110th Anniversary: Process Developments in Carbon Dioxide Capture using Membrane Technology

By

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Abstract

Carbon capture and storage has declined in prominence as a large scale response to climate change, but carbon dioxide capture will remain important into the future for the hydrogen economy, for steel and cement, as well as chemical production. Membrane technology can be a significant component of this industry if cost competitive. While most scientific research is focussed on developing novel materials for this application, it is the process design of the membrane operations that is much more critical in reducing these costs. In post combustion capture, this involves optimisation of the pressure driving force across the membrane, either through feed compression or permeate vacuum pumping, integration of downstream cryogenic purification and the use of combustion air sweeps. In pre-combustion capture, integration of the membrane into the water gas shift reactor is key. Membrane contactors can also play a role, but must be carefully engineered to ensure pressure drop control and to minimise capillary condensation of water.

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1. Introduction

The use of membranes to remove carbon dioxide from gas streams has been a commercial reality since the 1980s[1]. Carbon dioxide capture was first developed for the purification of natural gas streams and this application continues to expand market share today, as the quality of the available raw gas declines and as offshore fields become increasingly remote and in deeper waters.

The use of such membranes for the capture of carbon dioxide from flue gases first garnered interest around 1995 as a response to climate change[2, 3]. In many ways it has lost its lustre in more recent years, due to the rapid technological developments in solar photovoltaics, which have reduced the costs of these renewable technologies, relative to carbon capture and storage (CCS). However, it remains an essential component of any strategy to react to this critical global problem. The Fifth Assessment report from the Intergovernmental Panel on Climate Change shows that the majority of their scenarios that limit CO₂ concentrations to 500ppm require CCS to be part of the solution[4]. This report dates back to 2014 and since then, coal has continued to decline globally in prominence as a source of energy that might require this solution. However, CCS can still play a role in those countries which are heavily dependent upon coal[5]. Further, CCS will still be required for mitigating emissions from natural gas combustion, cement and steel production; and for the purification of biogas. Carbon capture will increasingly be used to generate pure CO₂ for chemical production, replacing fossil fuel resources and can also be utilised in microalgal culture to generate transport fuels.

A ‘hydrogen economy’ is also emerging globally which will require the production of large volumes of hydrogen for manufacturing and transport. While ultimately, this hydrogen can be produced through the electrolysis of water, production from coal or natural gas, with concurrent storage of the CO₂ is a likely interim measure. As one example, the Hydrogen Energy Supply Chain is a pilot project to produce hydrogen from Australian brown coal for export to Japan[6]. This requires ‘pre-combustion’ capture of CO₂, with this gas then stored underground.

2. Materials Development

There are thousands of articles in the scientific literature that describe the development of new materials for these carbon capture applications[7-9]. These articles tend to espouse their ability to leap the Robeson’s bound[10, 11], a tradeoff relationship between membrane permeability and selectivity as the basis for their novelty. However, on its own, this is a very poor criterion for success. The upper bound is based on pure gas permeabilities, rather than those of the

complex multicomponent mixture typical of flue gases. The other components in the gas stream can have a substantial impact upon performance through competitive sorption, plasticisation and concentration polarisation. In particular, the gas stream is almost inevitably saturated with water vapor. This is a highly condensable and mobile gas which permeates much faster than CO₂ and is thus a controlling factor in the performance of many systems.

Further, the performance of a glassy membrane, or a facilitated transport membrane is a function of the system pressure. The Robeson's bound was originally developed for pure gases tested at the standard laboratory conditions of 35°C and 10 Bar. These conditions are not representative of either post combustion capture (where CO₂ partial pressures are typically 0.1 Bar) or pre-combustion capture (CO₂ partial pressures of 20 Bar). As one example, facilitated transport membranes can readily overcome the bound at low CO₂ partial pressures, as they contain reactive groups which react with CO₂ to provide a rapid transport pathway, while other gases such as N₂ and H₂ can only pass via a solution diffusion mechanism. However, at higher partial pressures the reactive 'carrier' groups embedded in the membrane become saturated and so the CO₂ permeance and selectivity regresses towards the lower values provided by solution diffusion.

Another issue is that the Robeson's bound focuses on permeability, whereas the true process parameter of interest is the permeability divided by the membrane thickness[12]. A membrane with a permeability of 100 Barrer is ten times better than one of 1000 Barrer if the former can be readily processed into a film of 0.1 micron, while the latter can only be formed into a film of 10 micron. The ability to readily form defect free, mechanically robust thin films at industrial scale is a critical development needed for successful commercialisation of any membrane material.

It should further be recognised that it takes significant funding resources and many years of effort for any such material to gain commercial success. For this reason, only a handful of materials have been commercialised for carbon dioxide separation. The original membranes were prepared from cellulose triacetate, with polysulfone and polyimides emerging later. It is pleasing to see new entrants to this market in recent years, including polyether ether ketone (PEEK) membranes marketed by Air Liquide[13] and the polar rubbery membranes marketed by MTR as Polaris[14]. However, it is the process engineering of the capture plant, including any upstream pretreatment operations, that can have a much greater impact on the cost of capture. These developments form the focus of this paper.

3. Post Combustion Capture

Post combustion capture refers to the removal of CO₂ from flue gases downstream of either natural gas or coal combustion. There have been a number of recent review papers in this area, specifically those from Wang et al.[15] and Khalilpour et al. [16]. In this section, we consider gas separation membranes for this process, which follow the solution diffusion model (Equation 1).

$$J = \wp(p_f - p_e) \quad \text{Eq. 1}$$

Where J represents the volumetric CO₂ flux, $\wp$ is the membrane permeance and p_f and p_e represent the CO₂ partial pressure on the feed and retentate sides.

