

Two stage membrane system for post-combustion CO₂ capture application

CCTC 2015 Paper Number 1570087879

A. Hussain¹ and S. Farrukh²

^{1,2} School of Chemical and Materials Engineering, National University of Sciences and Technology (NUST), Islamabad, Pakistan

Abstract

This work evaluates the viability of a two stage process using a nitrogen selective membrane and a carbon dioxide selective membrane for post-combustion CO₂ capture. A novel cellulose acetate hybrid (CLSICA) membrane was developed with introduction of p-tert-butylcalix [4] arene immobilized silica (CL-Si) as filler. Gas permeation experiments of hybrid (CLSICA) membrane revealed its nitrogen selective character. A Fixed Site Carrier (FSC) membrane (PVAm cast on a porous polysulfone (PSf) support) has great potential to be used as CO₂ selective membrane. Based on the mentioned two membranes, a two stage membrane process is proposed in which N₂ selective membrane is used in 1st stage while a CO₂ selective membrane is used in 2nd stage. The techno-economic analysis show lower value of energy consumption (1.0 MJ/kg CO₂) and CO₂ capture cost (\$ 20.5/ton CO₂) by employing N₂ selective and CO₂ selective membrane. The concept of using modified silica with calixarene for the fabrication of hybrid CA membrane is novel and its viability for post-combustion CO₂ capture application has been reported first time.

Keywords: Hybrid membrane, FSC membrane, CO₂ capture, Techno-economic analysis

1. Introduction

The growing public concern on global warming plays a pivotal role to develop economical and environmental friendly techniques for CO₂ capture and storage. There are three major areas where CO₂ capture is more viable, namely; power generation (which is responsible for over 29% CO₂ emissions), industrial processing and fuel (natural gas) processing. Amine absorption is conventionally used as CO₂ capture technology, apart from some technical challenges in terms of higher energy costs and environmental impact. Membrane based CO₂ capture processes offer a great potential for CO₂ capture, despite few limitations in terms of their sensitivity towards high temperature/pressure and severe process conditions. Nevertheless membrane processes offer the benefit of their low capital investment, small footprints, ease of scale-up and low energy requirement. Process design and technical ease related to the process operation, along with CO₂ capture cost is a decisive factor while selecting the suitable capture technology. Numerous polymers have been used to fabricate membrane for CO₂ capture application including polyimide, polyamide, polyvinyl amine, polyvinyl alcohol, polyvinyl acetate and cellulose acetate [1]. There are only handful commercially available polymers for membrane fabrication because of the fact that lab scale synthesis of polymers to commercial scale production is very expensive [2]. It is vital that membrane has both good CO₂ selectivity and permeability to overcome the trade-off between permeability and selectivity [3]. It also needs to be easy to manufacture at a low cost [4]. Therefore selection of polymers, solvents and additives for membrane synthesis plays a vital role in the permselectivity of membrane.

2. Membranes for post-combustion CO₂ capture

2.1. N₂-selective (CLSICA) membrane

Hybrid membranes are a facile alternative to address the problem of low permselectivity. In this approach, inorganic media is added as filler in polymeric matrix to enhance both its selectivity and mechanical strength [5]. Calixarene is a synthetic supra-molecule, mainly recognized for its typical host-guest interaction with ionic as well as neutral guest species [6]. Immobilization of calixarene on to silica particle is beneficial in terms of its selectivity and reusability. The thermal, chemical and physical stability of silica under many experimental conditions make it suitable for filler purpose in gas separation. N₂-selective membrane is synthesized by incorporating silica (Si) and p-tert-butylcalix [4] arene immobilized silica (CL-Si) (see in Figure1) into CA matrix to explore their efficiency in gas permeation. Both CL-Si were introduced into CA matrix as filler following diffusion induced phase separation (DIPS) method [7]. Three different concentrations (3wt%,10wt%,30wt%) of CL-Si were blended with CA along with synthesis of pure CA membrane, which are nominated as M(c), M(d), M(e) and M(a) respectively. Si/CA hybrid membrane is indicated by M (b). Gas permeation experiments were carried out to examine the effect of impregnation of silica with calixarene. The CO₂, CH₄ and N₂ gases permeation behaviour of prepared membranes are presented in Figure 2-3.

