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Membrane Gas Separation Processes for CO_2 capture from Cement Kiln Flue Gas

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Abstract

The cement industry is a significant source of CO_2 emissions for the non-power sector. Carbon capture and storage has been proposed as a strategy to mitigate these CO_2 emissions. The high CO_2 partial pressure of the cement kiln flue gas enables more options than in other post-combustion capture scenarios. Here, three distinct process designs for membrane gas separation are simulated for the capture of CO_2 from cement kiln flue gas. The first design is based on a standard natural gas processing flowsheet and includes two membrane stages with a permeate recycle from the first stage. The second design uses a single membrane stage with downstream compression and cooling to achieve the necessary purity. The final design incorporates three membrane stages with similar downstream compression and cooling. It was found that the CO_2/N_2 selectivity of the membrane strongly influenced the performance of all three processes. The third design achieved the lowest energy demand of 1.2 MJ/kg of CO_2 captured for membranes with CO_2/N_2 selectivity above 50. Below a selectivity of 25 the second design with a single membrane stage had the lowest energy demand. However, a different trend was observed with cost of capture, where below a CO_2/N_2 selectivity of 25 the second design provided the lowest cost of capture while above this selectivity the first design was cheapest. This design could provide a cost of capture of US$ 74 per tonne of CO_2 avoided, based on current state-of-the art membrane permselectivity, which is competitive with solvent absorption carbon capture technologies. However, calcium looping and oxyfuel combustion would appear to have lower costs in this scenario.

Keywords: Membrane Gas Separation, Cement, post-combustion, Cost of Capture

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Introduction

The non-power industry sector is a significant source of global CO_2 emissions, of which the cement industry accounts for 5 – 7 % (IEA, 2009; Thambimuthu et al., 2005). There are two distinct sources of CO_2 associated with a cement kiln. The first is the result of the direct combustion of fossil fuels for heat energy which produces a flue gas of 4 to 15 vol% CO_2 depending upon the source of fuel. The second is the by-product of calcining of limestone to produce the clinker material (Hendriks et al., 1999), where stoichiometric quantities of carbon dioxide are produced according to the reaction:

$CaCO_3 \rightarrow CaO + CO_2$

Both of these sources emit roughly equal amounts of CO_2 per tonne of cement produced and therefore when combined generate a flue gas that is more concentrated in CO_2 than is generally found in the power generation industry (Thambimuthu et al., 2005). Typical total flue gas concentrations range from 22 to 28 mol%, with 900 kg of CO_2 emitted during production of 1000 kg of cement (Hassan et al., 2007).

A range of carbon reduction approaches has been proposed for the cement industry. These include improving efficiency and shifting to drier feed stocks, which reduce the CO_2 emissions per clinker produced, as well as changing to lower carbon fuels (Hendriks et al., 1999). Oxy-fuel firing of cement kilns is another approach that shows potential, as feeding pure O_2 to the cement kiln achieves an almost pure CO_2 flue gas (Bosoaga et al., 2009; IEA-GHG, 2008; Zeman and Lackner, 2006). This process however suffers from similar drawbacks to oxy-fuel firing of coal-fired power stations, in the form of extreme flame temperatures and the need for flue gas recycling. Carbon capture has also been proposed for the cement industry (Metz et al., 2005), which is analogous to post-combustion capture, given the low pressure of the flue gas. Reversible solvent absorption based on MEA has been applied to cement flue gas by Barker *et al*. (Barker et al., 2009), Hassan *et al*. (Hassan et al., 2007), and Ho *et al*. (Ho et al., 2011), while calcium looping technology has also been proposed by a number of authors (Bosoaga et al., 2009; Rodriguez et al., 2012; Romeo et al., 2011; Vatopoulos and Tzimas, 2012). The latter approach has the advantage that calcium oxide regeneration occurs within the cement kiln, because calcium carbonate is a clinker precursor.

To date, there is little in the literature on membrane gas separation technology being applied to cement flue gas, even though membrane technology has been considered for post-combustion capture from power station flue gas (Merkel et al., 2010; Scholes et al., 2013). Membrane gas separation is a conceptually simple process, where a semi-selective membrane allows one or more gases to pass through at the expense of other gases (Koros, 1991). This enables CO_2 to be

concentrated on one side of the membrane, and has the advantage of a smaller footprint than with other separation technologies. Importantly, the higher CO_2 partial pressure of the cement flue gas is advantageous for membrane-based carbon capture. Hence in this work, three process designs for membrane gas separation of cement kiln flue gas are simulated and compared with other carbon capture technologies in terms of energy demand and cost.

Simulation Methodology

The design basis is a 680,000 tonne per year cement kiln, with a combined flue gas of composition as shown in Table 1 (Hassan et al., 2007). The CO_2 mole fraction is approximately 22 %, which is almost double that from a pulverised coal fired power plant flue gas. It is assumed that the levels of SOx and NOx are below 20 ppm and hence these gases are not included in the simulation. All membrane processes are designed to ensure 90 % CO_2 recovery and produce a product purity of > 95 % CO_2 at 80 bar ready for transportation, in keeping with USA Department of Energy guidelines for CCS (Thambimuthu et al., 2005). As a result, the exit stream being vented to the environment always had a composition of N_2 > 94 mol% and CO_2 < 3 mol%.

All process simulations were undertaken with the Aspen HYSYS package, version 7.3, using the Peng-Robinson fluid package (AspenTech, USA) which provides the basis information for the total energy and cost calculations. The gas separation membrane process incorporated an in-house programmed module based on mass transfer equations, described in detail elsewhere (Chowdhury et al., 2005; Coker et al., 1998).

Membranes were operated under cross-flow conditions unless a sweep gas was applied in which case counter-current flow was used. All units were operated at their default parameters, with negligible pressure drop assumed for the piping; and compressors and turbo-expanders operating at 75 % efficiency. A pressure drop of 10 kPa was assumed across both sides of each membrane module and the heat exchangers. All membrane modules were assumed to operate at 35 ^{o}C. The CO_2 permeance of the membranes was set at 1000 GPU, while the CO_2 selectivity with respect to N_2 was varied. The O_2 permeability was assumed equal to that of N_2, which is reasonable given the low O_2 concentration, while the H_2O permeability was a factor of 100 greater than the CO_2 permeability, in keeping with the performance reported in the literature (Scholes et al., 2009). The membrane is assumed to be a polymeric composite with a thin active layer of thickness of 0.1 μm. A list of commercial gas separation membranes that have comparable performance to the CO_2 permeabilities and selectivities studied here is provided in Table 2.

Table 1

Table 2

Design 1 uses two membrane stages with a permeate recycle, as shown in Figure 1. A similar process is common in natural gas sweetening (Baker and Lokhandwala, 2008). The flue gas passes through a blower to ensure gas flow through the first CO_2-selective membrane stage. A vacuum of 22 kPa is applied to the permeate stream to generate the driving force across the membrane and CO_2 passes into the permeate stream, along with significant quantities of water. The majority of the N_2 and O_2 remain in the retentate side of the membrane and are vented to atmosphere. The use of a vacuum to generate the pressure difference has been shown to be the most cost effective approach for low pressure feed membrane systems (Ho et al., 2008). To achieve a high purity CO_2 product, the permeate stream from the first membrane stage is then passed through a second CO_2-selective membrane stage (of the same permselectivity as the first membrane stage). Again the pressure driving force is generated by vacuum on the second permeate stream. This concentrated CO_2 in the permeate stream is at high purity, while the retentate is recycled back to the flue gas feed to increase the CO_2 recovery. The final permeate stream is then compressed to 80 bar to produce transport ready CO_2. Heat exchangers are used to cool the gas with separator vessels removing liquid water from the process.

