IECM Technical Documentation:

Membrane-based CO_2 Capture Systems for Coal-fired Power Plants

September 2012

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Membrane-based CO_2 Capture Systems for Coal-fired Power Plants

Integrated Environmental Control Model Development
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MEMBRANE CAPTURE SYSTEMS

INTRODUCTION AND OBJECTIVES

Coal-fired power plants contribute nearly 50 percent of U.S. electricity supply and account for about a third of national emissions of carbon dioxide (CO_2) (EIA, 2012), the major greenhouse gas associated with global climate change. Post-combustion carbon capture and storage (CCS) could play an important role in deeply cutting CO_2 emissions from existing and new coal-fired power plants for mitigating climate change. However, adding commercial amine-based capture systems to pulverized coal power plants would significantly increase the cost of electricity by about 80 percent and lead to about 25 to 40 percent energy penalty (Rubin *et al*., 2007; Haszeldine, 2009; NETL, 2010a). Meanwhile, the addition of CCS would nearly double water use, which further intensifies pressure on water resources (NETL, 2010a; Zhai *et al*., 2011). Because the CO_2 partial pressure of flue gases is typically less than 0.15 atm., the thermodynamic driving force for CO_2 capture is low and then creates a technical challenge for cost-effective capture processes (Figueroa *et al*., 2008). To address these major drawbacks, there is a strong need to advanced cost-effective technologies for controlling CO_2 emissions. Thus, the U.S. Department of Energy is intensively supporting R&D programs of advanced CCS systems for coal-fired power plants (NETL, 2010b). Membranes have broad industrial applications such as air separation and natural gas purification, and have the potential for application to power plant flue gases (Gin and Noble, 2011). Innovative use of membranes is included among emerging carbon capture technologies for fossil fueled power plants (Figueroa *et al*., 2008).

In membrane applications, gas separation agrees with a solution-diffusion mechanism, in which gas components dissolve in the membrane material and then diffuse through the membrane; and the differences of two components in the solubility and diffusion rate drive a separation (Wijmans and Baker, 1995). To be effective for CO_2 capture, membrane materials should posses a number of features including high CO_2 permeability, high CO_2/N_2 selectivity, thermal and chemical stabilities, resistant to plasticization and aging, and so on (Powell and Qiao, 2006). However, there is a general tradeoff relation between membrane properties: more permeable polymers are generally less selective and vice versa (Freeman, 1999; Gin and Noble, 2011). The CO_2/N_2 selectivity for most types of those polymeric membrane materials is less than 50 to 70 (Powell and Qiao, 2006). The CO_2 permeability also changes substantially, even within the same type of membrane material. A novel thin-film, composite polymer membrane manufactured recently was reported to have a high CO_2 permeance of up to 1000 gas permeation unit number (*gpu*) or more with a CO_2/N_2 selectivity of 50 (Merkel *et al*., 2010).

The feasibility of membrane systems for removing CO_2 from flue gases from coal-fired power plants has been investigated increasingly (Van Der Sluijs *et al*., 1992; Hendriks 1994; Bounaceur *et al*, 2006; Ho *et al*., 2006; Favre, 2007; Ho *et al*., 2008; Zhao *et al*, 2008; Baker *et al*., 2009; Yang *et al*, 2009; Brunetti *et al*., 2010; Merkel *et al*., 2010; Zhao *et al*., 2010; Favre 2011). Due to the low CO_2 partial pressure of flue gases, it is difficult for using one-stage membrane systems to achieve the purity above 95% for CO_2 product simultaneously under the typical requirement of 90% CO_2 removal efficiency (Zhao *et al*., 2008). Even with an ideal CO_2/N_2 selectivity up to 200, the single-stage membrane process serving for the flue gas with a 10% mole fraction of CO_2 could not simultaneously achieve 90% removal efficiency and 90% purity (Favre, 2007). In contrast, membrane systems using two stages or more are able to simultaneously fulfill both the targets of removal efficiency and product purity for CO_2 (Yang *et al.*, 2009; Zhao *et al*., 2010). Minor gas components in real flue gases such as sulfur oxides (SO_x) and carbon monoxide (CO) might affect membrane separation performance through competitive sorption and plasticization (Scholes *et al*., 2009; Scholes *et al*., 2010; Scholes *et al*., 2011). However, their influences still remain largely unstudied. This lack of a general understanding limits efforts of system modeling to basically focus on only the separation of CO_2 and N_2 (Scholes *et al*., 2009; Favre, 2011).

Beyond separation modeling alone, some recent studies also evaluated energy penalties and costs for membrane-based capture systems. Using vacuum pumps in place of compressors to reduce energy penalties was proposed in some studies (Ho *et al*., 2008; Yang *et al.*, 2009; Merkel *et al*., 2010, Zhao *et al*., 2010). However, vacuum equipment is more capital intensive; and the optimum assumption of vacuum pressures less than 0.1 to 0.2 bar or lower in process designs may bias assessments of membrane system feasibility because it is hard to practically achieve such low vacuum pressures for a full-scale capture system (Merkel *et al*., 2010). Besides, the costing methods and scope for membrane systems analysis are not consistent across existing studies. For example, indirect capital costs and owner's costs are often ignored. CO_2 product compression is not included in the scope of some studies' energy and cost calculations, although it is one of major cost components of a CCS system.

The objectives of this study are to: (1) systematically evaluate performance and cost of two-stage polymeric membrane systems for CO_2 capture at coal-fired power plants; and (2) investigate the effects on membrane capture systems of key parameters and designs using a widely-used costing method that allows comparative assessment for different CO_2 capture technologies in a common framework.

SYSTEM MODELING AND COSTING METHODS

This section presents mathematical performance models and cost assessment approaches for membrane capture systems for coal-fired power plants.

Binary Gas Separation

A membrane gas separation process has no chemical reactions and thus no need for sorbent regeneration. Gas separation by polymeric membranes relies mainly on the permeability of membrane materials. The driving force for gas separation is the partial pressure *difference* between the feed side and the permeate side of a membrane. Transport flux through polymeric membranes is expressed as (Geankoplis, 1993):

$$J = \frac{P^*}{\delta}\left(xP_f - yP_p\right) \tag{1}$$

Where J is the volumetric flux (cm^3/(cm^2.s)); P^* is the gas permeability (cm^3.cm/(s.cm^2.cmHg)); δ is the membrane thickness (cm); P_f and P_p are the pressures in the feed and permeate sides (cmHg); and x and y are the concentrations of CO_2 in the feed and permeate streams (vol %). Membranes can be packed in modules to operate under different flow patterns such as cross-flow, concurrent flow, and countercurrent flow. Cross-flow modules shown in Figure 1 are most often used in industrial practice.