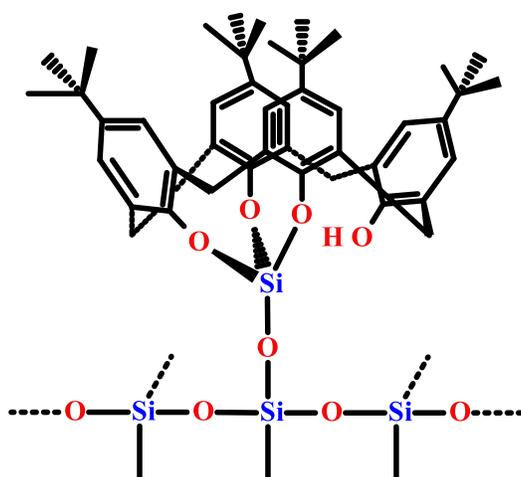


Figure 1. p-tert-butylcalix[4]arene immobilized silica.

It is evident from Figure 2 and 3 that CO₂ and CH₄ permeance in Si/CA and Si-CL/CA membranes are lower in comparison to pure CA. However, N₂ permeation of both Si/CA and Si-CL/CA membranes are high relative to pure CA. Figure 3 shows that N₂/CO₂ selectivity increases linearly with rise in Si-CL filler concentration while N₂/CH₄ selectivity firstly increases then drop at 30% Si-CL filler concentration. The possible explanation of this observation is intermolecular interaction of impregnated calixarene moiety with CO₂ that blocks its permeation through Si-CL/CA membrane. Conversely high N₂ permeation is expected due to its small kinetic radii relative to both CH₄ and CO₂.

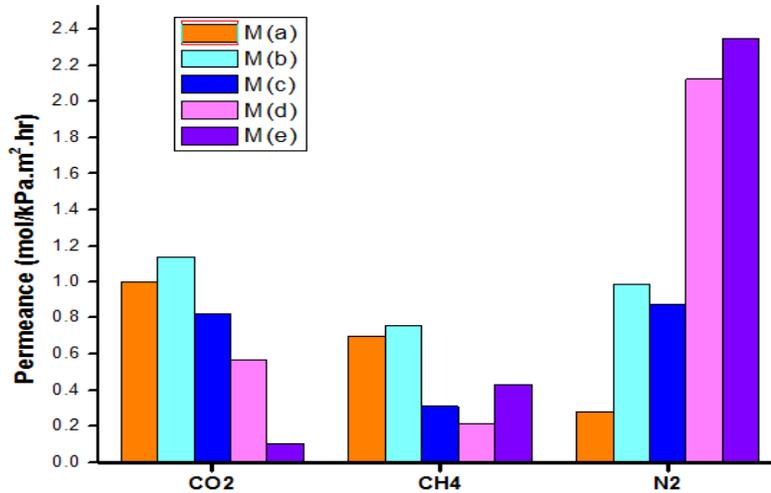


Figure 2: Permeance of different gases via fabricated membranes at 400kPa feed pressure [M(a): Pure CA, M(b): Si/CA hybrid, M(c): 3wt% CL-Si, M(d): 10wt% CL-Si, M(e): 30wt% CL-Si].

