO_2 partial pressure increases (Lin et al., 2006). This is due to carrier saturation. That is, as the CO_2 pressure increases, the proportion of carriers used by the facilitation reaction also increases until a point is reached where all carrier molecules are consumed. Further increases in CO_2 pressure will not lead to any increase in CO_2 flux and hence the measured permeability and selectivity will begin to decline (Chen et al. 2000). Thus while these membranes appear competitive under the test conditions used, their viability at the higher pressures prevalent in an IGCC process will not be as prospective.

Table 5

A further significant issue in facilitated transport membranes is loss of the transport mechanism. For example, the permeability of CO_2 decreases with increasing temperature due to water evaporation and therefore transport of the CO_2-facilitator complex through the membrane is increasingly hindered (Zou et al. 2007). Similarly, liquids typically cannot be maintained in the porous support when a large pressure difference is applied across the membrane, as will be the case in IGCC (Lin et al. 2006). Another problem is the loss of the facilitator through degradation due to reaction with minor components, such as NH_3 and H_2S (Scholes et al. 2009). These factors limit the viability of facilitated transport membranes for syngas applications and consequently these systems have yet to be commercialized.

3.2.3 Comparison of CO_2 selective Membranes

To achieve CO_2 selectivity for the IGCC process, polymeric membranes would appear to represent the best option, however as stated above (Section 3.1.4), the need to operate at low temperatures presents an energy liability into the IGCC process. Rubbery polymeric membranes, specifically PDMS and PEBAX, are current commercially available options that can achieve the desired separation, albeit with low selectivity. The high CO_2 permeabilities and selectivities of facilitated transport membranes may make them ideal candidates for the low CO_2 pressures prevalent in post-combustion capture, but they are less likely to be competitive at the high pressures prevalent in the IGCC operation. For all membrane types, information and additional research on actual performance in an IGCC process is required. In general, CO_2-selective membranes for an IGCC process are significantly less advanced than H_2-selective membranes, and considerable more research is required before they can be applied to the process.

4. Water Gas Shift (WGS) Membrane Reactors

In a fixed bed WGS reactor, the equilibrium CO conversion is a function of both the temperature and the H_2O / CO ratio (also known as the steam to carbon ratio S/C), as shown in Figure 3 (Xue et al. 1996). The exothermic nature of the forward WGS reaction means that high conversions are obtained at low temperatures, while increasing the amount of water present also produces more H_2. However, from an economic view, a H_2O/CO ratio between 0.9 – 1.5 has been claimed to be the most beneficial (Giessler et al. 2003), to maximize the calorific value of the exiting gas. Similarly, to maximize the combined cycle efficiency the temperature of the syngas is unlikely to fall below 200°C. Therefore, very high conversion of CO to maximize H_2 production does not generally occur in fixed bed WGS reactors.

The ability of a membrane to continually remove either H_2 or CO_2, is advantageous for the WGS reaction, because it provides the opportunity to overcome the thermodynamic constraints of the reaction, resulting in a higher CO conversion. Hence, a H_2 or CO_2-selective membrane may be incorporated into the WGS reactor as a membrane reactor (MR) (Bredesen and Peters 2008). In addition, the combination of WGS reaction and gas separation in the same unit reduces both operating and capital costs, and improves efficiency.

Figure 3

Generally, WGS-MR designs under development are similar to a shell and tube heat exchanger, where the membranes are a hollow fiber design (Bredesen and Peters 2008). Sweep gas is often used in the permeate stream if H_2 is the product, to dilute the stream and raise the membrane partial pressure difference. The sweep gas is commonly nitrogen, often obtained from the air separation unit supplying oxygen to the gasifier.

Low S/C ratios can lead to undesirable side reactions, producing carbon and methane (Xue et al. 1996). The following reactions can occur depending on the catalysis, system conditions and kinetics:

$$2CO \Leftrightarrow C + CO_2 \tag{4}$$

$$CO + H_2 \Leftrightarrow C + H_2O \tag{5}$$

$$2CO + 2H_2 \Leftrightarrow CO_2 + CH_4 \tag{6}$$

If these reactions are significant, they can lead to carbon blockage of the WGS-MR resulting in catalyst deactivation and decreasing gas flux through the membrane, as well as fouling of the equipment.

Catalysts are generally required to increase the kinetics of the WGS and there are a number of designs for incorporating the catalyst within a WGS-MR (Ross and Xue 1995). The use of a catalyst results in the majority of CO conversion and correspondingly the majority of the heat release, within the first ~20% of the reactor length. Over this initial length, the use of a membrane reactor is not very effective, as product H_2 and CO_2 concentrations are not high enough for significant permeation to occur (Oertel et al. 1987).

To counter this, a two-step WGS system has been suggested. Firstly the syngas passes through a standard fixed bed WGS reactor where the bulk of the CO conversion occurs and then enters a WGS-MR (Bracht et al. 1997; Ma and Lund 2003). The feed gas in the WGS-MR therefore has high product gas concentrations, leading to better gas permeation rates and conversion in this section can be extended over the thermodynamic equilibrium. In addition, since the majority of the reaction has already occurred; the membrane is not subject to large temperature gradients and frequent catalyst changes, increasing the lifetime of the unit. This process also has the added advantage of allowing two different types of catalyst to be used, for example Fe-Cr in the high temperature system and Cu-Zn in the WGS-MR (Xue et al. 1996). There are some other disadvantages to the WGS-MR design. Replacement of catalyst can be difficult without damage to the hollow-fiber membranes. The high temperatures and pressures can also make it difficult to form an adequate seal between the membrane and the rest of the reactor unit (Armor 1998). The seal between the membrane layers due to material incompatibility is often the most likely location for failure to occur. The complex design of a WGS-MR compared to a fixed bed reactor can also be a significant issue, given that a staged conventional reactor approach, with alternating membrane separation steps, can achieve many of the benefits of a WGS-MR (Middleton et al. 2005).

4.1 H_2-seletive WGS-MR

The influence of a H_2-selective membrane upon the theoretical conversion can be seen in Figure 4 as a function of S/C ratio, and H_2 selectivity (where Y corresponds to the fraction of H_2 removed by the membrane). Increased removal of H_2 drives the WGS reaction to produce more

CO, and a greater CO conversion is achieved. The most significant increase in conversion for amount of removed H_2 occurs around S/C ratio of 1, because at these conditions the thermodynamics most hinder the WGS reaction. Importantly, under any WGS-MR condition, greater conversion to H_2 is achieved compared with the thermodynamic equilibrium, and this highlights the advantage of a WGS-MR over standard WGS reactors for H_2 production.

Figure 4

Uemiya et al. (1991) investigated a Pd based WGS-MR, with the resulting CO-conversion to S/C ratio provided in Figure 5. Experimental performance is similar to the theoretical case in Figure 4, with the presence of the Pd membrane driving the WGS above the thermodynamic limit. Importantly, the same level of CO conversion in a conventional reactor at S/C=2 is achieved in a WGS-MR at S/C=1. Hence, the Pd membrane produces higher levels of conversion for more reasonable S/C ratios. CO conversion is dependent on the H_2 removal rate, which is related to the H_2 flux and therefore Pd thickness. Also studied is the effect of sweep gas flowrate, since this increases the partial pressure drop across the membrane. Naturally, the conversion increases with decreasing Pd thickness because of increased removal of H_2 driving the WGS reaction. However, H_2 concentration build-up in the permeate stream reduces the driving force across the membrane, resulting in a constant H_2 concentration observed for low membrane thicknesses. This reduces the removal of H_2 from the reaction, limiting conversion. Increasing the sweep gas rate dilutes H_2 concentration in the permeate stream, increasing H_2 removal from the reaction zone and improves conversion. The influence of the sweep gas flow rate can also be seen in the work of Basile et al. (1996) (Figure 6), where the CO conversion of a Pd WGS-MR increased with higher sweep flow, to similar levels observed above. In comparison, Basile et al. also test a microporous ceramic WGS-MR, and achieve a conversion performance well below equilibrium, especially at higher S/C ratios. This is attributed to water loss from the reaction zone through the membrane because of its porous structure.

Figure 5

Figure 6

A WGS reactor and WGS-MR (Pd) in series has been modeled by Lorenzo et al. (2008) as a function of S/C ratio (Figure 7). The majority of the WGS conversion occurs in the conventional reactor, as designed, to ensure a high H_2 pressure entering the MR and protect it from thermal stress. For S/C values greater than 2 the WGS reactor is responsible for virtually all CO conversion, since the thermodynamic equilibrium favors the products (Figure 3). However, as S/C falls, the reactor conversion decreases correspondingly with the change in the thermodynamic equilibrium, and the WGS-MR conversion increases monotonically as it removes H_2. Interestingly, even at S/C = 1, the WGS-MR contribution to the overall conversion is still less than 25% and it is unable to compensate for the lower conversion in the conventional reactor, evident in decreasing overall conversion.

Figure 7

For a porous inorganic WGS-MR operating under Knudsen diffusion, Ross and Xue (1995) have modeled the relative concentration of each gas component as it passes through the reactor, with comparison to a plug flow reactor with no membrane present. Across the inorganic membrane, 90% CO conversion is observed compared to 65% for plug flow conditions, for S/C =1. Hence, modeling demonstrates this membrane is able to increase the WGS reaction above its thermodynamic limit. However, its performance is not as high as that reported for Pd membranes.

To reduce the CO_2 concentration present in the resulting permeate, multiple porous inorganic membrane stages in series may be required. An example of the effect of multiple stages is shown in Figure 8, where the produced H_2 is a function of stage cut and the number of stages. Increasing the number of membrane units improves the purity, with calculations indicating that 5 or more may be required to achieve the same CO_2 level obtained with Pd membranes (Damle et al. 1994).

Figure 8

Inorganic membranes also allow some permeation of reactants, and if their concentration in the permeate becomes too high then the WGS-MR will stop functioning. Battersby et al. (2008)

doped porous silica with cobalt producing a membrane with a H_2/CO_2 selectivity of 3 and H_2/CO selectivity from 6 to 13 (dependent on temperature). The relative concentration of each component, as a function of CO conversion, for this membrane is shown in Figure 9. As CO is consumed, H_2 is produced and hence their concentrations move in opposite directions. At high CO conversions, concentrations of H_2 in both the retentate and permeate stream are high, while concentrations of CO in both the retentate and permeate streams are low. However, for low CO conversions, H_2 concentrations remain low and CO concentrations high and hence the WGS-MR performance is limited. For this membrane when conditions cause the WGS conversion to fall below 40%, the CO driving force across the porous membrane dominates over the H_2 driving force. Hence, the presence of the membrane now retards the performance of the WGS reaction.

Figure 9

A performance comparison between a Pd based WGS-MR and a mesoporous inorganic WGS-MR can be seen in Figure 10 (Criscuoli et al. 2000), along with a fixed bed reactor under a mixed gas composition of 32% CO, 12% CO_2, 4% H_2 and 52% N_2. The time factor is defined as the ratio of the amount of catalyst (g) to the molar flowrate of feed gas through the system (mol CO/min) and thus is comparable to a residence time. As expected the WGS-MRs obtain higher conversions than the traditional fixed bed reactor. However, for these conditions the equilibrium value can only be overcome for the Pd membrane operating at high time factors. The mesoporous inorganic membrane (Knudsen diffusion) only obtains the equilibrium limit at the highest time factor. Hence, a low CO flowrate through the membrane unit is needed to produce a large residence time that allows the reaction to proceed significantly. To overcome this limitation it may be necessary to consider internal recycle streams to ensure sufficient residence time within the reactor (McCandless 1985; Ross and Xue 1995; Stern et al. 1984; Tsuru and Hwang 1999).

Figure 10

The high temperatures found in the WGS reaction make the use of polymeric membranes difficult, given that most will undergo substantial degradation under these conditions. To the best of the authors' knowledge, no polymeric based WGS-MR have been reported for H_2 separation from syngas in a gasification process. Furthermore, the high temperature raises a number of design issues for the WGS-MR; one of the most significant is the seal between the membrane and housing being able to withstand conditions found there.

4.2 CO_2-seletive WGS-MR

The incorporation of a CO_2-selective membrane into a WGS-MR shifts the conversion of CO, similar to a H_2-selective WGS-MR. The difference is that CO_2 is generated at a low pressure, while H_2 is kept near gasification pressure. To date, the best candidate for these types of membrane reactors are those that incorporate facilitated transport, because they provide both a high CO_2 flux as well as high selectivity, to limit H_2 loss in the permeate stream. Huang et al. (2005) have modeled a facilitated transport membrane with a CO_2 permeability of 4000 barrers, and CO_2/H_2 selectivity of 40 to autothermal reforming within a fuel cell. The facilitated transport CO_2-selective membrane was able to enhance the H_2 concentration to 54.95 % (dry basis), producing a H_2 recovery of 97.38%. Rubbery polymers such as PDMS and PEBAX are also often considered as prospective in such a service. However, there appears to have been no experimental evaluations of either approach at WGS temperatures. Importantly, the low operational temperature of these polymeric membranes imposes a considerable cooling penalty on the syngas, which is a formidable economic disadvantage.