3.1 Partial Pressure driving Force Implications

A significant disadvantage in post combustion capture is the low total pressure of the flue gas stream (approximately atmospheric), relative to natural gas purification, where the total pressure is usually in excess of 40 Bar. It is feasible to use a blower to increase the pressure to around 150 KPa absolute. However, beyond this pressure a compressor is required. Given the very large feed gas volumes, this requires a significant capital cost as well as energy demand[17]. Many workers instead argue that it is more economic to reduce the pressure of the much smaller permeate stream using a vacuum pump such as a liquid ring system[17-19] (see Figure 1). Conversely, Belaissaoui et al.[20] show that if the pressure energy of the retentate stream can be recovered downstream using a turbo expander, feed compression to around 10 Bar can be more effective than the use of permeate vacuum for feed CO₂ concentrations of > 12 vol%. They conclude that both approaches lead to comparable energy requirements, but the membrane area is much smaller if feed compression was used. Indeed, Giordano et al.[21] show that the membrane area requirement for feed compression is only 20% of that required for vacuum pumping.

Even with feed compression to 15 Bar and the use of a permeate vacuum, the CO₂ partial pressure driving force ($p_f - p_e$).for a coal combustion flue gas of 15 vol% CO₂ is limited to around 2 bar. The process is constrained by this limited transmembrane pressure drop. As more CO₂ crosses the membrane in preference to other components (i.e. a high membrane selectivity), the CO₂ partial pressure on the permeate side (p_e) increases. In turn this reduces the partial pressure driving force for more mass transfer and hence the membrane flux (J). As shown in Figure 1, this means that CO₂/N₂ selectivities greater than 50 are of little or no value

to the process, a fact confirmed by many workers[18-20]. There is value in increasing membrane permeability but even here, there are diminishing returns as this permeability increases[17, 18].

Figure 1. Capture cost as a function of CO₂/N₂ selectivity for a high pressure single membrane stage (SMS) and for different vacuum membrane systems: Single membrane system (SMS) and a two stage two-stage cascade membrane system (TCMS). Reproduced with permission from Ho et al. [17]. Copyright (2008) American Chemical Society.

A further important recognition from this type of analysis is that the presence of water vapor in the flue gas stream is not necessarily a disadvantage when a permeate vacuum is used[18, 22]. Water is always more permeable than CO₂ and so it will tend to build in concentration within the permeate. The vacuum pump is limited only by the total feed pressure, usually to a minimum value of around 10 kPa. If no water vapor is present and the membrane has high CO₂/N₂ selectivity, the permeate may be essentially 10 kPa CO₂. However, if water vapor permeates, the flow to this pump may be 9kPa of water vapor and 1 kPa of CO₂. This increases the partial pressure driving force for CO₂ permeation and in turn, the membrane flux.

Hasse et al.[23] use an alternate type of sweep to overcome these partial pressure limitations in the absence of water vapour. In their case, they divert a small fraction (< 5% of the nitrogen-rich retentate into the permeate chamber of a hollow fibre membrane module. This reduces the partial pressure of CO₂ at this end of the exchanger (Figure 2).

Figure 2. A two dimensional axisymmetric computational fluid dynamics simulation of an Air Liquide hollow-fiber membrane module showing the CO₂ partial pressure difference along the module axial length. when a 2.5% sweep of retentate into the permeate is used. The partial pressure difference is color coded with the warmest colors (red) indicating the highest values and blue indicating the lower values. Reproduced under a Creative Commons License from Hasse et al. [23].

The advantages of vacuum permeate pumping are also lost if there is a significant pressure drop along the length of the membrane module on the permeate side, as the vacuum reduces along this length. This significantly constrains the design of the membrane module. While hollow fibre membranes offer the greatest membrane area per unit volume when used in natural gas separation, the fibre diameter and interfibre spacing required to minimise these pressure drops eliminates any such advantage in post-combustion capture[24]. Salim et al. [25] achieved pressure drops of less than 7 kPa per metre on the feed side and 9kPa per metre on the permeate side by using a spiral wound membrane module with a thicker permeate spacer (0.5 mm) compared to the feed spacer (0.25 mm), but even this permeate side pressure drop is probably too high for an effective process at scale.

The CO₂ concentration downstream of natural gas combustion is only around 4 vol%, giving a CO₂ feed partial pressure (p_f) of only 4 kPa absolute. This low feed partial pressure means that the use of gas separation membranes in post combustion here is extremely difficult, as the driving force is very limited[26]. Conversely, the CO₂ concentration in the flue gas from a cement plant is significantly higher than in coal combustion, typically 30 vol%. Membrane processes such as those described above are thus more prospective and can readily compete with solvent absorption[27]. However, in this instance calcium looping[28], or the use of an indirect fired kiln[29] are also options that may provide better economics.

3.2 Integration with Cryogenic Purification

Due to the partial pressure limitations described above, it is impossible to achieve a high CO₂ purity from a single stage membrane operation. Instead, many workers[20, 23, 30, 31] consider the use of downstream cryogenic operation to provide the required CO₂ purity, while also delivering a product suitable for compression and storage. The heat integration in one such cryogenic operation was recently optimised by Lee et al.[32], who claim that this approach can achieve a capture cost of US\$45 per tonne of CO₂ on a 2019 cost base, but with 29% of the power station output needed for the capture process.

Hasse et al.[23] make use of cryogenic temperatures to improve the separation performance of the membrane unit itself. By operating at subzero temperatures, they can increase membrane selectivity by 2 to fourfold with little change in permeance. Their process flowsheet incorporates a single membrane stage operating at -30°C with the total energy footprint minimised through both heat and pressure recovery. Cryogenic separation is again used downstream of the membrane to achieve the necessary CO₂ purity. However, due to the use of sub-ambient temperatures, water vapor must be removed upstream.

