Optimizing Methane Recovery: Techno-economic Feasibility Analysis of N_2-selective Membranes for the Enrichment of Ventilation Air Methane

Xuezhong He [1,2,*] and Linfeng Lei [3]

[1] Department of Chemical Engineering, Guangdong Technion Israel Institute of Technology (GTIIT), 241 Daxue Road, Shantou 515063, China

[2] The Wolfson Department of Chemical Engineering, Technion - Israel Institute of Technology, Haifa 32000, Israel

[3] Department of Chemical Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

*Corresponding author email: xuezhong.he@gtiit.edu.cn

Abstract: Utilization of the low concentration methane from coal-mining ventilation air is challenging but can significantly contribute to the mitigation of methane emissions to the atmosphere. This work focuses on the techno-economic feasibility analysis of N_2-selective membrane systems for the enrichment of ventilation air methane (VAM). The feed methane concentration and gas permeance are found to significantly influence the specific methane enrichment cost, while feed pressure has the lest effect. For a stand-alone membrane system, the optimal methane recovery of ca. 70 % is identified to achieve a higher methane purity at the same cost, which may gain an economic benefit when it is operated at high plant capacity. Although the SAPO-34 membrane system is technologically feasible for the enrichment of 1.5 vol.% VAM, novel membranes with a higher N_2/CH_4 selectivity of greater than 25 is required to reduce the membrane stages for the pre-concentration of a very diluted VAM of <1 vol.%. Considering a large-scale application in the methane recovery from the coal-mining ventilation air, carbon hollow fiber membranes may have the potential to address the challenges of the high production cost and the module up-scaling with large packing density that is faced by zeolite membranes.

Keywords: N_2-selective membranes; inorganic membranes; ventilation air methane; methane emissions; process simulation, methane recovery