4.3 Comparison of WGS-MRs

In any comparison between H_2-selective and CO_2-selective WGS-MRs for the IGCC process, the underlying membrane material is critical. As has been shown, the H_2-selective WGS-MRs, based on either metallic or porous inorganic membranes, are considerably more advanced than CO_2-selective WGS-MRs. Importantly, the inorganic nature of the membrane allows H_2-selective WGS-MRs to operate at high temperature, which is more favorable for the IGCC process. CO_2-selective WGS-MRs are generally designed to operate at near ambient temperatures because of the polymeric membrane. Hence, the H_2-selective WGS-MRs is closer to commercialization. However, facilitated transport based CO_2-selective WGS-MRs have the potential to achieve H_2 recovery greater than H_2-selective WGS-MRs, because of the greater selectivity of one gas over another, as the fuel cell application has demonstrated. If such CO_2-selective WGS-MRs can be adapted to operate at high temperatures and pressures then they present an attractive option for the IGCC process.

5. Membrane Processing Strategies and Economics

For membrane based pre-combustion capture to be viable, the process must be economical compared with alternative CO_2 capture technologies (Spillman and Grace 1989). This includes WGS-MR relative to a standard WGS reactor, with solvent scrubbing or other CO_2 removal technology, as well as the modifications required to an IGCC process for incorporation of the membrane separation.

5.1 H_2-selective membrane

The inclusion of a Pd metallic WGS-MR as part of a pre-combustion capture design has been modeled for two different syngas treatment designs (see Figure 11 and Table 6). Chiesa et al. (2007) considered a gasification process where the syngas undergoes quench cooling upon leaving the gasifier, removing particulates and increasing the S/C ratio. The syngas is then passed through a two stage WGS system, which includes a high temperature WGS reactor in series with the H_2-selective WGS-MR. The CO_2 rich retentate stream then enters a catalytic combustor, to recover energy from unconverted CO, non-permeated H_2, as well as minor components such as CH_4 and H_2S. The catalyst is required because of the very low heating value of this fuel. The exiting fuel gas is then cooled to condense H_2O, leaving CO_2 at a pressure similar to the gasification pressure which is then suitable for compression and transport for sequestration. This process strategy has very low CO_2 emissions, because the Pd membrane has very high selectivity.

In an alternative design, the CO_2 rich retentate is cooled to ambient temperature, removing water and then cryogenically cooled to $-53^{o}C$ to separate out CO_2 and H_2S. This design produced CO_2 and H_2S at low pressure, requiring recompression for storage, as well as a stream of incondensable H_2, CO, CH_4 and N_2 that is used as additional fuel in the combined cycle. There are still some CO_2 emissions observed for the WGS-MR with cryogenic capture (Table 6) due to the presence of the unconverted methane in the feed to the combined cycle. The performance of these membrane plants is heavily influenced by the membrane selectivity, for example porous inorganic membranes, even in series, will result in greater CO_2 emissions than obtained here for the Pd membrane. Naturally, the economics of the various WGS-MR designs remains the most significant criteria for design application.

Figure 11

Table 6

The power requirements of both of these membrane capture scenarios are significantly less than the conventional solvent absorption technology. However cryogenic cooling requires approximately double the power requirement of catalytic combustion. Indeed, when the WGS-MR retentate undergoes catalytic combustion, the generated steam provides additional power to the steam cycle and the net power output exceeds that of the process without CO_2 capture. A significant contribution to this outcome is the non-negligible heating contribution of H_2S, which is lost in both solvent absorption and WGS-MR cryogenic separation designs. However, this larger net power output of the catalytic combustion case does not result in a greater overall efficiency relative to the cryogenic process. This difference arises from the fate of the retentate stream; catalytic combustion generates steam for the steam cycle, whereas in the cryogenic process the incondensable gases go directly into the combined cycle, increasing turbine efficiency. Importantly, both membrane capture designs are more efficient than the conventional solvent absorption technology, even though both capture comparable volumes of CO_2 (>92%). However, it is clear that the energy integration of the plant design is important to the overall performance.

Lorenzo et al. (2008) undertook a similar study (Figure 12). In this case the syngas leaving the gasifier is cooled through radiant and convective heat exchangers, before entering a scrubber to remove corrosive components and increase the S/C ratio. Again, the syngas goes through a two stage WGS design which includes a high temperature WGS reactor followed by a Pd based WGS-MR. The H_2 permeate is sent to the combined cycle, while the CO_2 rich retentate enters a catalytic combustor and is then passed through a turbine to recover energy as electrical power. The turbine blades are cooled to maximize efficiency. This CO_2 stream is then cooled to condense out water, SO_2 is removed in a standard limestone slurry flue gas desulphurization unit, water is removed using glycol technology and the exit gas compressed to storage conditions.

Figure 12

Table 7

Compared to a design where the syngas is directly quenched with water (Chiesa et al. 2007), syngas cooling and scrubbing (Lorenzo et al. 2008) allowed greater steam generation, for the steam cycle, as well as lower S/C ratios. Such heat and energy integration, including the cooling of the retentate turbine blades, brings the WGS-MR design close to the efficiency obtained with PSA separation (Table 7) with a greater percentage of CO_2 captured. Hence, WGS-MRs can operate on a similar performance level to conventional technology, however considerable energy integration is required to ensure the heat duty of all streams is efficiently utilized.

The economics presented for these designs (Lorenzo et al. 2008) assumes a significant carbon emission tax. All have similar capital and operating costs. Importantly however, the resulting cost of producing H_2 is lower for the membrane designs compared to the PSA design. Both capital and operational costs for the syngas quenched case are reduced when compared to syngas cooling. This is due to the significant savings that are made in eliminating the specialized heat exchangers needed in syngas cooling. As a result, the cost of H_2 generation is greater for the syngas cooling design, even though it is more efficient.

5.2 CO_2-selective membrane plant

Corti et al. (2004) has modeled the performance of two plants that incorporate a CO_2-selective WGS-MR. The first strategy involves autothermal reforming of methane (that is steam methane reforming coupled with partial oxidation in a single reactor) while the latter examines standard steam reforming of methane. A PDMS membrane with a CO_2/H_2 selectivity of 6.4 is used. For the WGS-MR to obtain a CO_2 removal efficiency higher than 50%, membrane areas greater than 500 m^2 for the 39 MW steam reforming and 1000 m^2 for the 43 MW autothermal reforming are required. The larger area required for autothermal reforming is due to the higher feed flowrate compared to the steam reforming system. However, given the low selectivity of the membrane, significant amounts of H_2 enter the permeate stream diluting the CO_2 and decreasing the calorific value of the syngas remaining in the retentate. To counter this, the designs were modified to incorporate two membrane stages in series, with recirculation of the permeate stream from the second unit (Figure 13). This allows a more concentrated CO_2 stream to be taken as the permeate from the first unit.

Figure 13

To maximize the partial pressure of CO_2 in this permeate stream, the second membrane unit must have a larger area than the first. Even larger total membrane areas also become necessary (> 3000 m^2 for the autothermal case). Under optimized design conditions, efficiencies can reach 39% but only 40-48% of the CO_2 is separated. In comparison, the cycle efficiency of CO_2 removal by chemical absorption is quoted at 45% with 90% CO_2 separation efficiency (Fiaschi et al. 2002).

Improving the CO_2-selectivity of the membrane has a further beneficial effect on the cycle efficiency. When the PDMS membrane is changed to a PEBAX rubbery membrane (CO_2/H_2 of 9) or a facilitated transport membrane based on PVBTAF (CO_2/H_2 of 100) for the autothermal reforming system, at high compression ratios the efficiency approaches that quoted for chemical absorption. However, the required membrane area is very large, and may be impractical. Indeed, these authors conclude that CO_2 membrane technology is competitive with conventional CO_2 capture technologies only when the CO_2 concentration in the feed is higher than 10%.

5.3 Comparison of membrane plant

The economics of WGS-MR for a Pd-based membrane, relative to a conventional reactor, under two different S/C ratios 9.8 (MR1) and 2 (MR2) have been determined by Criscuoli et al. (2001) (Table 8). No carbon storage costs or carbon taxes are included in this analysis.

Table 8

The higher capital cost associated with the WGS-MR, compared to the conventional technology, is due to the expensive Pd membrane as well as the need for compressors (Criscuoli et al. 2001). Importantly, a saving is obtained on the amount of catalyst required compared to a conventional reactor, however this is not enough to offset the membrane cost. Operating at the lower S/C ratio reduces capital costs, because of the smaller membrane area, while still obtaining high CO conversions. The operating costs of the WGS-MR is also higher than conventional technology, mainly due to the replacement costs of the expensive Pd membrane. Hence minimizing the amount of Pd required will generate reduced capital and operating costs, making Pd-based WGS-MR more economical when compared to a conventional fixed bed WGS reactor. One approach is to reduce Pd thickness in the membrane, producing a higher flux which translates into less surface area and less metal required. Improving the permeability also benefits the operating cost of the WGS-MR, because less membrane area is required, as well as a reduction in the amount of catalyst required. There is also a limit to which the membrane thickness can be reduced, beyond which the economics becomes independent of these parameters, because the WGS-MR performance and flux through the membrane becomes catalytic rate limiting.

Bracht et al. (1997) has also compared the economics of a H_2 selective porous inorganic membrane having a H_2 permeability of $2x10^{-6}$ mol/ m^2 s Pa and H_2/CO_2 selectivity of 15, to conventional CO_2 solvent absorption (Table 9). In this case, the WGS-MR CO_2 removal system is found to be more efficient than conventional CO_2 capture (42.8% net electric efficiency compared to 40.5%), due to improved CO conversion. Similarly, the investment required per kW is less than the conventional capture case, due to savings made in process equipment. However, the percentage of CO_2 captured is lower (80% compared to 88%) so that the cost of CO_2 avoided in \$/tonne CO_2 may not be as positive. Naturally, the cost and energy penalty of capturing CO_2 means neither plant can compete in terms of efficiency and economics of the base case where no CO_2 capture is undertaken. However, the economic analysis does imply that porous inorganic membranes can be economically competitive with other separation technologies.

Table 9

The economics presented in Tables 7-9 should be used only to give a qualitative comparison of the costs of different processing strategies, as the effects of carbon taxes, currency and cost year can be significant. The capital cost estimates that underlie the economic assessments will vary substantially in methodology and scope. In addition, the effects of recent developments in construction costs, technology developments and current economic climate may have superseded their conclusions.

Importantly, none of the examples here provide data on the cost of CO_2 avoided, which is the most important parameter in a carbon-constrained world. The selectivity of many inorganic and polymer membrane systems is well below that of solvent absorption systems and this can lead to greater costs of CO_2 avoided due to lower recoveries and stream purities. It is therefore vitally important that the economics of membrane gas separation in pre-combustion be studied in more detail and the areas where economic sensitivities affect the viability of these technologies be explored fully.

7. Future directions

This review has shown that while membranes are prospective for pre-combustion capture, there remain a number of key issues that must be resolved before the technology can be considered competitive with solvent absorption processes.

At the laboratory scale, more research is required into high performance membranes that are firstly inexpensive and secondly resilient to syngas conditions. The minor components in the syngas can have an important influence on membrane performance (Scholes et al. 2009). This has been shown for sulfur on Pd, but is also true for water vapor in silica and carbon membranes (Lagorsse et al. 2005)) and polymeric membranes (e.g. hydrogen sulfide and carbon dioxide plasticization (Scholes et al. 2010)). These minor components can considerably alter the membrane performance compared to that reported in the literature, which is generally determined under ideal conditions. Another process problem for membranes is fouling, possibly due to liquid phase hydrocarbon or water and/or coal dust build up in and upon the membrane surface. This adds another resistance to gas transport through the membrane, reducing separation efficiency.