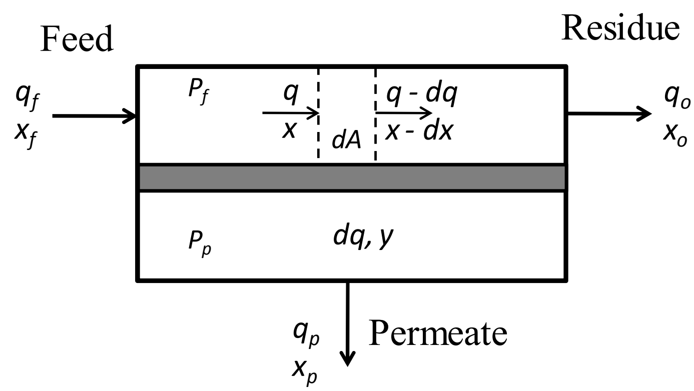

Figure 1 Schematic of a cross-flow membrane module

In formulating theoretical separation models, isothermal conditions, negligible pressure drop and constant gas permeability independent of pressure are generally assumed. The local permeation rate of either CO_2 or N_2 in a binary membrane system for the cross-flow pattern over a differential membrane area (dA) is described as (Geankoplis, 1993):

$$-ydq = J_{CO2}dA = \frac{P^*_{CO2}}{\delta}\left[xP_f - yP_p\right]dA \tag{2}$$

$$-(1-y)dq = J_{N2}dA = \frac{P^*_{N2}}{\delta}\left[(1-x)P_f - (1-y)P_p\right]dA \tag{3}$$

Dividing Equation (2) by Equation (3) yields:

$$\frac{y}{1-y} = \frac{\alpha(1-y/\phi)}{(1-x)-(1-y)/\phi} \tag{4}$$

where, A is the membrane area (cm^2); q is the gas flow rate (cm^3/s); α is the membrane selectivity (P^*_{CO2}/P^*_{N2}) for CO_2 versus N_2 gases; and ϕ is the pressure ratio (P_f/P_p) for feed versus permeate sides. The CO_2 of flue gas is enriched in the permeate stream through the CO_2-selective membrane. Equation (4) relates the concentrations of CO_2 in both feed and permeate streams. We can see that in terms of the governing equations above, membrane selectivity, pressure ratio and stage cut are the key parameters for a membrane gas separation process. Weller and Steiner applied mathematical transformations to obtain an analytical solution to the governing equations as (Geankoplis, 1993):

$$\frac{(1-\theta^*)(1-x)}{1-x_f} = \left(\frac{u_f - E/D}{u - E/D}\right)^R \left(\frac{u_f - \alpha + F}{u - \alpha + F}\right)^S \left(\frac{u_f - f}{u - f}\right)^T \tag{5}$$

Furthermore, the membrane area required was obtained as (Geankoplis, 1993):

$$A_m = \frac{tq_f}{P_f P^*_{N2}} \int_{i_o}^{i_f} \frac{(1-\theta^*)(1-x)}{(f_i - i)\left[\frac{1}{1+i} - \frac{1}{\phi}\left(\frac{1}{1+f_i}\right)\right]} di \tag{6}$$

Where:

$$\theta^* = 1 - \frac{q}{q_f}$$

$$i = \frac{x}{1-x}$$

$$u = -Di + \left(D^2 i^2 - 2Ei + F^2\right)^{0.5}$$

$$D = 0.5\left[\frac{(1-\alpha)}{\phi} + \alpha\right]$$

$$E = \frac{\alpha}{2} - DF$$

$$F = -0.5\left(\frac{1-\alpha}{\phi} - 1\right)$$

$$R = \frac{1}{2D-1}$$

$$S = \frac{\alpha(D-1)+F}{(2D-1)\left(\frac{\alpha}{2} - F\right)}$$

$$T = \frac{1}{1-D-E/F}$$

$$f_i = (Di - F) + (D^2 i^2 - 2Ei + F^2)^{0.5}$$

Given feed compositions, membrane properties, feed- and permeate- side pressure deigns and membrane module stage-cut, the CO_2 concentrations of permeate and residue streams and membrane area can be solved using the analytical approach above via an iterative process.

Power Use of Major Equipment

Power plants flue gases typically have 10% to 15% CO_2 by volume, which results in a low CO_2 partial pressure. The sufficient partial pressure difference of CO_2 between the feed and permeate sides can be generated by three strategies including feed-side compression, permeate-side vacuum pumping, and a combination of both the previous methods. The energy use for either compressors or vacuum pumps is estimated as (Vallieres *et al*, 2003; Bounaceur *et al*, 2006; Favre, 2007; Yang *et al*, 2009):

$$E = \frac{1}{\eta} Q \frac{\gamma RT}{\gamma - 1}\left[(\dot{\psi})^{\frac{\gamma-1}{\gamma}} - 1\right] \tag{7}$$

where, E is the equipment power use (W); Q is the gas flow rate through the equipment (mole/s); T is the operating temperature (K); η is the equipment efficiency (%); γ is the adiabatic expansion factor; and $\dot{\psi}$ is the pressure ratio across the compressor or vacuum pump. When a compressor is used in the feed side, the compression energy may be recovered partly from the residue stream using an expander. The recovered energy is estimated as:

$$E = \frac{1}{\eta} Q \frac{\gamma RT}{\gamma - 1}\left[1 - (\ddot{\psi})^{\frac{\gamma-1}{\gamma}}\right] \tag{8}$$

where $\ddot{\psi}$ is the pressure ratio across the expander. The equipment efficiency is typically assumed in the range from 0.85 to 0.90 in engineering studies (Favre, 2007). The specific heat ratio or expansion factor of a gas mixture is calculated as (Sutton and Biblarz, 2001):

$$C_{p,mix} = \frac{\sum_j^J n_j C_{p,j}}{\sum_j^J n_j} \tag{9}$$

$$\gamma = \frac{C_{p,mix}}{C_{p,mix} - R'} \tag{10}$$

Where C_p is the molar specific heat at constant pressure (e.g. 37.129 J/mol-K for CO_2 and 29.125 J/mol-K for N_2); n_j is the gas molar fraction; and R' is the universal gas constant (8.314 J/gram-mol-K).

The final CO_2 product stream needs to be compressed to a supercritical fluid for transport to a storage site. The energy requirements and cost of that compression are commonly attributed to the capture component of the CCS chain. The energy use for CO_2 product compression is estimated using the IECM (IECM, 2012).