Figure 1

Belaissaoui *et al*. (Belaissaoui et al., 2012) has proposed a single stage membrane process with permeate cooling and compression that achieves high CO_2 recovery and purity for post combustion flue gases. Design 2 is a version of this approach, modified for cement flue gas (Figure 2). The CO_2-selective membrane stage is used to concentrate CO_2 in the permeate stream, achieving 90 % CO_2 recovery in this single step. The permeate then undergoes multi-stage compression and cooling stages to achieve the necessary pressure (106 bar) that allows liquid CO_2 of high purity to be produced upon flashing in the separator vessel. Water is removed from the permeate stream after the vacuum and first compression stages. To minimise cooling duty both the liquid CO_2 and off gases

from the separator (N_2 and O_2) are used in the cross heat exchanger economizers to reduce the temperature of the permeate gas after multi-stage compression. The final CO_2 product stream is compressed to 80 bar to ensure consistency across all three processes.

Figure 2

Design 3 replicates that proposed by Merkel *et al*. (Merkel et al., 2010), shown in Figure 3. This process used a membrane stage to concentrate CO_2 in the permeate stream and then similarly uses compression and cryogenic cooling to achieve the necessary purity. The key distinction in the Merkel process is the use of a second membrane stage on the retentate from the first membrane stage. This ensures high CO_2 recovery is possible by recycling the CO_2 permeate from the second membrane stage back through the process. Importantly, this stage uses air for the combustion process as a sweep gas to generate the pressure driving force across the membrane, which avoids the need for a vacuum pump. The sweep gas picks up CO_2 which is recycled through the cement kiln. This increases the CO_2 partial pressure in the flue gas and hence also improves the separation performance of the first membrane stage. To ensure high CO_2 recovery, the off gas from the liquefaction stage also passes through a third membrane stage, where the permeate stream is recycled to the start of the liquefaction process and the retentate recycled back to the flue gas feed. The use of this third membrane stage means that the level of compression (25 bar) is not as high as required in the Belaissaoui process (Figure 2). The CO_2 product stream is finally compressed to 80 bar for consistency with the other two processes.

An important parameter in Design 3 is the amount of CO_2 being recycled from the second membrane stage. In post-combustion capture from a coal-fired power station, the amount being recycled is limited to 9 % CO_2 in the combustion air, because of burner-boiler efficiency limitations in handling diluted O_2 partial pressure (Spliethoff, 2010). In the present case, this restriction is not enforced, and a range of CO_2 mole fractions in the air for combustion are allowed.

Figure 3

The cost of the process equipment was evaluated using Aspen Economic Evaluator package, 2010 1st Quarter, with default parameters. The membrane cost was assumed to be US$ 50/m^2, with an installation factor of 1.6 (Merkel et al., 2010). The total equipment costs were the sum of the individual unit operations (membrane process plus CO_2 compression), plus $10 million for flue gas pre-treatment, consisting of ash removal and cooling. In addition, a loading of 25 % for instrumentation, piping and electrical costs, plus an additional 13 % for engineering and start-up costs are included. To estimate the total capital cost (CAPEX), an additional 10 % is added as a project contingency. In the operating costs (OPEX), the cost of electricity is assumed as US$ 42 / kWh. Also included in the OPEX is a 5 year replacement period for all membranes and 6 % fixed costs that includes maintenance and labour.

The cost of CO_2 avoided (in 2010 dollars) is calculated using the Net Present Value (NPV) method, based on tonnes of CO_2 avoided. The use of tonnes of CO_2 avoided enables the emissions from the energy usage of the capture plant to be taken into account. The electricity source is assumed to be from an onsite coal power plant with an emission intensity of 1.1 t/MWh. The project life is 25 years, with a 2 year construction period, and a discount rate of 7 % (real). The economics do not take into account CO_2 transportation or final compression of the CO_2 product stream for sequestration. Full details of the economic methodology can be found in Ho *et al*. (Ho et al., 2008).

Results and Discussion

Design 1

A critical parameter for Design 1 is the stage-cut of both membranes stages and their interdependence to achieve the desired CO_2 recovery and purity. A large stage-cut in Membrane 1 results in a significant permeate stream flowrate and hence recycle. The large recycle increases the duty of the vacuum pump and blower, and so it is vital to operate Membrane 1 at the lowest possible stage-cut. The energy duty is independent of membrane selectivity. However there is a minimum CO_2 mole fraction in the recycle that enables Membrane 2 to produce the desired CO_2 purity, as clearly shown in Figure 4. For example, if Membrane 1 has a CO_2/N_2 selectivity of 15, it must operate at a stage-cut above 0.65, while for a CO_2/N_2 selectivity of 50, the Membrane 1 stage-cut must be above 0.38, to ensure enough CO_2 enters the permeate so as to enable Membrane 2 to achieve > 95 % purity in its permeate stream. The increase in CO_2 mole fraction required as a function of Membane 1 stage-cut is due to the exponential increase in recycle flowrate and as a consequence the recycling of significant amounts of CO_2 around Membrane 1.

Figure 4

The total membrane area of the process is shown in Figure 5. Over 90 % of the membrane area is associated with Membrane 1, and it is for this reason that area increases with increasing stage-cut, as Membrane 1 must process a greater flowrate. The increase in membrane area with membrane selectivity reflects the need to ensure more than 90 % recovery in the process. At high CO_2 permeate concentrations the driving force for CO_2 permeation through the membrane decreases, because at high selectivities the 22 kPa vacuum provides a CO_2 partial pressure that is comparable to the CO_2 partial pressure in the retentate. It is therefore necessary to increase the membrane area to ensure the desired CO_2 recovery is achieved. Dilution of the permeate stream by N_2, which occurs at low selectivities, ensures the CO_2 partial pressure in the permeate is reduced and increases the driving force across the membrane, reducing membrane area. Hence, to minimise recycle flowrate and membrane area it is optimal to operate the process at the lowest possible stage-cut for Membrane 1, while still obtaining the purity of the CO_2 product stream.

The energy breakdown of the process is shown in Figure 6. For a CO_2/N_2 selectivity of 25 the energy demand is 1.6 MJ/kg of CO_2 captured, which decreases to 1.25 MJ/kg of CO_2 captured for a CO_2/N_2 selectivity of 50. These energy duties are comparable to other membrane processes for post-combustion capture from coal-fired power station flue gas. For example, the energy demand of a membrane-cryogenic hybrid process similar to that of Design 3 is 1 to 1.9 MJ/kg of CO_2 capture, dependent on selectivity (Scholes et al., 2013). Importantly, the vacuum pump on Membrane 1 makes the largest contribution to the energy of the process at low CO_2/N_2 selectivities. Minimising this duty by operating at the lowest stage-cut ensures the smallest energy demand is achieved. The energy demand for the vacuum pump on Membrane 2 is essentially constant as it produces the 95 % CO_2 product stream, and hence is not influenced by the flowrate of the recycle stream. Compression of the final CO_2 product from 1 bar to 80 bar requires a significant amount of energy.

Figure 5

Figure 6

Design 2

The performance of Design 2 is dependent on the selectivity of the membrane, as this dictates the amount of N_2 and O_2 entering the permeate stream and hence the duty of the downstream compression stages, as well as the membrane area required to achieve the necessary CO_2 recovery. For a CO_2/N_2 selectivity of 5, the membrane stage is only able to produce a permeate stream of 35 mol% CO_2 and hence the downstream compression and cooling is responsible for the majority of the separation (Figure 7). In contrast for a CO_2/N_2 selectivity of 100, the permeate stream is 56 mol% CO_2, which is 2.5 times the concentration of the flue gas. Current state-of-the-art post-combustion membranes have a selectivity of 50 (Merkel et al., 2010), and applying this selectivity in the process results in a permeate of 53 mol% CO_2, excluding 77 % of the N_2 from the downstream compression process. The membrane area increases with membrane selectivity, similar to results for Design 1. This area varies between 1.2×10^4 and 8.5×10^4 m^2 for the selectivities studied here (Figure 7). Hence for a CO_2/N_2 selectivity of 25, Design 2 requires an area that is two thirds of that needed for Design 1 (Figure 5). However, with increasing CO_2/N_2 selectivity the required area approaches that of Design 1.