The high capital cost of existing Pd-based membrane units, along with manufacturing volume limitations, make these membranes less economical when compared to conventional separation technology. In order to improve this, optimization of the membrane material and the membrane reactor performance is required. The optimal operational temperature, pressure, and feed gas composition need to be determined as these will influence CO conversion, gas permeation rate and ultimately process efficiency. This will allow increasing certainty in the design and construction of membrane units for CO_2 separation on an industrial scale. In addition, long time performance studies are required on many membranes reported in the literature. It is well known that performance degradation occurs over periods of months, even in pristine laboratory conditions, and therefore it is important that the reported performance is able to remain relatively constant for an extended period of time. Research is also required to resolve issues with sealing the often delicate membrane structures into a leak-proof housing in a cost effective manner.

One of the most significant issues for membrane capture of CO_2 in a pre-combustion scenario is the lack of pilot plant trials to test their feasibility. The majority of the results presented here are for small laboratory scale systems. However, only industrial trials of membrane separation and WGS-MRs will provide evidence on whether laboratory performance can be obtained upon scale up and under real industrial conditions. Future pilot plant trials should aim to provide information on unit performance under industrial conditions, such as CO conversion and operational efficiency, as well as membrane characterization, especially in the competitive permeability of minor components, subsequent composition of the permeate stream, and membrane degradation and lifetime.

The discussion on incorporating membrane capture into the IGCC process highlights the importance of energy integration. The information reported here clearly shows that pre-combustion performance is heavily associated with the extent of energy integration, and while these process designs are simplistic, they highlight the importance of future work in this area. Additional attention should be paid to CO_2 separation processes after the WGS-MR unit, since the options of catalytic combustion and cryogenic separation, presented here, may not be feasible. For example, the need for heat exchangers that can operate at high pressure with extremely acidic aqueous condensates may not be economical, and the energy and efficiency benefits may not be justified.

The broader design issue is whether the plant should produce high pressure CO_2 or H_2. In the former case compression for transport and storage is minimal, while in the latter case compression for the combined cycle is minimal. This will ultimately be an economic decision, based on the gasification process, size of the plant as well as the relative cost associated with CO_2 transport and storage. As it has been shown here, the current state of membrane technologies are not equal for each of these separations, and therefore more focus needs to be placed on membrane systems that have high selectivity for CO_2 over H_2. These are just some of the many significant technological hurdles that need to be overcome before carbon capture can be successfully implemented into the IGCC process.

8. References

Adhikari, S., Fernando, S., 2006. Hydrogen membrane separation techniques. Ind. Eng. Chem. Res. 45, 875-881.

Amano, M., Komaki, M., Nishimura, C., 1991. Hydrogen permeation characteristics of palladium-plated V-Ni alloy membranes. J. Less-Common. Met. 172, 727-731.

Andrew, P. L., Haasz, A. A., 1992. Models for hydrogen permeation in metals. J. Appl. Physics 72, 2749-2757.

Aoki, K., Kusakabe, K., Morooka, S., 1998. Gas permeation properties of A-type zeolite membrane formed on porous substrate by hydrothermal synthesis. J. Membr. Sci. 141, 197-205.

Armor, J. N., 1998. Applications of catalytic inorganic membrane reactors to refinery products. J. Membr. Sci. 147, 217-233.

Asaeda, M., Yamasaki, S., 2001. Separation of inorganic/organic gas mixtures by porous silica membranes. Sep. Purif. Techno. 25, 151-159.

Audus, H., Kaarstad, O., Skinner, G., 1998. CO2 capture by pre-combustion decarbonisation of natural gas. Series Interlaken, Switzerland.

Bai, H., Ho, W. S. W., 2009. New carbon dioxide-selective membranes based on sulfonated polybenzimidazole (SPBI) copolymer matrix for fuel cell applications. Ind. Eng. Chem. Res. 48, 2344-2354.

Baker, R. W., 2002. Future directions of membrane gas separation technology. Industrial & Engineering Chemistry Research 41, 1393-1411.

Basile, A., Criscuoli, A., Santella, F., Drioli, E., 1996. Membrane reactor for water gas shift reaction. Gas. Sep. Purif. 10, 243-254.

Battersby, S., Duke, M., Liu, S., Rudolph, V., Diniz da Costa, J. C., 2008. Metal doped silica membrane reactor: Operational effects of reaction and permeation for the water gas shift reaction. J. Membr. Sci. 316, 46-52.

Bondar, V. I., Freeman, B. D., Pinnau, I., 2000. Gas transport properties of poly(ether-b-amide) segmented block copolymers. J. Polym. Sci. B: Polym. Phys. 38, 2051-2062.

Bracht, M., Alderliesten, P. T., Kloster, R., Pruschek, R., Haupt, G., Xue, E., Ross, J. R. H., Koukou, M. K., Papayannakos, N., 1997. Water gas shift membrane reactor for CO2 control in IGCC systems: techno-economic feasibility study. Energy Convers. Mgmt. 38, S159-S164.

Brandup, J., 1999. Polymer Handbook. Series John Wiley & Sons, New York.

Bredesen, R., Peters, T. A., 2008. Membranes in Energy Systems with CO2 capture. ed. Peinemann, K.-V., Pereira Nunes, S., Eds., Series Wiley-VCH, Weinheim, Germany.

Brinker, C. J., Ward, T. L., Sehgal, R., Raman, N. K., Hietala, S. L., Smith, D. M., Hua, D. W., Headley, T. J., 1993. Ultramicroporous silica-based supported inorganic membranes. J. Membr. Sci. 77, 165-179.

Chen, H.; Kovvali, A.S.; Sirkar, K.K.; Selective CO_2 Separation from CO_2−N_2 Mixtures by Immobilized Glycine-Na−Glycerol Membranes, Industrial & Engineering Chemistry Research, 39 (2000) 2447-2458

Cheng, X. Y., Wu, Q. Y., Sun, Y. K., 2005. Hydrogen permeation behavior in a Fe3Al-based alloy at high temperature. J. Alloys Compd. 389, 198-203.

Chiesa, P., Kreutz, T. G., Lozza, G. G., 2007. CO2 sequestration from IGCC power plants by means of metallic membranes. J. Eng. Gas Turb. Power 129, 123-134.

Choi, Y.-J., Lee, H.-K., 2004. Separation of hydrogen-nitrogen gas mixture by PTMSP-silica-PEI composite membranes. Membrane J. 14, 304-311.

Chung, T.-S., Shao, L., Tin, P. S., 2006. Surface modification of polyimide membranes by diamines for H_2 and CO_2 separation. Macromol. Rapid Commun. 27, 998-1003.

Chung, T. S., Jiang, L. Y., Li, Y., Kulprathipanja, S., 2007. Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. Prog. Polym. Sci. 32, 483-507.

Choi, S., Coronas, J., Lai, Z., Yust, D., Onorato, F., Tsapatsis, M. Fabrication and gas separation properties of polybenzimidazole (PBI)/nano porous silicates hybrid membranes, J. Membr. Sci., 316 (2008) 145-152.

Choi, J.I., Jung, C.H., Han, S.H., Park, H.B., Lee, Y.M. Thermally rearranged (TR) poly(benzoxazole-co-pyrrolone) membranes tuned for high gas permeability and selectivity, J. Membr. Sci. 349 (2010) 358-368.

Coronas, J., Falconer, J. L., Noble, R. D., 1997. Characterization and permeation properties of ZSM-5 tubular membranes. AlChE J. 43, 1797-1812.

Corti, A., Fiaschi, D., Lombardi, L., 2004. Carbon dioxide removal in power generation using membrane technology. Energy 29, 2025-2043.

Criscuoli, A., Basile, A., Drioli, E., 2000. An analysis of the performance of membrane reactors for the water-gas shift reaction using a gas feed mixtures. Catal. Today 56, 53-64.

Criscuoli, A., Basile, A., Drioli, E., Loiacono, O., 2001. An economic feasibility study for water gas shift membrane reactor. J. Membr. Sci. 181, 21-27.

Cussler, E. L., 1994. Facilitated and active transport. ed. Paul, D. R., Yampol'skii, Y. P., Eds., Series CRC Press, Boca Raton, Fl.

Damle, A. S., Gangwal, S. K., Venkataraman, V. K., 1994. A simple model for a water gas shift membrane reactor. Gas. Sep. Purif. 8, 101-106.

Delassus, P. T., Grieser, D. J., 1980. Factors affecting the moisture barrier of vinylidene chloride-vinyl chloride copolymer films. J. Vinyl Technol. 2, 195-199.

Duthie, X.J., Kentish, S.E., Powell, C.E., Qiao, G.G., Nagai, K., Stevens, G.W., 2007a Plasticization Suppression in Grafted Polyimide-Epoxy Network Membranes, Industrial & Engineering Chemistry Research, 46, 8183-8192.

Duthie, X., Kentish, S., Powell, C.,Nagai, K., Qiao, G., Stevens, G. 2007b Operating temperature effects on the plasticization of polyimide gas separation membranes, Journal of Membrane Science, 294, 40-49.

El-Azzami, L. A., Grulke, E. A., 2008. Carbon dioxide separation from hydrogen and nitrogen by fixed facilitated transport in swollen chitosan membranes. J. Membr. Sci. 323, 225-234.

El-Azzami, L. A., Grulke, E. A., 2009. Carbon dioxide separation from hydrogen and nitrogen facilitated transport in arginine salt-chitosan membranes. J. Membr. Sci. 328, 15-22.

Fan, J., Ohya, H., Suga, T., Ohashi, H., Yamashita, K., Tsuchiya, S., Aihara, M., Takeuchi, T., Negishi, Y., 2000. High flux zirconia composite membrane for hydrogen separation at elevated temperature. J. Membr. Sci. 170, 113-125.

Fiaschi, D., Lombardi, L., Tapinassi, L., 2002. The R-ATR and the R-REF gas turbine power cycles with CO2 removal part 1: the R-ATR cycle. Proc. 47th ASME/IGTI Gas Turb. Conf. G-2002-30116.

Galuszka, J., Liu, D., 2001. Methane to syngas: development of non-coking catalyst and hydrogen-permselective membrane. Stud. Surf. Sci. Catal. 136(Natural Gas Conversion VI), 363-368.

Gavalas, G. R., Megiris, C. E., Nam, S. W., 1989. Deposition of H_2-permselective SiO_2 films. Chem. Eng. Sci. 44, 1829-1835.

Giessler, S., Jordan, L., Diniz da Costa, J. C., Lu, G. Q. M., 2003. Performance of hydrophobic and hydrophilic silica membrane reactors for the water gas shift reaciton. Sep. Purif. Technol. 32, 255-264.

Gryaznov, V., 1999. Membrane catalysis. Catal Today 51, 391-395.

Gu, X., Tang, Z., Dong, J., 2008. On-stream modification of MFI zeolite membranes for enhancing hydrogen separation at high temperature. Micro. Meso. Mat. 111, 441-448.

Guan, G., Tanaka, T., Kusakabe, K., Sotowa, K.-I., Morooka, S., 2003. Characterization of AlPO4 type molecular sieving membranes formed on a porous a-alumina tube. J. Membr. Sci. 214, 191-198.

Ha, H. Y., Suk, W. N., Hong, S.-A., Lee, W. K., 1993. Chemical vapor deposition of hydrogen-permselective silica films on porous glass supports from tetraethylorthosilicate. J. Membr. Sci. 85, 279-290.

Hara, S., Hatakeyama, N., Itoh, N., Kimura, H. M., Inoue, A., 2003. Hydrogen permeation through amorphous Zr36-xHfxNi64 alloy membranes. J. Membr. Sci. 211, 149-156.

Hara, S., Sakaki, K., Itoh, N. (2002), vol. 6478853.

Hashi, K., Ishikawa, K., Matsuda, T., Aoki, K., 2005. Microstructures and hydrogen permeability of Nb-Ti-Ni alloys with high resistance to hydrogen embrittlement. Mater. Trans. 46, 1026-1031.

Hirayama, Y., Kase, Y., Tanihara, N., Sumiyama, Y., Kusuki, Y., Haraya, K., 1999. Permeation properties to CO2 and N2 of poly(ethylene oxide)-containing and crosslinked polymer films. J. Membr. Sci. 160, 87-99.

Hirose, T., Mizoguchi, K., Kamiya, Y., 1985. Gas transport in poly(vinyl benzoate). J. Appl. Polym. Sci. 30, 401-410.

Holleck, G. L., 1970. Diffusion and solubility of hydrogen in palladium and palladium-silver alloys. J. Phys. Chem. 74, 503-511.

Hosseini, S. S., Teoh, M. M., Chung, T. S., 2008. Hydrogen separation and purification in membranes of miscible polymer blends with interpenetration networks. Polymer 49, 1594-1603.

Huang, J., El-Azzami, L. A., Ho, W. S. W., 2005. Modeling of CO2-selective water gas shift membrane reactor for fuel cell. J. Membr. Sci. 261, 67-75.