Heat Exchange

Challenging operation environment may affect the stability of membrane properties. For instance, the CO_2/N_2 selectivity may suffer a remarkable loss when membrane systems operate under high temperatures (Lin and Freeman, 2004). Compressing a feed-in gas stream in an adiabatic process increases the gas temperature. Therefore, heat exchangers are needed to maintain a stable operation. The adiabatic temperatures of a gas stream through pressure changing units such as compressors and vacuum pumps are related by (Geankoplis, 1993):

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \tag{11}$$

where T_1, T_2 are the temperature of a gas stream at the inlet and outlet, respectively; and P_1, P_2 are the inlet and outlet pressures of a gas stream (bar). The outlet temperature (T_2) is further adjusted based on the equipment efficiency. The rejected heat of a gas stream is estimated as:

$$q = \dot{m}C_{p,mix}\left(\acute{T}_2 - T_1\right) \tag{12}$$

where q is the rejected heat of a gas stream (J/sec); $\dot{m}$ is the gas stream flow rate (moles/sec); and $\acute{T}_2$ is the adjusted outlet temperature of a gas stream (^oK). The required area of a heat exchanger is estimated as:

$$A_{HeEx} = \frac{q}{U\,\dfrac{\Delta T_2 - \Delta T_1}{ln\left(\frac{\Delta T_2}{\Delta T_1}\right)}} \tag{13}$$

where A_{HeEx} is the heat exchange area (m^2); ΔT_1, ΔT_2 are the temperature difference between the gas stream and the cooling water at inlet and outlet (^oF), respectively; U is the heat transfer coefficient (W/m^2). The heat transfer coefficient is 110 W/m^2 for pressurized gases and 50 W/m^2 for atmospheric gases (Hendriks, 1994).

To briefly summarize, the analytical procedure used in this paper is as follows: given the flue gas flow rate and composition, membrane properties, pressure specifications, and CO_2 removal targets, the performance model is used to calculate permeate and residue flow rates and associated CO_2 concentrations, as well as the membrane size. The stream flow rates derived from the separation modeling also are used to estimate the power requirements of individual pieces of equipment. Subsequently, economic calculations are driven by parameters and results of the process performance modeling, primarily the membrane area and equipment power use.

Costing Method

The process performance models described above are linked to engineering-economic models that estimate the capital cost, annual operating and maintenance (O&M) costs and total levelized annual cost of the capture system and the overall power plant. The costing method and nomenclature in this study are based on the Electric Power Research Institute's (EPRI) Technical Assessment Guide (TAG), which has been adopted widely as an industry standard (EPRI, 1993). To outline the costing methodology, Figure 2 presents the technical and cost assessment framework for membrane capture systems.

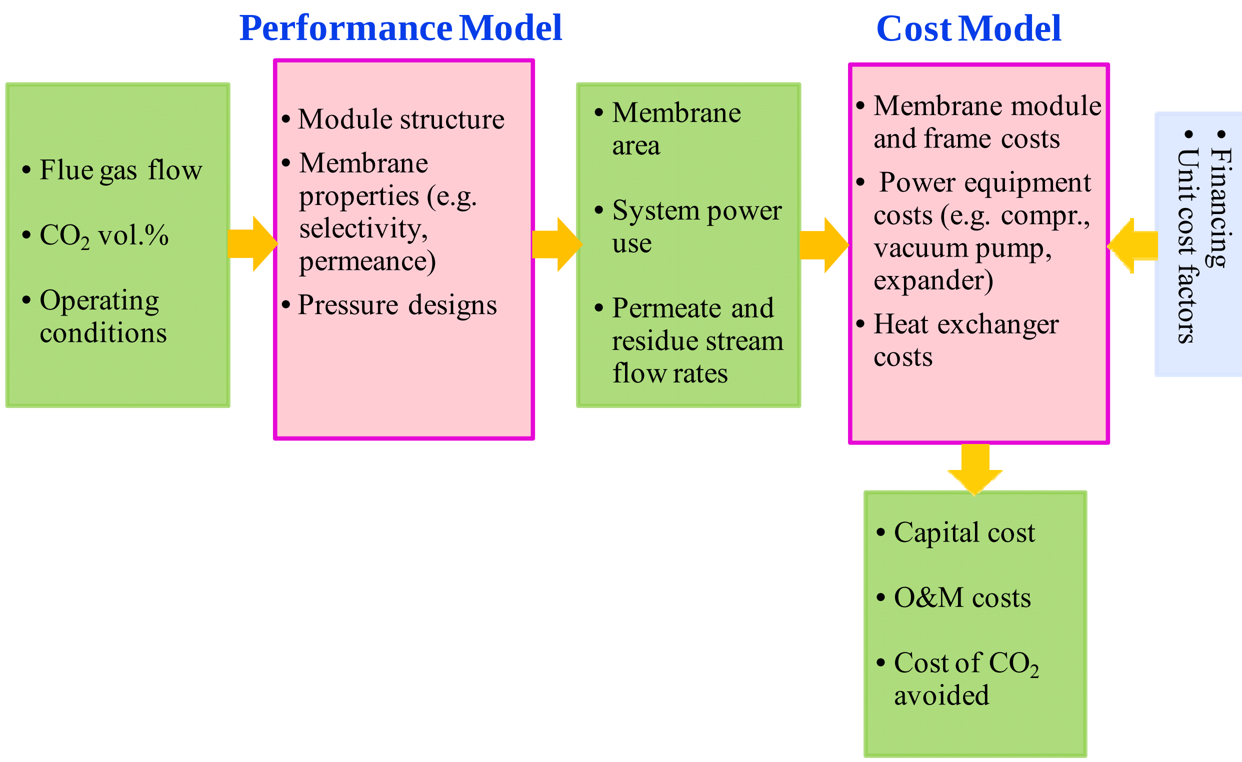

Figure 2 Technical and cost assessment framework for membrane capture systems

The total capital requirement (TCR) of a membrane-based capture system takes into account the direct costs of purchasing and installing process equipment (called the process facilities capital, PFC), plus a number of indirect costs such as the general facilities cost, engineering and home office fees, contingency costs and several categories of owner's costs. The major components of the PFC include the membrane module and frame, compressors, expanders, vacuum pumps and heat exchangers as well as CO_2 product compression. The indirect capital costs are commonly estimated as a percent of the PFC based on industry guidelines. Fixed O&M (FOM) costs include operating labor, maintenance costs, and overhead costs associated with administrative and support labor. Variable O&M (VOM) costs includes material replacement, electricity, and (where appropriate) CO_2 product transport and storage (T&S). Tables 1 and 2 summarize the approaches to capital, fixed and variable O&M cost estimates for membrane systems, respectively. The nomenclature is explained in detail in the EPRI's TAG (EPRI, 1993).