Figure 7

The energy duty of Design 2 decreases with increased membrane selectivity, because N_2 and O_2 concentrations in the permeate stream are reduced (Figure 8). The majority of the energy duty is associated with the downstream compressors. These account for between 55 and 60 % of the total energy demand of the process. The vacuum pump is the next biggest contribution and has the single largest energy demand per unit operation. Importantly, Belaissaoui *et al*. (2012) use a boost compressor – expander configuration that saves an additional 0.02 to 0.05 MJ/kg of CO_2 captured, dependent on membrane selectivity. The final CO_2 compression energy duty is lower than that required in Design 1, because the CO_2 product entering this stage is at 6 bar rather than 1 bar. The energy duty for Design 2 varies less with selectivity compared to Design 1. This is because the compressor duty is relatively insensitive to selectivity given the membrane process is focused on CO_2 recovery, while in Design 1 the duty of the first vacuum pump is dependent on the amount of N_2 being recycled, which is strongly dependent upon membrane selectivity, e.g. for a decrease in

selectivity from 50 to 15, the duty increases by 17%. Hence, below a selectivity of 32, Design 2 is more energy competitive compared to Design 1.

Figure 8

Design 3

One of the critical factors for Design 3 is the ability of the sweep gas to recycle CO_2 through the cement kiln and increase the CO_2 partial pressure of the flue gas. This produces a permeate stream exiting Membrane Stage 1 at a higher CO_2 concentration than is possible with just a single membrane stage (see Figure 9). Even at a CO_2/N_2 selectivity of 5, the permeate stream is at more than 84 % CO_2, which is a contrast to the 35 % CO_2 observed in the permeate stream in Design 2 (Figure 7). For membranes with selectivities above 100, the permeate stream is essentially a mixture of CO_2 and H_2O, which can achieve the desired CO_2 purity without the downstream cryogenic stage.

Figure 9

The membrane area is of a similar magnitude to that observed for Design 2 and less than that observed for Design 1. The majority of this area is associated with Membrane Stage 2, as it ensures high CO_2 recovery over the entire process and is dependent on the combustion air sweep gas to generate the partial pressure driving force, similar to that observed for the coal-fired power station study (Scholes et al., 2013). However, this process differs in that membrane area reduces with increasing selectivity. This is because the use of the sweep gas and subsequent recycle through the cement kiln overcomes the pressure driving force limitation observed in the other two processes. Hence, with Membrane stage 2 present, the overall area reduces as selectivity increases.

The energy duty of Design 3 is dependent on the amount of CO_2 being recycled into the combustion air supply (Figure 10). This is controlled by the stage-cut relationship between Membrane stages 1 and 2. Increasing the amount of CO_2 being recycled decreases the energy demand of the process by reducing the duty of the permeate vacuum pump and reducing the cooling duty of the cryogenic stage. Hence, it is more beneficial to operate Design 3 at a high CO_2 recycle level in the kiln air supply, 0.3 – 0.4 mole fraction for high membrane selectivities and 0.45 – 0.5 for low membrane

selectivities. Using these high CO_2 concentrations was also found to be beneficial in post-combustion capture from coal fired power station flue gas (Scholes et al., 2013). However, this will influence the combustion process and kiln temperature. Oxygen enrichment of the combustion air has been suggested to overcome this issue (Scholes et al., 2013) and in this case will add an extra 0.4 MJ/ kg of CO_2 captured to the energy duties reported here.

The energy duty breakdowns for Design 3 are provided in Figure 11 and are within the energy duty range reported by Scholes et al. (2013) for a coal fired power station flue gas capture with this design. Increasing the membrane selectivity reduces the compressor and vacuum pump duties considerably, because of the exclusion of N_2 and O_2 from the process units. Similarly, the cryogenic energy duty is reduced because there is less gas to cool. Importantly, the energy duty required to compress the final CO_2 product to 80 bar is almost negligible relative to the other energy duties, because the cryogenic process is operating at 25 bar. Hence, for current state-of-the-art membranes (selectivity = 50) the energy duty can be reduced to 1.3 MJ/kg of CO_2 captured.

Figure 10

Figure 11

Energy Duty and Economic Comparison

A comparison of the energy duty of the three processes (Figure 12) shows that for membrane selectivities greater than 25, Design 3 has the lowest energy duty, approaching 1.2 MJ/kg of CO_2 captured with increasing CO_2/N_2 selectivity. Interestingly, Design 1 is competitive only at around a CO_2/N_2 selectivity of 40. However, if Design 3 requires oxygen enrichment of the combustion air, then Design 1 is also competitive at selectivities above 25. Below a membrane selectivity of 25, Design 2 has the lowest energy duty at 1.4. MJ/kg of CO_2 captured. At these low selectivities there is a significant increase in the energy demand in Design 1 because large recycle rates are needed. Also, the energy demand increases for Design 3 because of the increase in cryogenic cooling duty.

Figure 12

All three membrane processes are competitive in terms of energy duty with other technologies applied to post-combustion capture from cement kiln flue gas. As the conversion efficiency of thermal energy to electrical energy is around 30 %, the thermal energy of the three designs varies from 4 to 4.7 MJ/kg. Traditional MEA solvent absorption of CO_2 from cement kiln gas has been estimated at a thermal energy demand of 3.7 – 4.4 MJ/kg of CO_2 captured as reported by Kuramochi *et al*. (Kuramochi et al., 2012), and 5 MJ/kg of CO_2 captured by Vatopoulos and Tzimas (Vatopoulos and Tzimas, 2012).

Conversely, the thermal energy demand for using calcium looping technology has been estimated at 2.7 MJ/kg of CO_2 captured (Vatopoulos and Tzimas, 2012), which is less than all three membrane processes studied here. The study by Vatopoulos and Tzimas (2012) reported oxy-combustion cement kiln firing to have a thermal energy demand that is even lower at 1 MJ/kg of CO_2 captured.

Economic evaluation of the three membrane processes was undertaken to enable further comparison and evaluation with other carbon capture technologies (Figure 13) and Table 3 summaries the capital and operating costs for Designs 1 to 3 at membrane selectivities of 50. Importantly, the reported costs of capture do not account for CO_2 transport, CO_2 storage or CO_2 compression at the injection site. They also do not include FGD or SGR pre-treatment costs. If FGD is required it will add an extra US$ 6 per tonne of CO_2 avoided to the costs of captured reported here and SGR will add an extra US$ 5 per tonne of CO_2 avoided, based on a SOx concentration of 390 ppm and a NOx concentration of 85 ppm.

The trends in capture costs deviate from the behaviour observed in energy duty. For membranes with CO_2/N_2 selectivity above 25, Design 1 provided the lowest cost of capture per tonne of CO_2 avoided. The lowest cost of capture was estimated at US$ 74 per tonne of CO_2 avoided for a membrane selectivity of 50. For membrane selectivity below 25, Design 2 provided the lowest cost of capture, between US$ 115 and 166 per tonne of CO_2 avoided. These costs are double the lowest observed for Design 1, highlighting the competitiveness of this approach for carbon capture from cement kiln flue gas. Design 3 always had a cost of capture greater than one of the other two processes.

Table 3

Figure 13

Design 1 was also found to be competitive compared to solvent absorption for this application provided membrane selectivities of greater than 40 are achieved. MEA solvent absorption for cement kiln flue gas is quoted by Barker *et al*. (2009) to have a cost of capture of US$ 140 per tonne of CO_2 avoided (€ 107.4 per tonne of CO_2 avoided) and by Ho *et al*. (2011) at US$ 68 per tonne of CO_2 avoided. However, it should be noted that the costs estimated by Ho et al. (2011) were for 2008 and the energy for capture was provided by a NGCC power plant. In contrast, Hassan *et al*. (Hassan et al., 2007) reported a MEA cost of capture of US$ 51 per tonne of CO_2 captured. However, Hassan *et al*. assumed that the MEA absorption process operated at extremely high solvent loadings. Reducing the loading to typical values increased the estimated cost of capture to about US$ 100 per tonne of CO_2 captured (Hassan, 2005). Unfortunately, Hassan *et al*. (2007) did not provide the energy penalty associated with CO_2 capture to enable a comparison of costs in terms of CO_2 avoided. These capture costs are considerably higher than those reported for post-combustion capture from coal-fired power stations (Scholes et al., 2013), the difference being due to the source of the electrical power. Rather than this power being generated on site, it is generated by a coal-fired power station. Hence, the coal-fired power station emissions partially offset the CO_2 captured, which impacts the cost of capture through the tonne of CO_2 avoided calculation.

