



Contents lists available at ScienceDirect

Engineering

journal homepage: [www.elsevier.com/locate/eng](http://www.elsevier.com/locate/eng)

Research  
Green Chemical Engineering—Perspective

# Polyvinylamine-Based Facilitated Transport Membranes for Post-Combustion CO<sub>2</sub> Capture: Challenges and Perspectives from Materials to Processes

Xuezhong He <sup>a,b</sup>

<sup>a</sup> Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim N-7491, Norway

<sup>b</sup> Department of Chemical Engineering, Guangdong Technion Israel Institute of Technology (GTIIT), Shantou 515063, China

## ARTICLE INFO

### Article history:

Received 26 May 2019

Revised 29 October 2019

Accepted 19 November 2019

Available online xxx

### Keywords:

Facilitated transport membranes

Flue gas

Hollow fiber

CO<sub>2</sub> capture

Process simulation

## ABSTRACT

Carbon dioxide (CO<sub>2</sub>) capture by gas-separation membranes has become increasingly attractive due to its high energy efficiency, relatively low cost, and environmental impact. Polyvinylamine (PVAm)-based facilitated transport (FT) membranes were developed in the last decade for CO<sub>2</sub> capture. This work discusses the challenges of applying PVAm-based FT membranes from materials to processes for post-combustion CO<sub>2</sub> capture in power plants and cement factories. Experiences learned from a pilot demonstration system can be used to guide the design of other membranes for CO<sub>2</sub> capture. The importance of module and process design is emphasized in the achievement of a high-performance membrane system. Moreover, the results from process simulation and cost estimation indicate that a three-stage membrane system is feasible for achieving a high CO<sub>2</sub> purity of 95 vol%. The specific CO<sub>2</sub> capture cost was found to significantly depend on the required CO<sub>2</sub> capture ratio, and a moderate CO<sub>2</sub> capture ratio of 50% presented a cost of 63.7 USD per tonne CO<sub>2</sub> captured. Thus, FT membrane systems were found to be more competitive for partial CO<sub>2</sub> capture.

© 2020 THE AUTHOR. Published by Elsevier LTD on behalf of Chinese Academy of Engineering and Higher Education Press Limited Company.

## 1. Introduction

In order to combat the serious environmental issue of global warming, the reduction of greenhouse gases (especially carbon dioxide, CO<sub>2</sub>) from power plants and energy-intensive industries (e.g., cement, iron, and steelmaking factories) should be implemented [1]. Different CO<sub>2</sub> capture technologies such as post-combustion, pre-combustion, and oxyfuel combustion, as well as CO<sub>2</sub> removal from industrial gases, have been designed and demonstrated [2]. Among them, post-combustion CO<sub>2</sub> capture is considered to be a feasible solution for retrofitting existing plants. At present, post-combustion CO<sub>2</sub> capture using chemical absorption with amine-based solvents is considered to be the most mature technology, and has been implemented at the large and full scales [3]. Great effort has recently been put into the development of next-generation and advanced solvents that can reduce the energy consumption of the whole capture process. However, the relatively high environmental impact and high capital expenditure (e.g., the absorber) still challenge the wide implementation of car-

bon capture. Several emerging separation technologies based on ionic liquid solvents [4,5], solid adsorbents [6–8], and chemical looping cycles (e.g., metal oxides) [9,10] have been developed for CO<sub>2</sub> capture with a potential cost-reduction benefit. Recently, there has been great interest in the development of solid adsorbents such as metal-organic frameworks (MOFs) [11] for CO<sub>2</sub> capture, as they present a higher CO<sub>2</sub> adsorption capacity and relatively low energy consumption compared with other sorbents. However, the relatively low selectivity of CO<sub>2</sub>/N<sub>2</sub> for solid sorbents hinders its upscaling [11]. Gas-separation membranes have already been used for air separation (Prism<sup>®</sup> from Air Products & Chemicals, Inc.), biogas upgrading (e.g., Evonik SEPURAN<sup>®</sup> Green), and natural gas sweetening (e.g., Separex<sup>™</sup>, Cynara<sup>®</sup>, and Medal) [12]; such membranes are regarded as one of the most mature and promising options for CO<sub>2</sub> capture in comparison with other technologies including cryogenic separation, chemical looping processes, and adsorption [13]. Great effort has been made in the membrane community to improve membrane performance for different CO<sub>2</sub> separation processes [14–18]. Special interest has been paid to the development of facilitated transport (FT) membranes made from polymers containing amino functional groups. These membranes

E-mail address: [xuezhong.he@gtiit.edu.cn](mailto:xuezhong.he@gtiit.edu.cn)

<https://doi.org/10.1016/j.eng.2020.11.001>

2095-8099/© 2020 THE AUTHOR. Published by Elsevier LTD on behalf of Chinese Academy of Engineering and Higher Education Press Limited Company.

present a high separation performance based on the extra FT contribution from the chemical reaction of CO<sub>2</sub> with the functional group [19–25]. Considering the commercialization of membrane technology for CO<sub>2</sub> capture, energy-efficient and low-cost membrane systems should be designed. Moreover, membrane materials should achieve long-term stability under exposure to the impurities of SO<sub>2</sub> and NO<sub>x</sub> in flue gas. At present, only a few types of membranes have been demonstrated at the pilot scale for CO<sub>2</sub> capture, such as the Polaris<sup>®</sup> membranes at Membrane Technology & Research, Inc. (MTR), fixed-site-carrier (FSC) membranes at Norwegian University of Science and Technology (NTNU) (licensed to Air Products and Chemicals, Inc.), and PolyActive<sup>®</sup> membranes at Helmholtz-Zentrum Geesthacht [1].

It should be noted that bringing membranes from the laboratory to pilot-scale demonstration is not straightforward and can easily take 10–15 years. For example, polyvinylamine (PVAm)-based FT membranes were initially developed in 2004 by coating a thin selective layer onto a flat-sheet polysulfone (PSf) support [26]. Since then, membrane performance has been continuously improved by the optimization of membrane-preparation conditions over ten years [19,20]. Several pilot demonstration systems have been tested in power plants [27] and cement factories [28,29] using plate-and-frame and hollow-fiber modules. Moreover, durability testing through exposure to high loads of SO<sub>2</sub> over 200 ppm was performed in real flue gas, and stable membrane performance with a CO<sub>2</sub> purity greater than 60 vol% in the permeate side over a long testing period was reported by Hägg et al. [29]. However, the testing results from those pilot systems indicate that module design is crucial in order to utilize the whole membrane area effectively for gas separation. Important module parameters such as fiber diameter, fiber length, and packing density must be optimized in order for the design of a high-efficiency hollow-fiber module based on mathematical modeling to be possible [30]. In addition to PVAm-based FT membranes, the membrane research group at Ohio State University (OSU) has reported a highly selective amine-containing FT membrane tailored for CO<sub>2</sub>/N<sub>2</sub> separation with a CO<sub>2</sub> permeance of 1450 gas permeation units (GPU, 1 GPU = 10<sup>-6</sup> cm<sup>3</sup>(STP)·(cm<sup>2</sup>·s·cmHg)<sup>-1</sup>, in which STP means standard temperature and pressure, 1 cmHg = 1.33 × 10<sup>3</sup> Pa) and a CO<sub>2</sub>/N<sub>2</sub> selectivity greater than 150 [31,32]. It should be noted that their estimation of the gas permeance, which was conducted by fitting the experimental data using COMSOL Multiphysics<sup>®</sup> [32], might be overestimated, as the average driving force was significantly underestimated. Nevertheless, those FT membranes have been demonstrated to have good performance for CO<sub>2</sub> capture from real flue gas, although the cost of a full-scale process needs to be evaluated in order to document the technology advance. Thus, in this work, the status and challenges of PVAm-based FT membranes from materials to module and pilot-system design and testing are discussed, and a process feasibility analysis of a three-stage FT membrane system is performed to provide guidelines for designing an efficient membrane system for CO<sub>2</sub> capture from flue gases.