Table 1 Capital cost estimation for membrane capture systems

Process Area/Cost	Method[a]
Membrane module (1)	$A_m \cdot c_m$
Membrane frame (2)	$\left(\frac{A_m}{2000}\right)^{0.7} \cdot c_{mf}$
Compressors (3)	$e_{cpr} \cdot c_{cpr}$
Expander (4)	$e_{exp} \cdot k_{exp} \cdot F_h$
Vacuum pumps (5)	$e_{vp} \cdot c_{vp}$
Heat exchangers (6)	$A_{HeEx} \cdot c_{HeEx}$
CO_2 product compression (7)	$e_{cmp} \cdot c_{cmp}$
Process Facilities Capital (PFC) (8)	**(1) +(2)+….+ (7)**
General facilities capital (9)	% of PFC
Eng. & home office fees (10)	% of PFC
Project contingency cost (11)	% of PFC
Process contingency cost (12)	% of PFC
Interest Charges (13)	
Royalty fees (14)	% of PFC
Preproduction cost (15)	
Inventory capital (16)	% of TPC[b]
Total Capital Requirement (TCR)	**(8) + (9) +…. + (16)**

[a] Notation:

A_{HeEx} = heat exchanger area (m^2);
A_m = membrane area (m^2);
c_{cmp} = installed unit cost of CO_2 product compression ($/kW).
c_{HeEx} = installed unit cost of heat exchanger ($\$/m^2$);
c_m = unit cost of membrane module ($\$/m^2$);
c_{mf} = referred frame cost (M$ 0.238) (Van Der Sluijs *et al*., 1992);
c_{cpr} = installed unit cost ($/kW);
c_{vp} = installed unit cost of vacuum pump ($/kW);
e_{cmp} = CO_2 product compression power use (kW); and
e_{cpr} = compressor power use (kW);
e_{exp} = expander power use (kW);
e_{vp} = vacuum pump power use (kW);
F_h = equipment cost factor for housing, installation, etc (1.8) ;
k_{exp} = unit cost ($/kW).

[b] TPC is the total plant cost, which is the sum of (8)+(9)+(10)+(11)+(12).

Table 2 Operation and maintenance cost estimation for membrane capture systems

Variable Cost Component	Method[a]	Fixed Cost Component	Method
Material replacement (1)	$(A_m \cdot \vartheta) \cdot c_{rm}$	Operating labor (4)	
Electricity (2)	MWh $\cdot$ COE	Maintenance labor (5)	% of TMC[b]
CO_2 transport & storage (when considered) (3)	$m_{CO2} \cdot c_{T\&S}$	Maintenance material (6)	% of TMC
		Admin. & support labor (7)	% of Total labor
Variable O&M Costs	**(1)+(2)+(3)**	**Fixed O&M Costs**	**(4)+(5)+(6)+(7)**

[a] Notation:

A_m = membrane area (m^2);
c_{rm} = material replacement cost ($\$/m^2$);
$c_{T\&S}$ = CO_2 transport and storage costs (\$/mt CO_2)
COE = cost of electricity (\$/MWh);
m_{CO2} = annual CO_2 captured (mt/yr);
MWh = annual system power use (MWh);
ϑ = annual material replacement rate (%).

[b] TMC is the total maintenance cost.

BASE CASE STUDIES

The IECM (v 7.0-beta) was used to conduct base case studies for illustrative supercritical PC power plants with and without a two-stage membrane CCS. Figure 3 presents schematic of a two-stage membrane CCS system that applies both compressors and vacuum pumps to produce driving force for membrane gas separation. The base plants comply with federal New Source Performance Standards for air and water pollutants. Table 3 summarizes major performance and economic assumptions for the base plants with a net power output of 550 MW.

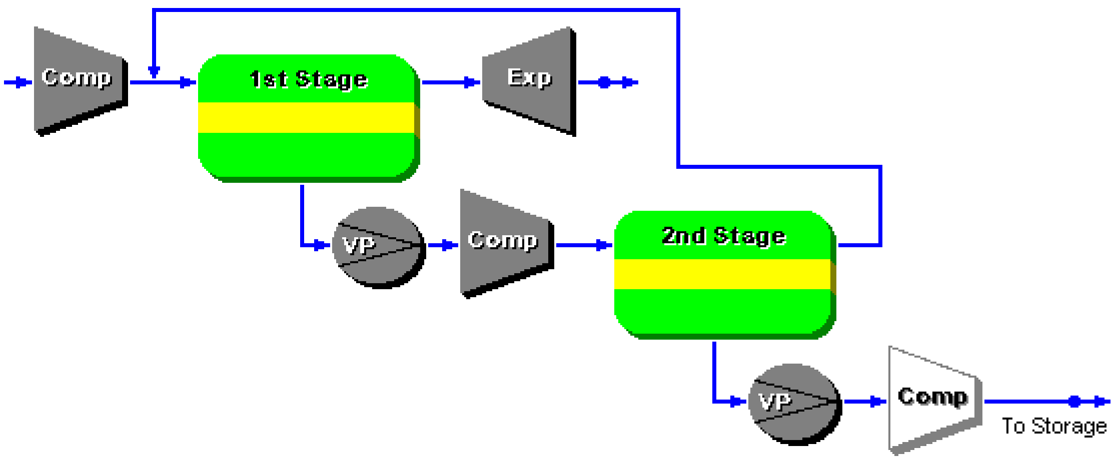

Figure 3 Schematic of a two-stage membrane capture system

The membrane system employed in the base capture case is configured with two stages operated for the cross-flow pattern. As shown in Figure 3, the residue stream out of the first stage is vented out to atmosphere. The residue stream out of the second membrane is recycled to the entrance of the capture system, and has the same CO_2 concentration as the inlet flue gas. The CO_2-rich permeate stream out of the second stage is further compressed via a multi-stage compressor before it is transported to a storage site. In this system the combination design of feed-side compression and permeate-side vacuum pumping is adopted to generate the driving force for CO_2/N_2 separation. Membrane properties and costs are based on recently reported data for polymeric membranes (Merkel *et al*, 2010). Cost data for other major process equipment are based on the literature and IECM estimates (Van Der Sluijs *et al*, 1992; Noble and Stern, 1995; Rao and Rubin, 2002; IECM 2012). Base case assumptions regarding indirect capital and O& M costs are similar to those of an amine-based capture system (Rao and Rubin, 2002; IECM 2012).Nominal values of major technical and cost metrics defining the membrane-based capture system are also presented in Table 3. The two stages of the capture system have identical material properties and pressure designs.