Calcium looping technology has been demonstrated to be relatively cheap, reflecting the lower energy duty in this application. Romeo *et al*. (2011) reported a cost of capture of US$ 16.2 per tonne of CO_2 avoided (€ 12.4 per tonne of CO_2 avoided), Rodriguez *et al*. (2012) quoted a cost of capture of US$ 23 per tonne of CO_2 avoided, and Kuramochi *et al*. (2012) demonstrates calcium looping achieves a cost less than US$ 35 per tonne of CO_2 avoided (€ 27 per tonne of CO_2 avoided). These costs of capture are all less than those estimated for the membrane processes studied here. However, calcium looping technology is less mature than membrane technology and there are greater uncertainties in estimating the costs. Therefore, it could be expected that the cost may increase with time as all factors about the process are taken into account and further uncertainties are accounted for in the economic analysis.

For oxy-firing at cement plants, Kuramochi *et al*. (2012) reported a cost of US$ 57 per tonne of CO_2 avoided (€ 44 per tonne of CO_2 avoided), while Barker *et al*. (2009) provided a cost of US$ 52 per tonne of CO_2 avoided (€ 40.2 per tonne of CO_2 avoided). However, Rodriguez *et al*. (2012) reported a much lower value of US$ 16 per tonne of CO_2 avoided, for the same technology as they did not

include the cost for the cement plant refurbishment. Based on literature, the membrane processes evaluated here are not economically competitive at this membrane price with oxy-firing. However, as reported by the IEA-GHG (2008), retrofitting oxy-firing to existing cement plants would require significant rebuilding of the core units. Hence, oxy-firing may be a more suitable option for new build plants.

One of the largest uncertainties in the economic analysis is the membrane price, as to date no membrane module has been commercialized for flue gas capture. Merkel *et al*. (2010) suggest a price of US$ 50 /m^2 for post-combustion capture, while commercial membranes have a price of between US$ 5 and 200 /m^2, for reverse osmosis and natural gas sweetening respectively (Baker, 2002). As expected, decreasing the membrane price reduces the cost of capture (Figure 14). For Designs 2 and 3, these changes are small, reflecting the minor contribution of the membrane to both CAPEX and OPEX relative to the costs for compression and cryogenic refrigeration. The changes in cost are more substantial for Design 1 because of the large membrane areas required for this process. At a membrane price of US$ 5 / m^2, this process has a cost of capture of US$ 61 per tonne of CO_2 avoided, which is extremely competitive with MEA solvent absorption and also oxy-firing. However, if the membrane module price is more costly; above US$ 150 /m^2, the cost of capture increases substantially to US$ 130 per tonne of CO_2 avoided, higher than the capture cost for the other two membrane processes. For a membrane price above US$ 125 /m^2, Design 3 provides the lowest cost of capture for a membrane with CO_2/N_2 selectivity of 50.

Figure 14

Conclusion

Three process designs were evaluated for post-combustion CO_2 capture from a cement kiln flue gas using membrane technology. These were a process with two membrane stages and permeate recycle, a single membrane stage with permeate stream compression and cooling and a more complex approach with three membrane stages combined with compression and cooling. It was shown that the CO_2/N_2 selectivity of the membrane heavily influenced both the energy demand of the process as well as the economic competitiveness of each process design. In terms of energy demand, for CO_2/N_2 selectivities above 25 the most complex design with three membrane stages had the lowest duty. Below this selectivity the single stage approach gave the minimum energy demand. In terms of cost of capture, the membrane area had a significant impact on the viability of

each design. It was found that for membranes with CO_2/N_2 selectivity below 25, the single stage approach had the lowest cost of capture; while above this selectivity the process with two membrane stages had the lowest cost of capture. These membrane processes were found to be competitive with MEA sorption technology, but both calcium looping and oxyfuel firing would appear to have advantages in this environment.

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Table Captions

Table 1: Flue gas conditions and composition from a cement kiln (Hassan et al., 2007).

Table 2: CO_2 permeance and CO_2/N_2 selectivity of commercially available gas separation membranes (Merkel et al., 2010; van der Sluus et al., 1992).

Table 3: Summary of CO_2 capture costs for a membrane CO_2/N_2 selectivity of 50, with Design 1 having a stage cut of 0.38, and Design 3 having 0.33 mole fraction of CO_2 in combustion air.

Figure Captions

Figure 1: Schematic of Design 1, based on common natural gas separation flowsheets (Baker and Lokhandwala, 2008).

Figure 2: Schematic of Design 2, based on (Belaissaoui et al., 2012).

Figure 3: Schematic of Design 3, based on (Merkel et al., 2010).

Figure 4: The CO_2 mol fraction in the pemeate stream from Membrane 1 as a function of Membrane 1 stage-cut and CO_2/N_2 selectivity, for Design 1.

Figure 5: Total membrane area (m^2) of Design 1 as a function of Membrane 1 stage-cut and CO_2/N_2 selectivity.

Figure 6: Energy Demand (MJ/kg of CO_2 captured) of Design 1 as a function of membrane selectivity. The stage cut used was the lowest possible that allowed specifications to be met.

Figure 7: Membrane area and permeate CO_2 mole fraction for Design 2, as a function of membrane CO_2/N_2 selectivity.

Figure 8: Energy duty of Design 2 as a function of membrane CO_2/N_2 selectivity, with the relative contribution of each component shown.

Figure 9: Membrane area and permeate CO_2 mole fraction for Design 3, as a function of membrane CO_2/N_2 selectivity.

Figure 10: Energy duty (MJ/kg of CO_2 captured) of Design 3 as a function of the CO_2 mole fraction in the air feed for combustion, and as a function of membrane CO_2/N_2 selectivity.

Figure 11: Energy duty of Design 3 as a function of membrane CO_2/N_2 selectivity, with the relative contribution of each component shown. The CO_2 mol fraction in the combustion air was between 0.3 and 0.5 for the selectivities studied.

Figure 12: Energy duty (MJ / kg of CO_2 captured) comparison of the three designs as a function of membrane CO_2/N_2 selectivity.

Figure 13: Cost of Capture in US$ per tonne of CO_2 avoided for the three designs as a function of membrane CO_2/N_2 selectivity, for a membrane price of US$ 50 /m^2. The stage cut used in Design 1 was 0.38, while the CO_2 mol fraction in the combustion air for Design 3 was 0.33.

Figure 14: Cost of Capture in US$ per tonne of CO_2 avoided for the three designs studied here as a function of membrane price (US$ /m^2), for a membrane of CO_2/N_2 selectivity = 50. The stage cut used in Design 1 was 0.38 while the CO_2 mol fraction in the combustion air for Design 3 was 0.33.

Tables

Flowrate (kg/hr)	2.53×10^5
Temperature (^oC)	160
Pressure (kPa)	101.3
Composition	Mole fraction
CO_2	0.224
N_2	0.681
O_2	0.023
H_2O	0.072

Table 1

Supplier	Tradename	CO_2 Permeance (GPU)	CO_2/N_2 Selectivity
MTR	Polaris	1000	50
Delair		375	19
Ube	B-H	100	43
Air Products	Prism	61	31

Table 2

	Design 1	Design 2	Design 3
Energy penalty (MJe/kg captured CO_2)	1.25	1.35	1.3
Capital costs (US$ million)	55	47	64
Operating costs (including electricity) (US$million/yr)	11.4	17.7	14.9
$US/t CO_2 avoided	74	98	96