3.3 Combustion Air Sweep

Merkel and co-workers was the first to identify that the air fed to the coal boiler could be used as a 'sweep gas' to remove some of the flue gas CO₂ (Figure 3) in a second membrane stage (Stage II in Figure 3)[18]. In turn, this increases the CO₂ concentration in the flue gas, which increases the driving force across the first stage (Stage I), which is operated with a vacuum permeate. A disadvantage of this process is that it reduces the oxygen content within the boiler, which may impact boiler performance. This reduction in oxygen occurs because of the addition of CO₂, but also because of some transfer of oxygen from the air sweep into the flue gas in Membrane Stage II. This loss of oxygen can be compensated by using oxygen enriched air, with an air separation membrane used on the inlet air to achieve these higher oxygen concentration[33, 34]. However, such modifications to both the air intake and the boiler itself can be difficult to implement if the capture operation is retrofitted to an existing power plant, rather than a greenfield operation. A further issue is that the standard spiral wound membranes cannot be used with a sweep gas, as there is no inlet port on the permeate side. This requires a modified design to be developed[35], similar to the designs which have been commercialised for forward osmosis in water treatment applications[36].

Merkel et al.[18] also identified that cryogenic separation could be readily used downstream to further separate other gases from the CO₂, so that the final product achieved the United States Department of Energy targets of 95% purity and 90% recovery. Their 2010 paper indicated that the combined process could achieve these targets using about 16% of plant energy at a cost as low as US\$23/ton CO₂. However, Zhai and Rubin[37] calculate significantly higher costs for a system with an air sweep but no cryogenic step, with a range from US\$52 to \$56 per tonne of CO₂ avoided in their 2013 paper.

Figure 3. Simplified flow diagram of a two-step counter-flow/sweep membrane process to capture and sequester CO₂ in flue gas from a coal-fired power plant. Reproduced with permission from Merkel et al. [18]. Copyright (2010) Elsevier.

3.4 The impact of Water Vapor

As discussed above, the presence of water vapor in a post combustion flue gas can be advantageous in providing a permeate pressure under vacuum conditions. The high water vapor content in post-combustion capture is also favourable for facilitated transport membranes, where the membrane must remain wet for the reactive carriers to be active. The group at Ohio State University have tested 1.4 m² spiral wound membranes on a coal derived flue gas, achieving 1450 GPU CO₂ permeance and 185 CO₂/N₂ selectivity at 67 °C with feed and permeate pressures of 4 and 0.3 atm, respectively[38]. However, these type of membranes

usually rely on the reactivity of amine groups[39] and these can be poisoned by SO₂ concentrations in the flue gas, which reduces performance over time[40].

While water vapor has these advantages, the vapor can significantly reduce the permeability of CO₂ in traditional gas separation membranes through competitive sorption and/or pore blocking mechanisms; while it can reduce selectivity through plasticisation. Further, the permeation of water through the membrane generates a highly corrosive mixture of CO₂ and water in the permeate, which can lead to the use of much more expensive, corrosion resistant materials downstream. This can add substantially to capital costs, particularly for the rotating equipment. The development of large scale vacuum pumps that are able to handle wet CO₂ gas streams and to produce a strong vacuum are not trivial tasks at scale. Similarly, the downstream compression train is likely to be more expensive if the CO₂ gas stream is wet. This means that there will be situations where it will be more effective to remove the water upstream.

3.5 Hybrid Systems

Some workers have considered the use of a membrane unit to concentrate the CO₂ upstream of a solvent capture plant (Figure 4)[41-43]. This approach can reduce the capital cost of the solvent plant – the column diameter is reduced by the smaller gas volume and the height reduces due to the increased mass transfer driving force. However, the fundamental energy demand of the solvent process does not change significantly, as this is based on the reaction of a certain number of CO₂ molecules with the solvent. Concentrating the flue gas does not change the number of molecules and hence the solvent flowrate and the operating cost for reboiling does not change significantly. While there are the savings in solvent plant capital cost, these costs are offset by the capital and operating costs for the blower, compressor and/or vacuum pump required to move the flue gas through the membrane. This means that such a hybrid approach is unlikely to be economic.

A collaboration between the University of Texas at Austin and MTR have also considered the use of a membrane unit in parallel with the solvent plant, or downstream of this plant[44]. This group again concluded that neither option is cheaper than a standalone solvent capture operation. Further, a hybrid operation is operationally more complex, likely to have a larger footprint and require a longer and more complex installation process[45].

Figure 4 Schematic and picture of a hybrid membrane/solvent absorption CO₂ capture unit, as tested on a 0.1 MW coal fired boiler. Reproduced with permission from Frimpong et al. [41]. Copyright (2019) Elsevier.

4. Pre Combustion Capture

Coal or natural gas can be converted to a mixture of CO, CO₂ and hydrogen known as syngas through steam reforming or partial oxidation. A water gas shift(WGS) reaction is then used to react the CO with water vapor to produce more hydrogen and CO₂. In pre-combustion capture, this gas mixture is then separated, with the hydrogen being combusted or used in downstream chemical production, while the CO₂ is sequestered.

It is possible to use both membranes that are CO₂ selective or hydrogen selective in these applications. CO₂ selective membranes can have application when very high purity hydrogen is required[12] or where there is a need to retain the hydrogen component at high pressure[46]. However, it is generally now accepted that hydrogen selective membranes offer greater potential and the remainder of this section focuses on this approach.

Membranes have an advantage over solvents such as Selexol or Rectisol in that they can operate at higher temperatures (up to 500°C), avoiding the need to cool the gas[47, 48]. Further, if the gas is kept hot, it can also contain more water vapor. If a polymeric membrane is used, this vapor permeates with the hydrogen and adds mass to the feed stream to the turbine, which improves turbine efficiency[47]. A nitrogen sweep gas can also be used on the permeate side to increase the partial pressure driving force for hydrogen permeation and to add even more mass to the turbine feed. The CO₂ is also maintained at pressure (40 – 60 Bar) which reduces the energy required to compress this stream for downstream sequestration.