## 2. Facilitated transport membranes

Flat-sheet FT membranes based on PVAm polymers were initially developed by the Memfo group at NTNU [33], and their good performance for CO<sub>2</sub>/CH<sub>4</sub> separation was reported by Kim et al. [26]. The influence of the molecular weight of PVAm was found to be significant for CO<sub>2</sub> permeation through membranes, and PVAm membranes with a higher molecular weight presenting a relatively low gas permeance due to the lower mobility of the longer polymer chains, but a much higher selectivity [26]. In general, those membranes presented a relatively low CO<sub>2</sub> permeance of 0.014 m<sup>3</sup>(STP)·(m<sup>2</sup>·h·bar)<sup>-1</sup> (1 bar = 1 × 10<sup>5</sup> Pa). Later on,

ultra-thin PVAm/polyvinylalcohol (PVA)-blend FT membranes were reported by Deng et al. [20], with a significantly improved CO<sub>2</sub> permeance performance (Fig. 1). Those membranes showed a good CO<sub>2</sub>/N<sub>2</sub> selectivity of up to 174 and a CO<sub>2</sub> permeance of 0.58 m<sup>3</sup>(STP)·(m<sup>2</sup>·h·bar)<sup>-1</sup> through mixed gas permeation tests at 2 bar and 25 °C. It should be noted that the membranes were tested under humidified conditions, and the feed gas humidity was reported to have a great effect on the membrane separation performance [20]. In 2013, Kim et al. [19] reported that the pH of the casting solution had a significant influence on the performance of FT membranes, as the protonated amino group (–NH<sub>3</sub><sup>+</sup>) does not contribute to the CO<sub>2</sub> FT. They successfully prepared bench-scale membranes (30 cm × 30 cm flat-sheet) from high-pH solutions, which presented a much higher CO<sub>2</sub> permeance of 5 m<sup>3</sup>(STP)·(m<sup>2</sup>·h·bar)<sup>-1</sup> at 1.1 bar. These high-performance PVAm-based membranes showed great potential for CO<sub>2</sub> capture from flue gas, and were tested in real flue gas [17,27–29]. Among them, a 4.2 m<sup>2</sup> pilot module was tested in real flue gas to document the dependence of the CO<sub>2</sub> flux on the driving force (partial pressure difference), as reported by He et al. [17]. Their testing results clearly indicated a significant FT contribution to the CO<sub>2</sub> flux, especially in the low feed pressure region (i.e., a low driving force). The CO<sub>2</sub> permeate flux,  $J_{\text{CO}_2}$ , is the sum of both the Fickian diffusion and FT diffusion, and can be expressed as follows [17]:

$$J_{\text{CO}_2} = \frac{D_{\text{CO}_2}}{l} (c_{\text{CO}_2,0} - c_{\text{CO}_2,l}) + \frac{D_{\text{CO}_2-c}}{l} (c_{\text{CO}_2-c,0} - c_{\text{CO}_2-c,l}) \quad (1)$$

$$J_{\text{CO}_2} = P_{\text{CO}_2}^{\text{S-D}} \Delta p_{\text{CO}_2} + P_{\text{CO}_2}^{\text{FT}} \Delta p_{\text{CO}_2} = P_{\text{CO}_2}^{\text{A}} \Delta p_{\text{CO}_2} \quad (2)$$

where  $D_{\text{CO}_2}$  and  $D_{\text{CO}_2-c}$  are the diffusion coefficients of the Fickian and the FT diffusion, respectively;  $l$  is the thickness of the selective layer of a FT membrane;  $c_{\text{CO}_2,0}$  and  $c_{\text{CO}_2,l}$  are the CO<sub>2</sub> concentrations in the feed side and the permeate side, respectively;  $c_{\text{CO}_2-c,0}$  and  $c_{\text{CO}_2-c,l}$  are the concentrations of the CO<sub>2</sub>-carrier complex in the feed side and the permeate side, respectively;  $P_{\text{CO}_2}^{\text{S-D}}$  is the CO<sub>2</sub> permeance based on the contribution from the solution-diffusion (S-D) transport mechanism. The other gas molecules, such as N<sub>2</sub> and O<sub>2</sub>, can only pass through membranes based on the S-D mechanism. This FT contribution is currently estimated by the partial pressure difference in experiments, as  $P_{\text{CO}_2}^{\text{FT}} \Delta p_{\text{CO}_2}$  [17]. It is notable that the FT-contributed CO<sub>2</sub> permeance,  $P_{\text{CO}_2}^{\text{FT}}$ , is quite high due to the large amount of carriers and water molecules available in the membrane matrix, which contribute to the CO<sub>2</sub> reaction. Thus, a high apparent CO<sub>2</sub> permeance ( $P_{\text{CO}_2}^{\text{A}}$ ) can be obtained from Eq. (2) when the partial pressure driving force is very low. Under the same driving force, the FSC membrane showed a higher CO<sub>2</sub> flux than that

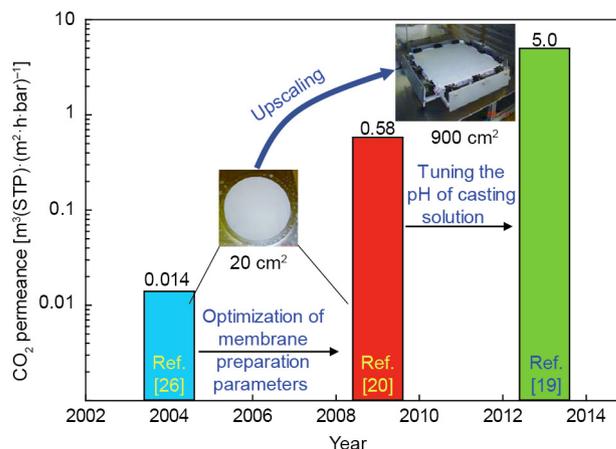


Fig. 1. Timeline of the development of PVAm-based FT membranes.