Table 3

Figures

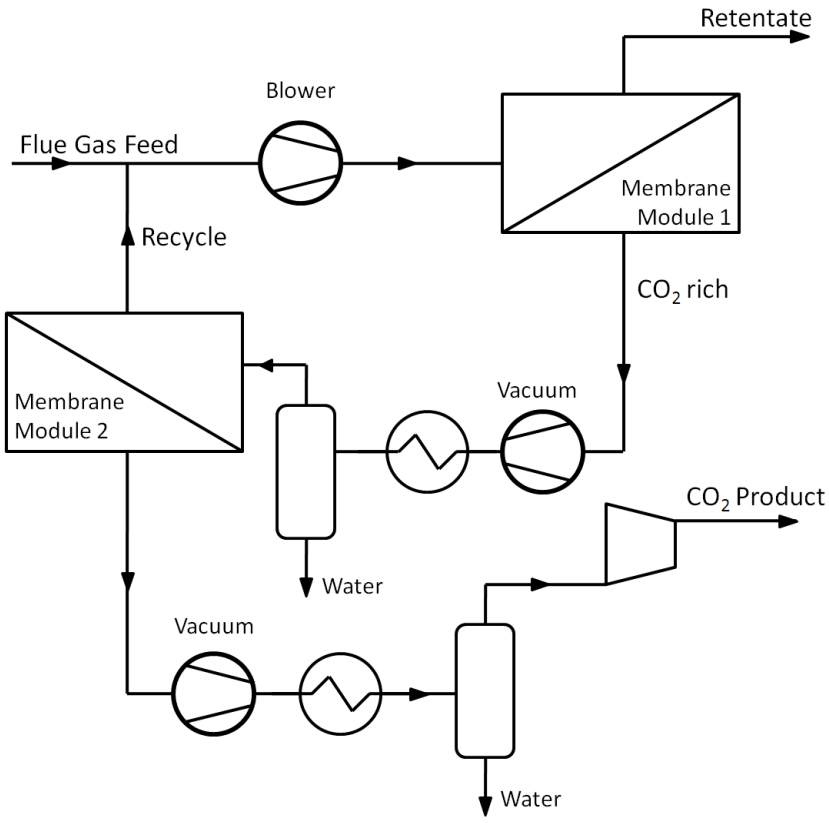

Figure 1

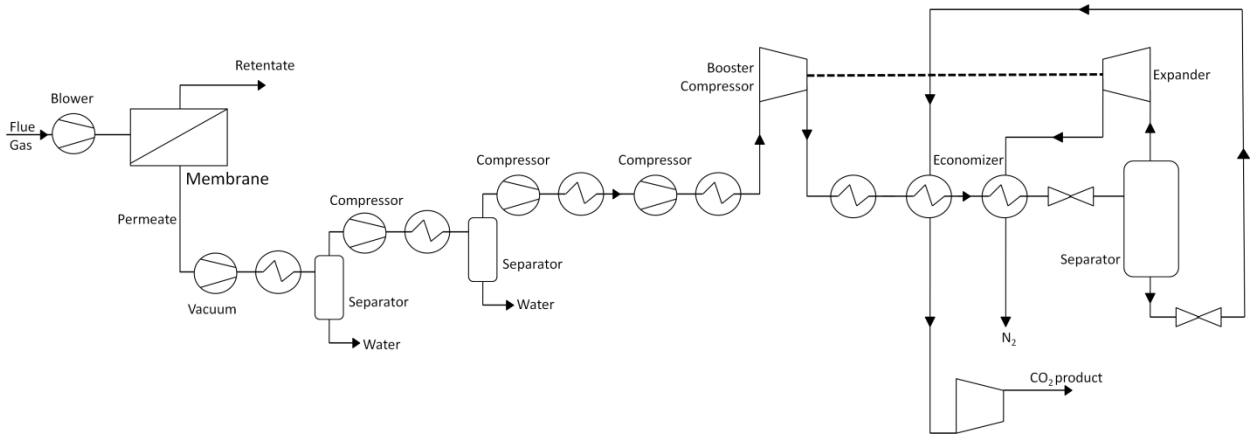

Figure 2

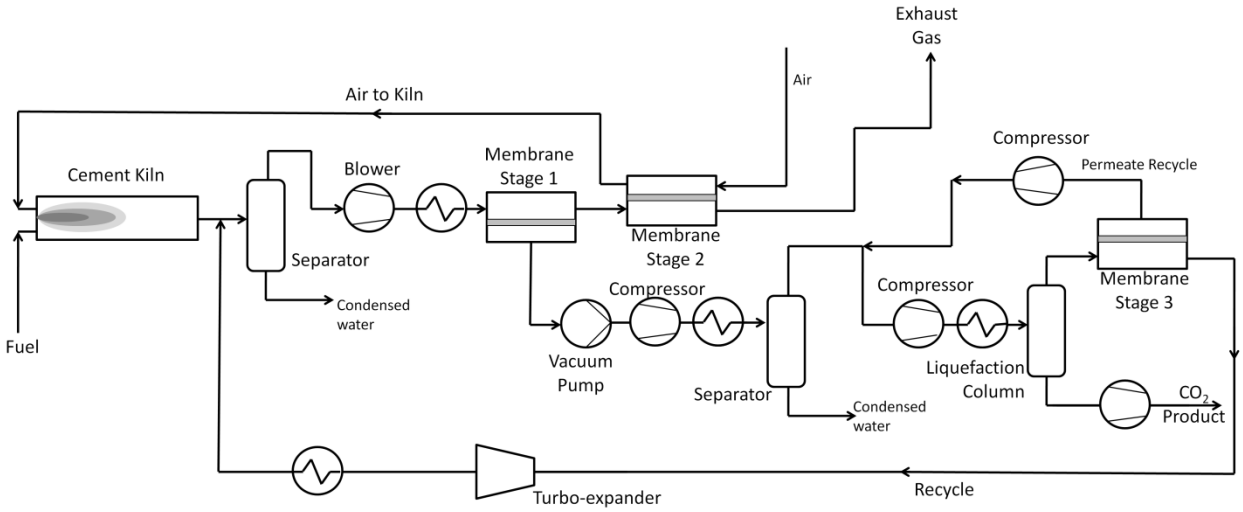

Figure 3

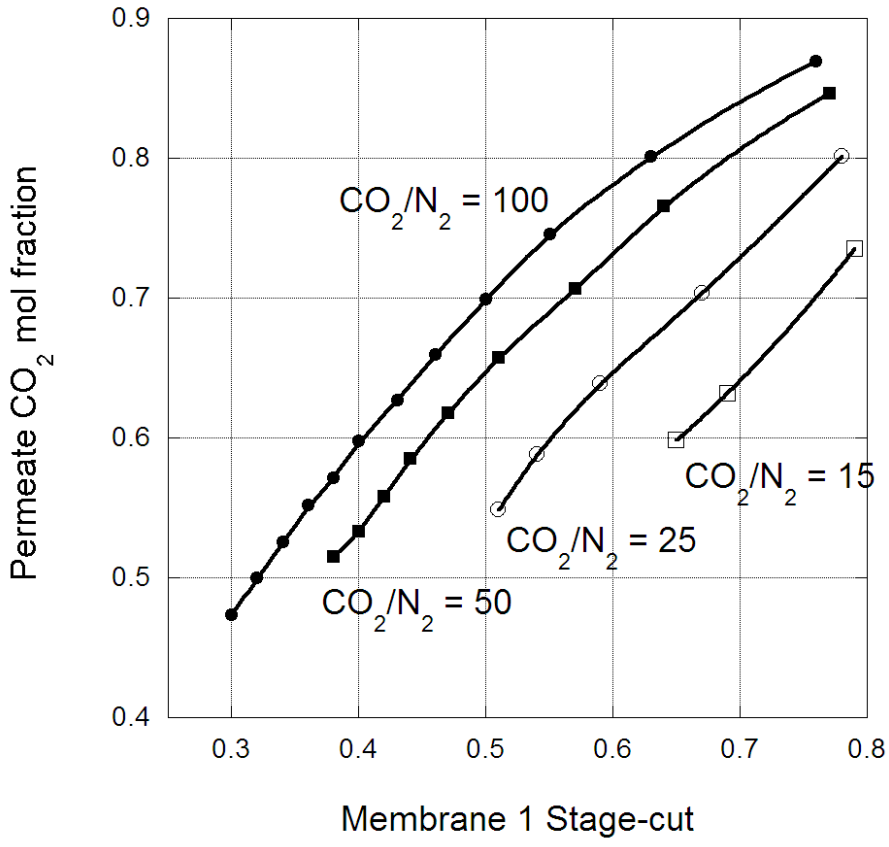

Figure 4

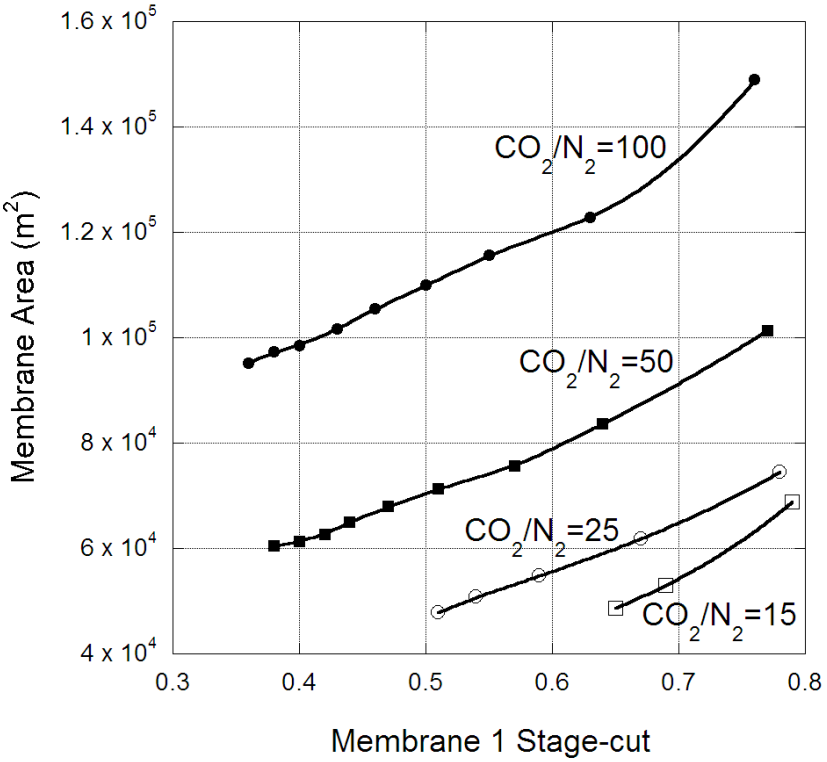
1.6 x 10^5
1.4 x 10^5
1.2 x 10^5
1 x 10^5
8 x 10^4
6 x 10^4
4 x 10^4
Membrane Area (m^2)
CO2/N2=100
CO2/N2=50
CO2/N2=25
CO2/N2=15
0.3
0.4
0.5
0.6
0.7
0.8
Membrane 1 Stage-cut