1. Introduction

Methane is responsible for about one-quarter of global warming, which is a dense greenhouse gas that has 25 times the global warming potential compared to CO_2 [1]. Today, global atmospheric methane concentration exceeds 1875 ppb [2], and is 2.5 times increase compared to that in the 1850s. Methane is emitted during the production of coal, natural gas and oil, and emissions also result from agriculture, animal feeding house gas and manure storage headspace. The reduction of methane emissions from the industrial sector is urgently needed as the methane concentration in the atmosphere will continuously increase by 30 % until 2050 if no reduction measure is taken [3]. However, it would be possible to reduce 38 % of methane emissions by implementing available technologies to mitigate or capture methane from different scenarios [4]. Reducing methane loss has already been considered in most of the natural gas and biogas production plants. While less effort has been put into the mitigation and utilization of methane in the coal mining processes. It should be noted that the methane emissions from the coal mining processes account for 8 % of the total global human-related methane emissions. Moreover, methane is a safety hazard to the mining production as it is explosive in a concentration ranging from 5 to 15 vol.% in the air [5]. Therefore, coal mining usually employs large-scale ventilation systems by blowing fresh air into mining wells to dilute methane, which maintains a safe working environment below the lower explosive limit. Thus, the ventilation air exhausts usually contain diluted methane (typically <1 vol.% [6]). Due to the huge exhaust flow rate in many mines, ventilation air methane (VAM) becomes the largest single source of methane emissions to the atmosphere, which needs to be first tackled. Therefore, the deployment of methane capture from coal-mining ventilation air is crucial to recover low-carbon energy resources and combat global warming in terms of greenhouse gas emissions. Several technologies such as catalytic and thermal oxidation, and biological oxidation [7-11] can be used to mitigate VAM emissions (i.e., VAM destruction). Regenerative thermal oxidation is the commercially available technology of using VAM as a primary fuel at methane concentrations of below 1.5 vol.%. However, the conversion efficiency of direct oxidation using such low content methane is low, and it requires much bigger reactors due to the existence of the large amount of inert gas N_2. Moreover, VAM destruction systems often need additional fuels to maintain a continuous operation as the methane concentration and flow rate in coal mining processes are highly unstable. The enrichment of VAM as an energy source can potentially expand its business in the downstream end-users. Many countries, such as China and India, gained great economic benefits of methane recovery from coal mining [4]. It should be noted that the methane captured from VAM will be more economically feasible compared to the direct air capture (DAC) due to the two reasons: 1) methane is a more valuable low-carbon energy source compared to CO_2, and; 2) methane emission to the atmosphere has a much high global warming potential compared to CO_2. Therefore, it is crucial to capture methane from coal-mining ventilation air compared with the direct carbon capture from air. Currently, different methods such as pressure swing adsorption (PSA) [12-15], hydrate crystallization [16, 17], cryogenic distillation [18], mechanical tower [4, 19], and membrane separation [20-22] have been investigated for the VAM capture. The main challenge of VAM recovery and enrichment using these separation technologies is the high operating cost due to a very diluted methane stream and a large gas volume to be processed. Hybrid systems by combining the bulk enrichment of VAM using membranes with the ultimate purification using PSA or cryogenic distillation may reduce the overall energy consumption and provide a more energy-efficient solution on the recovery of VAM. Great effort has recently been put into the development of novel membranes for the bulk methane enrichment of N_2/CH_4 separation [21-25] as it accounts for a large part of the total energy consumption. However, due to the similarity of the two gas molecules of N_2 and CH_4 in their physical properties such as molecular size and condensability, it makes their separation very challenging [25]. Recently, several thermally rearranged (TR) membranes [24, 26] has been reported to present a moderate N_2/CH_4 selectivity and their overall separation performances approach the 2008 Robeson upper bound, as is indicated in Fig. 1. Inorganic membranes provide a higher N_2/CH_4 selectivity based on the molecular sieving transport mechanism [20-22, 27-29]. Lei et al. reported that the cellulose-based carbon hollow fiber membranes presented a high N_2/CH_4 selectivity of >10, but N_2 permeability is quite low [21], which needs to be further enhanced to bring down the membrane unit cost. Zong et al. reported the high performance silicoaluminophosphate-34 (SAPO-34) zeolite membranes with a N_2 permeance of 1300 GPU and a reasonably good N_2/CH_4 selectivity of 7.4 [22] (as shown in Fig. 1). In general, carbon membranes present a similar N_2 permeability compared to TR polymers, but a higher N_2/CH_4 selectivity as indicated in Fig. 1. While the SAPO-34 membranes present a comparable selectivity with carbon membranes, but a much higher N_2 permeability, which makes it very promising for the enrichment of VAM. However, the main challenges hindering its commercialization is the high production cost as well as the difficulty in the up-scaling of membrane production related to the controlling of in-situ crystal growth.