IPCC, 2007. Intergovernmental Panel on: Climate Change 2007: The physical science bases. Contribution of Working Group 1 to the fourth assessment report of the Intergovernmental Panel on climate change. Series Cambridge University Press, Cambridge, United Kingdom and New York, USA.

Ito, Y., 1961. Permeability of high polymer films to gases and vapors. Kobunshi Kagaku 18, 124-132.

Jansen, K. C., Coker, E. N., 1996. Zeolitic membranes. Curr. Opin. Solid St. Mat. Sci. 1, 65-68.

Kesting, R. E., Fritzche, A. K., 1993. Polymeric Gas Separation Membranes. Series Wiley, New York.

Kim, J. H., Ha, S. Y., Lee, Y. M., 2001. Gas permeation of poly(amide-6-b-ethylene oxide) copolymer. Journal of Membrane Science 190, 179-193.

Koros, W. J., 1991. Gas Separation. ed. Baker, R. W., Ed., Series William Andrew Publishing, Park Ridge.

Laciak, D. V., Quinn, R., Pez, G. P., Appleby, J. B., Puri, P. S., 1990. Selective permeation of ammonia and carbon dioxide by novel membranes. Sep. Sci. Technol. 25, 1295-1305.

Lagorsse, S., Magalhaes, F. D., Mendes, A., 2005. Water adsorption on carbon molecular sieve membranes. Experimental data and isotherm model. Carbon 43, 2769-2779.

Lee, K. H., Hwang, S. T., 1986. The transport of condensible vapors through a microporous Vycor glass membrane. J. Colloid Interf. Sci. 110, 544-555.

Lee, L.-L., Tsai, D.-S., 2001. Synthesis and permeation properties of silicon-carbon based inorganic membrane for gas separation. Ind. Eng. Chem. Res. 40, 612-616.

Li, A., Liang, W., Hughes, R., 1998. Characterisation and permeation of palladium/stainless steel composite membranes. J. Membr. Sci. 149, 259-268.

Li, D., Hwang, S.-T., 1992. Gas separation by silicon based inorganic membrane at high temperature. J. Membr. Sci. 66, 119-127.

Lin, H., Freeman, B. D., 2004. Gas solubility, diffusivity and permeability in poly(ethylene oxide). J. Membr. Sci. 239, 105-117.

Lin, H., Freeman, B. D., 2005. Materials selection guidelines for membranes that remove CO2 from gas mixtures. J. Mol. Struct. 739, 57-74.

Lin, H., Van Wagner, E., Freeman, B. D., Toy, L. G., Gupta, R. P., 2006. Plasticization-enhanced hydrogen purification using polymeric membranes. Science 311, 639-642.

Linkov, V. M., Sanderson, R. D., Jacobs, E. P., 1994. Highly asymmetrical carbon membranes. J. Membr. Sci. 95, 93-99.

Lorenzo, L. D., Kreutz, T. G., Chiesa, P., Williams, R. H., 2008. Carbon-free hydrogen and electricity from coal: options for syngas cooling in systems using a hydrogen separation membrane reactor. J. Eng. Gas Turb. Power 130, 031401-031401 - 031401-031410.

Low, B. T., Xiao, Y., Chung, T. S., 2009. Amplifying the molecular sieving capability of polyimide membranes via coupling of diamine networking and molecular architecture. Polymer 50, 3250-3258.

Lu, G. Q., Diniz da Costa, J. C., Duke, M., Giessler, S., Socolow, R., Williams, R. H., Kreutz, T. G., 2007. Inorganic membranes for hydrogen production and purification: a critical review and perspective. J. Colloid Interf. Sci. 314, 589-603.

Luebke, D., Myers, C., Pennline, H., 2006. Hybrid membranes for selective carbon dioxide separation from fuel gas. Energ. Fuel 20, 1906-1913.

Luebke, D. R., Pennline, H. W., 2003. CO2-selective hybrid membranes by silation of alumina. Proc. A. Int. Pitts. Coal Conf. 20, 787-805.

Ma, D., Lund, C. R. F., 2003. Assessing high-temperature water-gas shift membrane reactors. Ind. Eng. Chem. Res. 42, 711-717.

Maier, G., 1998. Gas separation with polymer membranes. Angew. Chem. Int. Ed. 37, 2961-2974.

McCandless, F. P., 1985. A comparison of some recycle permeators for gas separation. J. Membr. Sci. 24, 15-28.

Megiris, C. E., Glezer, J. H. E., 1992. Synthesis of H2-permselective membranes by modified chemical vapor deposition. Microstructure and permselectivity of SiO2/C/Vycor membranes. Ind. Eng. Chem. Res. 31, 1293-1299.

Meldon, J. H., Stroeve, P., Gregoire, C. E., 1982. Facilitated transport of carbon dioxide: a review. Chem. Eng. Commun. 16, 263-300.

Merkel, T. C., Gupta, R. P., Turk, B. S., Freeman, B. D., 2001. Mixed-gas permeation of syngas components in poly(dimethylsiloxane) and poly(1-trimethylsilyl-1-propyne) at elevated temperatures. J. Membr. Sci. 191, 85-94.

Middleton, P., Hurst, P., Walker, G., 2005. GRACE: Pre-combustion De-carbonisation Hydrogen Membrane Study. ed. Thomas, D. C., Benson, S., Eds., Series Elsevier Science, Netherlands.

Morooka, S., Yan, S., Kusakabe, K., Akiyama, Y., 1995. Formation of hydrogen-permselective SiO2 membrane in macropores of a-alumina support tube by thermal decomposition of TEOS. J. Membr. Sci. 101, 89-98.

Myers, C., Pennline, H., Luebke, D., Ilconich, J., Dixon, J. K., Maginn, E. J., Brennecke, J. F., 2008. High temperature separation of carbon dioxide/hydrogen mixtures using facilitated supported ionic liquid membranes. J. Membr. Sci. 322, 28-31.

Nagai, K., Freeman, B. D., Cannon, A., Allcock, H. R., 2000. Gas permeability of poly(bis-trifluoroethoxyphosphazene) and blends with adamantane amino/trifluoroethoxy (50/50) polyphosphazene. J. Membr. Sci. 172, 167-176.

Naito, M., Nakahira, K., Fukuda, Y., Mori, H., Tsubaki, J., 1997. Process conditions on the preparation of supported microporous SiO2 membranes by sol-gel modification techniques. J. Membr. Sci. 129, 263-269.

Nakamura, A., 1985. Polymer membranes for gas separation. Hydrogen. Kobunshi Kako 34, 141-153.

Nam, S. E., Lee, K. H., 2000. A study on the palladium/nickel composite membrane by vacuum electrodeposition. J. Membr. Sci. 170, 91-99.

Neoff, T. M., Spontak, R. J., Aberg, C. M., 2006. Membranes for hydrogen purification: an important step toward a hydrogen-based economy. MRS Bulletin 31, 735-741.

Nishimura, C., Komaki, M., Hwang, S., Amano, M., 2002. V-Ni alloy membranes for hydrogen purification. J. Alloys Compd. 330-332, 902-906.

Noble, R. D., Koval, C. A., 2006. Review of Facilitated Transport Membranes. ed. Yampol'skii, Y. P., Pinnau, I., Freeman, B. D., Eds., Series John Wiley & Sons, West Sussex.

Oertel, M., Schmitz, J., Weirich, W., Jendryssek-Neumann, D., Schulten, R., 1987. Steam reforming of natural gas with integrated hydrogen separation for hydrogen production. Chem. Eng. Technol. 10, 248-255.

Orme, C. J., Stone, M. L., Benson, M. T., Peterson, E. S., 2003. Testing of polymer membranes for the selective permeability of hydrogen. Sep. Sci. Technol. 38, 3225-3238.

Osada, K., Ohnishi, T., Shin, Y., Yoshino, J., Kurpishi, N., 1999. Development of inorganic membranes by sol-gel method for CO2 separation. Proc. Int. Conf. Greenhouse Gas Control Technol. 2, 43-45.

Ozaki, T., Zhang, Y., Komaki, M., Nishimura, C., 2003. Hydrogen permeation characteristics of V-Ni-Al alloys. Int. J. Hydrogen Energ. 28, 1229-1235.

Paglieri, S. N., Way, J. D., 2002. Innovations in Palladium membrane research. Sep. Purif. Methods 31, 1-169.

Park, H. B. P., Chul, H. J., Lee, Y. M., Hill, A. J., Pas, S. J., Mudie, S. T., Wagner, E. V., Freeman, B. D., Cookson, D. J., 2007. Polymers with cavities tuned for fast selective transport of small molecules and ions. Science 318, 254-258.

Perry, J. D., Nagai, K., Koros, W. J., 2006. Polymer membranes for hydrogen separations. MRS Bulletin 31, 745-749.

Pesiri, D. R., Jorgensen, B., Dye, R. C., 2003. Thermal optimization of polybenzimidazole meniscus membranes for the separation of hydrogen, methane, and carbon dioxide. J. Membr. Sci. 218, 11-18.

Petersen, J., Matsuda, M., Haraya, k., 1997. Capillary carbon molecular sieve membranes derived from Kapton for high temperature gas separation. J. Membr. Sci. 131, 85-94.

Petropoulos, J. H., 1994. Mechanisms and theories for sorption and diffusion of gases in polymers. ed. Paul, D. R., Yampol'skii, Y. P., Eds., Series CRC Press, Boca Raton.

Phair, J. W., Donelson, R., 2006. Developments and design of novel (non-palladium based) metal membranes for hydrogen separation. Ind. Eng. Chem. Res. 45, 5657-5674.

Pinnau, I., He, Z., 2004. Pure and mixed gas permeation properties of polydimethylsiloxane for hydrocarbon/methane and hydrocarbon/hydrogen separation. J. Membr. Sci. 244, 227-233.

Powell, C., Qiao, G., 2006. Polymeric CO2/N2 gas separation membranes for the capture of carbon dioxide from power plant flue gases. J. Membr. Sci. 279, 1-49.

Quinn, R., Appleby, J. B., Pez, G. P., 1995. New facilitated transport membranes for the separation of carbon dioxide from hydrogen and methane. J. Membr. Sci. 104, 139-146.

Quinn, R., Laciak, D. V., 1997. Polyelectrolyte membranes for acid gas separation. J. Membr. Sci. 131, 49-60.

Rao, M. B., Sircar, S., 1993. Nanoporous carbon membranes for separation of gas mixtures by selective surface flow. J. Membr. Sci. 85, 253-264.

Renate, M. d. V., Verweij, H., 1998. High-selectivity, high-flux silica membranes for gas separation. Science 279, 1710-1711.

Roa, F., Way, D. J., McCormick, R. L., Paglieri, S. N., 2003. Preparation and characterization of Pd-Cu composite membranes for hydrogen separation. Chem. Eng. J. 93, 11-22.

Robertson, W. M., 1973. Hydrogen permeation, diffusion and solution in nickel. Zeitschrift fur Metallkunde 64, 436-443.

Ross, J. R. H., Xue, E., 1995. Catalysis with membranes or catalytic membranes? Catal. Today 25, 291-301.

Scholes, C. A., Chen, G. Q., Stevens, G. W., Kentish, S. E., 2010. Plasticization of ultra-thin polysulfone membranes by carbon dioxide. J. Membr. Sci. 346, 208-214.

Scholes, C. A., Kentish, S. E., Stevens, G. W., 2009. Effects of minor components in carbon dioxide capture using polymeric gas separation membranes. Sep. Purif. Reviews 38, 1-44.

Shao, L., Chung, T. S., 2009. In situ fabrication of cross-linked PEO/silica reverse-selective membranes for hydrogen purification. Int. J. Hydrogen Energ. 34, 6492-6504.

Shao, L., Lau, C.-H., Chung, T. S., 2009. A novel strategy for surface modification of polyimide membranes by vapor-phase ethylenediamine (EDA) for hydrogen purification. Int. J. Hydrogen Energy. 34, 8716-8722.

Shao, L., Low, B. T., Chung, T. S., Greenberg, A. R., 2009. Polymeric membranes for the hydrogen economy: Contemporary approaches and prospects for the future. Journal of Membrane Science 327, 18-31.

Shelly, S., 2009. Capturing CO2: membrane systems move forward. Chem. Eng. Prog. 105, 42-47.

Shkolnik, I. V., Kulsartov, T. V., Tazhibaeva, I. L., Shestakov, V. P., 1998. Investigation of the surface element composition influence on hydrogen permeability through vanadium alloy VCr4Ti4. Fusion Technol. 34, 868-871.