Figure 5

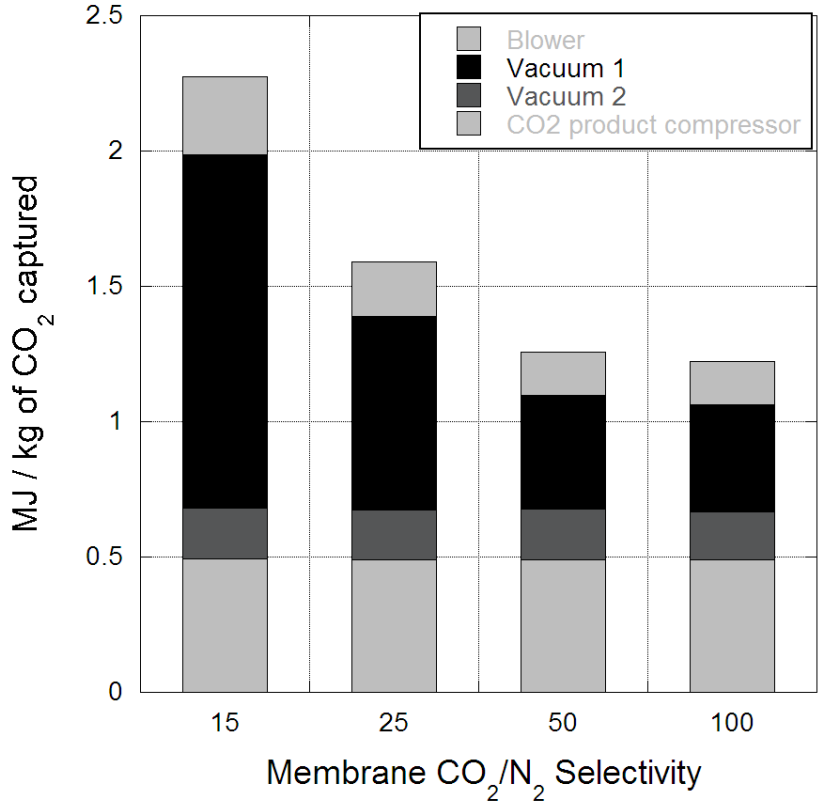
Blower
Vacuum 1
Vacuum 2
CO2 product compressor
MJ / kg of CO2 captured
2.5
2
1.5
1
0.5
0
15
25
50
100
Membrane CO2/N2 Selectivity

Figure 6

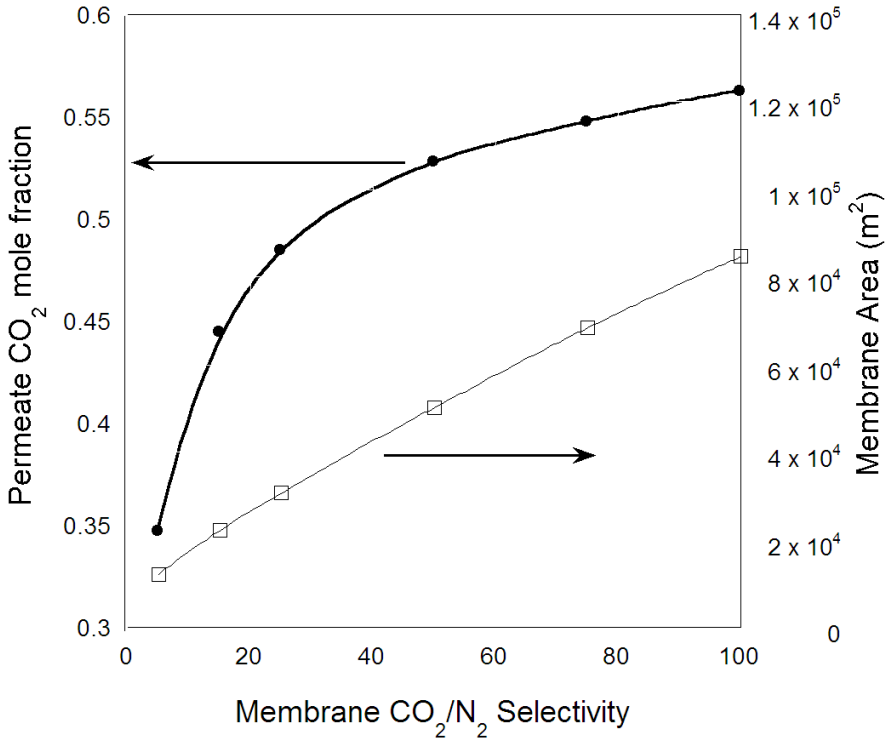
0.6
0.55
0.5
0.45
0.4
0.35
0.3
Permeate CO_2 mole fraction
1.4 x 10^5
1.2 x 10^5
1 x 10^5
8 x 10^4
6 x 10^4
4 x 10^4
2 x 10^4
0
Membrane Area (m^2)
0
20
40
60
80
100
Membrane CO_2/N_2 Selectivity