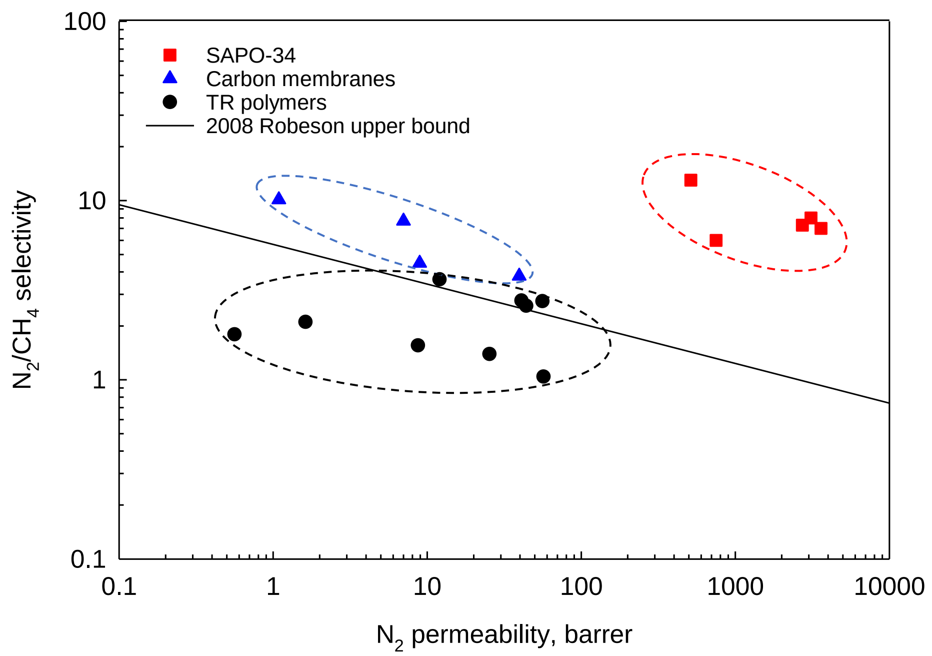

Fig. 1 N_2/CH_4 upper bound performance for the state-of-the-art membrane materials. TR polymers (●) from Refs. [24, 26], carbon membranes (▲) from refs. [20, 21], and SAPO-34 membranes (■) from refs. [22, 27].

In order to identify the most suitable membrane materials for VAM recovery, techno-economic feasibility analysis should be conducted to estimate the energy consumption and capital cost. Therefore, different inorganic membranes such as carbon molecular sieve membranes and SAPO-34 membranes were investigated for N_2/CH_4 separation based on HYSYS simulation in this work. Moreover, the process parametric optimization of feed and permeate pressures and gas composition was also investigated to determine the optimal operating conditions. The results can be used to guide the design and development of advanced membrane materials and processes for the membrane recovery from ventilation air exhausts.

2. Method

2.1. Process description and membrane system design

VAM derived from the coal mining is usually kept quite low in the ventilation air. The main components of raw VAM are N_2 and CH_4, together with some impurities of CO_2, O_2, and H_2O. Both N_2 and CH_4 are non-condensable and have similar physical and chemical properties, which are difficult to be separated at room temperature. In order to develop energy-efficient and cost-effective membrane processes for the methane enrichment from ventilation air, process design and optimization are crucial besides the development of advanced membrane materials. A single-stage membrane unit (see Fig. 2a) is proposed for the enrichment of VAM containing low content methane of <1.5 vol.%. The methane-enriched gas is produced in the retentate and followed by a further purification unit using membranes or other technologies of PSA or cryogenic distillation to produce high purity methane for vehicle fuels or blending nature gas. While the permeate with very low-content methane can be vented to the atmosphere under a controlled methane loss. If a single-stage membrane system cannot achieve the separation requirement, two- or multi-stage membrane systems are usually designed to produce the enriched methane at an acceptable methane loss as shown in Fig. 2b. The permeate in the second-stage membrane unit contains high-concentration CH_4, which should be recycled back to the first-stage membrane unit to avoid the high methane emissions. As the ventilation air usually has a low pressure exhausting from coal mining, it should be compressed to get a high driving force for the gas transportation before feeding into the membrane units.

