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CO_2 capture by sub-ambient membrane operation

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Abstract

Air Liquide is developing a cost effective hybrid CO_2 capture process based on sub-ambient temperature operation of a hollow fiber membrane in combination with cryogenic distillation. Operation of these commercial Air Liquide membranes at low temperatures provides an unprecedented combination of CO_2 permeability and selectivity. Both high membrane module productivity and high selectivity are critical for cost-efficient CO_2 capture. High selectivity reduces the energy cost of CO_2 capture while high module productivity reduces the capital cost of the membrane system. The proposed hybrid CO_2 capture process concept couples the unique high performance membrane with cryogenic processing technology to efficiently capture at least 90% of the CO_2 in the flue gas from an air fired power plant.

This paper describes a successful long-term (8 month) test of the enhanced CO_2 separation capability of the Air Liquide membrane at low temperatures. This demonstration was carried out with commercial scale membrane modules using a synthetic CO_2/N_2 feed and is an important milestone in development of the cold membrane process. The membrane selectivity and permeance validated through bench scale testing was fed into with process simulation studies coupled with process equipment cost estimates. These results indicate that the cold membrane process concept is promising for CO_2 removal from flue gas generated by coal power plants.

Keyword: membrane, CO2, cryogenic

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1. Introduction

Air Liquide is developing a cost effective hybrid CO_2 capture process based on sub-ambient temperature operation of a hollow fiber membrane in combination with cryogenic distillation. The development program utilizes several key Air Liquide strengths: an existing program for coal oxy-combustion with CO_2 recovery [1,2], cryogenic processing expertise and membrane manufacturing through MEDAL™, an Air Liquide subsidiary. The cold membrane development work [3] is supported through an U.S. DOE / NETL program aimed at CO_2 recovery by retrofitting existing pulverized coal fired power plants.
For most membrane materials, permeability decreases and selectivity increases with a decrease in operating temperature. However, measurements of commercially available Air Liquide membranes operated at temperatures below -20˚C show two to four times increase in CO_2/N_2 selectivity with minimal CO_2 permeance loss compared to ambient temperature values. Operation of these commercial Air Liquide membranes at low temperatures provides an unprecedented combination of CO_2 permeability and selectivity.
Both high membrane module productivity and high selectivity are critical for cost-efficient CO_2 capture [4-8]. High selectivity reduces the energy cost of CO_2 capture while high module productivity reduces the capital cost of the membrane system. The proposed hybrid CO_2 capture process concept couples the unique high performance membrane with cryogenic processing technology to efficiently capture at least 90% of the CO_2 in the flue gas from an air fired power plant. The ultimate target is to achieve this degree of CO_2 capture with increase in the levelized cost of electricity of less than 35%.
The process concept is illustrated in the simplified process block flow diagram as shown in Figure 1.

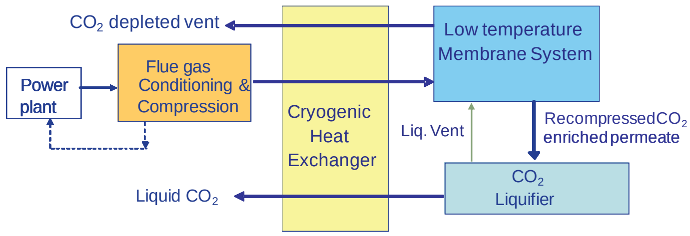

Figure 1. Sub-Ambient Membrane System for CO_2 separation

Nomenclature

BFW	Boiler feed water
CPU	Cryogenic purification unit
E_P	Activation energy for permeation
FGD	Flue gas desulphurization
LCOE	Levelized cost of electricity

As in some previous literature [9, 10], the membrane serves as a CO_2 pre-concentrator sending a small CO_2-rich stream to the cryogenic purification unit (CPU). However, in contrast to previous membrane schemes, the membrane is now operated at cold temperatures. The process is feasible because of the exceptional permeance-selectivity characteristics of the commercial Air Liquide (AL) polyimide membrane when operated at sub-ambient temperatures. Simulations and preliminary cost analyses show that an integrated carbon capture process scheme can take advantage of these membrane properties.