Simril, V. L., Hershberger, A., 1950. Permeability of polymeric films to gases. Modern Plastics 27, 95-102.

Smaihi, M., Schrotter, J.-C., Lesimple, C., Prevost, I., Guizard, C., 1999. Gas separation properties of hybrid imide-siloxane copolymers with various silica contents. J. Membr. Sci. 161, 157-170.

Spillman, R. W., Grace, W. R., 1989. Economics of gas separation membranes. Chem. Eng. Prog. 85, 41-62.

Steeneveldt, R., Berger, B., Torp, T. A., 2006. CO2 capture and storage. Closing the knowing-doing gap. Chem. Eng. Res. Des. 84(A9), 739-763.

Stern, S., 1994. Polylmers for gas separation: the next decade. J. Membr. Sci. 94, 1-65.

Stern, S. A., Perrin, J. E., Naimon, E. J., 1984. Recycle and multimembrane permeators for gas separation. J. Membr. Sci. 20, 25-43.

Steward, S. A., “Review of hydrogen isotope permeability through materials” (U.S. Department of Commerce, 1983).

Suda, H., Yamauchi, H., Uchimaru, Y., Fujiwara, I., Haraya, K., 2006. Preparation and gas permeation properties of silicon carbide-based inorganic membranes for hydrogen separation. Desalination 193, 252-255.

Suzuki, H., Tanaka, K., Kita, H., Okamoto, K., Hoshino, H., Yoshinaga, T., Kusuki, Y., 1998. Preparation of composite hollow fiber membranes of poly(ethylene oxide)-containing polyimide and their CO2/N2 separation properties. J. Membr. Sci. 146, 31-37.

Takano, T., Ishikawa, K., Matsuda, T., Aoki, K., 2004. Hydrogen permeation of eutectic Nb-Zr-Ni alloy membranes containing primary phases. Mater. Trans. 45, 3360-3362.

Thambimuthu, K., Soltanieh, M., Abandas, J. C., 2005. IPCC special report on carbon dioxide capture and storage. Series Cambridge University Press, Cambridge.

Tikhomirov, B. P., Hopfenberg, H. B., Stannett, V., Williams, J. L., 1968. Permeation, diffusion and solution of gases and water vapor in unplasticized poly (vinyl chloride). Makromol. Chem. 118, 177-188.

Tong, H. D., Gielens, F. C., Gardeniers, J. G. E., Jansen, H. V., Rijn, C. J. M. V., Elwenspoek, M. C., Nijdam, W., 2004. Microfabricated palladium-silver alloy membranes and their application in hydrogen separation. Ind. Eng. Chem. Res. 43, 4182-4187.

Tsuru, T., Hwang, S.-T., 1999. Permeators and continuous membrane columns with retentate recycle. J. Membr. Sci. 98, 57-67.

Uemiya, S., Sato, N., Ando, H., Kikuchi, E., 1991. The water gas shift reaction assisted by a palladium membrane reactor. Ind. Eng. Chem. Res. 30, 585-589.

Uhlhorn, R. J. R., Zaspalis, V. T., Keizer, K., Burggraaf, A. J., 1992. Synthesis of ceramic membranes. Part II: Modifcation of alumina thin film: reservoir method. J. Material Sci. 27, 538-552.

Waack, R., Alex, N. H., Frisch, H. L., Stannett, V., Szwarc, M., 1955. Permeability of polymer films to gases and vapors. Ind. Eng. Chem. 47, 2524-2527.

Wallace, P. S., Kasbaum, J. L., Johnson, K. A., 2002. Hydrogen recycle and acid gas removal using a membrane. US Patent No. 6416568.

Wang, Z., Chen, T., Xu, J., 2000. Gas transport properties of novel cardo poly(aryl ether ketone)s with pendant alkyl groups. Macromolecules 33, 5672-5679.

Xiao, Y., Low, B. T., Hosseini, S. S., Chung, T. S., Paul, D. R., 2009. The strategies of molecular architecture and modificaiton of polyimide-based membranes for CO2 removal from natural gas - a review. Prog. Polym. Sci. 34, 561-580.

Xue, E., O'Keeffe, M., Ross, J. R. H., 1996. Water-gas shift conversion using a feed with a low steam to carbon monoxide ratio and containing sulphur. Catal. Today 30, 107-118.

Yamamoto, M., Kusakabe, K., Hayashi, J., Morooka, S., 1997. Carbon molecular sieve membrane formed by oxidative carbonization of a copolyimide film coated on a porous support tube. J. Membr. Sci. 133, 195-205.

Yamaura, S.-I., Shimpo, Y., Okouchi, H., Nishida, M., Kajita, O., Inoue, A., 2004. The effect of additional elements on hydrogen permeation properties of melt-spun Ni-Nb-Zr amorphous alloys. Mater. Trans. 45, 330-333.

Yan, Y., Davis, M. E., Gavalas, G. R., 1997. Use of diffusion barriers in the preparation of supported zeolite ZSM-5 membranes. J. Membr. Sci. 126, 53-65.

Yasuda, H., Rosengren, K., 1970. Isobaric measurement of gas permeability of polymers. J. Appl. Polym. Sci. 14, 2839-2877.

Yazawa, T., Kishimoto, M., Inoue, T., Mineshige, A., Kobune, M., Kuraoka, K., 2007. Preparation of CO2-selective separation membranes with highly chemical and thermal stability prepared from inorganic-organic nanohybrids containing branched polyethers. J. Mater. Sci. 42, 723-727.

Zhang, Y., Gwak, J., Murakoshi, Y., Ikehara, T., Maeda, R., Nishimura, C., 2006. Hydrogen permeation characteristics of thin Pd membrane prepared by microfabrication technology. J. Membr. Sci. 277, 203-209.

Zou, J., Huang, J., Ho, W. S. W., 2007. CO2-selective water gas shift membrane reactor for fuel cell hydrogen processing. Ind. Eng. Chem. Res. 46, 2272-2279.

Table Captions

Table 1: Hydrogen permeability through a range of pure and alloyed metallic membranes.

Table 2: Hydrogen permeance through a range of inorganic membranes. All data is based on single gas measurements and ideal selectivities. 1 GPU = 10^{-6} cm^3(STP).cm/cm^2 s cmHg

Table 3: Hydrogen permeability (1 barrer = 10^{-10} cm^3(STP)/cm^2 s cmHg) through a range of polymeric membranes. All data is based on single gas measurements and ideal selectivities except where otherwise stated.

Table 4: Carbon dioxide permeability through a range of polymeric membranes.

Table 5: Carbon dioxide permeability through a range of facilitated transport membranes.

Table 6: Performance of pre-combustion capture designs with syngas quenching (Chiesa et al. 2007).

Table 7: Performance of three plants for hydrogen production. The first employs direct syngas quenching with a WGS-MR, the second syngas cooling using heat exchangers for steam generation with a WGS-MR and the third a similar plant with syngas cooling but Pressure Swing Adsorption(PSA) for H_2 separation (Lorenzo et al. 2008). Cost estimations are based on \$5.5/tonne CO_2 for pipeline transport and aquifer storage costs and a carbon tax of 96.2 \$/tonne of carbon. All costs in 2006 US\$.

Table 8: Economic analysis of Pd-based WGS-MR compared to conventional WGS reactor (Criscuoli et al. 2001).

Table 9: Economic analysis of porous inorganic WGS-MR, compared to conventional CO_2 capture in an IGCC system (Bracht et al. 1997). All costs in US\$ July 1996.

Tables

Table 1

	Permeability (mol / s m $Pa^{1/2}$)	Temperature (K)	H_2 Pressure (kPa)	Reference
Pure Metal				
Cu	5×10^{-12}	773	<0.2	(Phair and Donelson 2006)
Ni	2×10^{-12}	500		(Robertson 1973)
Fe	2×10^{-9}	260-700	20-500	(Steward 1983)
Pd	9×10^{-9}	500	13	(Holleck 1970)
Pt	8.1×10^{-7}	705-827	100	(Steward 1983)
Alloy				
Ni-Pd	2×10^{-12}	500	20	(Zhang et al. 2006)
Fe_3Al	1×10^{-10}- 6×10^{-11}	300	101	(Cheng et al. 2005)
$Zr_{24}Hf_{12}Ni_{64}$	2×10^{-9} – 6×10^{-10}	673-473	100 – 300	(Hara et al. 2003)
$Nb_{29}Ti_{31}Ni_{40}$	1.5 – 7×10^{-9}	523-673	100-200	(Hashi et al. 2005)
$Nb_{21}Ti_{50}Ni_{29}$	1×10^{-8} - 9×10^{-10}	673- 523	100-200	(Hashi et al. 2005)
VCr_4Ti_4	1×10^{-5} – 1×10^{-8}	773-923		(Shkolnik et al. 1998)
$V_{85}Ni_{15}$	2-3×10^{-8}	673-473	<300	(Amano et al. 1991; Nishimura et al. 2002)
$(Ni_{0.6}Nb_{0.4})_{45}Zr_{50}Cu_5$	2.3×10^{-8}	673	< 300	(Yamaura et al. 2004)
$(Ni_{0.6}Nb_{0.4})_{45}Zr_{50}Co_5$	2.5×10^{-8}	673	< 300	(Yamaura et al. 2004)
$Nb_{20}Zr_{45}Ni_{45}$	2.7×10^{-8}	623	100-550	(Takano et al. 2004)
$V_{85}Ni_{15}$	3-4×10^{-7}	673-423	10 – 200	(Ozaki et al. 2003)
$V_{85}Ni_{10.5}Al_{4.5}$	5-7×10^{-7}	673-423	10 -200	(Ozaki et al. 2003)
Pd-Ni	7×10^{-6}	723	53	(Nam and Lee 2000)
Pd-Cu	6×10^{-5}	723	670	(Rao and Sircar 1993)
Pd-Ag	5×10^{-5}	723	20-75	(Tong et al. 2004)
$Hf_{34}Ni_{61}Cu_5$	1.5×10^{-3}	623	100 – 300	(Hara et al. 2002)

Table 2

Membrane	Permeance (GPU)	H_2 / CO_2	Temperature (ºC)	H_2 Pressure (kPa)	Ref
Silica (hydrophilic)	20	11	200	101	(Giessler et al. 2003)
Carbon	50	29	250	600	(Petersen et al. 1997)
PDMS coated Carbon	80	42	250	600	(Petersen et al. 1997)
SiO_2 on alumina	300	4	600	0.2	(Morooka et al. 1995)
ZSM-5 Zeolite	300		185		(Jansen and Coker 1996)
Zeolite – A	300	10	35	101	(Aoki et al. 1998)
Zirconia	300	3.5	25	150	(Fan et al. 2000)
MFI Zeolite	560	18	450	101	(Gu et al. 2008)
AlPO4-5 Zeolite	1000	24	35		(Guan et al. 2003)
Silica (Si600)	1500	-	200		(Renate and Verweij 1998)
Silica on porous silica	4000	8	300	200	(Asaeda and Yamasaki 2001)
Silica on zirconia	4000	4	300	200	(Asaeda and Yamasaki 2001)
Silica (hydrophobic)	4500	6	200	101	(Giessler et al. 2003)
Silica (Si400)	6000	7	200		(Renate and Verweij 1998)
Silicone composite	22500 barrer	2	130	103	(Li and Hwang 1992)

Table 3

Membrane	H_2 permeability (barrer)	H_2 / CO_2	Temp. (^oC)	Pressure (atm)	Ref
Poly benzimidazole	0.09 13 11	9 20 3	20 270 320	3.4	(Pesiri et al. 2003)
Poly(2,2'-(1,3-phenylene)-5,5'-bibenzimidazole	0.6	3.8	35	3.5	(Hosseini et al. 2008)
Poly (tetrafluorochloroethylene)	0.94	4.5			(Ito 1961)
polybenzimidazole (PBI)/nano porous silicate mixed matrix	1	45	35		(Choi et al. 2008)
Poly (vinyl chloride)	1.7	11			(Tikhomirov et al. 1968)
Poly (vinyl chloride)	2	11	30		(Nakamura 1985)
Poly (methyl methacrylate)	2.4	4	30	2.04	(Orme et al. 2003)
Poly (vinylidene fluoride)	2.4	2	30	2.04	(Orme et al. 2003)
Polyimide	3	2.6	90	1.9	(Smaihi et al. 1999)
Cellulose acetate	3.5	0.15			(Waack et al. 1955)
Poly (isobutylene)	7	1.4	30		(Nakamura 1985)
Poly (vinyl benzoate)	8.7	1.6	25		(Hirose et al. 1985)
DMPEK-C	10	4	30	5	(Wang et al. 2000)
6FDA-Durene modified by liquid-phase PDA crosslinking	10	100	35	3.5	(Chung et al. 2006)
Poly (benzyl methacrylate)	11	1.4	30	2.04	(Orme et al. 2003)
PEK-C	12	4.3	30	5	(Wang et al. 2000)
Poly sulfone	12	2	30	2.04	(Orme et al. 2003)