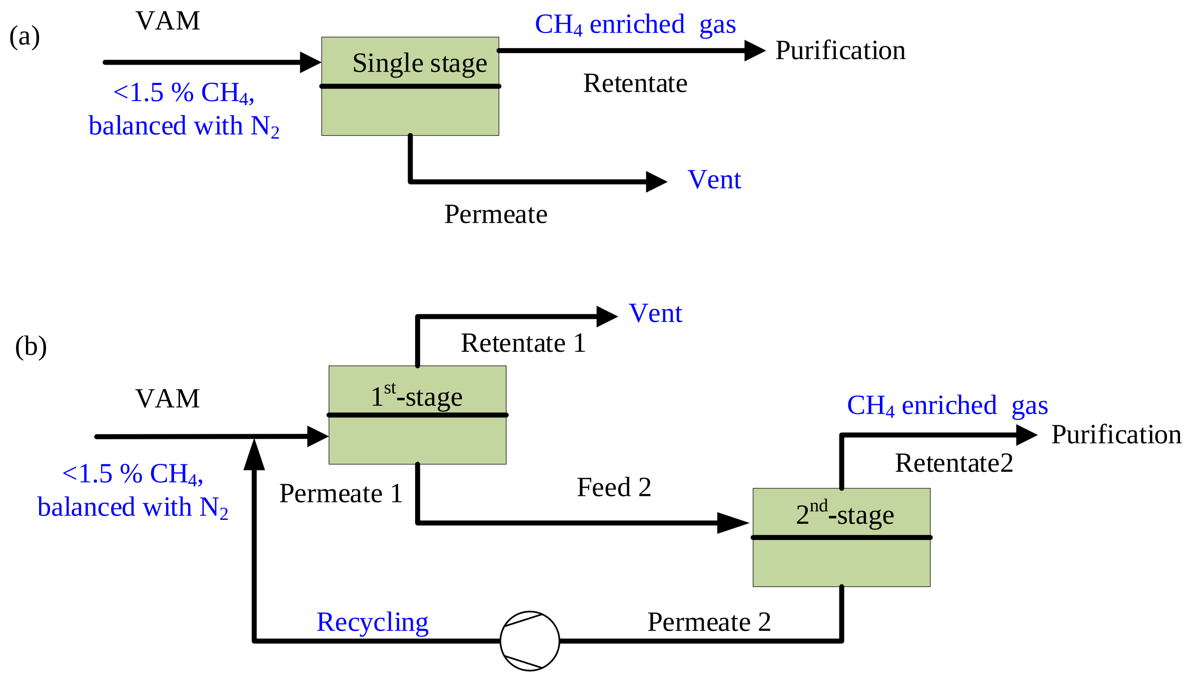

Fig. 2 Membrane processes for the enrichment of VAM. (a) single-stage membrane system with high N_2/CH_4 selectivity; (b) two-stage membrane system with low N_2/CH_4 selectivity

2.2. Simulation basis

A gas flow rate of 10,000 m^3 (STP)/h ventilation air methane at 1 bar was chosen as the simulation basis. Only the main component of N_2 and CH_4 in feed gas was considered in the process simulations to achieve the separation requirement listed in Table 1. Tubular and hollow fiber modules mounted with SAPO-34 membranes and carbon membranes, respectively, were chosen to model the membrane separation units. The separation performances of carbon membranes and SAPO-34 membranes that are given in Fig. 1 were used as the simulation input. Marin et al. reported that the process operating parameters such as feed pressure and CH_4

concentration influenced the system separation performance [30], which have been investigated in this work. Moreover, it is expected that the membrane material performances will also affect the separation efficiency and the required membrane area. Therefore, the chemometric methods based on a 2^{4-1} factorial design and multivariate analysis were introduced to systematically investigate the influences of the membrane material and process parameters such as N_2 permeance, N_2/CH_4 selectivity, feed pressure, and feed methane content on the membrane system performance. The factors and levels used in the factorial design are listed in Table 2. Each parameter has two levels in which the low level (-1) and the high level (+1) are selected. In total eight scenarios with different combinations of membrane separation performances and process operating conditions were simulated. A methane recovery of 70 % and a methane enrichment of 10 vol.% were defined as the separation targets from different scenarios with various feed methane concentrations (0.5–1.5 vol.%). For the sensitivity analysis, varying plant capacity, methane purities and recoveries, membrane separation performance as well as membrane material cost were conducted in process simulation. The following assumptions were applied in the simulations.

1) Gas permeance was kept constant for a specific membrane in the investigated pressure range.
2) The counter-current flow pattern was used to model gas transport through membranes, and no pressure drop is applied on both feed and permeate sides.
3) The pressure drops for coolers were negligible in all simulation scenarios.
4) The compressor adiabatic efficiency of 75 % was applied, and no pressure drop on heat exchangers.
5) The plug flow model was applied in both the feed and permeate side of membrane modules, and no radial velocity distribution is considered.

Table 1 The simulation basis for the enrichment of VAM using SAPO-34 based membrane system

Parameters	Values

Feed flow, m^3(STP)/h	10,000
Feed composition	0.5–1.5 vol.% CH_4 balanced with N_2
Feed gas pressure, bar	1
Feed temperature, °C	30
Gas permeance	See Table 2
Methane enrichment, vol.%	10*
Methane recovery, %	70*

*: only set in the factorial design, and it varies in the sensitivity analysis.