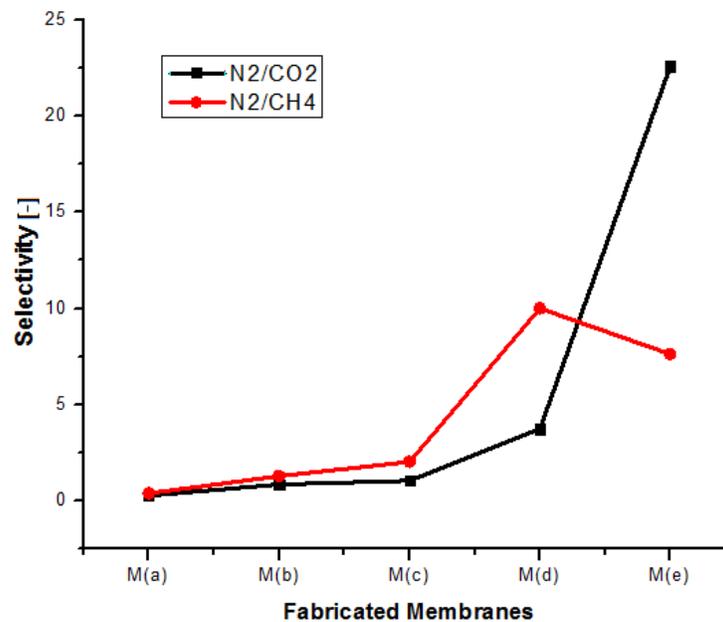


Figure 3. Selectivity of different gases via fabricated membranes at 400kPa feed pressure.

2.2. CO₂-selective (FSC) membrane

Polymeric fixed-site-carrier (FSC) membranes have carriers covalently bonded directly to the polymer backbone; hence the carriers have restricted mobility and therefore more stable. Amines are one of the possible carriers for CO₂ capture in FSC membranes. The transport mechanism illustrated in Figure 4 suggests that the CO₂ reacts with the water and form bicarbonate. The water will at the same time protonate the primary amine in the polyvinylamine. The bicarbonate will hop from amine to amine sites and then will convert back into CO₂ by reversible reaction and CO₂ is released at the permeate side. [8].

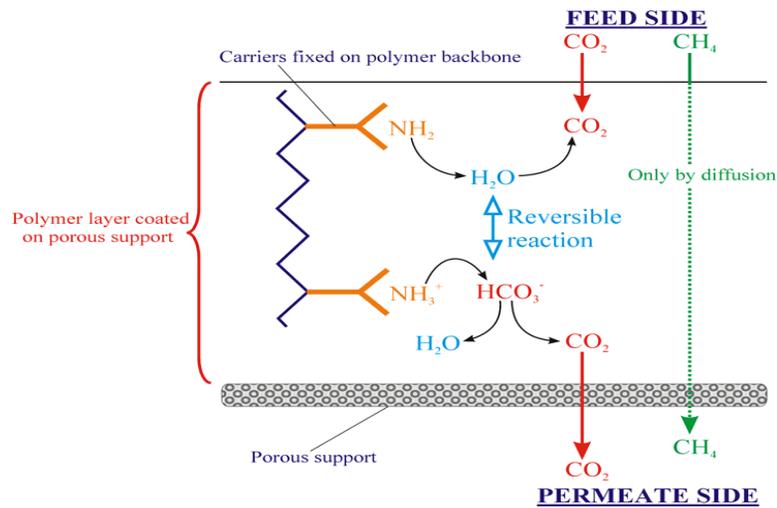


Figure 4. Schematic transport through FSC membrane.

FSC (fixed-site-carrier) membranes have shown a promising performance in terms of high flux as well as high selectivity in favour of CO₂ [4]. PVAm based FSC membrane has been developed for the specific purpose of CO₂ capture from flue gas [8-12]. The membrane consists of a selective layer of polyvinylamine (PVAm) on a microporous polysulfone (PSf) support. The membrane has previously showed a selectivity for CO₂/N₂ of 200 and a CO₂ permeance up to 1 m³ (STP)/m² h bar [10-12].