Table 3 Technical and economic assumptions for base power plant and membrane system

Category	Variable	Value
Power plant (w/o CCS)	Plant type	Supercritical
	Coal type	Illinois #6
	Environmental controls	SCR + ESP + FGD[a]
	Cooling system	Wet tower
	Capacity factor (%)	75
	Net electrical output (MW)	550
	CO_2 molar concentration in flue gas (%)	11.8
	Flue gas pressure (bar)	1.0
	Fixed charge factor	0.113
	Dollar year/type	2010/constant
Membrane system	CO_2 permeance (S.T.P. gpu)[c]	1000
	CO_2/N_2 selectivity (S.T.P.)	50
	System operating temperature (^oC)	30
	CO_2 product compression (kWh/mt CO_2)	93
	Membrane module price ($\$/m^2$)	50
	Gas compressor installed cost ($/hp)	500
	Gas vacuum pump installed cost ($/hp)	1000
	Gas expander unit cost ($/kW)	500
	Heat exchanger capital cost ($\$/m^2$)	300
	Product compression installed cost ($/kW)	900
	General facilities capital (% of PFC)	10
	Engineering & home office fees (% of PFC)	7
	Project contingency cost (% of PFC)	15
	Process contingency cost (% of PFC)	5
	Royalty fees (% of PFC)	0.5
	Pre-production costs	
	Months of fixed O&M	1
	Months of variable O&M	1
	Misc. capital cost (% of TPI[d])	2
	Inventory capital (% of TPC[d])	0.5
	CO_2 transport and storage costs ($/mt)	5.0
	Material replacement rate (%)	20
	Material replacement cost ($\$/m^2$)	10
	Number of operating jobs (jobs/shift)	2
	Number of operating shifts (shifts/day)	4.75
	Total maintenance cost (TMC) (% of TPC)	2.5
	Maint. cost allocated to labor (% of TMC)	40
	Administrative & support cost (% total labor)	30
	Labor rate ($/hr)	34.65

[a] SCR = selective catalytic reduction; ESP =electrostatic precipitator device; and FGD = flue gas desulfurization;

[b] The S.T.P. indicates the standard temperature and pressure conditions (0^oC and 1 atmospheric pressure);

[c] 1 gas permeation unit (gpu) = 10^{-6} cm^3 (S.T.P.)/($cm^2 \cdot s \cdot cmHg$);

[d] TPC is the total plant cost, and TPI is the total plant investment.

A wide range of process scenarios are designed to explore the potential operational space of the two-stage membrane-based capture process and characterize key input-output response relations. The reduced-order models (ROMs) are then formulated and embedded in the IECM. The detailed ROMs also are available in the appendix.

Table 4 Performance and cost results of coal-fired power plant with and without two-stage membrane system for 90% CO_2 capture

Parameter	Carbon capture and storage (CCS)	
	Without	**With**
Gross electrical output (MW)	589.7	883.2
Net electrical output (MW)	550.0	550.0
Net plant efficiency(%, HHV)	38.4	25.7
CO_2 emission rate (kg/kWh)	0.816	0.122
Two-stage membrane CCS system		
Pressure ratio for permeate versus feed sides	n/a	20.5
Feed-side pressure (bars)	n/a	4.1
System power use (% of MWg)	n/a	31.1
Plant cost of electricity (COE) ($/MWh)	59.4	117.0
Added COE for CCS ($/MWh)		57.6
Cost of CO_2 avoided ($/mt)		83

When the two-stage membrane CCS is added to the PC plant for 90% removal efficiency and 95% product purity for $CO_{2,}$ the pressure ratio for feed versus permeate side is required to be about 20 for the given membrane properties in Table 3. To achieve this pressure ratio, the feed stream is compressed to be 4.1 bars and the permeate stream is vacuumed to be 0.2 bar. The results in Table 4 show that with the addition of CCS, the net plant efficiency (HHV) decreases from 38.4% to 25.7% mainly because the power us of the capture system accounts for 31% of the gross power output. As a result of adding CCS, the levelized cost of electricity (COE) of the base plant increases by 97%, which is larger than that for the current amine-based capture system (Rubin *et al*, 2007). The resulting cost of CO_2 avoided for the PC plants with and without capture is $83 per metric tonne of $CO_{2,}$ which is a widely-used cost metric for inter- and intra-technology comparisons. Because a number of factors affect the capture system performance and cost, we next undertake a series of parametric analyses to examine the effects of various parameters and designs on the plant performance and the cost of CO_2 avoided by membrane systems.

SENSTIVITY ANALYSIS

Parametric analyses also were conducted to investigate the effects of feed-side pressure, membrane properties and price on the power plant and membrane capture system. In each capture case of fulfilling the desired separation of 90% removal efficiency and 95% product purity for CO_2, other parameters were kept at their base case values, unless otherwise noted.

Feed-side Pressure

We first examine how different feed-side pressure designs affect the plant performance and the cost of CO_2 avoided by the two-stage membrane system. For the fixed pressure ratio of 20, the feed-side pressure is varied from 2.0 bars to 10.0 bars. To elevate the feed-side pressure significantly increases the system power requirements, although it reduces the required membrane area. Figure 4 shows that as a result of increasing the feed-side pressure by compressors, the net plane efficiency (HHV) decreases from 27.8% to 20.1%, and the cost of CO_2 avoided for the PC plants with and without capture increases from $73 to $141 per metric tonne of CO_2. These results imply that using compressors alone would make the capture system's overall energy penalty far too large to be affordable, even if an expander is used to recover part of the energy.

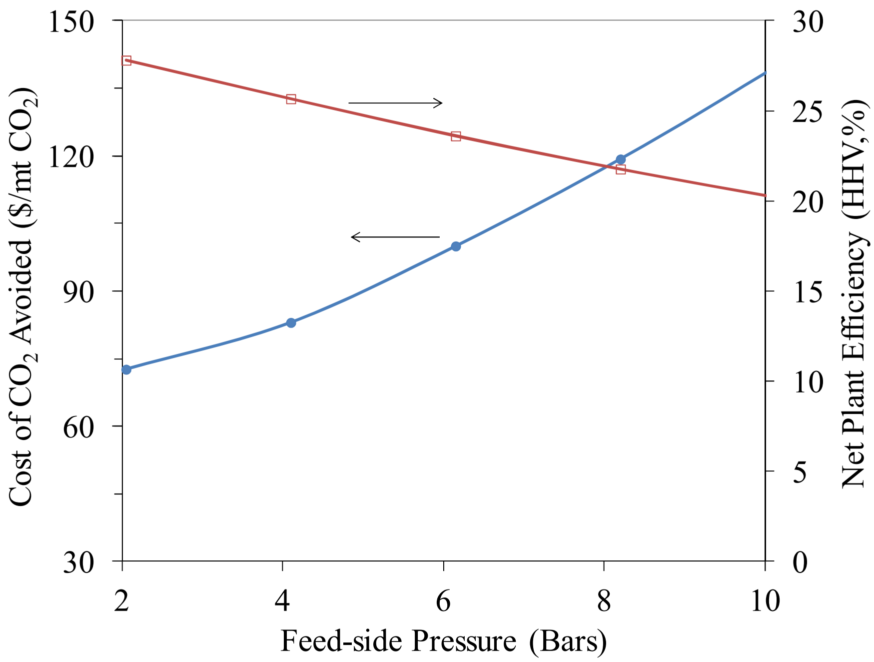

Figure 4 Effects of feed-side pressure of two-stage membrane system on net plant efficiency and cost of CO_2 avoided