of a common S-D membrane [17]. Therefore, lower feed pressure operation is preferred in order for PVAm-based FSC membranes to achieve a high membrane performance, and can avoid high energy consumption for the compression of a huge amount of flue gas. Moreover, a higher water content (i.e., a higher relative humidity at a given condition) in feed gas enhances the FT of CO<sub>2</sub> through the membranes, as water molecules act as a catalyst for the reaction of CO<sub>2</sub> with amino functional groups (-NH<sub>2</sub>). Thus, the challenge of maintaining a high water vapor content in feed gas should be addressed in real-life applications in order to achieve a high membrane separation performance. From an engineering point of view, increasing the driving force (i.e., the partial pressure across a membrane) can improve the CO<sub>2</sub> flux, and can reduce the necessary membrane area for a specific separation requirement. However, too high (pressure) of a driving force will saturate the carriers, causing the CO<sub>2</sub> permeance to decrease due to the lower contribution from the FT mechanism. On the other hand, while a lower (pressure) driving force results in a higher CO<sub>2</sub> permeance, the total CO<sub>2</sub> flux calculated from Eq. (2) will be lower. Although this membrane has been demonstrated to have a high performance for CO<sub>2</sub>/N<sub>2</sub> separation at the lab scale and bench scale, its performance is dependent on the quality of the purified PVAm (e.g., polymer purity and molecular weight). The large-scale production of PVAm through a quality-controlled process is one of the challenges for the commercialization of FSC membranes at a low cost.

### 3. The challenges of membrane module upscaling

A plate-and-frame module (Fig. 2(a)) designed by Deng [34] was used for the lab-scale gas permeation testing of FT membranes. The cell is mounted with a circular cut membrane between its two parts, which forms a feed and a permeate gas chamber. A porous metal support is placed on the circular edge of the bottom of the support membrane, and a flat-sheet FT membrane is sealed with a rubbery O-ring. It is expected that the efficiency of this lab-scale module will be quite low due to its small effective membrane area based on a cross-flow mode. Moving the plate-and-frame modules from the lab scale to the small pilot scale is quite challenging, which is related to the sealing and gas distribution inside the module. A pilot plate-and-frame module (Fig. 2(b)) with a membrane area of 2 m<sup>2</sup> was designed by Yodfat Engineers for testing at the EDP's power plant [27] and the Norcem cement factory [28]. The pilot-testing results indicated that it was very challenging to achieve good gas distribution inside the module, and the effective membrane area was found to be much smaller than the estimated apparent membrane area. Thus, PSf hollow-fiber modules (provided by Air Products & Chemicals, Inc.) were introduced in order to reach high module efficiency with a counter-current mode. It should be noted that the *in situ* coating of PVAm selective layers on the PSf hollow fibers inside modules is quite challenging,

as the coating procedure cannot easily be transferred from flat-sheet membranes to hollow fibers. Nevertheless, 4.2 m<sup>2</sup> PSf hollow-fiber membrane modules (Fig. 2(c)) were finally successfully produced, and were tested for CO<sub>2</sub> capture from two different flue gases [17,29]. Even though the PVAm-based FSC membranes were found through testing to present a good performance at the pilot scale, further research work on controlling the quality of coated modules is still needed.

The space between hollow fibers is quite small, and has been estimated to be 0.82 mm based on a square pitch mode [17]. Therefore, it is expected that uniformly coating PVAm thin layers on the outside of PSf hollow fibers is quite challenging, due to the high packing density. Inside coating may provide more uniform selective layers on the support. However, other support membranes are required, as the currently used PSf membranes (ultrafiltration MWCO 50K) have their own outer selective layer, and the pore size of the inner layer is much too large, which makes it difficult to coat a thin PVAm inner layer without significant pore penetration. Moreover, for shell-side feeding, the experimentally measured pressure drops in the shell and bore side were 70 and 6.7 mbar, respectively, which indicated that the pressure drops for their hollow-fiber modules are quite low. It was also reported that the membrane module performance was not optimized, even though good membrane material performance was documented and was found to be comparable with the lab-scale testing results [17].

Mathematical modeling of a hollow-fiber module design was reported by Chu et al. [30], whose results indicated that the hollow-fiber inner diameter and length significantly influenced the pressure drop in the bore side. Moreover, the module packing density may have a great influence on the pressure drop in the shell side. It should be expected that the pressure drop for low-pressure operations (i.e., post-combustion carbon capture) will be much more significant than those for high-pressure scenarios (e.g., natural gas processing). A relatively low absolute pressure drop (e.g., 200 mbar) along the module length may cause a large reduction in the driving force, and thus increase the required membrane areas dramatically. Therefore, future work on designing energy-efficient modules without a significant pressure drop in both the feed and permeate sides is essential to improve module performance. A potential solution for reducing CO<sub>2</sub> capture cost could be the reduction of the required membrane area operated at elevated temperature with better-designed modules (e.g., to achieve higher gas permeance with the same selectivity); this is an engineering challenge for future work.

### 4. Pilot membrane testing examples

A tailor-made test rig was designed and constructed by the company of Yodfat Engineers, and was installed at Norcem's Brevik site in January 2014 [28]. After an extended start-up phase, a six-

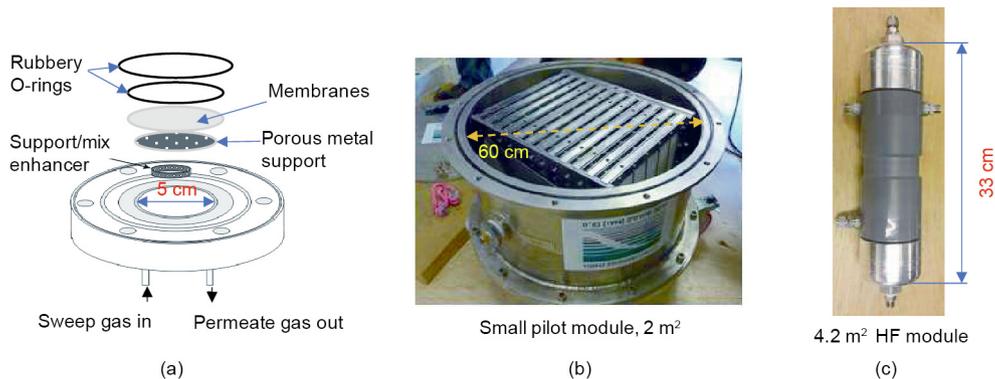


Fig. 2. Plate-and-frame modules at (a) the lab scale [34] and (b) the small pilot scale [27]; (c) a 4.2 m<sup>2</sup> hollow-fiber (HF) module [17].