2. Membrane performance at cold temperatures

For most commercial membrane gas separations (CO_2/CH_4, He/N_2, O_2/N_2), gas diffusion through the polymer rather than gas solubility in the polymer is the controlling phenomena determining the overall gas permeability. Solubility depends on the penetrant activity and affinity for the polymer matrix. Diffusivity depends on molecular mobility, i.e. the molecular size of the penetrant and free-volume morphology of the polymer. The permeation activation energy, E_P, can be expressed in terms of the activation energy for diffusion E_D and the enthalpy H_S of solution [$E_P = E_D + H_S$]. Since diffusivity is usually the controlling parameter, the general rule is that overall permeability decreases and selectivity increases with a decrease in operating temperature. It is possible to deviate from this text-book rule for gases such as CO_2 which have high affinity for polyimides. In such a case, the high exothermic heat of solution compensates for the diffusion activation energy leading to lower or even negative values of E_P.

Several commercial AL polyimide membranes show similar phenomena in that CO_2 permeance begins to level off as the temperature decreases. As a result, at temperatures < -20˚C; the CO_2 permeance is ~ 2x higher than the value predicted by a simple Arrhenius extrapolation of ambient and higher temperature (20˚-70˚C) data. CO_2/N_2 selectivity continues to increase as temperature decreases. The net effect of cold temperature operation is as if a new material had been discovered with unprecedented permeance-selectivity characteristics on the Robeson[11] trade-off plot, as illustrated in Figure 2.

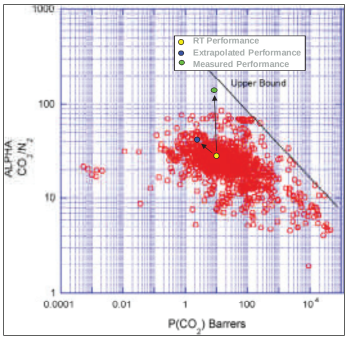

Figure 2. Plot of back-calculated equivalent permeability and selectivity at ambient temperature (yellow) and at -30˚C (green) on a Robeson [11] plot for CO_2/N_2. The cold temperature estimate was made by estimating effective skin thickness of the hollow fiber from ambient temperature data for the fiber and dense film. The blue point shows the performance at -30˚C predicted by extrapolation of data from 20-50˚C while the green point is the actual performance at -30˚C.

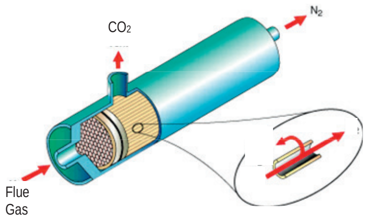

Figure 3. Air Liquide hollow-fiber membrane module for gas separation

The hollow fiber membrane module configuration (Figure 3), used by AL, is the most economic configuration in terms of cost/membrane area. This is particularly important for flue gas treatment. Due to the small hollow fiber size and the module construction method, commercial AL hollow fiber modules have an order of magnitude advantage in packing density (membrane area /module volume) over competing spiral wound configurations and an even greater advantage over plate and frame membranes. Typical AL hollow fiber modules contain as much as 10x more active membrane area compared to a typical multi-leaf spiral wound module.

Low membrane installed costs are particularly important because of the sheer volumes associated with flue gas processing. Commercial large-scale CO_2 separation membrane systems based on hollow fiber modules are operated at capacities approaching the flue gas volumes expected from power plants. For example, at a commercial facility in Grissik, Indonesia operating since 2000, Air Liquide membranes remove CO_2 from ~ 12,000 tons/day of natural gas [12]. The small footprint and operational simplicity of such compact membrane units is very advantageous in retrofitting existing power plants with space limitations, such as those in cities or other populated areas.

3. Hybrid integrated Membrane + Cryogenic Process Concept and Description

Air Liquide is proposing a novel integrated sub-ambient membrane and cryogenic CO_2 recovery process which takes advantage of the high membrane permeance to capture CO_2 from flue gas of air-fired coal power plants. The CO_2 capture process concept is described below in general terms.