Membrane Properties

We conduct additional sensitivity analyses to evaluate the effects of membrane CO_2/N_2 selectivity and CO_2 permeance on the cost of CO_2 avoided by the two-stage membrane system. Here the CO_2/N_2 selectivity is changed from 40 to 70, while the CO_2 permeance is evaluated at 1000, 2000 and 3000 gpu. In this analysis, the permeate-side pressure is held at 0.20 bar for all cases. The required pressure ratio decreases from 29.3 to 14.3 and the net plant efficiency (HHV) increases from 23.4% to 27.5%, when the selectivity increases within the selected range. Figure 3 shows the cost of CO_2 avoided as a function of the membrane selectivity. Figure 5 shows that for a given permeance, the cost decreases up to a selectivity of 60, then remains roughly constant. For a given selectivity, increasing the CO_2 permeance reduces the cost of CO_2 avoided by decreasing the required membrane area. These results clearly indicate the cost of CO_2 avoided is highly affected by membrane properties.

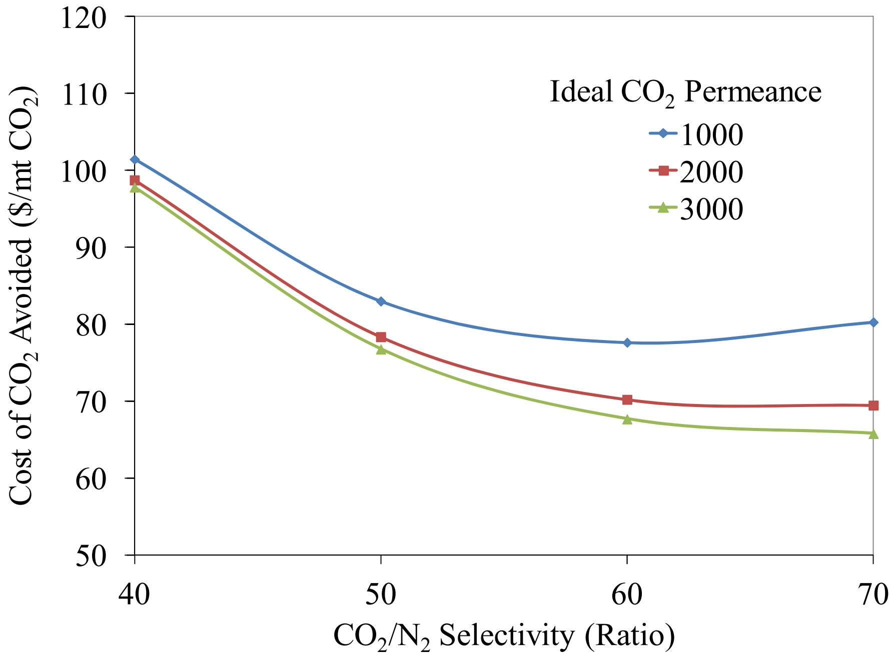

Figure 5 Effect of membrane properties on cost of CO_2 avoided by two-stage membrane system

Membrane Module Price

The assumption of membrane module price directly affects cost estimates. Figure 6 shows that effect of membrane price for three CO_2 permeances. To reduce the cost of producing membrane modules decreases the cost of CO_2 avoided by the capture system. For example, for a permeance of 1000 gpu the cost of CO_2 avoided decreases from $98.4/mt to $76.9/mt as the unit price falls from $150 to $10 per square meter. At higher values of CO_2 permeance the cost is relatively less sensitive to the membrane price because the required membrane area decreases with increasing permeance. When the membrane module price approaches to the smallest value, the cost of CO_2 avoided is still high up to more than $70/mt CO_2, which is mainly accounted for by the costs of major equipments including the compressors, vacuum pumps and an expander as well as the CO_2 product compression and storage.

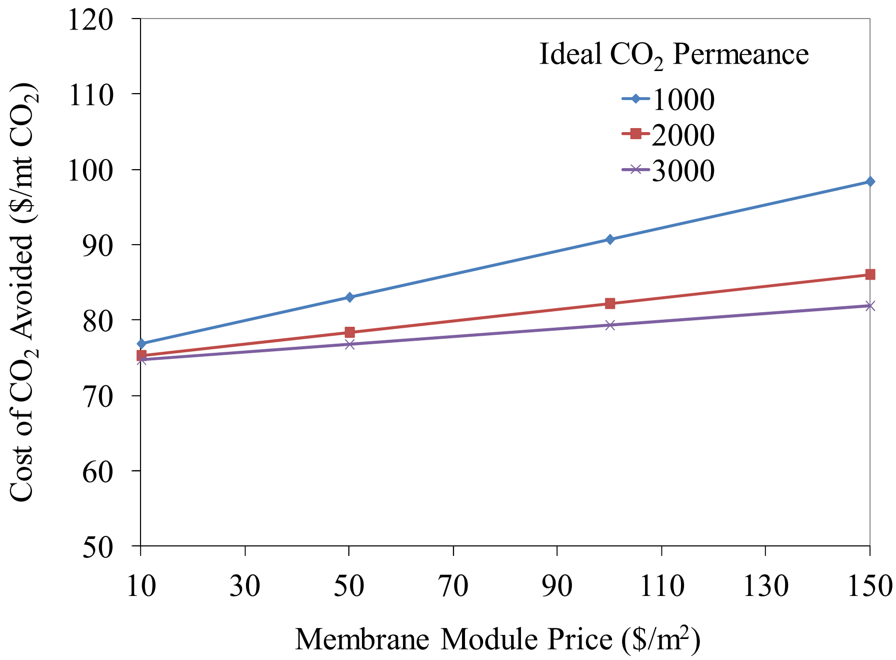

Figure 6 Effect of membrane module price on cost of CO_2 avoided by two-stage membrane system

SUMMARY

The system analyses demonstrate the feasibility of multi-stage membrane systems for CO_2 capture at coal-fired power plants. However, potential impacts of minor air pollutants in real flue gases on the membrane system performance are not taken into account. To simultaneously achieve 90% capture and 95% product purity for CO_2, adding a two-stage membrane system to a PC power plant nearly doubles the plant COE and incurs a high energy penalty up to about 30% of the gross electrical output. A series of parametric analyses exhibits that the driving force design of using both compressors and vacuum pumps to lower the feed gas compression pressures is effective with reducing the capture system's energy penalty and cost of CO_2 avoided; and improving membrane properties, along with lowering the cost of producing highly permeable membranes would further decrease the capture cost and enhance the viability of membrane technology.

