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CO_2 Capture by Hollow Fibre Carbon Membranes: Experiments and Process Simulations

Xuezhong He, Jon Arvid Lie, Edel Sheridan, May-Britt Hägg*

Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

Abstract

Hollow fibre carbon membranes (HFCMs) were fabricated from deacetylated cellulose acetate precursors based on a multi-dwell carbonization protocol. Membrane structure and morphology were characterized by scanning electronic microscope (SEM), and membrane separation performances for single gas and gas mixtures were tested by the in-house gas test setup. Simulations of CO_2 capture by hollow fibre carbon membranes were conducted based on Aspen Hysys® integrated with ChemBrane. The characteristic diagrams and optimal configuration were obtained, and the process was optimized based on the necessary membrane area, energy demands for the compressor and cooler, recovery and purity of CO_2, and capital cost.

Keywords: Hollow fibre carbon membrane; Power plant; Flue gas; CO_2 Capture; Process simulation

1. Introduction

Energy Information Administration (EIA) 2008 predicts a 50% increase of energy demand from 2005 to 2030 due to more countries becoming industrialized [**1**]. Global CO_2 emissions continue to increase steadily in the International Energy Outlook 2008 reference case, from 28.1 billion metric tons in 2005 to 34.3 billion metric tons in 2015 and 42.3 billion metric tons in 2030. The control of anthropogenic emissions of greenhouse gases (GHGs) is one of the most challenging environmental issues facing industrialized countries owing to the implications of GHGs for global climate change. Among these GHGs, CO_2 is the largest contributor in the atmosphere, contributing to 60% of global warming effects, although methane and chlorofluorocarbons have much higher greenhouse effect as per mass of gases [**2**]. There are three options to reduce CO_2 emissions into the atmosphere: To reduce energy intensity, to reduce carbon intensity, and to capture and store CO_2. The first two options require efficient usage of energy and a switch to non-fossil fuels such as hydrogen and renewable energy respectively. The third option requires the development of new efficient technologies for CO_2 capture and sequestration (CCS). The main application of CO_2 capture is likely to be at fossil fuel power plants. Such plants emit large quantities of CO_2; for

* Corresponding author. Tel.: +47-73594033; fax: +47-73594080.
E-mail address: may-britt.hagg@chemeng.ntnu.no.

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example the fossil fuel power plants are responsible for roughly 40% of the total CO_2 emissions, with coal-fired plants being the main contributor.

Since CO_2 separation is the most energy intensive step of CCS, much research has been conducted to improve the current technologies or develop new methods for CO_2 capture. Different technologies such as chemical and physical absorption, low-temperature distillation, and gas separation membranes can be used to capture CO_2. Membranes have been widely used in various industrial separations during the last two decades. Polymer membranes are dominated in current industries. Recent research is mainly focused on the development and application of inorganic membranes such as carbon, silica, zeolite and metallic membranes, facilitated transport membranes and mixed-matrix membranes. Yang et al. reviewed the progress in CO_2 separation and capture: They concluded that the membrane process is energy-saving, space-saving, easy to scale-up, and could be the future technology for CO_2 separation [**3**]. Some literature reported that the research work about CO_2 capture by membrane technology in power plants [**4, 5, 6, 7, 3**]. In this work, high performance hollow fibre carbon membranes will be prepared and tested, and the simulation of CO_2 capture by this carbon membrane in a post-combustion process will also be conducted.

2. Experimental methods and results

Carbon membranes have the ability to separate gases based on small differences in the size and shape of the gas molecules, and the separation performance is superior to the conventional polymeric membranes. Moreover, carbon membranes have high chemical and thermal stability. Hollow fibres will be preferable because of its high packing density (up to 30,000 m^2/m^3) and easier module assembly. An additional advantage is that the carbonization of the precursors can be carried out in a continuous process [**8**]. Therefore, hollow fibre carbon membranes (HFCMs) based on a deacetylated cellulose acetate precursor will be prepared and tested at lab scale.