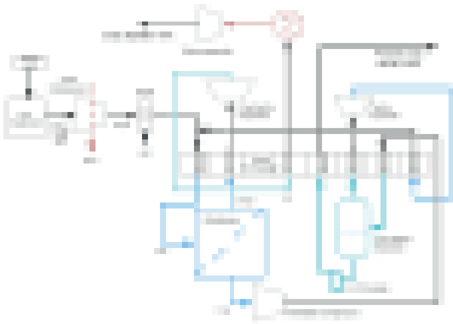

Figure 4. Schematic diagram of proposed membrane-based CO_2 CPU process.

The highly selective cold membrane provides efficient pre-concentration of CO_2 prior to CO_2 partial condensation in a liquefaction unit. The CO_2 enriched permeate stream from the membrane is re-compressed, cooled in a heat exchanger and undergoes phase separation in the cryo-phase separator. Liquid CO_2 is pumped from the separator to provide a sequestration-ready CO_2 product at > 60 bar and 20°C. The cryogenic heat exchanger system provides energy integration between the membrane and CO_2 liquefaction system. Simulations show that the high membrane selectivity achieved by low temperature operation greatly increases efficiency of the subsequent CO_2 liquefaction, thereby reducing the specific energy required for CO_2 capture. The required process cooling requirements are obtained by cryo-expansion of the pressurized residue stream and gas-gas heat exchange.

For simplicity, Figure 4 assumes that the flue gas is available after bag-house filtration and acid component removal (FGD and SCR), and has been filtered further to meet the particulate specifications of the compressor manufacturer.

The pre-treated flue gas is compressed to 16 bar. The heat of compression is captured in boiler feed water raising the water temperature to 147˚C. The compressed flue gas is then dried in a dehydration unit to prevent water condensation when the stream is cooled in the economizing heat exchanger to -30˚C. The cooled, dried, compressed flue gas is then fed to the membrane to produce a residue stream with 1.6% CO_2 at 15 bar and a permeate stream with 60-70% CO_2 at 1-2 bar.

After the residue stream is sent through one pass of the heat exchanger, further cooling and energy recovery is done via a series of turbo-expanders with the resulting cold residue stream at -57˚C sent through the heat exchanger. Finally, the excess pressure energy remaining in the warmed residue is partly recovered in a warm turbo-expander before venting. A fraction of the vent gas is heated by the compression-heated water and used to regenerate the drier. The permeate stream is re-compressed, cooled in the heat exchanger and undergoes phase separation in a one pot separator. Liquid CO_2 is pumped from the separator through the heat exchanger to extract more energy and provide a sequestration-ready product at 150 bar and 20°C. The overhead from the cryogenic separator is warmed through the heat exchanger and undergoes energy recovery in a turbo-expander. This stream is mixed with the incoming dried flue gas; this recycle raises the mixed feed concentration entering the membrane to 18% CO_2. The higher CO_2 content improves the membrane separation.

4. Cold Membrane Bench scale testing

The cold membrane performance described in section 2 has been consistently measured during Air Liquide laboratory testing with minipermeators. Stable performance was measured over a year proving that the membrane fiber is stable at the proposed operating conditions. The current project phase focuses on reproducing the excellent laboratory scale membrane performance with commercial modules (a 10^4 scale up in membrane area). Successful testing of commercial bundles with a synthetic CO_2/N_2 feed is an important milestone before field testing with real flue gas.

A bench-scale test system was constructed for long term testing of commercial Air Liquide membrane modules with CO_2/N_2 mixtures at sub-ambient conditions. Air Liquide MEDAL™ 12” and 6” modules were tested at pressures as high as 15 bar and temperatures down to -45°C. As shown in Figure 5, the feed CO_2/N_2 mixture was recirculated through a heat exchanger and membrane module in a cold box. The cooling required was provided mainly by Joule-Thomson cooling from expansion of the pressurized residue. The cold expanded residue and permeate are used to cool the ambient temperature feed entering the heat exchanger. These streams are then mixed and recirculated through the compressor.