3. Principle of membrane gas separation

The principle of membrane gas separation is based on Solution-Diffusion Model, which is widely accepted transport mechanism for gas permeation through polymer membranes [13]. The governing flux equation for the permeation (eq. 1) is based on Fick's law where driving force is the difference in partial pressures over the membrane. The flux, J (m³ (STP)/m²h), is expressed as,

$$\frac{q_{p,i}}{A_m} = \frac{q_p y_{p,i}}{A_m} = J_i = \frac{P_i}{l} (p_h x_i - p_l y_i) \quad (1)$$

where q_p is the volume of the permeating gas (i) (m³ (STP)/h), P_i is the permeability of gas component i (m³ (STP)m/(m².h.bar)), l is the thickness of the membrane (m), p_h and p_l are pressure on the feed and permeate sides (bar), x_i and y_i are the fractions of component i on the feed and permeate sides, respectively, and A_m (m²) is the required membrane permeation area. The general definition of permeability (P) of gases through membrane is defined as the product of diffusion, D (m²/s) and solubility, S (m³ (STP)/m³.bar) coefficients for the gas in the membrane material. The intrinsic membrane selectivity " α " is estimated by the ratio of pure gas permeabilities (P_i, P_j).

$$P = D.S \quad (2)$$

$$\alpha = \frac{P_i}{P_j} \quad (3)$$

The recovery (R) of desired component (in this work $i = \text{CO}_2$) by a membrane separation process is calculated by eq. 4,

$$R = \theta \cdot y_i / x_i \quad (4)$$

Where y_i is the mole fraction of desired component (in this work CO_2) in permeate and feed.

4. CO_2 capture by membrane technology

The current cost of post-combustion CO_2 capture is perceived to be high. To reduce the impact of CO_2 capture cost, it is aimed to design a less expensive capture process. Flue gas treatment process requires a quite large capture system by size and volume since it is at atmospheric pressure and the partial pressure of CO_2 is relatively low. Moreover, the capture systems must be flexible for simple retrofit without requiring tedious modifications to the original plant. The key issue for membrane based post-combustion CO_2 capture process is the energy requirement which must be competitive to the energy required by amine absorption process (3-4 MJ/kg CO_2) to prove its feasibility [14-15]. The simulation analysis showed that the proposed process design can give 98% pure N_2 on the permeate side at 1st stage, 90% pure CO_2 on the 2nd stage. Retentate from 1st stage is fed to 2nd stage. The retentate from 2nd stage contains predominantly Nitrogen (78%) and Oxygen (18%) which can be released into the atmosphere. The flue gas mixture data has been taken from a 500 MW coal fired power plant which contains 11.93% CO_2 , 4.86% O_2 , 70.60% N_2 and 12.60% water. The flue gas mixture also contained 235 mg/dNm³ SO_2 and 298 mg/dNm³ NO_x , however in this analysis traces of SO_2 and NO_x have been ignored due to unavailability of experimental data for these gases.

4.1. Process conditions and simulations method

The CO_2 concentration in flue gas can vary from 7-30% depending on the source [16]. A flue gas mixture containing 11.93% CO_2 , 4.86% O_2 , 70.60% N_2 and 12.60% water is considered in this work. Apart from flow rates, temperature and compositions, other process variables when using polymeric membranes, are pressure ratio (ψ) between the upstream (p_h) and downstream (p_l) pressure over the membrane. A process flow diagram of the proposed two stage membrane separation process is depicted in Figure 5. In a post-combustion scenario depending on the emissions source, flue gas flow rates can be huge [17]. Therefore, the feed (flue) gas flow rate is taken 1.725×10^6 kg/h (1200 MMSCFD) which is realistic and has been reported earlier [18]. It is assumed that the membrane permeability is independent of pressure and concentration and the pressure drop on the feed side is nominal. The feasibility of proposed process design is evaluated with an in-house membrane program interfaced within process simulation program (AspenHysys) by calculating the energy demand and flue gas processing cost. The input data is mainly based on process conditions, feed gas composition and gas permeance values for both membranes. The simulations are based on the SRK (Soave-Redlich-Kwong) equation of state and the program has the possibility to utilize Hysys capability to calculate and couple energy balances in the process model. Adiabatic efficiency for compressors has been assumed as 85%.