2.1. Fabrication of hollow fibre carbon membranes

Based on the cellulose acetate dope solution, the hollow fiber membranes were spun using well-known dry-wet spinning method [**9, 10**]. The prepared hollow fiber precursors were then treated with NaOH for deacetylation [**11, 12**].The deacetylated precursor fibres were carbonized in a tubular furnace (Carbolite® TZF 12/100/900) based on a working tube of alumina and a quartz container, which was described elsewhere [**13**]. A multi-dwell carbonization protocol with CO_2 purge gas was executed for the carbonization procedure. The protocol was optimized with respect to mechanical properties of the carbon membranes and its separation properties. The furnace was heated at 1°C/min, with a final temperature of 650°C (maintained for 2 hrs), then the system was allowed to cool naturally to a temperature less than 50 ℃ before taking out the HFCMs from the furnace.

2.2. SEM

A Zeiss SUPRA 55VP scanning electron microscope (SEM) was used to qualitatively assess structural and morphological characteristics of the produced HFCMs. Backscatter and secondary electron images were obtained using an acceleration potential of 5keV. The samples measured had not been used in gas permeation tests, but were taken from the same carbonization batch as those used for permeation.

2.3. Gas performance tests

The prepared HFCMs were loaded into an in-house module, and the gas permeability were tested at 30 ℃ and a feed pressure of 2 bar (permeate side evacuated) in a standard pressure-rise setup (MKS Baratron® pressure transducer, 0–100 mbar range) with LabView® data logging. The tests were run from several minutes or several hours to several days, to ensure that the transient phase of diffusion was passed and steady state obtained (dp/dt tends to a constant). The gas permeance, P (m^3 (STP)/ (m^2.h.bar)) can be calculated using the following equation:

$$P = \frac{9.828V\left(dp/dt\right)}{\mathrm{D}pAT_{\mathrm{exp.}}} \tag{1}$$

Where V is the permeate side volume (cm^3) that can be measured with a pre-calibrated permeation cell reported elsewhere [**14, 15**], dp/dt and A are the collection volume pressure increase rate (mbar/s) and total active area of membrane sample (cm^2) respectively, ΔP (bar) the pressure head and T_{exp} the experimental temperature (K). In this work, the ideal selectivity is defined as the ratio of the pure gas permeance:

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{2}$$

2.4. Experimental results

Cross-sectional views of the prepared hollow fibre carbon membrane are given in Fig. 1. The permeability for single gases was measured and the ideal selectivity was calculated by Eq. (2). The experimental results are given in Table 1, which will be used for the process simulation. Carbonization of a polymer precursor under optimal carbonization conditions generates a carbon membrane with narrow pore constrictions (<4 Å) and a narrow pore size distribution, which makes the possibility to separate gases with very similar molecular size such as CO_2 (3.3 Å), O_2 (3.46 Å) and N_2 (3.64 Å). The high separation performance of these carbon membranes provides the potential application in CO_2 capture from flue gas in fossil-fired power plants.

Table 1 Membrane performance for gases used in the simulations

Membrane type	Gas mixture	Permeance of CO_2 (m^3(STP)/(m^2.h.bar))	Selectivity	Temperature (℃)	Pressure (bar)
HFCMs	CO_2-N_2	0.022	34.4	30	2
	CO_2-O_2	0.022	3.1	30	2

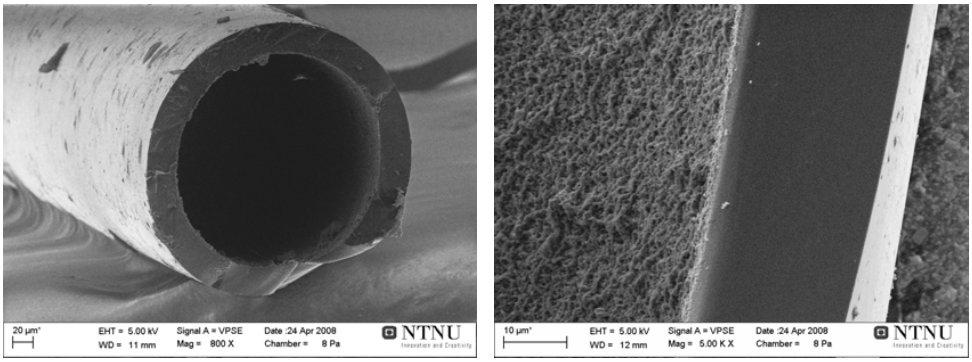

Fig. 1 Cross-sectional structure for HFCM

3. Simulation of selected case

3.1. CO_2 capture by membrane systems

Membrane technology can reduce the cost greatly for CO_2 separation. Membrane-based CO_2 capture systems can be classified according to membrane type basically as polymeric or inorganic membranes. Industry applications are dominated by polymeric membranes. However, recent research directed at the development and application of