Table 2 The material performances and process operating parameters and levels used in the membrane system design

Factor	Material and process parameter	High level (+1)	Low level (-1)
A	N_2 permeance (GPU)*	1300	100
B	N_2/CH_4 selectivity*	10	6
C	Feed pressure (bar)	15	5
D	Feed methane concentration (%)	1.5	0.5

*: based on the SAPO-34 membranes in Fig. 1

2.3. Process simulation and cost estimation

The above-designed scenarios were simulated by Aspen HYSYS integrated with a customized membrane unit of ChemBrane ([31-33]). It is expected that the ventilation air from coal mining should be compressed before entering membrane units if the permeate is operated at the atmospheric pressure (vacuum operation is not included). A higher feed pressure (or a high transmembrane-pressure difference) can potentially enhance the purification performance and reduce the required membrane area. However, the operating cost related to the compressor power demand increases accordingly. Therefore, cost estimation based on the power demand of compressors and the required membrane area should be conducted to identify the optimal operating conditions for a specific separation scenario.

The cost evaluation was conducted by the capital expenditure (CAPEX) estimation of the major equipment of compressors and membrane units by CAPCOST 2012 program [34]. The cost model reported in the previous work [35] was introduced in this work to estimate the methane recovery from ventilation air. The centrifugal compressors (450–3000 kW) with carbon steel materials were selected for low- to medium-pressure operation (up to 15 bar), and its purchasing cost (C_p^0) is dependent on the required compressor capacity Q (kW) ($log_{10}C_p^0 = K_1 + K_2 log_{10}(Q) + K_3[log_{10}(Q)]^2$ [34]), and the total module cost (C_{TM}) is calculated by,

$$C_{TM} = 1.18 \sum_{i=1}^{n} C_{BM,i}\ ,\ C_{BM} = C_p^0 F_{BMCS} \tag{1}$$

where C_{BM} is the bare module cost, K_1, K_2, K_3, and the carbon material factor (F_{BMCS}) are given in Table 3. The chemical engineering plant cost index (CEPCI) of 603.1 (2018) for the equipment was used to adopt all inflation adjustments.

Table 3 The parameters for the cost estimation of centrifugal compressors [34]

Compressor type	K_1	K_2	K_3	F_{BMCS}*	W_{min}, kW	W_{max}, kW
Centrifugal	2.2891	1.3604	-0.1027	2.7	450	3000

*: the bare module factor using carbon steel material.

Apart from compressors, the membrane unit cost of $500/m^2 was used considering the high production cost of SAPO-34 membrane materials, while $100/m^2 was chosen for carbon hollow fiber membranes [33, 36]. The sensitivity analysis on the membrane material cost was conducted for the SAPO-34 membranes from $300-2500/m^2 and carbon membranes from $20-200/m^2, respectively. The membrane lifetime of 10 years was also applied. Other equipment such as heat exchanger, cooler, and mixer have not been included as those unit costs are expected to be much lower compared to compressors and membrane units. The annual capital-related cost (CRC) was estimated based on a loan interest of 7 % at a project lifetime of 20 years. The electricity price of $0.05/kWh was used to estimate the operating expenditure

(OPEX) of compressors [37]. It is worth noting that the cooling unit cost is negligible as the cooling water used in a membrane process for the enrichment of VAM is very small. Thus, the specific methane enrichment cost (C^S, \$/m^3 enriched methane) from coal-mining ventilation air is estimated by:

$$C^S = \frac{CRC+OPEX}{Annual\ total\ enriched\ methane\ production} \tag{2}$$

2.4. Theory basis and statistical analysis

Experimental design and multivariate analysis methods have been widely used in the process engineering field to systematically investigate the significance of different factors on response variables. The factorial design method has the advantage of obtaining quantitative information by running reduced investigations. Based on the obtained simulation results, statistical analysis using linear regression of the response variables to the factors was conducted by Minitab® 19 based on the method reported in our previous work [38]. The main effects of different factors were analyzed by the Pareto Charts of Standard Effects and Main Effects Plot. In the Pareto Charts, the parameters are statistically significant if their bars exceed the reference line determined by the significance level (e.g., α=5 %) and the degree of freedom of parameters.