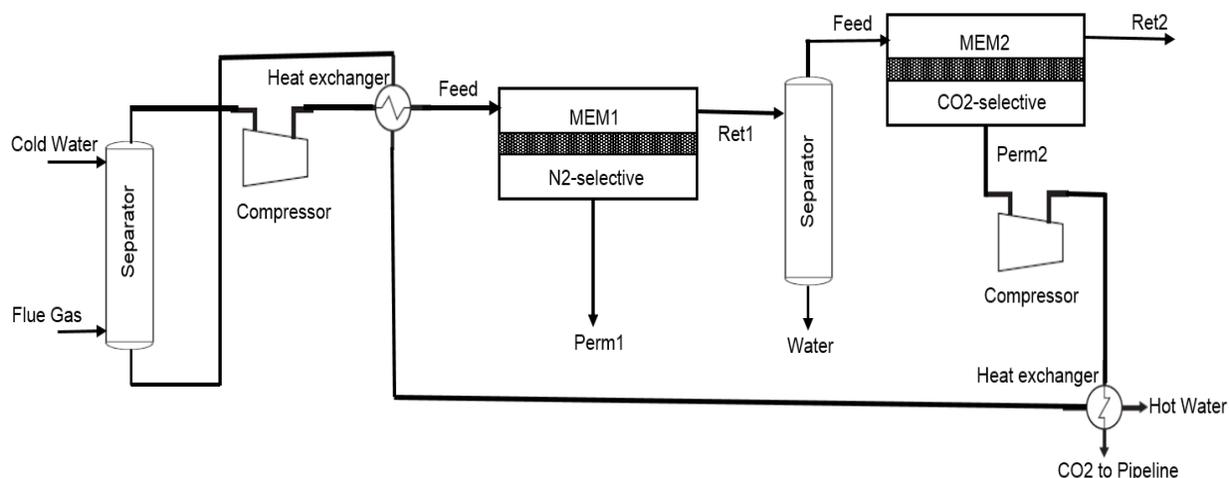


Figure 5. Simplified single stage membrane separation process.

The feed gas (flue gas) at 1 bar and 50°C is fed to a direct contact condenser which brings the flue gas temperature from 50°C to down to 20°C. This process step contributes towards the removal of appreciable amount of water in the original flue gas mixture and washes away some trace gases and fly ash from the flue gas, thus bringing down the H₂O content in flue gas from 12.6% to 2.1%. Flue gas is then compressed to 4 bar and cooled to 35°C before being fed to the 1st membrane stage (MEM1). In this analysis, upstream pressure and downstream pressures at 1st stage are kept at 4 bar and 1 bar respectively. The permeate from 1st membrane stage (MEM1) contains 98% N₂ and 2% CO₂. The retentate from 1st membrane stage is first fed to a separator to strip off water from the stream and then fed to 2nd membrane stage (MEM2) for further CO₂ separation. At the 2nd membrane stage (MEM2) the upstream pressure is 4 bar while the downstream pressures is set 0.2 bar. An overview of process conditions and compositions in different process streams is tabulated in Table 1.

Table 1. Process conditions of major flow streams in the system.

Two Stage Process								
Name Stream	Flue Gas	Feed MEM1	Perm1	Ret1	Feed MEM2	Ret2	Perm2	CO2 to Pipeline
Vapour Fraction	0.89	0.99	1	0.95	1	0.99	1	1
Temperature [C]	20	35	40	35	35	35	49	69
Pressure [bar]	1.1	4.05	1.05	4	4	4	0.2	1.05
Molar Flow [MMSCFD]	1200	1071	642.9	428.2	411.7	272.8	138.9	138.9
Mass Flow [kg/hr]	1.725x10 ⁶	1.61x10 ⁶	9.1x10 ⁵	7.01x10 ⁵	6.86x10 ⁵	3.92x10 ⁵	2.94x10 ⁵	2.94x10 ⁵
Name Stream	Flue Gas	Feed MEM1	Perm1	Ret1	Feed MEM2	Ret2	Perm2	CO2 to Pipeline
Nitrogen	0.706	0.792	0.978	0.511	0.532	0.775	0.053	0.053
CO ₂	0.119	0.134	0.021	0.303	0.315	0.019	0.896	0.896
Oxygen	0.049	0.054	0.000	0.133	0.139	0.184	0.051	0.051
Water	0.126	0.020	0.001	0.053	0.015	0.022	0.000	0.000