Figure 7

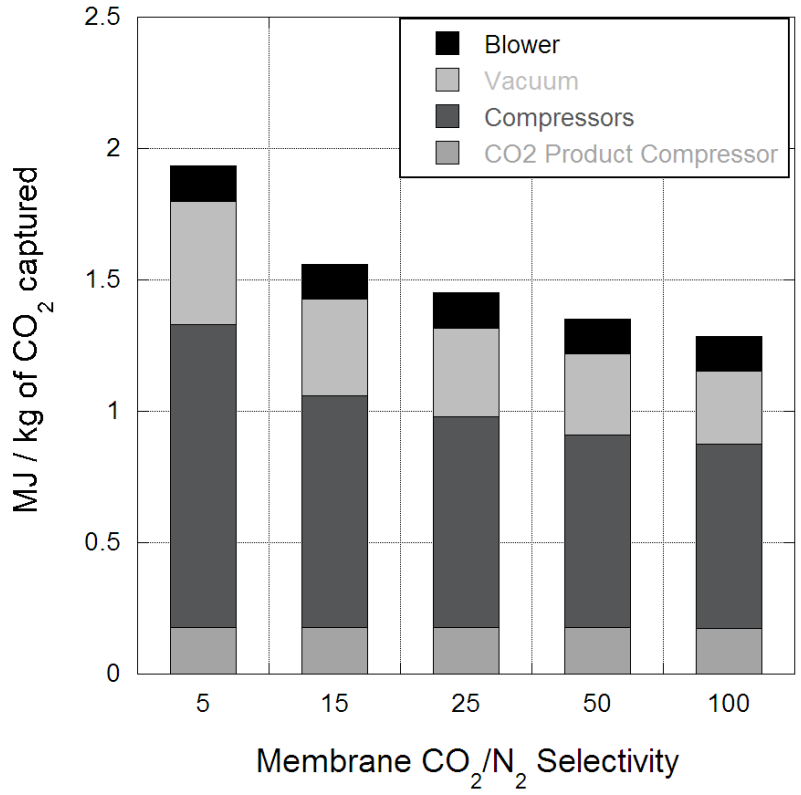

Figure 8

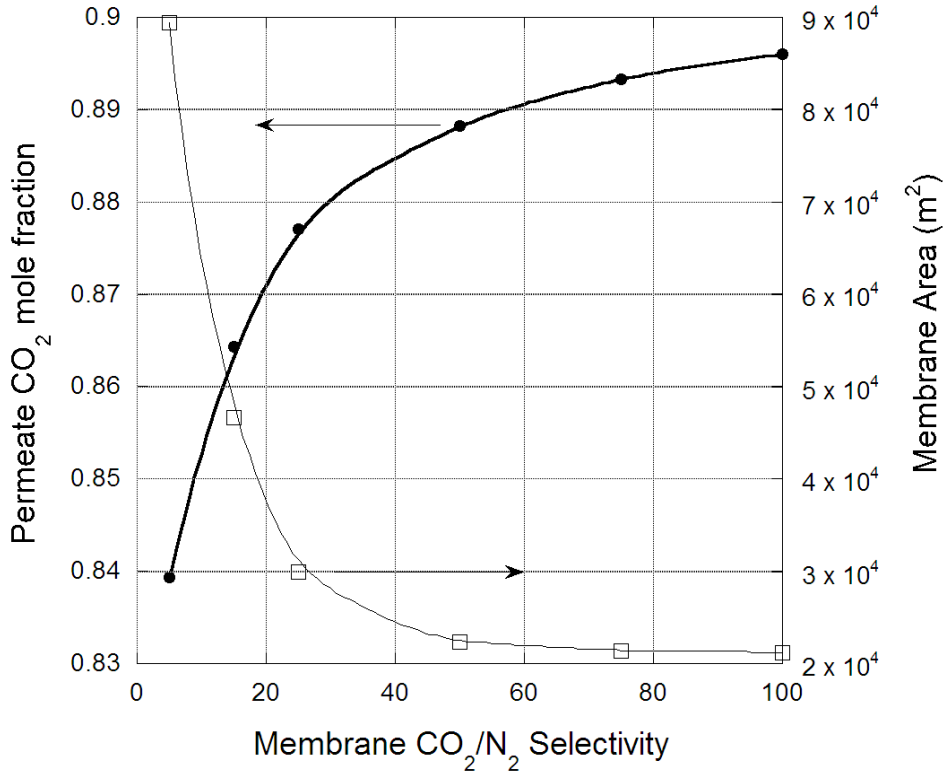

Figure 9

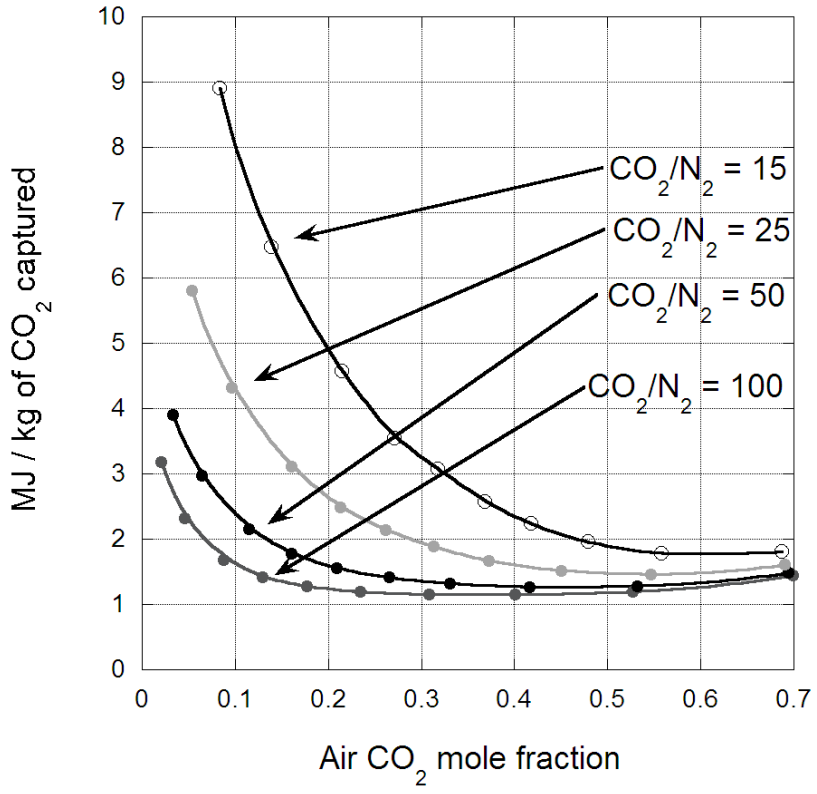
MJ / kg of CO2 captured
Air CO2 mole fraction
CO2/N2 = 15
CO2/N2 = 25
CO2/N2 = 50
CO2/N2 = 100
0
1
2
3
4
5
6
7
8
9
10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7

Figure 10

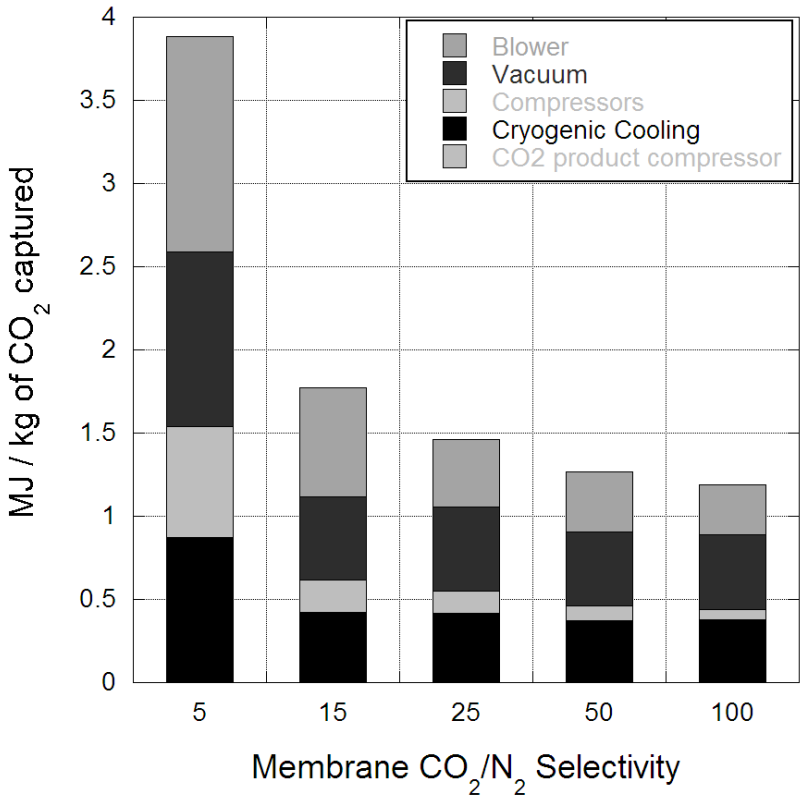
Blower
Vacuum
Compressors
Cryogenic Cooling
CO2 product compressor
MJ / kg of CO2 captured
0
0.5
1
1.5
2
2.5
3
3.5
4
5
15
25
50
100
Membrane CO2/N2 Selectivity