3. Results and discussion

3.1. Statistical analysis of parameter influences

HYSYS simulations were conducted for the eight scenarios at different conditions, and the enriched methane purity of 10 vol.% with a methane recovery of 70 % was set as the separation requirements. The process simulation results are given in Table 4, and the major output variables such as the compressor power demands, the required membrane area, and the production rate are used to calculate the specific methane enrichment cost based on Eq. (2), and the specific power demand (E^S, kWh/m^3 enriched methane produced). Factorial analysis in Minitab 19 was performed to identify the significant parameters that affect the specific cost and E^S. The single-parameter linear regression models are obtained in Eqs. (3) and (4) with the R^2 of 98.3 % and 94.3%, respectively, which indicates a high prediction accuracy within the defined factor levels. The Pareto Chart of Standardized Effects (Fig. 3 Left) indicates that the specific methane enrichment cost is mainly dependent on the two significant factors (i.e., the feed methane concentration (factor D) and the N_2 permeance (factor A)), and the methane enrichment from a highly diluted VAM dramatically increases the cost. Thus, scenario 2 operated at a high level for all parameters that were chosen for the sensitivity analysis in terms of both coal-mining plant capacity and separation requirement. It is surprising that the membrane performance of both N_2 permeance and N_2/CH_4 selectivity (in the investigated ranges) has no significant influence on the specific cost, which is probably due to the assumption of the pressure-independent membrane performance, and a low separation requirement set in the first-stage membrane unit. It should be noted that most of the membranes present a reduced separation performance with the increase of feed pressure because of either the membrane compaction (e.g., polymeric membranes) or the reduction of gas solubility coefficient (e.g., inorganic membranes). The membrane performances reported in the literature were mainly obtained from a low feed-pressure testing of ca. 2 bar [22], and the extrapolation to a moderate- or high-pressure of 10-15 bar may have significant deviations, which should be further investigated when more experimental data is available. Nevertheless, the developed model can be used for the preliminary prediction of the processing cost when the plant ventilation air has different methane concentrations. Moreover, the specific power demand was also found to be significantly dependent on the feed methane concentration (Fig. 3 Right). It is worth noting that higher N_2 permeance leads to a higher E^S due to a positive effect of the factor A given in Eq. (4), which indicates that highly-permeable membranes may increase the operating cost significantly even though it can reduce the required membrane area. As expected, the increase in feed pressure (factor C) results in higher power demand (and thus

OPEX). However, it has a minor influence on the overall specific cost as the reduced membrane capital cost can largely offset the increased OPEX.

$$\ln(C^S) = -1.455 - 0.174\,A - 0.100\,B - 0.0675\,C - 0.690D \quad (3)$$

$$E^S = 2.773 + 0.367\,A - 0.138\,B + 0.246\,C - 1.697\,D \quad (4)$$

Table 4 The process simulation results of all the scenarios defined in the 2^{4-1}factorial design

Scenarios	Factors				Major output variables			Response variables	
	A	B	C	D	Compressor power demand (kW)	Membrane areas (m^2)	Enriched methane flow rate (m^3/h)	C^S ($\$/m^3$ enriched methane)	E^S (kWh/m^3 enriched methane)
1	1	-1	-1	1	1010.5	755.5	920.0	0.101	1.10
2	1	1	1	1	989.9	234.3	1028.8	0.082	0.96
3	1	-1	1	-1	1622.9	173.8	287.4	0.451	5.65
4	-1	-1	1	1	1398.2	2439.3	938.7	0.151	1.49
5	-1	1	1	-1	1303.6	2291.5	328.0	0.405	3.97
6	-1	1	-1	1	803.9	7537.5	1066.7	0.151	0.75
7	-1	-1	-1	-1	1108.6	9773.0	325.4	0.648	3.41
8	1	1	-1	-1	1753.0	561.5	361.6	0.397	4.85