month period of stable operation took place with a water-saturated feed gas by applying a humidifier in the feed line. The pilot system produced a high CO<sub>2</sub> purity of up to 72 vol% for a short period during which the whole system worked properly [28]. It was also reported that stable operation was more difficult to achieve than expected, the CO<sub>2</sub> permeate flux and purity were lower than expected, and the durability and other parameters were difficult to determine because of the relatively short time of the testing and other phenomena that influenced the testing [28]. Therefore, a phase II project was launched in July 2015 to test a new pilot system using PVAm-based hollow-fiber membranes. Three modules with a total membrane area of 20 m<sup>2</sup> were installed in the pilot system using a compressor instead of a blower to provide flexibility for changing the feed pressure [29]. Even though the compressor had a design capacity of up to 7 bar, the system was not tested at high pressures over 5 bar due to the expected high energy consumption needed for the compression of a huge amount of flue gas. Hägg et al. [29] reported stable membrane performance with a CO<sub>2</sub> purity greater than 60 vol% in the permeate side over a long testing period, as shown in Fig. 3(a). Moreover, another pilot system was tested for CO<sub>2</sub> capture from flue gas in a propane burner plant at Tiller (Trondheim, Norway), where the feed CO<sub>2</sub> content is much lower (ca. 9.6 vol%) [17]. That pilot system provided more flexibility through varying process parameters such as gas composition, feed flow, and operating pressure and temperature. Based on the testing results from these two pilot systems, PVAm-based membranes were found to be more economically feasible for CO<sub>2</sub> capture from flue gases with higher CO<sub>2</sub> content (e.g., cement factories) than from flue gases with lower CO<sub>2</sub> content (e.g., power plants). Moreover, a membrane system that was operated at a relatively warmer temperature presented higher gas permeance without a significant loss of selectivity, as shown in Fig. 3 (b) [17], which indicates that a moderate operating temperature is preferred for such a system. Future work on testing membrane systems at warmer temperatures is required to improve membrane system performance. However, maintaining a high water vapor content of the feed gas stream with no condensation in the whole system at a higher temperature is an engineering challenge. The key findings from the pilot testing [17,28] can be summarized as follows:

- (1) Flue gas pretreatment units (e.g., particle filters and condensers) should be implemented to protect membrane units.
- (2) Any water condensation inside a membrane system after the condenser/cooler should be avoided to protect all the instruments, controllers, and compressors, as condensed (acidic) water will result in serious corrosion of the hardware and reduce membrane performance and lifetime.
- (3) A moderate operating temperature is preferred in order for an FT membrane system to function with high performance, if the membrane materials can tolerate a higher temperature.

(4) Design and optimization of the module and process are crucial to achieve high module performance in real-life applications.

Based on the pilot-testing results, the use of PVAm-based FT membranes for CO<sub>2</sub> capture from flue gas was evaluated at a technology readiness level (TRL) of 5 thus far; advancing to the next stage of a TRL of 6–7 with two- or multi-stage membrane systems should be further demonstrated before moving on to full-scale implementation. Again, process design related to inter-stage re-compression and re-humidification should be thoroughly considered for this membrane. Moreover, a configuration using sweep gas instead of a vacuum pump might be applicable to reduce energy consumption.

## 5. Plant-scale membrane system design and simulation

### 5.1. Process description and simulation basis

Membrane systems are usually located downstream of the flue gas pretreatment units so that most of the impurities, such as SO<sub>2</sub> and NO<sub>x</sub>, are removed [35]. Flue gas pretreatment units (e.g., particle filters and condensers) should be implemented to protect the membrane unit. A flue gas containing 9.6% CO<sub>2</sub>/80.9% N<sub>2</sub>/5% O<sub>2</sub>/4.5% H<sub>2</sub>O by volume at a feed flow rate of  $2.2 \times 10^5 \text{ Nm}^3 \cdot \text{h}^{-1}$  (Nm<sup>3</sup> means normal cubic meter) was simulated. In flue gas, all these gas species compete in the separation. High O<sub>2</sub> content in flue gas will make it challenging to obtain high-purity CO<sub>2</sub>, as CO<sub>2</sub>/O<sub>2</sub> selectivity is usually low (<10 [36]), and may be unable to achieve the purity requirement for CO<sub>2</sub> compression and pipe transportation. Water is crucial in most FT membranes, as it promotes the reaction with the neutral amino carriers, but too much condensing water may hinder gas transport through the membranes. Moreover, if the water permeance is too high, the membrane may become dry (with a very low relative humidity) and thereby less efficient toward the outlet in the retentate side. Thus, controlling the process conditions to maintain a high water vapor content in the feed gas through the whole membrane area is crucial.

It should be noted that no pressure drop was set for the heat exchangers/coolers, even though this is typically about 10 mbar per step. Any pressure drop would result in increased energy consumption by the compressors (e.g., 60 kW per step). However, this value is negligible, as a pressure drop of 200 mbar (bore-side feeding [30]) was set inside the membrane models, which has a dominating effect on the total energy consumption. All the simulations were conducted according to the simulation basis provided in Tables 1 and 2. It should be noted that a high vacuum operation (e.g., 200 mbar) in the permeate side will pull too much water through the membranes, so that many fewer water molecules will be available for FT contribution. This will result in a

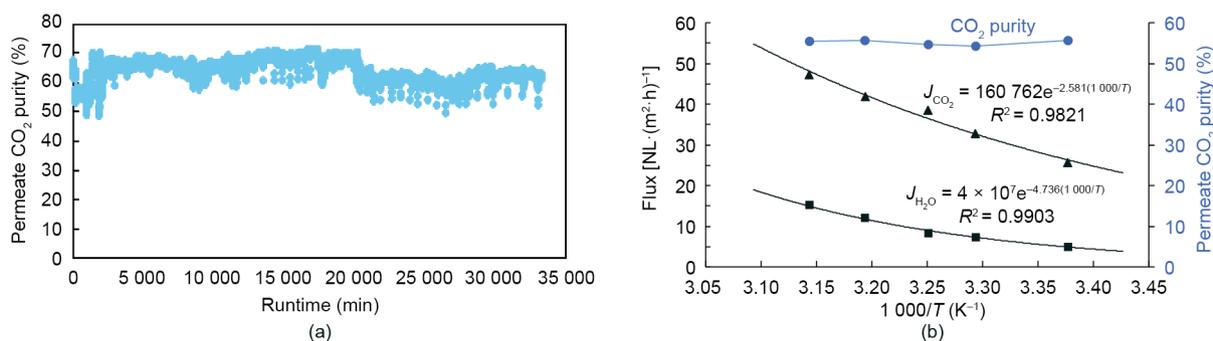


Fig. 3. (a) Durability testing results of the pilot system [29]; (b) temperature influence of PVAm-based membranes [17]. NL: normal liter.