inorganic membranes is advancing faster because of the demand in new application fields, such as membrane reactors, and high-temperature separations. Both polymeric and inorganic membrane separation processes are more efficient than the conventional chemical absorption processes [**16**]. The most attractive feature for a membrane process is the simplicity of the process, and there is no need for the additional chemical absorbent and stripping. The governing flux equation for gas separation by membranes is based on the Fick's law, and the flux of component *i* (J_i) can be described as follows,

$$J_i = \frac{P_i}{l}(x_{i,f} p_H - y_{i,p} p_L) \tag{3}$$

Where P_i is the membrane permeability for gas *i,* and *l* is the membrane thickness, and p_H and p_L are the pressures in the feed and permeate flow, respectively. $x_{i,f}$ and $y_{i,p}$ are the molar fraction of component *i* on the high pressure side and the low pressure side, respectively.

3.2. Process design and simulation

Post-combustion CO_2 capture with membranes is a "tail-end" process. This means that for a coal fired power plant, the membrane separation module should be located in the downstream of the flue gas desulphurization (FGD) unit. A typical schematic diagram for a pulverized coal (PC) power plant for post-combustion with CO_2 capture from flue gas by membrane separation units is shown in Fig. 2.

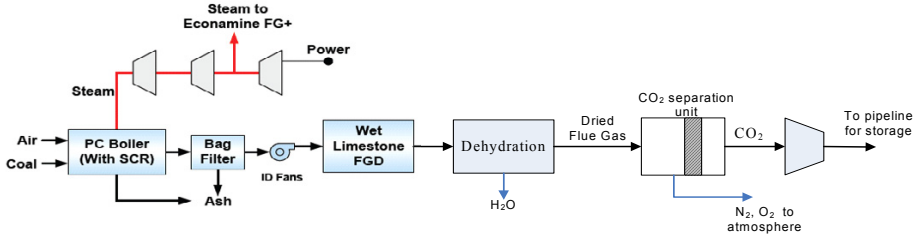

Fig. 2 Flow sheet for a plant with post-combustion capture

When post-combustion capture technology is integrated with the power plant, it enables the capture up to 95% of CO_2 created during energy production. After cooling and cleaning the flue gas, the CO_2 is captured, compressed, transported and stored. Now, CO_2 capture and storage in geological formations is being examined around the world as one way of stabilizing atmospheric levels of CO_2. The process design in this study was based on a typical coal fired power plant (400MWe). The main components of the coal fired power plant flue gases are N_2, CO_2, water vapor and O_2 , and shown in Table 2. Process simulations were executed using a membrane module that was developed by the MEMFO group of the Norwegian University of Science and Technology for use in Aspen Hysys®.

3.3. Economic evaluation

The main equipments like membrane modules and compressors were only considered for evaluating the capital cost. The membrane module cost was calculated based on 15\$/m^2. This is somewhat lower than that given by Koros (20\$/m^2) [**17**], but is justified by large equipment scale and decreasing prices for membranes. The lifetime for carbon membranes is 5 years. The annual capital cost was calculated by an interest rate of 6% and a project lifetime of 20 years, together with the annual CO_2 recovery (330 days per year). Therefore, the total cost per ton CO_2 avoided (C_{CO2}) can be calculated as follows.

$$C_{CO_2} = \frac{C_T}{20 \times F_{CO_2} \times 24 \times 330} (\$/\text{t CO}_2 \text{ avoided}) \tag{4}$$

Where C_T and F_{CO2} are toatl cost ($) and mass flow of CO_2 to pipeline (t/h). The computer program of CAPCOST can be used to calculate the capital cost for single equipment based on the equipment module approach [**18**].

Table 2 Flue gas characteristics for a typical coal fired power plant

Parameters		Wet-base	Dry-base
Flow (Nm^3/h)		1.2×10^6	1.0×10^6
Pressure(bar)		1.003	
Temperature (℃)		80	
CO_2 transport pressure (bar)		80	
Recovery (%)		Min 80	
CO_2 purity (%)		Min 90	
Composition (%, vol)	CO_2	12.5	15
	N_2	68	81
	O_2	3.5	4.0
	H_2O	16	0

4. Simulation results and discussion

The simulations were conducted with an in-house membrane program integrated with Aspen Hysys®. Therefore, it has the possibility to use Hysys's capacity. The input data for the membrane simulations were based on the experimental results. The initial measurements indicated that the pressure (2-5bar) and temperature (30-50℃) variations can be negligible.