REFERENCES

(1) Energy Information Administration. *Annual Energy Outlook 2012 with projections to 2035*; DOE/EIA-0383(2012); U.S. Department of Energy's Energy Information Administration: Washington, DC, June 2012.
(2) Bounaceur, R.; Lape, N.; Roizard, D.; Vallieres, C.; Favre, E. Membrane processes for post-combustion carbon dioxide capture: a parametric study. *Energy* **2006**, 31, 2556–2570.

(3) Brunetti, A.; Scura, F.; Barbieri, G.; Drioli, E. Membrane technologies for CO_2 separation. *J. Membr. Sci.* **2010**, 359(1-2), 115–125.
(4) *Carnegie Mellon University's Integrated Environmental Control Model (IECM) Website*. http://www.cmu.edu/epp/iecm/index.html (accessed May 2012).
(5) Electric Power Research Institute (EPRI). *TAG™ –Technical Assessment Guide Vol.1: Electricity Supply, Rev.7*; ReportNo.TR-102276-VIR7; Electric Power Research Institute, Palo Alto, CA, June 1993.
(6) Favre, E. Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption? *J. Membr. Sci.* **2007**, 294, 50–59.
(7) Favre, E. Membrane process and postcombustion carbon dioxide capture: challenges and prospects. *Chem. Eng. J.* **2011**, 171(3), 782–793.
(8) Figueroa, J. D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R. D. Advances in CO_2 capture technology – the U.S. Department of Energy's Carbon Sequestration Program. *Int. J. Greenhouse Gas Control* **2008**, 2, 9–20.
(9) Freeman, B. D. Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes. *Macromolecules* **1999**, 32, 375–380.
(10) Geankoplis, C. J. *Transport Processes and Unit Operations*, 3rd Edition. Prentice Hall, **1993**.
(11) Gin, D. L.; Noble, R.D. Designing the next generation chemical separation membranes. *Science* **2011**, 332, 674–676.
(12) Haszeldine, R. S. Carbon capture and storage: how green can black be? *Science* **2009**, 325, 1647–1652.
(13) Hendriks, C. F. *Carbon Dioxide Removal from Coal-fired Power Plants*. Kluwer Academic Publishers, 1994.
(14) Ho, M. T.; Leamon, G.; Allinson, G. W.; Wiley, D. E. Economics of CO_2 and mixed gas geosequestration of flue gas using gas separation membranes. *Ind. Eng. Chem. Res.* **2006**, 45, 2546–2552.
(15) Ho, M. T.; Allinson, G. W.; Wiley, D. E. Reducing the cost of CO_2 capture from flue gases using membrane technology. *Ind. Eng. Chem. Res.* **2008**, 47, 1562–1568.
(16) IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK, New York, NY, 2005.
(17) Lin, H. and B. D. Freeman. Gas solubility, diffusivity and permeability in poly (ethylene oxide). *J. Membr. Sci.* **2004**, 239(1):105-117.
(18) National Energy Technology Laboratory*, Cost and performance baseline for fossil energy plants, Rev. 2*; DOE/NETL-2010/1397; U.S. Department of Energy's National Energy Technology Laboratory: Pittsburgh, PA, November 2010a.
(19) National Energy Technology Laboratory. *DOE/NETL carbon dioxide capture and storage RD& D roadmap*; U.S. Department of Energy's National Energy Technology Laboratory: Pittsburgh, PA, December 2010b.
(20) Noble, R. D.; Stern, S. A. Membrane Science and Technology Series 2: Membrane Separations Technology Principles and Applications, Elsevier Science B.V., Netherlands, 1995.
(21) Merkel, T. C.; Lin, H.; Wei, X.; Baker, R. Power plant post-combustion carbon dioxide capture: an opportunity for membranes. *J. Membr. Sci.* **2010**, 359(1-2), 126–139.
(22) Powell, C. E.; Qiao, G. G. Polymeric CO_2/N_2 gas separation membranes for the capture of carbon dioxide from power plant flue gases. *J. Membr. Sci.* **2006**, 279, 1–49.

(23) Favre, E. Membrane process and postcombustion carbon dioxide capture: challenges and prospects. *Chem. Eng. J.* **2011**, 171(3), 782–793.
(24) Hussain, A.; Hägg, M-B. A feasibility study of CO_2 capture from flue gas by a facilitated transport membrane. *J. Membr. Sci.***2010**, 359, 140-148.
(25) Geankoplis, C. J. *Transport Processes and Unit Operations*, 3rd Edition. Prentice Hall, **1993**.
(26) Pan, C. Y.; Habgood, H. W. An analysis of the single-stage gaseous permeation process, *Ind. Eng. Chem. Fundam.* **1974**, 13, 323–331.
(27) Rao, A. B.; Rubin, E. S. A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. *Environ. Sci. Technol.* **2002**, 36 (20), 4467– 4475.
(28) Rubin E. S.; Chen, C.; Rao, A. B. Cost and performance of fossil fuel power plants with CO_2 capture and storage. *Energy Policy* **2007**, 35, 4444–4454.
(29) Scholes, C. A.; Kentish, S. E.; Stevens, G. W. Effects of minor components in carbon dioxide capture using polymeric gas separation membranes. *Sep. Purif. Rev.* **2009**, 38(1), 1–44.
(30) Scholes, G. A.; Kentish, S. E.; Stevens, G. W. The effects of minor components on the gas separation performance of polymeric membranes for carbon capture. Chapter 11, *Membrane Gas Separation*, Edited by Yampolskii, Y. and Freeman, B. D. John Wiley & Sons Ltd, 2010.
(31) Scholes, C. A.; Chen, G. Q.; Tao, W. X.; Bacus, J.; Anderson, C.; Stevens, G. W.; Kentish, S. E. The effects of minor components on the gas separation performance of membranes for carbon capture. *Energy Procedia* **2011**, 4, 681–687.
(32) Sutton, George P., Biblarz, Oscar. *Rocket Propulsion Elements*, 7th Edition. 2001, John Wiley & Sons.
(33) Vallieres, C.; Favre, E.; Arnold, X.; Roizard, D. Separation of binary mixtures by dense membrane processes: influence of inert gas entrance under variable downstream pressure conditions. *Chem. Eng. Sci.* **2003**, 58, 2767–2775.
(34) Van Der Sluijs, J. P.; Hendriks, C. A.; Blok, K. Feasibility of polymer membranes for carbon dioxide recovery from flue gases. ***Energy Convers. Manage.*** **1992**, 33(5-8), 429–436.
(35) Wijmans, J. G.; Baker, R. W. The solution-diffusion model: a review. *J. Membr. Sci.* **1995**, 107, 1-21.
(36) Yang, D.; Wang, Z.; Wang, J.; Wang, S. Potential of two-stage membrane system with recycle stream for CO_2 capture from postcombustion gas. *Energy Fuels* **2009**, 23, 4755–4762.
(37) Zhai, H.; Rubin, E. S.; Versteeg, P. L. Water use at pulverized coal power plants with post-combustion carbon capture and storage. *Environ. Sci. Technol.* **2011**, 45, 2479-2485.
(38) Zhao, L.; Riensche, E.; Menzer, R.; Blum, L.; Stolten, D. A parametric study of CO_2/N_2 gas separation membrane processes for post-combustion capture. *J. Membr. Sci.***2008**, 325, 284–294.
(39) Zhao, L.; Riensche, E.; Blum, L.; Stolten, D. Multi-stage gas separation membrane processes used in post-combustion capture: energetic and economic analyses. *J. Membr. Sci.* **2010**, 359(1-2), 160–172.