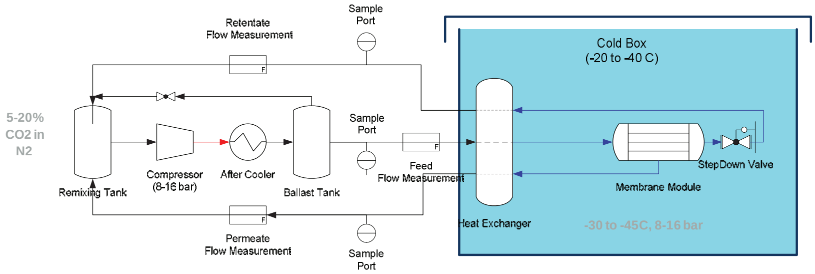

Figure 5. Schematic of cold membrane test skid

The membrane modules exhibited the same cold temperature response as previously observed for laboratory minipermeators. Enhanced perm-selectivity has been observed with a commercial module over 8 months continuous cold temperature testing. Parametric testing (temperature, pressure, flow, CO_2 concentration) was performed to develop the membrane performance map.

Parametric tests were performed at the 1 month and 6 month mark of the long term test with the 6" bundle. These tests indicate that the membrane performance will be best at the coldest temperature (see Figure 6) and highest feed pressure that can be achieved. These are the conditions that correspond to the highest available CO_2 feed-side activity. In our testing, the minimum temperature (-45˚C) and highest feed pressure (210 psig) were limited respectively by the membrane vessel rating and by the compressor capability. In terms of the process choice, the optimized variables will also depend on the energy and capital costs of achieving these desirable pressure / temperature conditions.

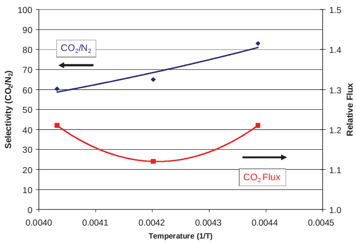

Figure 6. Summary of temperature effect on CO_2 permeance and selectivity between -25˚C to -45˚C developed as a result of parametric testing. Feed gas was 18% CO_2 /N_2 at 200 psi. Right hand Y axis shows CO_2 permeance relative to ambient temperature value.

Membrane longevity was confirmed by a total 8-month long exposure of the 6" bundle to sub-ambient temperature operating conditions. The majority of the testing was run at 200 psi, -45°C and 18% CO_2 feed. These pressure and temperature conditions were indicated to be the optimum by the first parametric study. The membrane performance at test conditions was stable with no decline in either permeance or selectivity (see Figure 7). This better than expected performance with synthetic feed is motivation for pursuing cold membrane technology development in general and field testing in particular

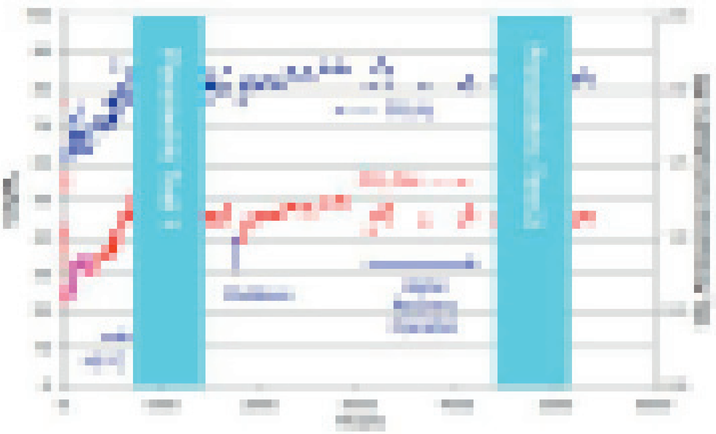

Figure 7. CO_2 permeance (normalized) and CO_2 / N_2 selectivity for MEDAL™ membrane module during long term testing. The normal test conditions were -45°C, 200 psig, 18% CO_2 in feed. The right-side Y-axis shows normalized permeance (CO_2 permeance at cold conditions /permeance at initial ambient temperature).