4.1. Characteristic diagrams

Based on the membrane transport model described in section 3.1, a dimensionless parameter can be represented by applying the Buckingham π theorem to characterize the performance of one stage or multi-stage membrane separation processes.

$$\phi = \frac{p_F}{p_P} \tag{5}$$

Where Φ is the pressure ratio between feed and permeate side. The process parameters, such as CO_2 purity, CO_2 recovery, energy demands and required membrane areas obtained from the process simulation, are used to plot the

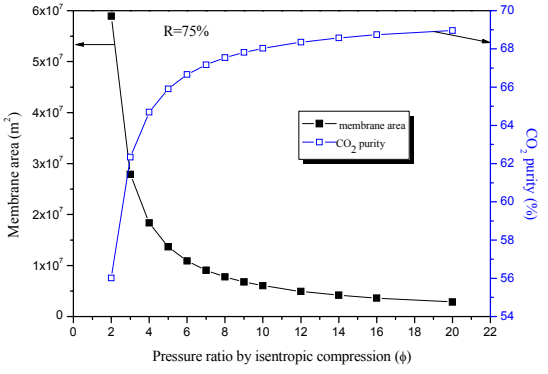

Fig. 3 Membrane areas and CO_2 purity as a function of pressure ratio

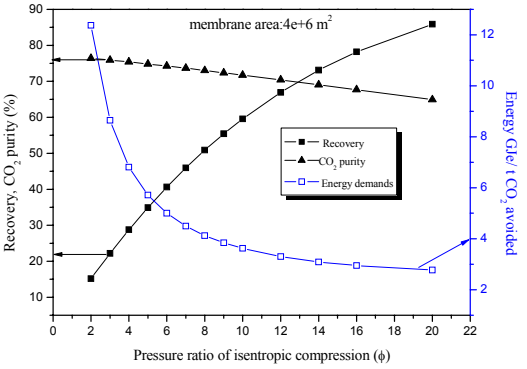

Fig. 4 CO_2 recovery and energy demands as a function of pressure ratio

characteristic diagrams for different separation processes. In this work, the characteristic diagrams are investigated based on a single stage process where the driving force is generated by feed compression, keeping the permeate side at ambient pressure (1 bar). The hollow fibre carbon membranes have been used in this process. The flue gas with the specified composition as listed in Table 2 is compressed to appropriate pressures (various Φ) and cooled down to 30℃, and the condensate is removed before the gas mixture enters the membrane separation unit. Figs. 3-4 give the simulated characteristic diagrams which can be easily used to calculate some important process parameters. From these two figures, we can conclude that an appropriate pressure ratio should be determined to optimize the process. In this work, the feed pressure was set to 5 bar according to the consideration for these process parameters (energy demands, membrane area, CO_2 recovery and purity).

4.2. Configuration selection

ChemBrane is a User Operation module for use in Aspen Hysys®. It includes three different membrane configurations: 1) co-current (plug-flow both shell and bore side), 2) perfect-mixed (plug flow on the bore side, perfectly mixed on the shell side) and 3) counter-current (plug-flow on both sides) [**19**]. The hollow fibre carbon membranes with three kinds of configurations were simulated to obtain the optimal configuration. The operation conditions in table 2 were used for the simulation and the results are given in Table 3. From this table, we can find that the counter-current configuration shows the best performance compared to the other two configurations based on the required membrane area and total energy demands.