**Table 1**  
Simulation basis.

Parameter	Value
Flue gas flow rate (Nm <sup>3</sup> ·h <sup>-1</sup> )	2.2 × 10 <sup>5</sup>
Temperature (°C)	45
Feed pressure (bar)	2
Flue gas composition <sup>a</sup> (vol%)	
CO <sub>2</sub>	9.6
N <sub>2</sub>	80.9
O <sub>2</sub>	5.0
H <sub>2</sub> O	4.5
CO <sub>2</sub> purity requirement (vol%)	95
CO <sub>2</sub> capture ratio (%)	30–90

<sup>a</sup> Impurities of SO<sub>2</sub>, NO<sub>x</sub>, and fly ashes are not included here.

low CO<sub>2</sub> permeance (first-stage membrane) and low selectivity, compared with those during operation at a relatively low vacuum (e.g., 350 mbar) in the second- and third-stage membranes (Table 2). However, the CO<sub>2</sub> flux will be lower at a lower vacuum, which usually leads to a larger required membrane area. The water permeance was set to 10 times the CO<sub>2</sub> permeance for all simulations, which is higher than the tested H<sub>2</sub>O/CO<sub>2</sub> selectivity of 5 at a feed pressure of 2 bar [17]. A CO<sub>2</sub> purity of 95 vol% was set for either storage or utilization in the downstream processes. For example, the captured CO<sub>2</sub> could be compressed and transported to greenhouse plants and used as a liquid CO<sub>2</sub> source for a beneficial implementation of CO<sub>2</sub> capture technology. It is worth noting that pursuing a very high CO<sub>2</sub> capture ratio of greater than 90% will dramatically increase the CO<sub>2</sub> capture cost [37], and was not considered in this work.

## 5.2. Process design and simulation

In order to document the techno-economic feasibility of the PVAm-based FT membranes for post-combustion CO<sub>2</sub> capture, a three-stage membrane system (Fig. 4) was designed to complete the separation requirement. It should be noted that two-stage membrane systems with this membrane performance cannot achieve a CO<sub>2</sub> purity of greater than 95 vol% at a reasonable recovery. The flue gas (F1) was compressed to 2 bar and fed into the first-stage membrane unit to pre-concentrate the CO<sub>2</sub>. The CO<sub>2</sub> capture ratio was controlled by adjusting the membrane area using the ADJ-1 to adjust the stage-cut (where ADJ is the adjust unit in HYSYS and 1 indicates the first-stage membrane unit). The permeate gas of P1 (i.e., the permeate gas stream in the first-stage membrane unit) was then recompressed to 1.5 bar for further purification in the second- and third-stage units. The ADJ-2 was also used to control the CO<sub>2</sub> capture ratio, while the ADJ-3 was used to achieve the CO<sub>2</sub> purity requirement of greater than 95 vol%. It should be noted that the stage-cut is crucial in achieving the separation requirement in terms of both CO<sub>2</sub> purity and capture ratio [35]; it should be adjusted by tuning the process parameters and membrane areas. A permeate pressure of 350 mbar was set for the vacuum pumps of the VP-2 and VP-3 (Fig. 4). Moreover, a pressure drop of 200 mbar was set for each stage of the membrane system. The third-stage retentate (R3) was raised to 1.5 bar and recycled back to the second-stage feed, as the

**Table 2**  
Membrane performance used for simulation.

Membrane stages	Feed/permeate pressure (bar)	Temperature (°C)	Permeance <sup>a</sup> [Nm <sup>3</sup> ·(m <sup>2</sup> ·h·bar) <sup>-1</sup> ] [17]		
			CO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>
1	2.0/0.2	45	0.63	0.018	0.095
2 & 3	1.50/0.35	40	2.18	0.023	0.105

<sup>a</sup> H<sub>2</sub>O permeance is assumed to be 10 times the CO<sub>2</sub> permeance.

retentate CO<sub>2</sub> concentration in the third stage is higher than the feed of the second stage; doing this can achieve a higher CO<sub>2</sub> capture ratio when necessary. Even though controlling the water content in feed gas is important to maintain a high overall membrane system performance, re-humidification between membrane stages was not included in the simulation, as the humidifier cost is significantly lower than other major equipment costs. The following assumptions were made in the process simulations:

- The membrane performance obtained from Tiller pilot system [17] was used for simulation.
- The efficiency of the compressor, expander, and pump was assumed to be 85%.
- The counter-current configuration in ChemBrane was chosen.
- The captured CO<sub>2</sub> was compressed to 110 bar for pipeline transportation and, potentially, for CO<sub>2</sub> storage or other end-users such as greenhouse plants.
- The membrane separation in each stage utilized a single membrane module with a pressure drop of 200 mbar.

Based on the gas-separation performance data (mainly gas permeance and selectivity) obtained from the lab- and/or pilot-scale experiments, the next step is to conduct process simulations to evaluate the techno-economic feasibility of the membrane system for post-combustion CO<sub>2</sub> capture at full scale. In this work, process simulations for CO<sub>2</sub> capture from flue gas were performed by HYSYS integrated with ChemBrane [38] to evaluate the required membrane area and energy consumption. Cost estimation was also conducted to evaluate the economic feasibility and to provide possible recommendations for further research and development.

## 5.3. Cost and footprint estimation model

A cost model reported in the literature was used for the estimation of the CO<sub>2</sub> capture cost in this work, and the major equipment cost of the compressors and membrane units was calculated based on the CAPCOST 2012 program [39]. Moreover, a membrane module cost of 35 USD·m<sup>-2</sup> was applied, considering the cheaper materials used for large-scale membrane production, while the membrane skid cost was estimated at a moderate price of 50 USD·m<sup>-2</sup> membrane surface area (this covers the cost for mounting the membranes into the module and pipe connection, but does not include pretreatment units or control instruments). A membrane lifetime of 5 years was estimated based on the pilot durability testing results. The annual capital related cost (CRC) was estimated to be 20% of the grassroots cost, which covers the depreciation, interest, and equipment maintenance (for a membrane unit, 30% is assumed, considering a short lifetime). It is worth noting that the cooling unit operation has a negligible influence on the cost and was thus not included. (Cooling towers are normally built in industrial plants (e.g., power plants), and the cost of cooling water used in the membrane process is very small.) The operating expenditure (OPEX) was mainly estimated based on the electricity cost for the driving equipment. The specific CO<sub>2</sub> capture cost (USD per tonne CO<sub>2</sub>) was then estimated using the following equation:

$$\text{CO}_2 \text{ capture cost} = \frac{\text{CRC} + \text{OPEX}}{\text{Annual captured CO}_2} \quad (3)$$