Figure 11

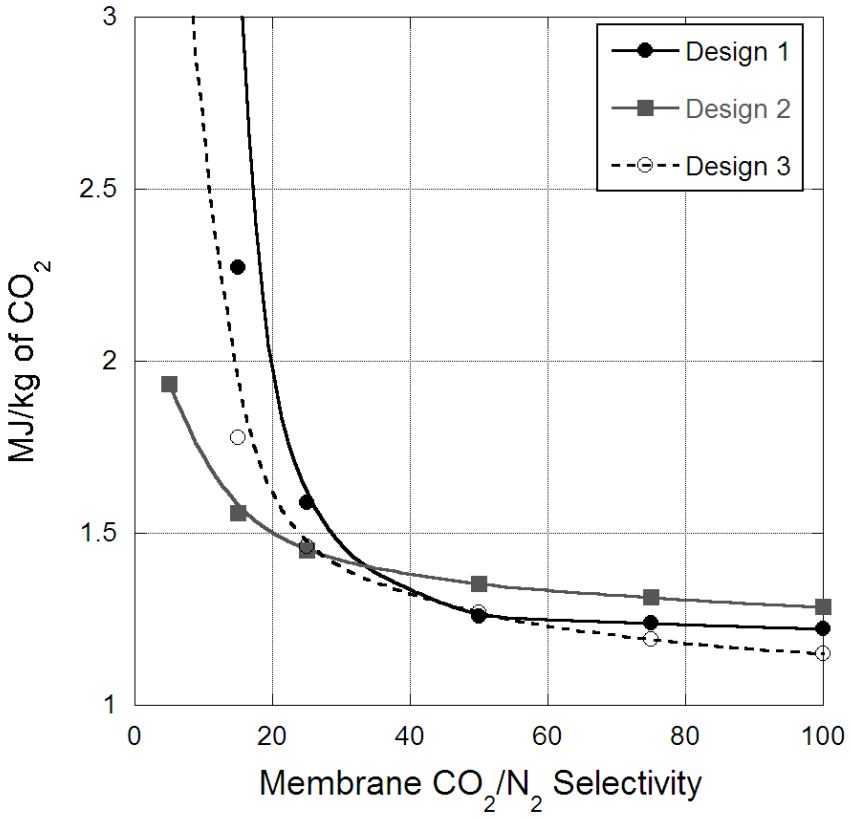
Design 1
Design 2
Design 3
MJ/kg of CO_2
Membrane CO_2/N_2 Selectivity
3
2.5
2
1.5
1
0
20
40
60
80
100

Figure 12

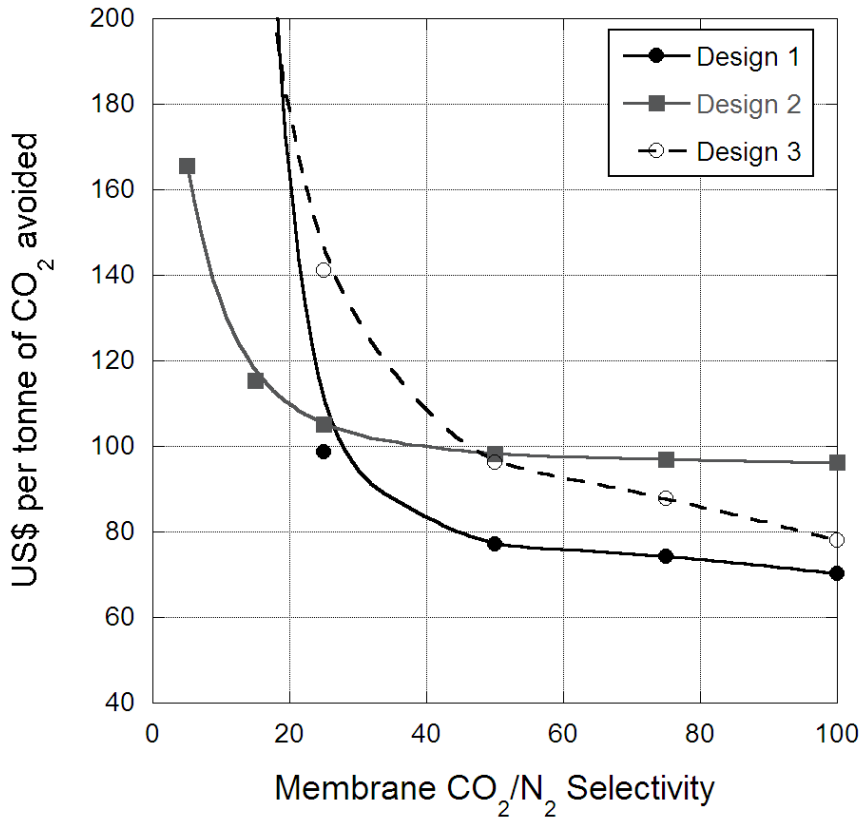
200
180
160
140
120
100
80
60
40
0
20
40
60
80
100
US$ per tonne of CO2 avoided
Membrane CO2/N2 Selectivity
Design 1
Design 2
Design 3

Figure 13

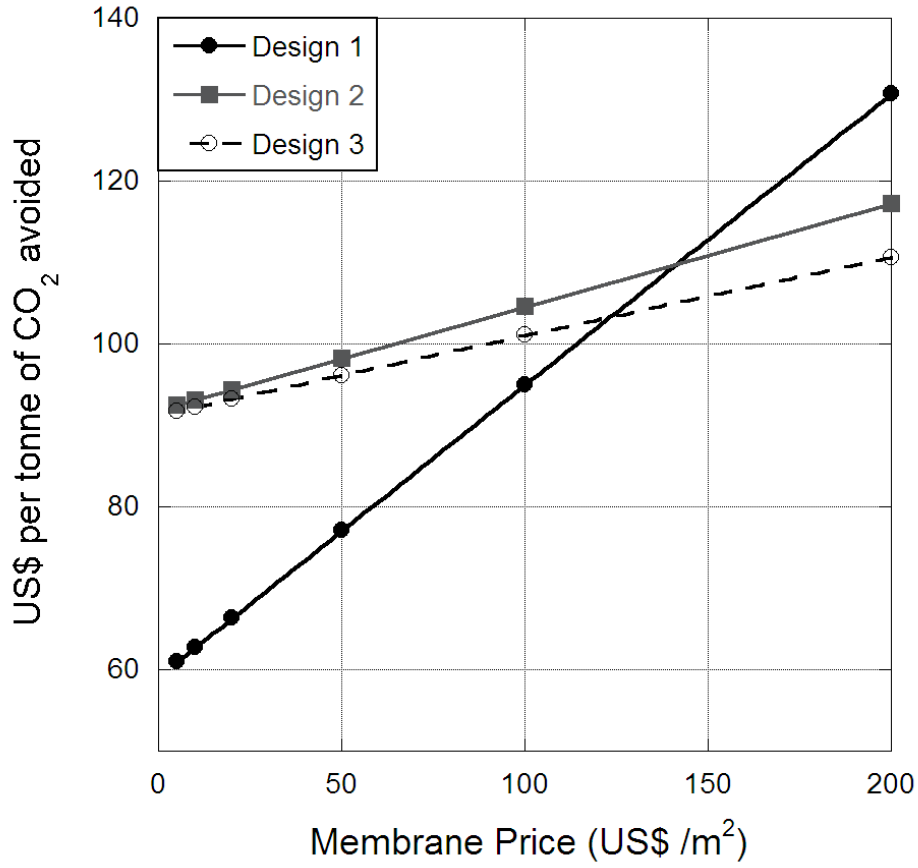
Design 1
Design 2
Design 3
US$ per tonne of CO2 avoided
Membrane Price (US$ /m2)
140
120
100
80
60
0
50
100
150
200

Figure 14