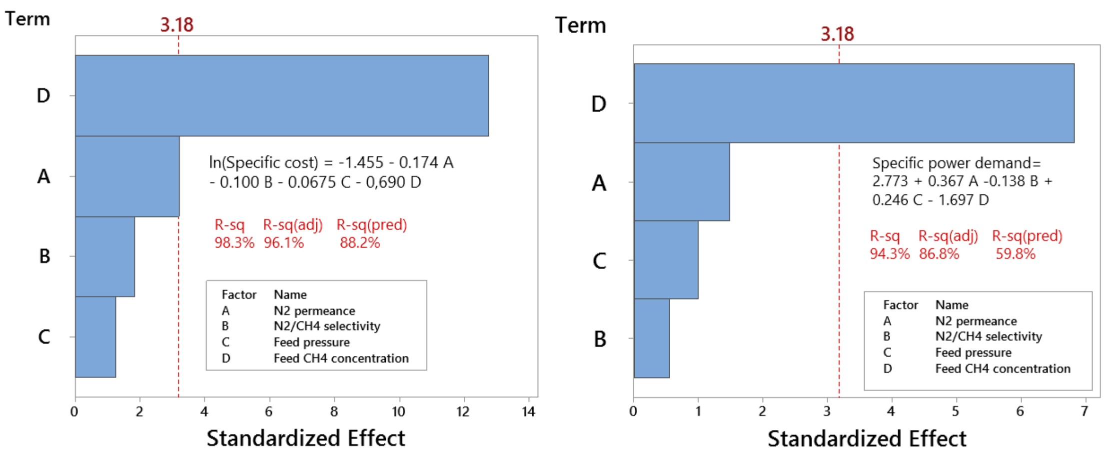

Fig. 3 The Pareto Chart of Standardized Effects on the specific methane enrichment cost (Left) and the specific power demand (Right) at a 95 % confidence level

3.2. Sensitivity analysis

3.2.1. Separation requirement

Methane recovery is an important parameter in controlling the methane emissions of coal mining industries, which needs to be balanced between the environmental impact of greenhouse gas and the economic benefit of fuels. Moreover, methane purity after the enrichment process is another key performance index to determine the suitable end-users (e.g., the feedstocks for thermal oxidation and combined heating and power (CHP), or vehicle fuels). Therefore, the influences of these two parameters on the specific methane enrichment cost were conducted by process simulation of scenario 2 at the methane recovery of 35–90 % and the methane purity of 10–96 vol.%. The simulation results are shown in Fig. 4, it can be found that the specific cost increases with the increase of methane purity at a given recovery, and the optimal methane recovery of ca. 70 % is identified to achieve a higher methane purity at the same cost. The stand-alone membrane system is technologically feasible for the methane enrichment to different purities from VAM. However, pursuing a higher methane purity increases the cost accordingly. It is worth noting that the same cost (e.g., 1.4 $\$/m^3$ enriched methane) can achieve a combination of both high recovery (>80 %) and methane purity (80 vol.%) compared to the process with a lower recovery (~45 %), which is mainly attributed to the recycling of the second-stage membrane unit (Fig. 2b). In this work, the cost of other operation units such as recycling and cooling have not been included, which may underestimate the overall cost of those processes integrated with permeate recycling. Moreover, the low recovery scenarios at the same purity require no recycling unit, which can enhance the process operation stability, and reduce the footprint of the whole system.

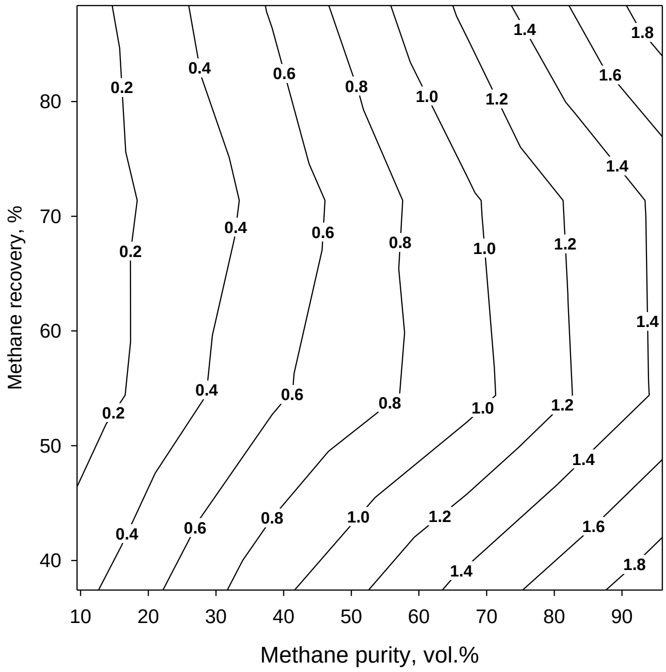

Fig. 4 The influences of separation requirement on the specific methane enrichment cost