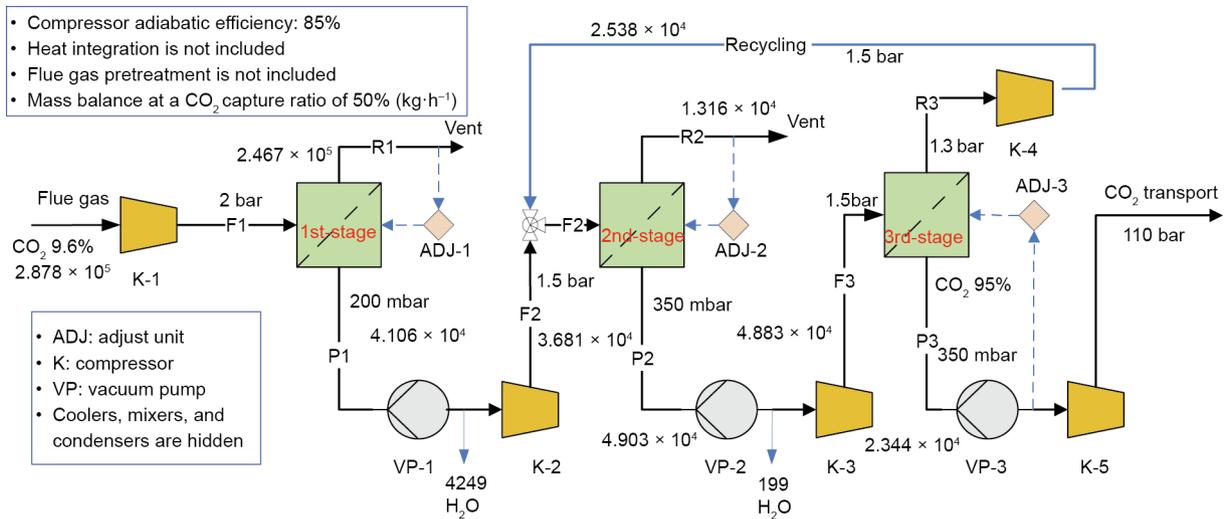


Fig. 4. Process flow diagram of a three-stage membrane system for CO<sub>2</sub> capture.

Table 3

Key simulation results.

CO <sub>2</sub> capture ratio (%)	Total power consumption for compressors and pumps (kW)	Total membrane area (m <sup>2</sup> )	Footprint (number of containers)	CO <sub>2</sub> capture flow (kmol·h <sup>-1</sup> )	Specific energy consumption (GJ <sub>e</sub> per tonne CO <sub>2</sub> captured)
30	$9.84 \times 10^3$	$1.81 \times 10^5$	4	282.48	2.85
50	$1.26 \times 10^4$	$3.79 \times 10^5$	8	472.83	2.18
70	$1.58 \times 10^4$	$6.88 \times 10^5$	15	659.71	1.96
90	$2.03 \times 10^4$	$1.35 \times 10^6$	29	847.71	1.96

In order to estimate the footprint of this membrane system, a 40 ft container (12.2 m length) [29] (inner volume of 67.5 m<sup>3</sup>) with a hollow-fiber module with a packing density of 2000 m<sup>2</sup>·m<sup>-3</sup> was employed. A factor of three was used to cover the manifolding and valves connection between modules, as well as the large header of each group membrane module. Therefore, an apparent module packing density of 700 m<sup>2</sup>·m<sup>-3</sup> for this type of container was employed.

#### 5.4. Techno-economic feasibility analysis

Table 3 summarizes the key simulation results of the total power consumption for the compressors and the total membrane area for different CO<sub>2</sub> capture ratios ranging from 30% to 90%. It can be seen that an increase in the CO<sub>2</sub> capture ratio dramatically increases the required membrane area and total power consumption of the compressors. It should be expected that the incremental cost would not offset the increased CO<sub>2</sub> productivity. Therefore, the membrane system is more economically feasible for a scenario with a low-to-medium CO<sub>2</sub> capture ratio, which aligns with the results reported by Roussanaly et al. [37]. Moreover, the specific energy per tonne of captured CO<sub>2</sub> was found to be higher than the results reported in our previous work [29,40], which is mainly due to the relatively low gas permeance obtained from the pilot testing. Based on the obtained total required membrane surface area, the footprint of the membrane units was estimated to be 4–30 containers, which is acceptable, especially for the scenario with a moderate CO<sub>2</sub> capture ratio of 50%. It should also be noted that the operating pressure was chosen based on the pilot-testing conditions in this work.

Process optimization cannot simply be conducted without experimental data under different testing conditions, as the FT membrane performance is operating-parameter dependent. Therefore, the process condition-dependent gas permeance should be

obtained in future work, in order to investigate the technology feasibility of this membrane further. Moreover, it is worth noting that a CO<sub>2</sub> capture process is more challenging for flue gases with a high O<sub>2</sub> content, as the CO<sub>2</sub>/O<sub>2</sub> selectivity is quite low for the tested FT membranes. It should be expected that the impurity of O<sub>2</sub> in the captured CO<sub>2</sub> will be quite low, especially for the enhanced oil recovery (EOR) process. Therefore, a final purification with cryogenic distillation may be applied.

Based on the energy consumption and the required membrane area listed in Table 3, the annual CRC, operating cost, and specific CO<sub>2</sub> capture cost were estimated (Fig. 5). It was found that the specific CO<sub>2</sub> capture cost is significantly dependent on the capture ratio, such that pursuing a very high CO<sub>2</sub> capture ratio will dramatically increase the capture cost—especially the capital cost of the membrane units. Thus, it is recommended that a moderate CO<sub>2</sub>

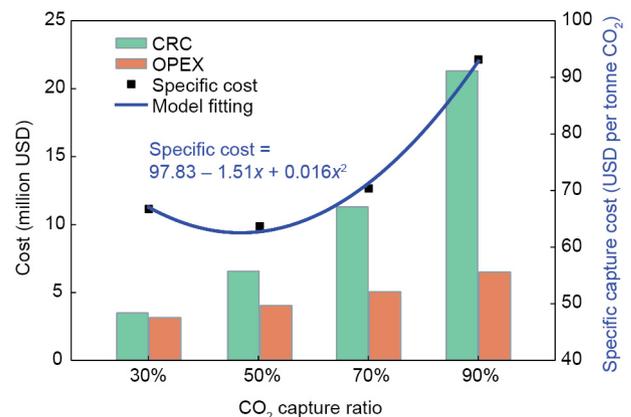


Fig. 5. Dependence of cost on the CO<sub>2</sub> capture ratio.