Poly sulfone	14	2.5	30	5	(Wang et al. 2000)
Poly vinyl acetate	15	1.2	30	2	(Orme et al. 2003)
TMPEK-C	22	4.0	30	5	(Wang et al. 2000)
Poly (styrene)	22	2.15	35		(Yasuda and Rosengren 1970)
Poly styrene	24	2.3	30	2	(Orme et al. 2003)
Matrimid	27	4	35	3.5	(Hosseini et al. 2008)
6FDA-Durene modified by vapor-phase EDA crosslinking	33 19*	102 17*	35	3.5	(Shao et al. 2009)
Poly (propylene)	41	4.5	35		(1999)
Poly (butadiene)	42	0.3	30		(Nakamura 1985)
IMPEK-C	43	2.2	30	5	(Wang et al. 2000)
6FDA-Durene modified by liquid-phase EDA crosslinking	120	5	35	3.5	(Chung et al. 2006)
6FDA-Durene	600	1	35	3.5	(Chung et al. 2006)
Thermally rearranged (TR) poly(benzoxazole-co-pyrrolone	1680	3.2	25	1	(Choi et al. 2010)

* mixed gas value

Table 4

Membrane	CO_2 permeability (barrer)	CO_2 / H_2	Temp. (°C)	Pressure (atm)	Ref
Poly (vinyl alcohol)	0.012	1.4			(Simril and Hershberger 1950)
Cellulose nitrate	2.1	1.0			(Ito 1961)
Poly (tetrafluoroethylene)	10	1.0			(Delassus and Grieser 1980)
Poly (oxymethylene)	12	1.2	30		(Nakamura 1985)
Poly (styrene-co-butadiene)	15	1.9	30	2	(Orme et al. 2003)
Poly (ethylene oxide) – semicrystalline	17	9.9	35	14.6	(Lin and Freeman 2004)
Poly (urethane rubber)	18	2.9	30		(Nakamura 1985)
Poly (amide-6-b-ethylene oxide) PEBAX© 3533	20	6.1	25	4	Kim et al. (2001)
Cellulose acetate	23	6.6			(Waack et al. 1955)
Poly (chloroprene)	26	1.9	30		(Nakamura 1985)
Gutta percha	35	2.5	30		(Nakamura 1985)
Butadiene-acrylonitrile rubber	63	2.5	30		(Nakamura 1985)
Ethyl cellulose	113	1.3			(Ito 1961)
Styrene-butadiene rubber	121	3	30		(Nakamura 1985)
Poly (cis-isoprene)	134	2.7	35	5	(Bondar et al. 2000)
Polyl (butadiene)	138	3.3			(1999)
Poly ethylene – poly amide copolymer	200	4	35	5	(Bondar et al. 2000)
PEGMEA-PEGDA copolymer	440	9.4	35	17	(Lin et al. 2006)
PTFEP	470	3.6	35	13.6	(Nagai et al. 2000)
Crosslinked poly(ethylene glycol) acrylate (XLPEO)	570	12	35	1	Lin and Freeman (2005)
PDMS	1300	3.5	30	2.04	(Orme et al. 2003)

PDMS	3100	4.3	35	5	(Bondar et al. 2000)
PDMS	3200	3.4	35	1.36	(Merkel et al. 2001)
Silicone rubber	3240	5	30		(Nakamura 1985)
PTMSP	18200	1.5	35	1.36	(Merkel et al. 2001)

Table 5

Membrane	CO_2 permeability (barrer)	CO_2/H_2	Temp. (°C)	Pressure (atm)	Ref
PVBTAF composite	6.0	87	23	0.5	(Quinn and Laciak 1997)
$[(C_2H_5)_4N]CH_3CO_2.4H_2O$	247	5.5	50	0.3	(Quinn et al. 1995; Quinn and Laciak 1997)
$[(CH_3)_4N]F.4H_2O$	445	10	50	0.3	(Quinn et al. 1995; Quinn and Laciak 1997)
Chitosan membrane	482	43	110	1.5	(El-Azzami and Grulke 2008)
[hmim][Tf2N]	900	7	100	1	(Myers et al. 2008)
$[H_2NC_3H_6min][tf2N]$	1000	10	100	1	(Myers et al. 2008)
PEI-SPBI composite	1262	50	100	2	(Bai and Ho 2009)
Arginine-sodium-chitosan	1500	144	110	1.5	(El-Azzami and Grulke 2009)

Table 6

	Conventional (No capture)	**Conventional (solvent absorption)**	**WGS-MR (catalytic combustion)**	**WGS-MR (cryogenic capture)**
S/C in WGS	—	2.390	2.462	2.459
Gas turbine airflow (kg/s)	536.0	553.9	495.1	532.8
Gas turbine power (MW)	294.3	293.7	315.5	300.2
Steam turbine power (MW)	178.6	179.3	266.3	181.0
Syngas expander (MW)	9.5	9.8	0.0	0.0
ASU consumption (MW)	-26.3	-28.5	-41.4	-27.6
O_2 compressor (MW)	-16.8	-18.2	-26.4	-17.6
N_2 compressor (MW)	-33.3	-28.5	-68.4	-45.5
Auxiliaries (MW)	-15.9	-17.2	-20.2	-16.1
CO_2 capture & compr. (MW)	—	-28.6	-3.8	-7.8
Net power output (MW)	390.1	361.9	421.5	366.6
LHV fuel input (MW)	908.2	983.7	1098.1	949.4
Plant efficiency (% LHV)	42.95	36.79	38.38	38.61
Carbon removed (%)	0.00	92.02	100.00	92.15
CO_2 emissions (kg/kWh)	0.752	0.070	0.000	0.066
Membrane area (m^2)	—	—	33202	34337

Table 7

	Syngas Quench	Syngas Cool with WGS-MR	Syngas Cool with PSA
Net electric power output (MW_e)	-3.8	62.2	73.8
Total steam generated (MW_{th})	37.5	394.4	—
Hydrogen produced (MW_{th}, LHV)	1089	1037	1032
Steam to Carbon (S/C) ratio	2.39	0.89	1.48
Effective efficiency (% LHV)	60.3	63.8	64.7
CO_2 produced (kg/GJ H_2 LHV)	147.9	158.4	142
CO_2 emissions (kg/GJ H_2 LHV)	0	0	13.8
Total Plant Investment $M US	929	1242	1218
Total Cost of Hydrogen Production ($/kg H_2)	1.14	1.32	1.41

Table 8

	Conventional WGS reactor	**WGS-MR (S/C = 9.8)**	**WGS-MR (S/C = 2)**
CO conversion (%)	98	99.3	94.9
Reactor (M€)	0.77	6.40	2.45
Compressor (M€)	—	0.36	0.36
Separation units (M€)	1.03	—	—
Capital costs (M€)	1.16	6.78	2.82
Membrane replacement (M€/year)	—	2	0.78
Total Operating costs (M€/year)	2.43	6.97	3.72

Table 9

	No capture	Conventional solvent absorption capture	WGS-MR CO_2 capture
CO_2 recovery (%)		88	80
New power output (MW)	379	355	433
Net efficiency (% LHV)	46.7	40.5	42.8
Specific investment ($/kW)	1228	1472	1255
Cost of electricity generation ($/kWh)	0.062	0.068	0.066

Figure Captions

Figure 1: IGCC and pre-combustion carbon capture, with standard water-gas shift reactor.

Figure 2: Hydrogen permeability of a range of metallic membranes with temperature (reprinted with permission from Adhikari and Fernando (2006).

Figure 3: Equilibrium CO conversion in the water gas shift reaction as a function of temperature and the H_2O/CO ratio (R) (reprinted with permission from Xue et al. (1996).

Figure 4: CO conversion of a H_2-selective WGS-MR as a function of S/C ratio (reprinted with permission from Xue et al. (1996). Y is the fraction of H_2 separated into the permeate stream.

Figure 5: Effect of S/C ratio on CO conversion through a Pd based WGS-MR, compared to thermodynamic equilibrium (reprinted with permission from Uemiya et al. (1991).

Figure 6: CO conversion of Pd based WGS-MR against S/C ratio with varying N_2 sweep flow rate, compared to thermodynamic equilibrium and a ceramic based WGS-MR (reprinted with permission from Basile et al. (1996).

Figure 7: CO conversion contribution of a WGS reactor (WGSR) and H_2-selective WGS-MR (HSMR) in series as a function of S/C ratio (reprinted with permission from Lorenzo et al. (2008).

Figure 8: H_2 production for Knudsen diffusion membranes in series as a function of stage cut, for a S/C ratio of 3 and a membrane pressure ratio of 20 (reprinted with permission from Damle et al. (1994).

Figure 9: Concentration of WGS components in the permeate and retenate as a function of CO conversion, for a membrane operating under Knudsen diffusion (reprinted with permission from Battersby et al. (2008).

Figure 10: Effect of the time factor on the CO conversion for three WGS systems under mixed gas conditions (reprinted with permission from Criscuoli et al. (2000).

Figure 11: Detailed design of a syngas quenching plant with a WGS-MR followed by catalytic combustion (reprinted with permission from Chiesa et al. (2007).

Figure 12: Detailed design of a syngas cooling plant with a WGS-MR followed by catalytic combustion (reprinted with permission from Lorenzo et al. (2008).

Figure 13: Two stage membrane separation system for use in autothermal reforming of methane (reprinted with permission from Corti et al. (2004).