APPENDIX

REDUCED-ORDER MODELS FOR TWO-STAGE MEMBRANE SYSTEMS

The two-stage membrane system mainly consists of two membrane modules and a variety of equipments including feed-side compressors, an expander, vacuum pumps, and heat exchangers. Besides, the concentrated CO_2 product stream obtained from membrane separation is compressed and dried using a multi-stage compressor, and then is transported to a storage site. In the IECM, both the membrane modules have identical materials and pressure designs; the gas flow out of the second membrane at the residue end is recycled to the entrance of the capture system, and has the same CO_2 concentration as the inlet plant flue gas.

A wide range of process scenarios are designed to explore the potential operational space of a two-stage membrane-based capture process and characterize key input-output response relations. The CO_2 product purity is designed to be 95 percent for all the process scenarios. The reduced-order models (ROMs) are formulated based on the process modeling results, and then embedded into the IECM to evaluate the performance of membrane-based capture systems. It, in turn, allows comparative assessment for different CO_2 capture technologies in a common framework.

Table A1 summarizes the major input and output variables included in the ROMs. Each of the input parameters is varied over a range to cover possible operation conditions. For the given ranges of key input variables shown in Table A1, there are a total of 960 scenarios designed and modeled for quantifying input-output response relations among the major process parameters.

Table A1 Summary of Key Input and Output Variables for Reduced-Order Models

Parameter	Symbol	Unit	Variable Type	Range
CO_2 removal efficiency	η	%	Input	60-95
CO_2 concentration of inlet Flue gas	x	Molar fraction	Input	10-15
Membrane CO_2 permeance	τ	gpu	Input	500-5000
Membrane CO_2/N_2 selectivity	φ	ratio	Input	40-75
Permeate-side pressure	P_p	bar	Input	0.2
Pressure ratio	α	ratio	Output	
Pressure-side pressure	P_f	bar	Output	
Stage-cut 1	$\emptyset_1$	fraction	Output	
Stage-cut 2	$\emptyset_2$	fraction	Output	
Permeate CO_2 concentration @Stage 1	y	Molar fraction	Output	
Membrane area @ Stage 1	$\tilde{a}_1$	m^2/m^3 of flue gas[a]	Output	
Membrane area @ Stage 2	$\tilde{a}_2$	m^2/m^3 of flue gas[a]	Output	

[a] That represents the total flue gas flow rate into the membrane capture system.

Regression Equations

The data collected from the process modeling results were used to develop multivariate regression equations using a statistical package called Minitab. The resulting regression equations for major parameters are:

The pressure ratio for feed side to permeate side is estimated as a function of inlet CO_2 concentration of flue gas, CO_2 removal efficiency, and membrane CO_2/N_2 selectivity:

$$\mathrm{Ln}(\alpha) = 10.5 - 36.6x + 93.6x^2 - 6.73\eta + 5.63\eta^2 - 0.0889\varphi + 0.000590\varphi^2 \quad \text{(A1)}$$

(R-Sq(adj) = 93.0%, Sample size: 384)

The stage cut at the first module is estimated as a function of CO_2 removal efficiency, inlet CO_2 concentration of flue gas, membrane CO_2/N_2 selectivity, and pressure ratio:

$$\emptyset_1 = -0.249 + 1.29x + 0.336\eta + 0.000732\varphi - 0.0123\mathrm{Ln}(\alpha) \quad \text{(A2)}$$

(R-Sq(adj) = 97.3%, Sample size: 384)

The stage cut at the second module is estimated as a function of CO_2 removal efficiency, membrane CO_2/N_2 selectivity, and stage cut:

$$\emptyset_2 = 0.900 - 0.207\eta - 0.00295\varphi - 0.331\emptyset_1 \quad \text{(A3)}$$

(R-Sq(adj) = 97.4%, Sample size: 384)

The CO_2 concentration of the permeate flow out of the first module is estimated as a function of inlet CO_2 concentration of flue gas, CO_2 removal efficiency, membrane CO_2/N_2 selectivity, pressure ratio, and stage cut:

$$y = 0.589 + 1.51x - 0.0337\eta - 0.00164\varphi + 0.0131\text{Ln}(\alpha) - 0.794\emptyset_1 \quad \text{(A4)}$$

(R-Sq(adj) = 98.7%, Sample size: 384)

The product of normalized membrane area and membrane CO_2 permeance is estimated as a function of inlet CO_2 concentration of flue gas, CO_2 removal efficiency, membrane CO_2/N_2 selectivity, pressure ratio, and stage cut:

$$\text{Ln}(\tilde{a}_1\tau) = 13.3 + 7.17\,x + 2.67\,\eta + 0.0282\,\varphi - 1.18\text{Ln}(\alpha) - 0.00167\emptyset_1 \quad \text{(A5)}$$

(R-Sq(adj) = 99.8%, Same size: 960)

$$\text{Ln}(\tilde{a}_2\tau) = 10.5 + 15.7\,y + 1.73\,\eta + 0.0155\,\varphi - 1.14\text{Ln}(\alpha) - 11.9\emptyset_2 \quad \text{(A6)}$$

(R-Sq(adj) = 99.8%, Same size: 960)

When the permeate-side pressure differs from the scenario value (0.20 bar), but other parameters and process designs are kept at their values in the scenarios above, the membrane area is estimated as:

$$A_m = A_m^o\left(\frac{0.20}{P_P}\right) \quad \text{(A7)}$$

where A_m^o is the membrane area (m^2) referred to the base case in which the permeate-side pressure is 0.20 bar; A_m is the membrane area (m^2) with a permeate-side pressure different from the base value, and P_P is the actual permeate-side pressure (bar).