**Table 4**  
Comparison of simulation results with the literature.

CO <sub>2</sub> capture cost (USD per tonne CO <sub>2</sub> )	Membrane system	Membrane performances		Operating pressure (bar)	Ref.
		CO <sub>2</sub> permeance [m <sup>3</sup> (STP)·(m <sup>2</sup> ·h·bar) <sup>-1</sup> ]	Selectivities		
63.7 (capture ratio of 50%)	Three-stage with recycling	Table 2	Table 2	1st stage: 2/0.2; 2nd stage: 1.5/0.35	This work
43.98 (capture ratio of 80%)	Two-stage with recycling	0.17 Nm <sup>3</sup> ·(m <sup>2</sup> ·h) <sup>-1</sup> (CO <sub>2</sub> flux)	CO <sub>2</sub> /N <sub>2</sub> = 87 O <sub>2</sub> /N <sub>2</sub> = 14 H <sub>2</sub> O/N <sub>2</sub> = 167 (feed composition: 19.4% CO <sub>2</sub> /74.8% N <sub>2</sub> /4% O <sub>2</sub> /1.8% H <sub>2</sub> O)	1st & 2nd stages: 3.3/0.2 (feed pressure drop of 0.5 bar)	[29]
47.87 (capture ratio of 80%)	Two-stage with recycling and heat integration	2	CO <sub>2</sub> /N <sub>2</sub> = 135 (feed composition: 12.9% CO <sub>2</sub> /87.1% N <sub>2</sub> )	1st & 2nd stages: 2.5/0.25	[35]
47.3 (capture ratio of 90%)	Two-stage with recycling	2	CO <sub>2</sub> /N <sub>2</sub> = 135 CO <sub>2</sub> /O <sub>2</sub> = 30 CO <sub>2</sub> /H <sub>2</sub> O = 1 (feed composition: 13.74% CO <sub>2</sub> /72.88% N <sub>2</sub> /3.65% O <sub>2</sub> /9.73% H <sub>2</sub> O)	1st & 2nd stages: 2.5/0.25	[40]
20.5 (capture ratio of 90%)	Two-stage with recycling	1	1st stage: N <sub>2</sub> /CO <sub>2</sub> = 20 2nd stage: CO <sub>2</sub> /N <sub>2</sub> = 200 (feed composition: 11.9% CO <sub>2</sub> /70.6% N <sub>2</sub> /4.9% O <sub>2</sub> /12.6% H <sub>2</sub> O)	1st stage: 4/1; 2nd stage: 4/0.2	[41]

capture ratio should be applied to a membrane system for CO<sub>2</sub> capture. The specific CO<sub>2</sub> capture cost of 63.7 USD per tonne CO<sub>2</sub> captured was obtained at a capture ratio of 50% using the FT membranes. It was also found that the estimated CO<sub>2</sub> capture costs (63–93 USD per tonne CO<sub>2</sub>) were higher than the literature-reported CO<sub>2</sub> capture costs [35,40], as shown in Table 4. This difference is mainly due to the use of more realistic membrane performances (lower gas permeance and selectivity) based on field-testing under specific conditions. Moreover, Hussain et al. [41] reported the lowest CO<sub>2</sub> capture cost of 20.5 USD per tonne CO<sub>2</sub> by using two different membrane materials. It should be noted that N<sub>2</sub>/CO<sub>2</sub> selective membranes were still in an earlier research phase in the work of Hussain et al., and the selectivities of CO<sub>2</sub> over O<sub>2</sub> and H<sub>2</sub>O were not provided, which makes it difficult to compare the results. However, their reported membrane area of  $6.9 \times 10^5$  m<sup>2</sup> was very close to the results obtained at a 70% CO<sub>2</sub> capture ratio in this work. It should also be expected that the high feed pressure of 4 bar used in their work requires higher operating and capital costs for the compressors. Therefore, their reported lower cost is probably due to the different cost models applied. It should be noted that the estimated CO<sub>2</sub> capture cost based on the pilot-testing results is still quite high, and is less cost competitive than amine absorption. However, the membrane material, module, and process performance can be improved to some extent by designing better modules and optimizing the process conditions—especially the uniformly coated modules and the operating temperature. Moreover, the designed three-stage membrane system can be optimized further by varying the operating pressure if membrane performances under other testing conditions are available. In addition, introducing sweep gas might be an option to reduce the energy consumption of the whole system.

## 6. Conclusions and perspectives

PVAm-based FT membranes were identified as a promising gas-separation membrane for post-combustion CO<sub>2</sub> capture. The high membrane material performance is attributed to the unique properties that come from the combination of the S-D and FT mechanisms. The challenge of *in situ* coating was identified for the upscaling of hollow-fiber FT membranes, which should be well addressed in order to control membrane repeatability. Future work on inside coating may provide FSC membranes with uniform and quality-controlled selective layers. Moreover, designing energy-efficient hollow-fiber modules with lower pressure drops in both

the shell and bore sides should be pursued to improve module performance. The PVAm-based FT membranes for CO<sub>2</sub> capture were evaluated at a TRL of 5 at present; advancing to the next stage of a TRL at 6–7 with two- or multi-stage membrane systems should be conducted before bringing this type of membrane into commercial application. However, process design related to inter-stage re-humidification should be thoroughly considered.

Based on the process simulation and cost estimation, it was found that PVAm-based FT membranes can achieve a high CO<sub>2</sub> purity of 95 vol% using a three-stage membrane system. The CO<sub>2</sub> capture cost was significantly dependent on the required CO<sub>2</sub> capture ratio. Pursuing a very high CO<sub>2</sub> capture ratio will dramatically increase the capture cost, which may result in a loss in the competition with state-of-the-art amine technology. Therefore, it is recommended to implement FT membrane systems for partial CO<sub>2</sub> capture. Although the CO<sub>2</sub> capture cost based on process simulation is still quite high, a future research focus on improving membrane system performance by the optimization of module design, process design, and operating conditions should be pursued, in order to enhance the competitiveness of membrane technology for post-combustion CO<sub>2</sub> capture.

## Acknowledgements

The author acknowledges the Research Council of Norway for funding this work through the CO2Hing project (#267615) and Department of Chemical Engineering at Norwegian University of Science and Technology for conducting this work.

## References

- [1] He X. A review of material development in the field of carbon capture and the application of membrane-based processes in power plants and energy-intensive industries. *Energy Sustain Soc* 2018;8(1):34.
- [2] He X, Yu Q, Hägg MB. CO<sub>2</sub> capture. In: Hoek EMV, Tarabara VV, editors. *Encyclopedia of membrane science and technology*. Hoboken: John Wiley & Sons, Inc.; 2013. p. 1–29.
- [3] Anselmi H, Mirgaux O, Bounaceur R, Patisson F. Simulation of post-combustion CO<sub>2</sub> capture, a comparison among absorption, adsorption and membranes. *Appl Phys Lett* 2019;42(4):797–804.
- [4] Aghaie M, Rezaei N, Zendejboudi S. A systematic review on CO<sub>2</sub> capture with ionic liquids: current status and future prospects. *Renew Sustain Energy Rev* 2018;96:502–25.
- [5] Anthony JL, Maginn EJ, Brennecke JF. Solubilities and thermodynamic properties of gases in the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate. *J Phys Chem B* 2002;106(29):7315–20.