Figures

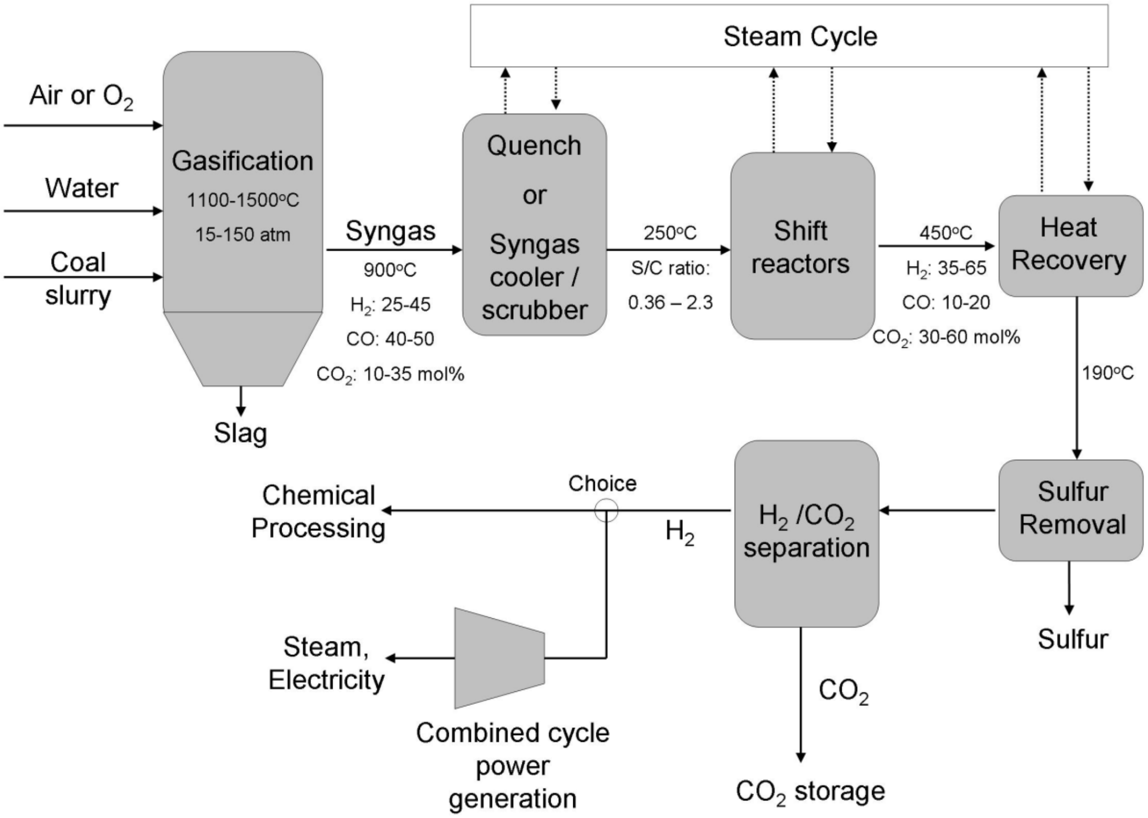


Figure 1

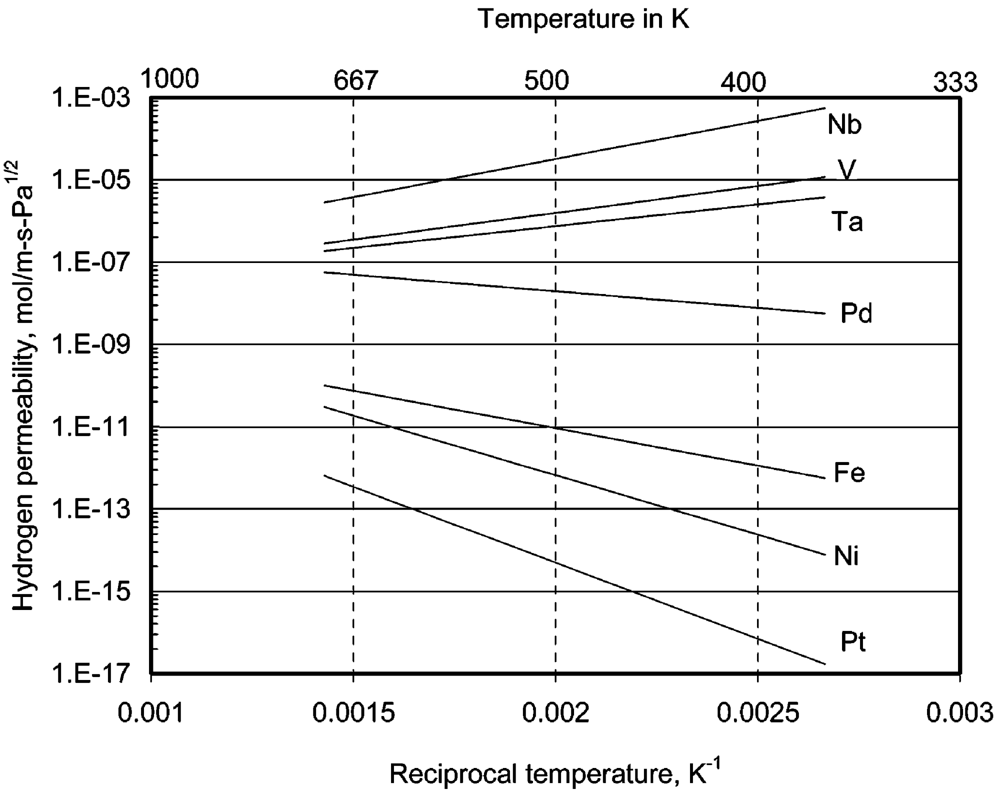


Figure 2

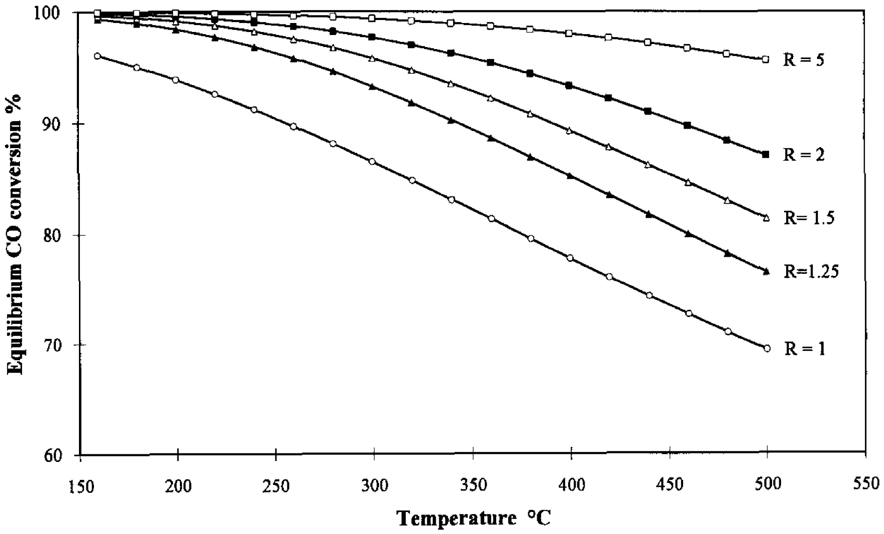


Figure 3

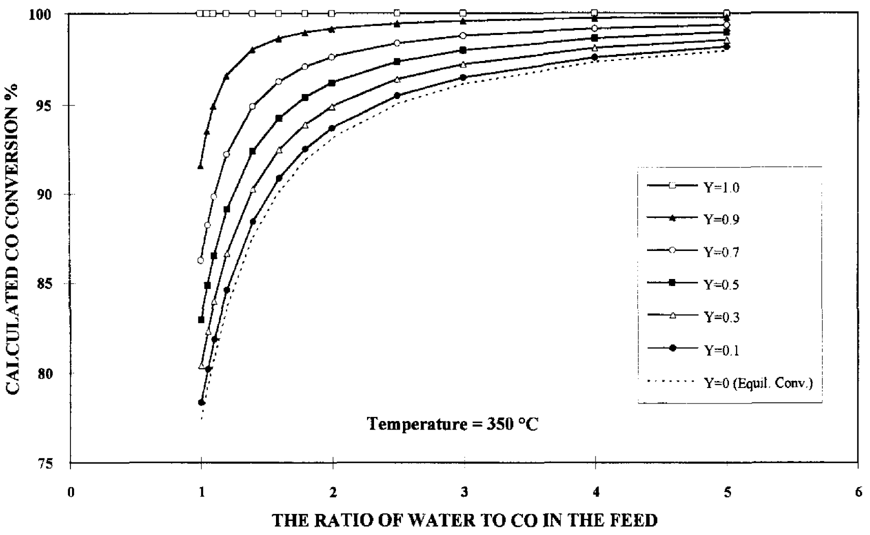


Figure 4

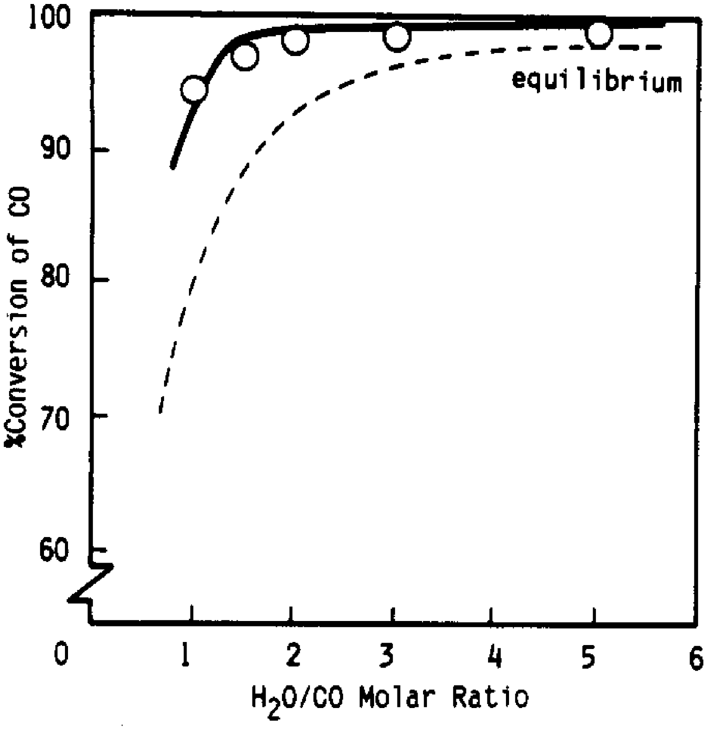


Figure 5

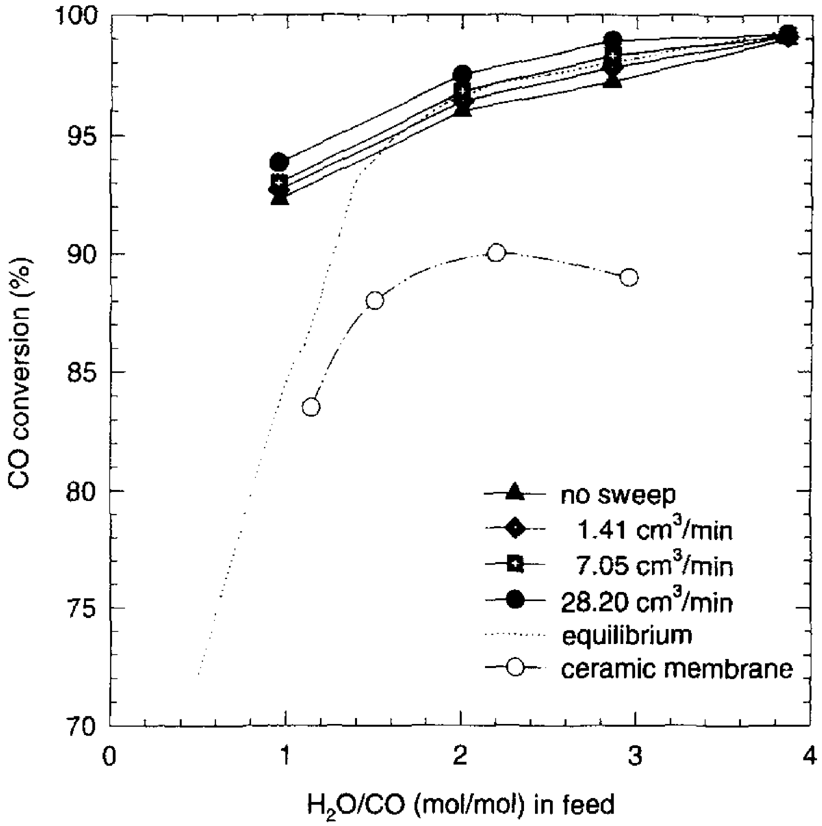


Figure 6

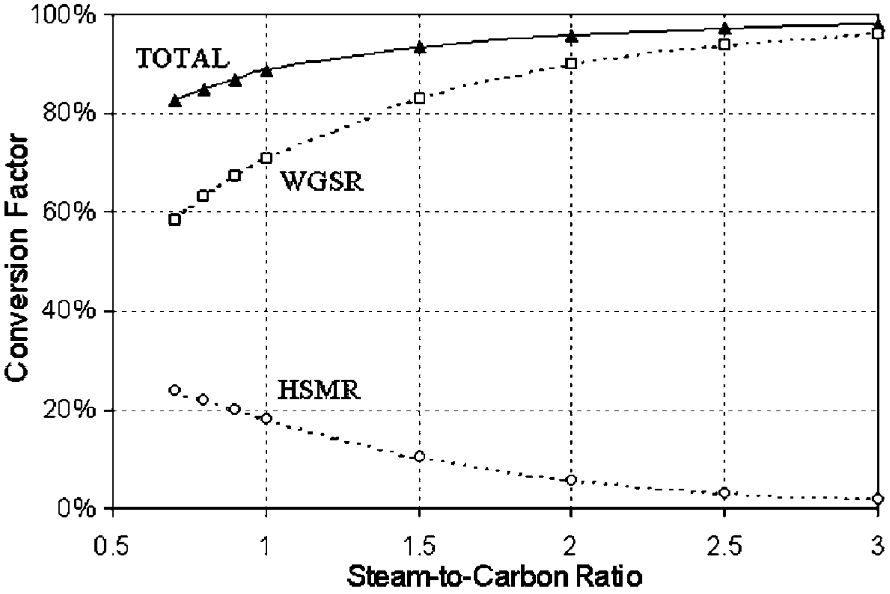


Figure 7

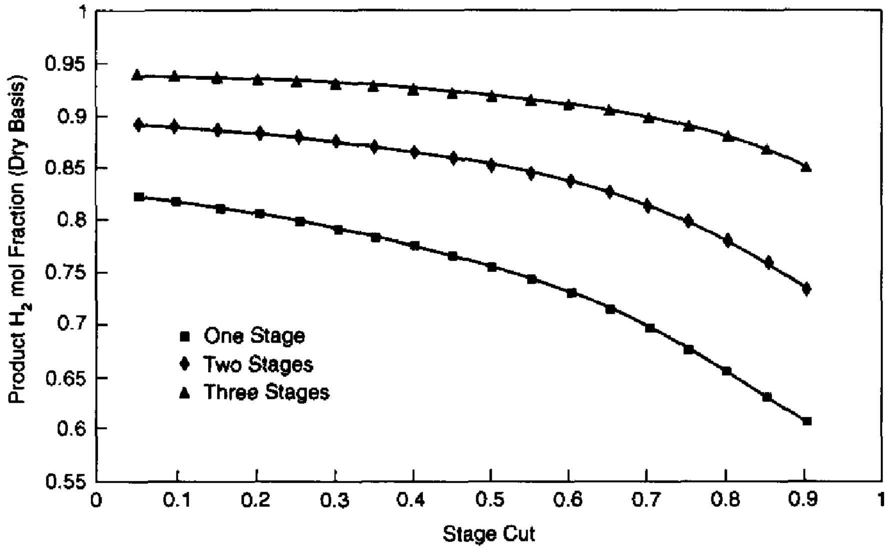


Figure 8

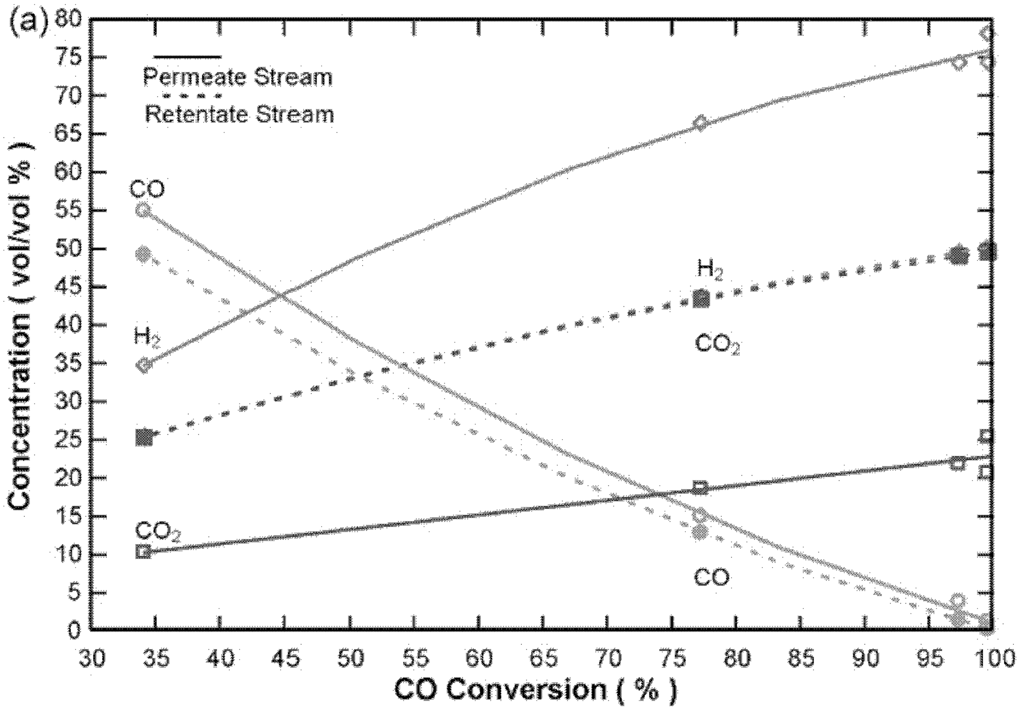
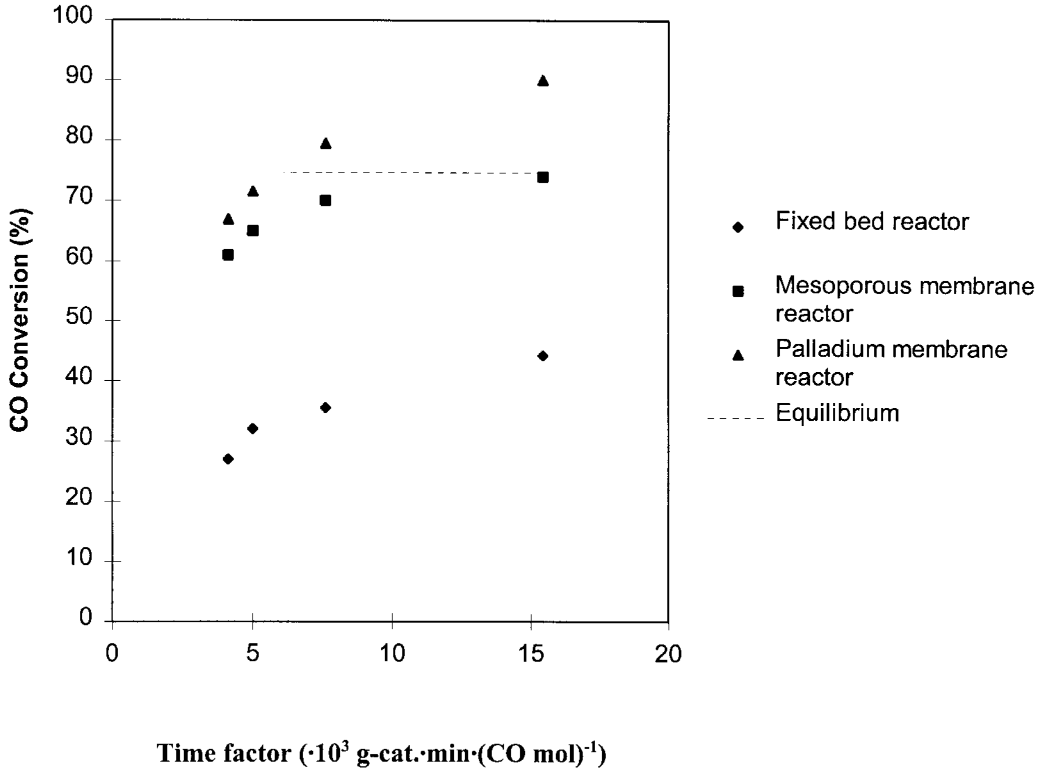


Figure 9



100
90
80
70
60