5. Results and discussions

Separation efficiency (*in terms of energy required per kg of CO₂ captured (recovered)*) and Flue Gas Processing Cost (FGPC) of the membrane process has been evaluated. The flue gas processing cost (FGPC) is comprised of required membrane area and energy along with other operational and fixed costs. In this analysis, FGPC defined as the cost per MSCF (1000 Standard Cubic Foot) of product is based on Total Plant Investment cost (TPI), Variable Operating & Maintenance cost (VOM) and Capital Related Costs (CRC). In this analysis membrane modules and compressors are considered as the major equipment in the system to evaluate the capital cost. The cost of electricity was calculated as utility cost in this analysis. Table 2 shows the values of economic and process parameters along with calculation methodology. This methodology is based on the values assigned to the selected process/economic parameters which might differ considerably for different evaluators [19].

In general, the gas processing cost is reported to be around \$1.5/MSCF [20]. The literature review on the economics of CO₂ sequestration shows that the primary capture cost is not the transportation and injection rather due to separation, capture and compression [21]. It has been estimated that the total capital and operating cost for CO₂ capture, from a coal-fired flue gas based on a standard design 1000 t/d Econamine FG CO₂ plant, to be \$1.71/MSCF [22]. The cost to add and operate a drying and CO₂ compression facility (up to 130 bars) increase the gas processing cost by approximately \$0.42/MSCF [21].

It is evident from Table 3 that total membrane area required for post-combustion CO₂ capture by the proposed design is 6.43×10^5 m². The total energy demand (1.05 MJ/kg CO₂) for the proposed process design is almost 3 times less compared to energy demand for CO₂ capture by amine absorption process which requires 3-6 MJ/kg CO₂ [24-25, 34-35] and considerably lower than the energy demand (6-8.8 MJ/kg CO₂) reported by other CO₂ capture techniques [23]. It is worth mentioning here that energy demand reported in this work (1.05 MJ/kg CO₂) is much less compared to the similar process design reported recently (1.1 GJ/metric ton CO₂) [24]. Table 3 shows the energy consumed and the capture cost for the process. It can be stipulated that it is possible to attain 90% CO₂ recovery and purity at FGPC less than \$0.21/MSCF at all pressure ratios and permeate recycle conditions. It's worth mentioning here that membrane based CO₂ capture technology is already being tested at pilot scale at a cement plant in southern Norway. It is hoped that technology may be available for commercial applications in next 5 years.

EIC Climate Change Technology Conference 2015

Table 2. Economic and Process parameters for Flue Gas Processing Cost (FGPC)

Total Plant Investment (TPI)	
Membrane module cost, including cost of membrane element (MC)	\$5/ft ²
Installed Compressor Cost (CC)	\$8650 X (HP/η) ^{0.82}
Fixed Cost (FC)	MC + CC
Base Plant Cost (BPC)	1.12 X FC
Project Contingency (PC)	0.20 X BPC
Total Facilities Investment (TFI)	BPC + PC
Start-up Cost (SC)	0.10 X VOM
TPI	TFI + SC
Annual Variable Operating & Maintenance Cost (VOM)	
Contract & Material maintenance Cost (CMC)	0.05 X TFI
Local Taxes & Insurance (LTI)	0.015 X TFI
Direct Labor Cost (DL) based on 8h/day per 25MMSCFD	\$15/h
Labor Overhead Cost (LOC)	1.15XDL
Membrane replacement costs, (MRC)	\$3/ft ² of membrane
Utility Cost, \$/kWh, (UC)	0.07/kWh
VOM	CMC + TI+DL+LOC+MRC+UC
Annual Capital related cost (CRC)	0.2 X TPI
Flue Gas Processing Cost, \$/MSCF of processed flue gas (FGPC)	(CRC +VOM) / [365 X OSF X Q_f X (1-SCE) X 1000]
Other assumptions	
On-Stream Factor (OSF)	96%
Net Feed flow rate, MMSCFD, (Q _p)	1068 MMSCFD
Stage Cut Equivalent, (net permeate flow rate)/(net feed flow rate), (SCE)	Q _p /Q _f
Membrane life (t)	4 years