Palladium based membranes have been tested for this application for a number of decades due to their very high selectivity towards hydrogen[49-56]. An issue has been achieving a leak free connection to the connecting piping, but this issue now appears resolved[57]. Shell and CRI/Criterion have tested palladium membranes for up to one year producing hydrogen at greater than 99 mol% purity at 430 °C[48]. However, one analysis suggests that there is insufficient palladium reserves worldwide for large scale deployment of these membranes[58]. SRI International has tested polybenzimidazole based polymeric hollow fibre membranes, developed at Los Alamos National Laboratory[59], for pre-combustion capture at up to 225°C and 14 Bar transmembrane pressure, using 23 kg/hr of coal derived syngas, achieving H₂/CO₂ selectivities of up to 40[60]. This company estimates a capture cost of under US\$40, versus US\$52 per tonne of CO₂ captured for a standard Selexol solvent based capture process.

Air Liquide has also commercialised hydrogen selective polyimide membranes to treat the off-gas from a pressure swing adsorption (PSA) unit placed downstream of a steam reformer[61, 62]. Compression and cryogenic distillation generates high pressure liquid CO₂, while the membranes operate on the non-condensed gas, allowing the permeated hydrogen to be recycled to the PSA unit.

A further advantage in pre-combustion capture occurs if the membrane is incorporated into either the steam reforming reactor of a natural gas process (Figure 5 (a)), or the water gas shift reactor of a coal or natural gas process (Figure 5 (b)). These approaches draw the hydrogen away from the reaction zone and thus shift the equilibrium further towards a mixture of CO₂ and H₂, increasing the conversions that can be achieved. A recent article by Pichardo et al.[63] suggests that the incorporation of these membrane reactors into a standard coal Integrated Gasification Combined Cycle (IGCC) operation with CCS produces 2.2% more power, with lower capital cost. However, operating costs increase significantly, primarily due to the cost of replacement membranes. Other workers have shown that the use of membrane reactors can produce a slightly lower cost of electricity, relative to a Selexol absorption process[64, 65].

Figure 5. Working principle of hydrogen membrane reactors for CO₂ capture. A (a) membrane reformer and (b) membrane water gas shift. The open circles represent catalyst particles. Reproduced under a Creative Commons License from Dijkstra et al. (2011) [66].

There are an increasing number of publications that describe a Sorbent Enhanced Water Gas Shift Reactor (SEWGS) where an adsorbent is combined with the WGS shift catalyst, to remove CO₂ and other acidic gas components as they form, thus again shifting the WGS equilibria. Some workers have combined the SEWGS with a hydrogen selective membrane to simultaneously remove both hydrogen and CO₂ from the reaction zone, but this approach has not proved successful to date (see Figure 6)[67, 68].

Figure 6. A schematic representation of a sorption enhanced water gas shift (SEWGS) reactor with a hydrogen selective membrane reactor. Reproduced with permission from García-García et al. [68]. Copyright (2014) Elsevier.

5. Membrane Contactors

Membrane gas absorption (MGA) is a form of solvent absorption, but where a membrane replaces a packed column in providing the mass transfer contact area between the gas and the solvent. The membrane is porous and if the pores are gas filled, it offers little resistance to mass transfer – it serves only to separate the gas and liquid phases. This approach has been shown to significantly reduce the capital cost of absorption, due to the high mass transfer area per unit volume[69, 70], but does not generally influence operating costs. The approach was

first trialled at pilot scale for CO₂ separation from a natural gas stream around 20 years ago, using porous PTFE membranes[71, 72]. A significant issue identified during this trial was controlling the pressure difference between the gas and the liquid side. Variations in this pressure cause either the gas to bubble through the liquid solvent, or for the liquid to fill the pores of the membrane. Pore wetting is of particular importance, as once the pores are wet, the mass transfer resistance for CO₂ transfer increases by orders of magnitude. Further, it is very difficult once the pores are wetted, for this to be reversed. While pore wetting was exacerbated in these early pilot trials by the very large pressure difference between the natural gas and the solvent, many other authors have noted similar issues. In our own pilot scale trials, we were unable to control this pressure drop during the start-up period even with lower pressure flue gases and hence pore wetting commenced even before steady state had been achieved[73, 74].

The use of an ultrathin non-porous layer on top of the porous layer has been used to reduce the impact of the pore wetting issue. The non-porous layer adds a mass transfer resistance, but this is minimal if the film is thin. The non-porous layer prevents solvent intrusion, particularly during process startups and upsets. However, pore wetting can still occur by water vapor permeating through the non-porous layer and condensing within the porous support[75]. To avoid this latter affect, the support layer must be hydrophobic and have large pores to reduce the capillary pressures that drive water condensation [76, 77].

The Gas Technology Institute have used a porogen-based process that generates a porous membrane with very small pores (~20nm) at the membrane surface [78, 79]. Further, the membrane is coated with a perfluoro oligomer that generates superhydrophobicity[80]. These poly(ether ether ketone) (PEEK) hollow fiber membranes have been tested for gas absorption at a pilot scale equivalent to 0.5MW electricity generation from coal [80]. However, some water vapor capillary condensation was still observed[81].

Much less attention has been paid to the use of membrane contactors to replace the stripping column, where CO₂ is removed from the solvent [75, 82]. Importantly, the use of a partial vacuum in this format may reduce the regeneration energy demand by up to 20%, relative to a standard packed column[83]. The Gas Technology Institute trials successfully tested their PEEK membranes for desorption at pilot scale at 104°C and with a transmembrane pressure drop of 4 Bar[80].