- [6] Trickett CA, Helal A, Al-Maythalyon BA, Yamani ZH, Cordova KE, Yaghi OM. The chemistry of metal–organic frameworks for CO<sub>2</sub> capture, regeneration and conversion. *Nat Rev Mater* 2017;2(8):17045.
- [7] Sumida K, Rogow DL, Mason JA, McDonald TM, Bloch ED, Herm ZR, et al. Carbon dioxide capture in metal–organic frameworks. *Chem Rev* 2012;112(2):724–81.
- [8] Kazemi S, Safarifar V. Carbon dioxide capture in MOFs: the effect of ligand functionalization. *Polyhedron* 2018;154:236–51.
- [9] Li J, Zhang H, Gao Z, Fu J, Ao W, Dai J. CO<sub>2</sub> capture with chemical looping combustion of gaseous fuels: an overview. *Energy Fuels* 2017;31(4):3475–524.
- [10] Mantripragada HC, Rubin ES. Chemical looping for pre-combustion and post-combustion CO<sub>2</sub> capture. *Energy Procedia* 2017;114:6403–10.
- [11] Samanta A, Zhao A, Shimizu GKH, Sarkar P, Gupta R. Post-combustion CO<sub>2</sub> capture using solid sorbents: a review. *Ind Eng Chem Res* 2012;51(4):1438–63.
- [12] He X. Membranes for natural gas sweetening. In: Drioli E, Giorno L, editors. *Encyclopedia of membranes*. Berlin: Springer; 2016. p. 1266–7.
- [13] Roussanaly S, Anantharaman R, Lindqvist K, Zhai H, Rubin E. Membrane properties required for post-combustion CO<sub>2</sub> capture at coal-fired power plants. *J Membr Sci* 2016;511:250–64.
- [14] Khalilpour R, Mumford K, Zhai H, Abbas A, Stevens G, Rubin ES. Membrane-based carbon capture from flue gas: a review. *J Clean Prod* 2015;103:286–300.
- [15] Prasetya N, Donose BC, Ladewig BP. A new and highly robust light-responsive Azo–UiO-66 for highly selective and low energy post-combustion CO<sub>2</sub> capture and its application in a mixed matrix membrane for CO<sub>2</sub>/N<sub>2</sub> separation. *J Mater Chem A* 2018;6(34):16390–402.
- [16] Merkel TC, Wei X, He Z, White LS, Wijmans JG, Baker RW. Selective exhaust gas recycle with membranes for CO<sub>2</sub> capture from natural gas combined cycle power plants. *Ind Eng Chem Res* 2013;52(3):1150–9.
- [17] He X, Lindbräthen A, Kim TJ, Hägg MB. Pilot testing on fixed-site-carrier membranes for CO<sub>2</sub> capture from flue gas. *IJGGC* 2017;64:323–32.
- [18] Pohlmann J, Bram M, Wilkner K, Brinkmann T. Pilot scale separation of CO<sub>2</sub> from power plant flue gases by membrane technology. *IJGGC* 2016;53:56–64.
- [19] Kim TJ, Vrålstad H, Sandru M, Hägg MB. Separation performance of PVAm composite membrane for CO<sub>2</sub> capture at various pH levels. *J Membr Sci* 2013;428:218–24.
- [20] Deng L, Kim TJ, Hägg MB. Facilitated transport of CO<sub>2</sub> in novel PVAm/PVA blend membrane. *J Membr Sci* 2009;340(1–2):154–63.
- [21] Tong Z, Ho WSW. Facilitated transport membranes for CO<sub>2</sub> separation and capture. *Sep Sci Technol* 2017;52(2):156–67.
- [22] Qiao Z, Zhao S, Sheng M, Wang J, Wang S, Wang Z, et al. Metal-induced ordered microporous polymers for fabricating large-area gas separation membranes. *Nat Mater* 2019;18(2):163–8.
- [23] Tong Z, Ho WSW. New sterically hindered polyvinylamine membranes for CO<sub>2</sub> separation and capture. *J Membr Sci* 2017;543:202–11.
- [24] Shen Y, Wang H, Liu J, Zhang Y. Enhanced performance of a novel polyvinyl amine/chitosan/graphene oxide mixed matrix membrane for CO<sub>2</sub> capture. *ACS Sustain Chem Eng* 2015;3(8):1819–29.
- [25] Taniguchi I, Kinugasa K, Toyoda M, Minezaki K. Effect of amine structure on CO<sub>2</sub> capture by polymeric membranes. *Sci Technol Adv Mater* 2017;18(1):950–8.
- [26] Kim TJ, Li B, Hägg MB. Novel fixed-site-carrier polyvinylamine membrane for carbon dioxide capture. *J Polym Sci B* 2004;42(23):4326–36.
- [27] Sandru M, Kim TJ, Capala W, Huijbers M, Hägg MB. Pilot scale testing of polymeric membranes for CO<sub>2</sub> capture from coal fired power plants. *Energy Procedia* 2013;37:6473–80.
- [28] Hägg MB, He X, Sarfaraz V, Sandru M, Kim TJ. CO<sub>2</sub> capture using a membrane pilot process at cement factory. In: *Proceedings of the 8th Trondheim CCS Conference*; 2015 Jun 16–18; Trondheim, Norway; 2015.
- [29] Hägg MB, Lindbräthen A, He X, Nodeland SG, Cantero T. Pilot demonstration-reporting on CO<sub>2</sub> capture from a cement plant using hollow fiber process. *Energy Procedia* 2017;114:6150–65.
- [30] Chu Y, Lindbräthen A, Lei L, He X, Hillestad M. Mathematical modeling and process parametric study of CO<sub>2</sub> removal from natural gas by hollow fiber membranes. *Chem Eng Res Des* 2019;148:45–55.
- [31] Han Y, Wu D, Ho WSW. Simultaneous effects of temperature and vacuum and feed pressures on facilitated transport membrane for CO<sub>2</sub>/N<sub>2</sub> separation. *J Membr Sci* 2019;573:476–84.
- [32] Han Y, Salim W, Chen KK, Wu D, Ho WSW. Field trial of spiral-wound facilitated transport membrane module for CO<sub>2</sub> capture from flue gas. *J Membr Sci* 2019;575:242–51.
- [33] Hägg MB, Kim TJ, Li B, inventors. Membrane for separating CO<sub>2</sub> and process for the production thereof. WIPO patent WO 2005089907A1. 2005 Sep 29.
- [34] Deng L. Development of novel PVAm/PVA blend FSC membrane for CO<sub>2</sub> capture [dissertation]. Trondheim: Norwegian University of Science and Technology; 2009.
- [35] He X, Fu C, Hägg MB. Membrane system design and process feasibility analysis for CO<sub>2</sub> capture from flue gas with a fixed-site-carrier membrane. *Chem Eng J* 2015;268:1–9.
- [36] Robeson LM. The upper bound revisited. *J Membr Sci* 2008;320(1–2):390–400.
- [37] Roussanaly S, Anantharaman R. Cost-optimal CO<sub>2</sub> capture ratio for membrane-based capture from different CO<sub>2</sub> sources. *Chem Eng J* 2017;327:618–28.
- [38] Grainger D. Development of carbon membranes for hydrogen recovery [dissertation]. Trondheim: Norwegian University of Science and Technology; 2007.
- [39] Turton R, Bailie RC, Whiting WB, Shaiwitz JA, Bhattacharyya D. Analysis, synthesis, and design of chemical processes. 4th ed. New Jersey: Pearson Education; 2013.
- [40] He X, Hägg MB. Energy efficient process for CO<sub>2</sub> capture from flue gas with novel fixed-site-carrier membranes. *Energy Procedia* 2014;63:174–85.
- [41] Hussain A, Farrukh S, Minhas FT. Two-stage membrane system for post-combustion CO<sub>2</sub> capture application. *Energy Fuels* 2015;29(10):6664–9.