Table 3. Required membrane area, energy consumed and gas processing cost for the process

1st Stage Membrane Area [m²]	8.19x10⁴
2nd Stage Membrane Area [m²]	5.61x10⁵
Total Membrane Area [m²]	6.43x10⁵
E (MJ/kg CO₂ captured)	1.05
Flue Gas Processing Cost ((\$/MSCF)	0.21
Capture cost (\$/ton)	20.4

6. Conclusion

The objective of this work is to shift the paradigm related post-combustion CO₂ capture by designing a process which utilizes the potential of both N₂-selective and CO₂-selective membrane. A novel cellulose acetate hybrid (CLSICA) membrane revealed its nitrogen selective character with introduction of p-tert-butylcalix[4]arene immobilized silica (CL-Si) as filler. Whereas, a CO₂ selective Fixed Site Carrier (FSC) membrane (PVAm cast on a porous polysulfone (PSf) support) has already been developed and evaluated. It can be concluded from this work that it is possible to attain 90% purity and 90% CO₂ recovery from flue gas with considerably low energy requirement and gas processing cost by the proposed process design which is simple and cost effective. The energy penalty for this process design is considerably low (1MJ/kg CO₂) and the capture cost amounts to be \$ 20.4/ton). The proposed process has the potential to be competitive to amine absorption and other CO₂ capture processes because of its simplicity and cost-effectiveness. This simulation analysis has been conducted while considering the realistic process design and operation parameters which reflect the dimensions of a real flue gas treatment facility. Hence, a higher feed flow rate has been taken in this work to correspond to huge CO₂ emission sources.

7. References

- [1] Yampolskii, Y., Polymeric Gas Separation Membranes, *Macromolecules* 2012, 45, 3298–3311
- [2] Drioli, E., Barbier, G., *Membrane Engineering for the Treatment of Gases: Volume 1: Gas-separation Problems with Membranes*, RSC Publishers, 2011.
- [3] Robeson, L.M., Correlation of separation factor versus permeability for polymeric membranes, *Journal of Membrane Science*, 62 (1991), 165-185.
- [4] Taek-Joong Kim, Mohammad WashimUddin, Marius Sandru and May-Britt Hägg, The effect of contaminants on the composite membranes for CO₂ separation and challenges in up-scaling of the membranes, *Energy Procedia* 4 (2011) 737–744.
- [5] Chung, T.S., Jiang, L.Y. and Li, Y. (2007) 'Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, *Progress in Polymer Science*, Vol. 32, pp.483–507.
- [6] Graham, B.F., Harrowfield, J.M., Tengrove, R.D., Lagalante, A.F. and Bruno, T.J. 'Evidence of a Host:Guest Complex between p-t-Butylcalix[4]arene and Carbon Dioxide, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, Vol.43 (2002) 179-182.
- [7] Kools, W., *Membrane formation by phase inversion in multi component polymer systems mechanisms and morphologies*, PhD thesis, Chem. Engg Uni. of Twente, Netherlands (1998).
- [8] Taek-Joong Kim, Baoan Li, May-Britt Hägg, Novel Fixed -Site-Carrier Polyvinylamine Membrane for CO₂ Capture, *J. of Poly. Sci. Part B-Polymer Physics* 42 (2004) 4326–4336.