While most work has focused on the use of membrane contactors in post-combustion capture, these can also be used in pre-combustion capture[74, 84]. However, the need for elevated

temperatures here make these less attractive. While many membrane materials can handle temperatures of up to 300°C, it is difficult to find the adhesives needed for this temperature range[74].

6. Concluding Remarks

For membrane technology to be successful in flue gas carbon capture, effective process design, such as that described above, is key. The focus in the scientific literature is currently too heavily biased towards materials synthesis, when so very few materials will ever become commercial. What is needed instead is effective techno-economic analysis of process flowsheets, optimised design of membrane modules and pilot scale assessment of each design using real flue gas streams. Consideration needs to be given to how this design will change for a retro-fitted plant versus a greenfield installation and how the presence of water vapor in the acidic gas streams will affect the cost and design of the rotating machinery that is needed for large scale capture.

References

- [1] P. D, Membrane CO₂ separation proves out at SACROC tertiary recovery project, *Oil and Gas Journal*, (1984) 85-88.
- [2] P.H.M. Feron, A.E. Jansen, Capture of carbon dioxide using membrane gas absorption and reuse in the horticultural industry, *Energy Convers. Manage.*, 36 (1995) 411-414.
- [3] P.W.F. Riemer, W.G. Ormerod, International perspectives and the results of carbon dioxide capture, disposal and utilisation studies, *Energy Convers. Manage.*, 36 (1995) 813-818.
- [4] R.P.-M. Edenhofer O., Y. Sokona, S. Kadner, J. C. Minx, S. Brunner, S. Agrawala, G. Baiocchi, I. A. Bashmakov,, J.B. G. Blanco, T. Bruckner, M. Bustamante, L. Clarke, M. Conte Grand, F. Creutzig, X. Cruz-Núñez, S. Dhakal, N. K., P.E. Dubash, E. Farahani, M. Fischedick, M. Fleurbaey, R. Gerlagh, L. Gómez-Echeverri, S. Gupta, J. Harnisch, K., F.J. Jiang, S. Kartha, S. Klasen, C. Kolstad, V. Krey, H. Kunreuther, O. Lucon, O. Masera, Y. Mulugetta, R. B. Norgaard, A., N.H.R. Patt, K. Riahi, J. Roy, A. Sagar, R. Schaeffer, S. Schlömer, K. C. Seto, K. Seyboth, R. Sims, P. Smith, E. Somanathan,, C.v.S. R. Stavins, T. Sterner, T. Sugiyama, S. Suh, D. Ürge-Vorsatz, K. Urama, A. Venables, D. G. Victor, E., D.Z. Weber, J. Zou, and T. Zwickel, Technical Summary, in: O. Edenhofer, R. Pichs-Madruga, Y. Sokona, E. Farahani, S. Kadner, K. Seyboth, A. Adler, I. Baum, S. Brunner, P. Eickemeier,, J.S. B. Kriemann, S. Schlömer, C. von Stechow, T. Zwickel and J. C. Minx (Eds.) *Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA., 2014.
- [5] O. Edenhofer, J.C. Steckel, M. Jakob, C. Bertram, Reports of coal's terminal decline may be exaggerated, *Environmental Research Letters*, 13 (2018) 024019.
- [6] H.E. Australia, *Hydrogen Energy Supply Chain*, in, 2019.
- [7] E.P. Favvas, F.K. Katsaros, S.K. Papageorgiou, A.A. Sapalidis, A.C. Mitropoulos, A review of the latest development of polyimide based membranes for CO₂ separations, *React. Funct. Polym.*, 120 (2017) 104-130.
- [8] X. Gong, Y. Wang, T. Kuang, ZIF-8-Based Membranes for Carbon Dioxide Capture and Separation, *ACS Sustainable Chem. Eng.*, 5 (2017) 11204-11214.