Laboratory work has verified the impact of contaminants (SO_2 , NO , NO_2) at levels relevant to coal fired power plants on membrane performance. Experimental results were used to refine the integrated process simulation.

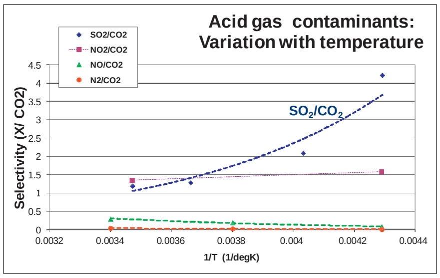

Figure 8. Permeance of various flue gas constituents relative to CO_2 permeance as a function of temperature in the range of 20º to -40ºC. Data was measured with mini-permeators at ~ 140 psi with CO_2 /N_2 gas mixtures containing ~ 100 ppm of various acid gases (SO_2, NO_2, NO).

5. Summary and Process concept evaluation

The process concept shown in Figure 4 is very different from most previous schemes [4-10] which also use membranes to recover or concentrate CO_2 from flue gas. The two main differences are that this scheme operates the membrane at colder temperature and higher pressure conditions than previously envisaged.

Cold membrane operation requires all the feed gas to be cooled to sub-ambient temperature. To be viable, this scheme requires good heat integration. As shown in Figure 4, the cold temperatures used to cross-exchange the feed stream are generated by turbo-expansion of the pressurized membrane residue stream. The heat exchanger and required pre-treatment is an important cost item.

Previous schemes also limit the membrane operating pressure since feed compression is the dominant energy cost. It is well known from membrane modeling that operation at the correspondingly low feed/permeate pressure ratios limits the separation ability of the membrane. There is little benefit of high membrane selectivity when operating at low pressure ratios across the membrane. Hence previous membrane schemes envisage the use of membranes with extremely high permeance but modest selectivity. The extremely high permeance is required to keep membrane capital cost within acceptable limits. The low pressure ratio mode of operation increases the process energy penalty compared to a high pressure/high membrane selectivity mode of operation .

Figures 9a-b show illustrative calculations for the permeate /feed ratio and permeate CO_2 concentration as a function of selectivity for two different pressure ratios. At higher pressure ratio, there is a clear advantage to more selective membranes in terms of increased permeate CO_2 purity and the lower amount of total gas permeated.

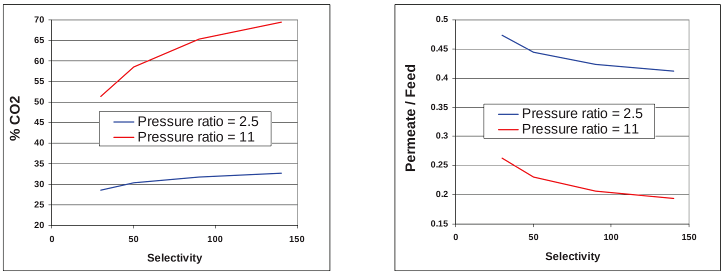

Figure 9a-b. Illustrative calculation of CO_2 purity in permeate and permeate flow as a fraction of feed flow for various assumed membrane selectivity values at feed/permeate pressure ratios of 2.5 and 11.

With a less selective membrane, the CO_2 composition of the permeate is lower. There are two consequences of lower permeate concentration. As shown in Figure 10, a higher pressure is required in the subsequent liquefaction step if the incoming CO_2 purity is low. In addition, the higher amount of inerts that permeate the membrane also increase the flow rate from the liquefier vent that need to be recycled. A more selective membrane step decreases this energy cost because the total recycle is reduced.