EIC Climate Change Technology Conference 2015

- [9] Liyuan Deng, Taek-Joong Kim, May-Britt Hägg, Facilitated transport of CO₂ in novel PVAm/PVA blend membrane, *Journal of Membrane Science*, 349 (2009) 154-163.
- [10] Marius Sandru, Taek-Joong Kim, May-Britt Hägg, High molecular fixed-site-carrier PVAm membrane for CO₂ capture, *Desalination* 240 (2009) 298-300.
- [11] Jon Arvid Lie, Terje Vassbotn, May-Britt Hägg, David Grainger, Taek-Joong Kim, Thor Mejdell, Optimization of a membrane process for CO₂ capture in the steelmaking industry, *International Journal of Greenhouse Gas Control* 1 (2007) 309-317.
- [12] Arshad Hussain, May-Britt Hägg, A feasibility study of CO₂ capture from flue gas by a facilitated membrane, *Journal of Membrane Science* 359 (2009) 140-148.
- [13] Wijmans, J.G.; Baker, R.W. (1995) The solution-diffusion model: a review. *J. Membr. Sci.*, 107: 21–25.
- [14] Page, S.C.; Williamson, A.G.; Mason, I.G. (2009) Carbon capture and storage: Fundamental thermodynamics and current technology. *Energy Policy*, 37 (9): 3314–3324.
- [15] Blomen, E.; Hendriks, C.; Neele, F. (2009) Capture technologies: Improvements and promising developments. *Energy Procedia*, 1:1505–1512.
- [16] Davison, J.; Thambimuthu, K. (2004) Technologies for capture of carbon dioxide. In: *Proceedings of the Seventh Greenhouse Gas Technology Conference*, Vancouver, Canada, International Energy Association (IEA), Greenhouse Gas R&D Program, (www.ghgt7.ca).
- [17] Favre, E. (2007) Carbon dioxide recovery from post-combustion processes: Can gas permeation membrane compete with absorption? *J. Membr. Sci.*, 294: 50–59.
- [18] Lin, H.; Merkel, T.; Baker, R. (2007) *The Membrane Solution to Global Warming*, Sixth Annual Conference on Carbon Capture & Sequestration, May 7–10, Pittsburgh, Pennsylvania.
- [19] Hao, J.; Rice, P.A.; Stern, S.A. (2008) Upgrading low quality natural gas with H₂S and CO₂ selective membranes, Part II. Process design, economics, and sensitivity study of membrane stages with recycle streams. *J. Membr. Sci.*, 320: 108–122.
- [20] Gozalpour, F.; Ren, S.R.; Tohidi, B. (2005) CO₂ EOR and storage in oil reservoirs. *Oil & Gas Science and Technology*, 60: 537–546.
- [21] Wong, S.; Gunter, W.D.; Mavor, M.J. (2000) Economics of CO₂ Sequestration in Coal bed Methane Reservoirs, SPE 59785 SPE-CERI Gas Tech. Symp. Calgary, Canada (April 3–5, 2000).
- [22] Chapel, D.; Ernest, J.; Mariz, C. (1999) Recovery of CO₂ from Flue Gases: Commercial Trends, paper 340, 49th Canadian Society of Chemical Engineers annual meeting October 4–6, 1999, Saskatoon, Saskatchewan, Canada.

EIC Climate Change Technology Conference 2015

- [23] Merel, J.; Clause, M.; Meunier, F. (2008) Experimental investigation on CO₂ post-combustion capture by indirect thermal swing adsorption using 13X and 5A zeolites. *Ind. Eng. Chem. Res.*, 47: 209–215.
- [24] Yuan, M.; Narakornpijit, K.; Haghpanah, R., Wilcox, J. (2014) Consideration of a nitrogen-selective membrane for post combustion carbon capture through process modeling and optimization. *Journal of Membrane Science* 465 (2014)177–184.

8. Acknowledgements

The authors would like to thank Dr.L. Deng, Dr. T-J. Kim, S.Farrukh and F. Minhas for their excellent experimental work.

9. Biography

Dr. Arshad Hussain did his MS and PhD in Chemical Engineering from Germany. As a Research Fellow at Center for Marine CNG, St. Johns, Canada and at the department of Chemical Engg., NTNU Trondheim, Norway. He is working on process design and feasibility analysis of CO₂ Capture from Natural Gas/Flue Gases by employing polymer membranes.