- [9] D.F. Sanders, Z.P. Smith, R. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B.D. Freeman, Energy-efficient polymeric gas separation membranes for a sustainable future: A review, *Polymer*, 54 (2013) 4729-4761.
- [10] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, *J. Membr. Sci.*, 62 (1991) 165-185.
- [11] L.M. Robeson, The upper bound revisited, *J. Membr. Sci.*, 320 (2008) 390-400.
- [12] K. Xie, Q. Fu, G.G. Qiao, P.A. Webley, Recent progress on fabrication methods of polymeric thin film gas separation membranes for CO₂ capture, *J. Membr. Sci.*, 572 (2019) 38-60.
- [13] A.L.A. Separations, *Membrane Technology*, in, 2019.
- [14] T. Merkel, E. Wagener, T. Wu, M. Zhou, J. Jin, J. Wheeldon, S. Thomas, A. Haldeman, S. Datta, H. Lin, V. Klep, S. Robert, A. Serbanescu, J. Vu, K. Amo, Novel Polymer Membrane Process For Pre-Combustion CO₂ Capture From Coal-Fired Syngas, in: N. U.S. Department of Energy (Ed.) Final Report Award Number DE-FE0001124, Membrane Technology and Research, Inc., 2011.
- [15] Y. Wang, L. Zhao, A. Otto, M. Robinius, D. Stolten, A Review of Post-combustion CO₂ Capture Technologies from Coal-fired Power Plants, *Energy Procedia*, 114 (2017) 650-665.
- [16] R. Khalilpour, K. Mumford, H. Zhai, A. Abbas, G. Stevens, E.S. Rubin, Membrane-based carbon capture from flue gas: a review, *Journal of Cleaner Production*, 103 (2015) 286-300.
- [17] M.T. Ho, G.W. Allinson, D.E. Wiley, Reducing the Cost of CO₂ Capture from Flue Gases Using Membrane Technology, *Industrial & Engineering Chemistry Research*, 47 (2008) 1562-1568.
- [18] T.C. Merkel, H. Lin, X. Wei, R. Baker, Power plant post-combustion carbon dioxide capture: An opportunity for membranes, *Journal of Membrane Science*, 359 (2010) 126-139.
- [19] C.A. Scholes, M.T. Ho, D.E. Wiley, G.W. Stevens, S.E. Kentish, Cost competitive membrane-cryogenic post-combustion carbon capture, *International Journal of Greenhouse Gas Control*, 17 (2013) 341-348.
- [20] B. Belaissaoui, Y. Le Moullec, D. Willson, E. Favre, Hybrid membrane cryogenic process for post-combustion CO₂ capture, *Journal of Membrane Science*, 415-416 (2012) 424-434.
- [21] L. Giordano, D. Roizard, R. Bounaceur, E. Favre, Evaluating the effects of CO₂ capture benchmarks on efficiency and costs of membrane systems for post-combustion capture: A parametric simulation study, *International Journal of Greenhouse Gas Control*, 63 (2017) 449-461.
- [22] B.T. Low, L. Zhao, T.C. Merkel, M. Weber, D. Stolten, A parametric study of the impact of membrane materials and process operating conditions on carbon capture from humidified flue gas, *Journal of Membrane Science*, 431 (2013) 139-155.
- [23] D. Hasse, J. Ma, S. Kulkarni, P. Terrien, J.-P. Tranier, E. Sanders, T. Chaubey, J. Brumback, CO₂ Capture by Cold Membrane Operation, *Energy Procedia*, 63 (2014) 186-193.
- [24] C.A. Scholes, A. Qader, G.W. Stevens, S.E. Kentish, Membrane pilot plant trials of CO₂ separation from flue gas, *Greenhouse Gases: Science and Technology*, (2015).
- [25] W. Salim, V. Vakharia, Y. Chen, D. Wu, Y. Han, W.S.W. Ho, Fabrication and field testing of spiral-wound membrane modules for CO₂ capture from flue gas, *Journal of Membrane Science*, 556 (2018) 126-137.
- [26] R.W. Baker, B. Freeman, J. Kniep, X. Wei, T. Merkel, CO₂ capture from natural gas power plants using selective exhaust gas recycle membrane designs, *International Journal of Greenhouse Gas Control*, 66 (2017) 35-47.
- [27] R.W. Baker, B. Freeman, J. Kniep, Y.I. Huang, T.C. Merkel, CO₂ Capture from Cement Plants and Steel Mills Using Membranes, *Industrial and Engineering Chemistry Research*, 57 (2018) 15963-15970.
- [28] C.A. Scholes, M.T. Ho, A.A. Aguiar, D.E. Wiley, G.W. Stevens, S.E. Kentish, Membrane gas separation processes for CO₂ capture from cement kiln flue gas, *International Journal of Greenhouse Gas Control*, 24 (2014) 78-86.
- [29] Calix, *A New Nano Technology*, in, 2009.

- [30] C. Song, Y. Sun, Z. Fan, Q. Liu, N. Ji, Y. Kitamura, Parametric study of a novel cryogenic-membrane hybrid system for efficient CO₂ separation, *International Journal of Greenhouse Gas Control*, 72 (2018) 74-81.
- [31] C. Song, Q. Liu, N. Ji, S. Deng, J. Zhao, Y. Li, Y. Kitamura, Reducing the energy consumption of membrane-cryogenic hybrid CO₂ capture by process optimization, *Energy*, 124 (2017) 29-39.
- [32] S. Lee, S. Yun, J.-K. Kim, Development of novel sub-ambient membrane systems for energy-efficient post-combustion CO₂ capture, *Applied Energy*, 238 (2019) 1060-1073.
- [33] R.W. Baker, J.G. Wijmans, T.C. Merkel, H. Lin, R. Daniels, S. Thompson, Gas separation process using membranes with permeate sweep to remove CO₂ from combustion gases, in, *Membrane Technology and Research Inc United States*, 2009.
- [34] C. Scholes, M. Ho, D. Wiley, G. Stevens, S. Kentish, Cost competitive membrane-cryogenic post-combustion carbon capture, *International Journal of Greenhouse Gas Control*, 17 (2013) 341-348.
- [35] L.S. White, K.D. Amo, T. Wu, T.C. Merkel, Extended field trials of Polaris sweep modules for carbon capture, *Journal of Membrane Science*, 542 (2017) 217-225.
- [36] G.Q. Chen, A. Artemi, J. Lee, S.L. Gras, S.E. Kentish, A pilot scale study on the concentration of milk and whey by forward osmosis, *Separation and Purification Technology*, (2019) 652-659.
- [37] H. Zhai, E.S. Rubin, Techno-Economic Assessment of Polymer Membrane Systems for Postcombustion Carbon Capture at Coal-Fired Power Plants, *Environmental Science & Technology*, 47 (2013) 3006-3014.
- [38] Y. Han, W. Salim, K.K. Chen, D. Wu, W.S.W. Ho, Field trial of spiral-wound facilitated transport membrane module for CO₂ capture from flue gas, *Journal of Membrane Science*, 575 (2019) 242-251.
- [39] X. He, A review of material development in the field of carbon capture and the application of membrane-based processes in power plants and energy-intensive industries, *Energy, Sustainability and Society*, 8 (2018) 34.
- [40] K. Ramasubramanian, W.S.W. Ho, Recent developments on membranes for post-combustion carbon capture, *Current Opinion in Chemical Engineering*, 1 (2011) 47-54.
- [41] R.A. Frimpong, B.D. Irvin, H. Nikolic, K. Liu, J. Figueroa, Integrated hybrid process for solvent-based CO₂ capture using a pre-concentrating membrane: A pilot scale study, *International Journal of Greenhouse Gas Control*, 82 (2019) 204-209.
- [42] C.A. Scholes, C.J. Anderson, R. Cuthbertson, G.W. Stevens, S.E. Kentish, Simulations of Membrane Gas Separation: Chemical Solvent Absorption Hybrid Plants for Pre- and Post-Combustion Carbon Capture, *Separation Science and Technology (Philadelphia)*, 48 (2013) 1954-1962.
- [43] P.K. Kundu, A. Chakma, X. Feng, Effectiveness of membranes and hybrid membrane processes in comparison with absorption using amines for post-combustion CO₂ capture, *International Journal of Greenhouse Gas Control*, 28 (2014) 248-256.
- [44] B. Freeman, P. Hao, R. Baker, J. Kniep, E. Chen, J. Ding, Y. Zhang, G.T. Rochelle, Hybrid Membrane-absorption CO₂ Capture Process, *Energy Procedia*, 63 (2014) 605-613.
- [45] B. Freeman, J. Kniep, R. Baker, T. Merkel, P. Hao, G. Rochelle, E. Chen, Y. Zhang, J. Ding, B. Sherman, Bench Scale Development of a Hybrid Membrane-Absorption CO₂ Capture Process, in: *CO₂ Capture Technology Project Review Meeting, National Energy Technology Laboratory (NETL), Omni William Penn Hotel, Pittsburgh, Pennsylvania*, 2018.
- [46] W. Salim, W.S.W. Ho, Hydrogen purification with CO₂-selective facilitated transport membranes, *Current Opinion in Chemical Engineering*, 21 (2018) 96-102.
- [47] G. Krishnan, D. Steele, K. O'Brien, R. Callahan, K. Berchtold, J. Figueroa, Simulation of a Process to Capture CO₂ From IGCC Syngas Using a High Temperature PBI Membrane, *Energy Procedia*, 1 (2009) 4079-4088.
- [48] P. Veenstra, M. Iyer, A. Nijmeijer, F. Geuzebroek, R. Moene, J. Saukaitis, Integrated Approach to CO₂ Capture: Fuel Gas Decarbonisation, *Energy Procedia*, 63 (2014) 2054-2059.