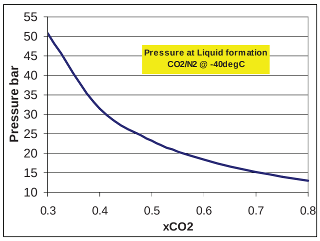

Figure 10. Illustrative calculation of liquefaction pressure of CO_2 /N_2 mixture at -40ºC as a function of CO_2 purity

Since the proposed scheme uses high feed compression, it needs a viable method of energy recovery is critical. The main energy input and recovery steps corresponding to the scheme in Figure 4 are summarized in Table 1. The process viability depends crucially on the compression and expander efficiencies as well as the valorization of the boiler feed water [5]. CO_2 capture energy was estimated through Hysys™ simulation of the cold membrane process operating on a FGD and SCR pre-treated flue gas from air-fired coal power plant. The high efficiency of the compression and expander rotating machines simulation was validated by corresponding manufacturers. Boiler feed water valorization (power plant equivalent kwh for BFW at 147ºC) was consistent with previous oxy-combustion studies (DOE/NETL 2007-1291 [13]). Sensitivity analysis was done assuming variations in the compressor efficiency and BFW valorization. The specific energy for CO_2 capture by this process ranged from 216 – 242 kWh/t of CO_2 captured. It is important to note that in this process, the CO_2 product for sequestration is not compressed as a gas; it is pumped as a liquid. By using a cryogenic process and maintaining a liquid product, the energy intensive step of product gas compression (estimated at 50-60 kWh/t CO_2) is avoided.

Table 1. Main energy usage and recovery elements in process corresponding to Figure 4.

Main Energy input operations	**Main energy recovery operations**
Feed compression (1.0 to 16.0 bar)	Cold pressurized residue turbo-expansion
Permeate re-compression from 1-2 bar to 17 bar	Final warm residue turbo-expansion
Drier adsorbent regeneration	Boiler feed water (BFW) credit from compression
Liquid CO_2 pump to 150 bar	Recycle stream turbo-expansion

The energy capture estimate was coupled with capital cost estimates to calculate the levelized cost of electricity (LCOE) for 90% CO_2 capture from a 550 MW net air-fired coal power plant. The costing methodology followed DOE/NETL study 2010/1397 [14]. Process equipment cost estimates were based on (i) vendor quotes for the major equipment and (ii) internal Air Liquide Engineering database for other equipment. Equipment sizes / number of trains were not optimized as we limited this exercise to current quotations at the scale available today. For most equipment, the budgetary cost estimates were valid within ± 20%. This is a conservative approach but is a useful bench-mark for the future. This analysis indicates increases in LCOE between 48% and 53%.

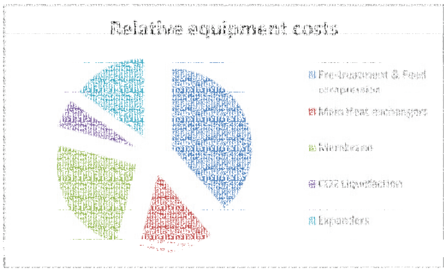

Figure 11. Relative capital cost (non-installed) for major equipment blocks of conceptual hybrid cryogenic + cold membrane process for 90% CO_2 recovery from a 550 MW (net) coal power plant.

Figure 11 shows the relative capital costs of the main process equipment blocks. The most significant capital costs are due to the (i) feed compression and associated gas pretreatment and (ii) membrane system. For both items, there is a realistic chance of cost reductions in the immediate future (0-5 years) as well as in the long term. The immediate cost reductions come from factors such as larger manufacturing economy of scale (especially for membrane manufacturing) as well as increased equipment (compression, pre-treatment) optimization.

6. Conclusion

Verification of the enhanced CO_2 separation capability of commercial Air Liquide membrane at low temperature is an important milestone in development of the cold membrane process. The enhanced membrane separation capability, seen originally at laboratory scale, has now been demonstrated on a commercial scale bundle with a synthetic gas mixture over a total of 8 months at sub-ambient temperatures.

The membrane selectivity and permeance, validated through bench scale testing, was fed into process simulation studies coupled with process equipment cost estimates. These results indicate that the hybrid cryogenic + cold membrane process concept is promising for CO_2 removal from flue gas generated by coal power plants. The proposed next steps are field testing of the membrane on flue gas and further refinement of the energy integration schemes.

Acknowledgements

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