50
40
30
20
10
0
CO Conversion (%)
0
5
10
15
20
Time factor (·10^3 g-cat.·min·(CO mol)$^{-1}$)
◆ Fixed bed reactor
■ Mesoporous membrane reactor
▲ Palladium membrane reactor
- - - - Equilibrium

Figure 10

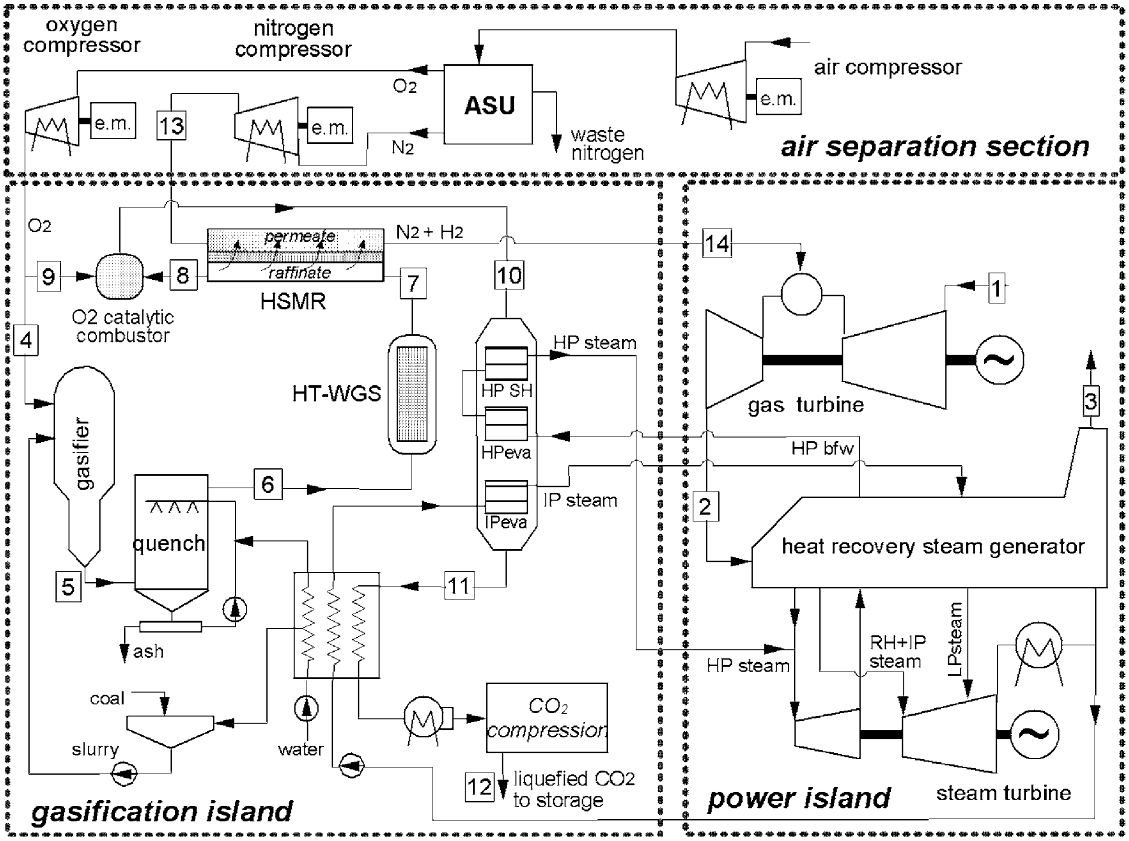
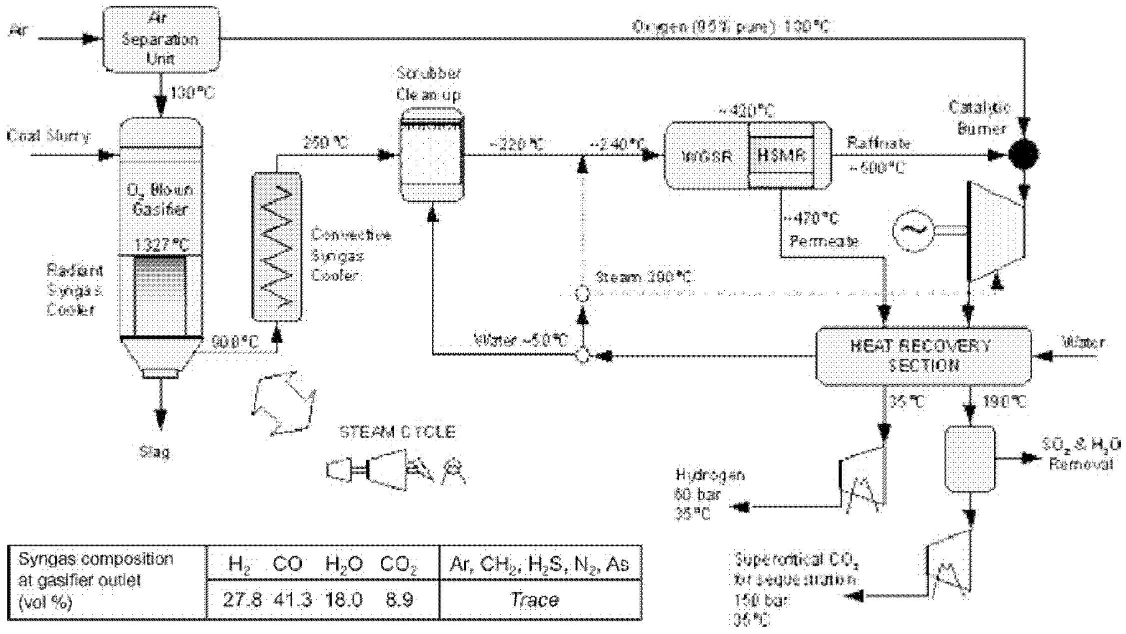
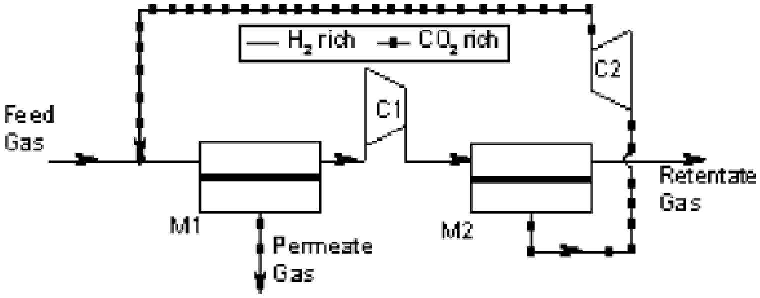


Figure 11



Syngas composition at gasifier outlet (vol %)	H_2	CO	H_2O	CO_2	Ar, CH_2, H_2S, N_2, As
	27.8	41.3	18.0	8.9	*Trace*

Figure 12



H2 rich
CO2 rich
Feed Gas
C1
C2
M1
M2
Permeate Gas
Retentate Gas

Figure 13