- [49] J. Boon, V. Spallina, Y. van Delft, M. van Sint Annaland, Comparison of the efficiency of carbon dioxide capture by sorption-enhanced water-gas shift and palladium-based membranes for power and hydrogen production, *Int. J. Greenhouse Gas Control*, 50 (2016) 121-134.
- [50] K.-R. Hwang, C.-B. Lee, S.-K. Ryi, J.-S. Park, Hydrogen production and carbon dioxide enrichment using a catalytic membrane reactor with Ni metal catalyst and Pd-based membrane, *Int. J. Hydrogen Energy*, 37 (2012) 6626-6634.
- [51] A. Iulianelli, A. Basile, H. Li, R.W. Van den Brink, Inorganic membranes for pre-combustion carbon dioxide (CO₂) capture, *Woodhead Publ. Ser. Energy*, 25 (2011) 184-213.
- [52] C.-H. Kim, J.-Y. Han, H. Lim, K.-Y. Lee, S.-K. Ryi, Methane steam reforming using a membrane reactor equipped with a Pd-based composite membrane for effective hydrogen production, *Int. J. Hydrogen Energy*, 43 (2018) 5863-5872.
- [53] P. Middleton, P. Hurst, G. Walker, GRACE: pre-combustion de-carbonisation hydrogen membrane study, in: Elsevier Ltd., 2005, pp. 409-425.
- [54] T.A. Peters, P.M. Roervik, T.O. Sunde, M. Stange, F. Roness, T.R. Reinertsen, J.H. Raeder, Y. Larring, R. Bredesen, Palladium (Pd) Membranes as Key Enabling Technology for Pre-combustion CO₂ Capture and Hydrogen Production, *Energy Procedia*, 114 (2017) 37-45.
- [55] C. Zhao, H. Xu, A. Goldbach, Duplex Pd/ceramic/Pd composite membrane for sweep gas-enhanced CO₂ capture, *J. Membr. Sci.*, 563 (2018) 388-397.
- [56] A.J. DeRosset, Diffusion of hydrogen through palladium membranes, *Ind. Eng. Chem.*, 52 (1960) 525-528.
- [57] A. Goldbach, F. Bao, C. Qi, C. Bao, L. Zhao, C. Hao, C. Jiang, H. Xu, Evaluation of Pd composite membrane for pre-combustion CO₂ capture, *Int. J. Greenhouse Gas Control*, 33 (2015) 69-76.
- [58] A. Helmi, F. Gallucci, M. van Sint Annaland, Resource scarcity in palladium membrane applications for carbon capture in integrated gasification combined cycle units, *Int. J. Hydrogen Energy*, 39 (2014) 10498-10506.
- [59] K.A. Berchtold, R.P. Singh, J.S. Young, K.W. Dudeck, Polybenzimidazole composite membranes for high temperature synthesis gas separations, *Journal of Membrane Science*, 415-416 (2012) 265-270.
- [60] I.S. Jayaweera, Development of Pre-Combustion CO₂ Capture Process Using High-Temperature Polybenzimidazole (PBI) Hollow-Fiber Membranes (HFMs), in: CO₂ Capture Technology Project Review Meeting, National Energy Technology Laboratory (NETL), Omni William Penn Hotel, Pittsburgh, Pennsylvania, 2018.
- [61] D. Pichot, L. Granados, T. Morel, A. Schuller, R. Dubettier, F. Lockwood, Start-up of Port-Jérôme CRYOCAP™ Plant: Optimized Cryogenic CO₂ Capture from H₂ Plants, *Energy Procedia*, 114 (2017) 2682-2689.
- [62] P. Terrien, F. Lockwood, L. Granados, T. Morel, CO₂ Capture from H₂ Plants: Implementation for EOR, *Energy Procedia*, 63 (2014) 7861-7866.
- [63] P.A. Pichardo, S. Karagöz, T. Tsotsis, R. Ciora, V.I. Manousiouthakis, Technical economic analysis of an intensified Integrated Gasification Combined Cycle (IGCC) power plant featuring a sequence of membrane reactors, *Journal of Membrane Science*, 579 (2019) 266-282.
- [64] J. Franz, P. Maas, V. Scherer, Economic evaluation of pre-combustion CO₂-capture in IGCC power plants by porous ceramic membranes, *Appl. Energy*, 130 (2014) 532-542.
- [65] M. Amelio, P. Morrone, F. Gallucci, A. Basile, Integrated gasification gas combined cycle plant with membrane reactors: Technological and economical analysis, *Energy Conversion and Management*, 48 (2007) 2680-2693.
- [66] J.W. Dijkstra, J.A.Z. Pieterse, H. Li, J. Boon, Y.C. van Delft, G. Raju, G. Peppink, R.W. van den Brink, D. Jansen, Development of membrane reactor technology for power production with pre-combustion CO₂ capture, *Energy Procedia*, 4 (2011) 715-722.
- [67] M. Marono, M.M. Barreiro, Y. Torreiro, J.M. Sanchez, Performance of a hybrid system sorbent-catalyst-membrane for CO₂ capture and H₂ production under pre-combustion operating conditions, *Catal. Today*, 236 (2014) 77-85.