Table 3 simulation results for configuration evaluation

Parameters	Co-current		Perfect-mixed		Counter-current	
	Flue gas	CO_2 pipeline	Flue gas	CO_2 pipeline	flue gas	CO_2 pipeline
CO_2 composition (%)	15	80	15	80	15	83
Pressure (kPa)	500	8000	500	8000	500	8000
CO_2 molar flow (kmol/h)	6.69×10^3	3.43×10^3	6.69×10^3	3.41×10^3	6.69×10^3	4.93×10^3
Total CO_2 recovery (%)	51.30		51.04		73.71	
Sweep water vapor molar flow (kmol/h)	1.05×10^4		1.05×10^4		1.05×10^4	
Total membrane area (m^2)	5.02×10^7		4.93×10^7		1.99×10^7	
Compressor duty to transport (kW)	2.29×10^4		2.27×10^4		3.15×10^4	
Total compressor duty GJe/t CO_2 avoided	3.37		3.37		2.36	

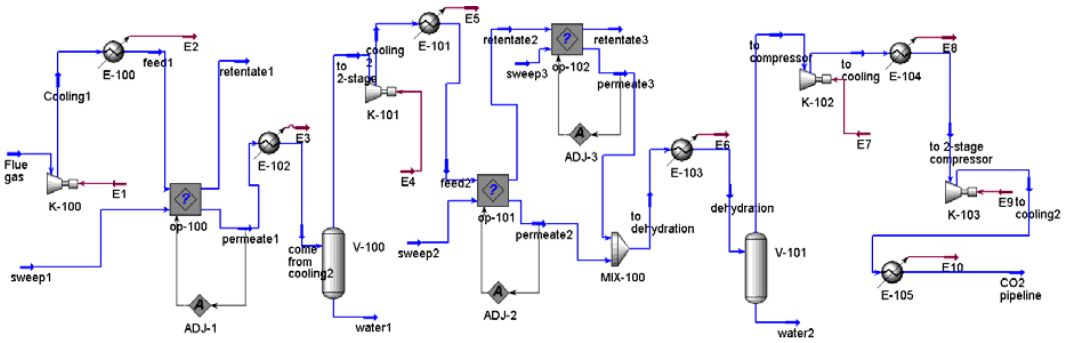

Fig. 6 Simulation PFD for optimal process

4.3. Process optimization

In order to balance the CO_2 recovery, purity, required membrane areas and energy demands, the process must be optimized by adjusting the operation conditions. The feed temperature and pressure for two membrane units are both set to 30℃ and 5 bar. Since the effect of water vapor on the permeability of the other gases has not been experimentally tested which may reduce their permeability due to competitive sorption, the flue gas was dried before feed into the membrane unit. The sweep gas with water vapor was fed into the membrane units in order to dilute the CO_2 concentration in the permeate stream in case the occurrence of inverse transport from the permeate side to retentate side. The optimal simulation process flow diagram (PFD) is shown in Fig. 5. Table 4 gives the simulation results based on this optimal process. Since the CO_2 recovery is still low, thus, the avoided cost will be higher for 80% recovery. Although a continuous run lasting several weeks indicated that the membrane is stable, long-term testing with real gas feeds is still required since the lifetime of the evaluated membrane is presently unknown. Moreover, in order to match the goal for CO_2 capture, the hollow fibre carbon membrane performance should be improved further in future work.

Table 4 Simulation results for optimal process

Parameter	Simulation results
CO_2 feed flow (kmol/h)	6.69×10^3
CO_2 to pipeline (kmol/h)	4.48×10^3
Recovery (%)	67
CO_2 Purity (%)	88
Total sweep gas (kmol/h)	2.57×10^4
Total membrane areas (m^2)	1.62×10^7
Total compressor duty (kW)	1.37×10^5
Total compressor duty GJe /t CO_2 avoided	2.5
Total capital cost \$/ t CO_2 avoided	197

5. Conclusions

Hollow fibres of deacetylated cellulose acetate were carbonized under CO_2 flow up to 550°C. The permeability for different gases (CO_2, N_2, O_2, etc) were tested and used as the input for process simulation. The simulation results illustrated that the hollow fibre carbon membranes show a potential application for CO_2 capture from flue gas in post-combustion power plant. The counter-current flow was evaluated as the optimal configuration. Moreover, the optimal process was obtained based on the economic evaluation. The CO_2 recovery is 67% with a total required hollow fibre carbon membrane area of 1.62×10^7 m^2 and a total compressor duty of 1.37×10^5 kW. The captured CO_2 with the purity of 88% was compressed to 80 bar for transport through pipeline. The total energy demands and capital costs are 2.5 GJe and 197 $ per ton CO_2 avoided. The performance of hollow fibre carbon membranes should be further improved in order to reduce the capital cost for CO_2 capture at an industrial scale.

Acknowledements

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