- [68] F.R. García-García, M. León, S. Ordóñez, K. Li, Studies on water–gas-shift enhanced by adsorption and membrane permeation, *Catalysis Today*, 236 (2014) 57-63.
- [69] B.W. Reed, M.J. Semmens, E.L. Cussler, Membrane contactors, in: R.D. Noble, S.A. Stern (Eds.) *Membrane Separations Technology. Principles and Applications.*, Elsevier Science, New York, 1995.
- [70] P.H.M. Feron, A.E. Jansen, CO₂ separation with polyolefin membrane contactors and dedicated absorption liquids: performances and prospects, *Separation and Purification Technology*, 27 (2002) 231-242.
- [71] O. Falk-Pedersen, H. Dannström, Separation of carbon dioxide from offshore gas turbine exhaust, *Energy Conversion and Management*, 38 (1997) S81-S86.
- [72] H. Herzog, O. Falk-Pedersen, The Kvaerner Membrane Contactor: lessons from a case study in how to reduce capture costs, in: D.J. Williams, R.A. Durie, P. McMullan, C.A.J. Paulson, A. Smith (Eds.) *Fifth International conference on Greenhouse Gas Control Technologies: GHGT-5*, CSIRO Energy Technology, Cairns, Australia, 2001.
- [73] C.A. Scholes, A. Qader, G.W. Stevens, S.E. Kentish, Membrane Gas-Solvent Contactor Pilot Plant Trials of CO₂ Absorption from Flue Gas, *Separation Science and Technology (Philadelphia)*, 49 (2014) 2449-2458.
- [74] C.A. Scholes, M. Simioni, A. Qader, G.W. Stevens, S.E. Kentish, Membrane gas-solvent contactor trials of CO₂ absorption from syngas, *Chemical Engineering Journal*, 195-196 (2012) 188-197.
- [75] M. Simioni, S.E. Kentish, G.W. Stevens, Membrane stripping: Desorption of carbon dioxide from alkali solvents, *Journal of Membrane Science*, 378 (2011) 18-27.
- [76] C.A. Scholes, S.E. Kentish, G.W. Stevens, D. deMontigny, Asymmetric composite PDMS membrane contactors for desorption of CO₂ from monoethanolamine, *International Journal of Greenhouse Gas Control*, 55 (2016) 195-201.
- [77] C.A. Scholes, S.E. Kentish, G.W. Stevens, D. deMontigny, Comparison of thin film composite and microporous membrane contactors for CO₂ absorption into monoethanolamine, *International Journal of Greenhouse Gas Control*, 42 (2015) 66-74.
- [78] Y. Yuan, Y. Ding, Functionalized porous poly(aryl ether ketone) materials and their use, in, PoroGen LLC, 2007.
- [79] Y. Ding, B. Bikson, Preparation and characterization of semi-crystalline poly(ether ether ketone) hollow fiber membranes, *Journal of Membrane Science*, 357 (2010) 192-198.
- [80] S. Li, T.J. Pyrzynski, N.B. Klinghoffer, T. Tamale, Y. Zhong, J.L. Aderhold, S. James Zhou, H.S. Meyer, Y. Ding, B. Bikson, Scale-up of PEEK hollow fiber membrane contactor for post-combustion CO₂ capture, *Journal of Membrane Science*, 527 (2017) 92-101.
- [81] S. Li, T. Pyrzynski, N. Klinghoffer, T. Tamale, J. Aderhold, S.J. Zhou, H. Meyer, Pilot Test of a Nanoporous, Super-Hydrophobic Membrane Contactor Process for Post-Combustion CO₂ Capture, in: *CO₂ Capture Technology Project Review Meeting*, National Energy Technology Laboratory (NETL), Omni William Penn Hotel, Pittsburgh, Pennsylvania, 2018.
- [82] S. Khaisri, D. deMontigny, P. Tontiwachwuthikul, R. Jiratananon, CO₂ stripping from monoethanolamine using a membrane contactor, *Journal of Membrane Science*, 376 (2011) 110-118.
- [83] Z. Wang, M. Fang, Q. Ma, Z. Zhao, T. Wang, Z. Luo, Membrane Stripping Technology for CO₂ Desorption from CO₂-rich Absorbents with Low Energy Consumption, *Energy Procedia*, 63 (2014) 765-772.
- [84] A. Padurean, C.-C. Cormos, P.-S. Agachi, Pre-combustion carbon dioxide capture by gas–liquid absorption for Integrated Gasification Combined Cycle power plants, *International Journal of Greenhouse Gas Control*, 7 (2012) 1-11.