3.2.2. Plant capacity

In order to investigate the process flexibility of membranes systems for the enrichment of VAM, the influence of plant capacity (5,000–30,000 m^3/h) on the specific methane enrichment cost was conducted using the same condition as scenario 2 in Table 4. The separation requirements were set to 10 vol.% and 70 % for the methane purity and recovery, respectively. Fig. 5 shows the dependence of the specific methane enrichment cost on the coal-mining plant capacity. It is found that the specific methane enrichment cost slightly decreases with increasing plant capacity, which indicates that the total annual cost is not linearly increased with the increase of plant capacity- this is probably due to the power function (the index <1) of the compressor purchase cost with its power demand ($C_P^0 = 1560Q^{0.749}$). Moreover, OPEX is relatively higher compared to annual CRC, and thus the power demands of membrane system have a great effect on the specific cost. Therefore, process operation at a lower feed pressure can potentially reduce the energy consumption for the compression of the huge amount of ventilation air. Since membrane systems are the module-based units, it can be readily scaled up and down to accommodate the variety of the ventilation air capacity in coal mining as there is no significant cost changes at different plant capacities.

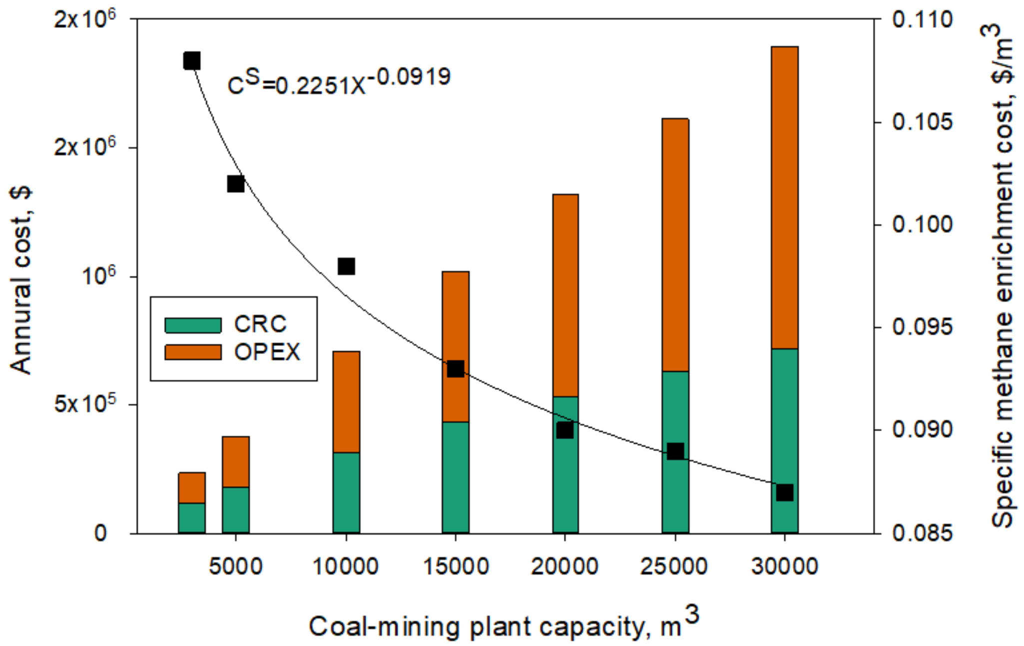

Fig. 5 The influence of coal-mining plant capacity on the specific methane enrichment cost

3.2.3. Membrane material performance influence

A single-stage membrane unit with the literature reported SAPO-34 membrane selectivity for N_2/CH_4 of 6–10 cannot attain a high methane enrichment from VAM (the ratio of methane purity between retentate and feed). Thus, multi-stage membrane systems are needed to achieve the separation requirement of a given methane purity and recovery, which boosts the process operation complexity and cost, and the footprint. In order to reduce the required membrane stages, membrane material performance under the real testing conditions (e.g., moderate pressures) should be further improved besides the optimization of process conditions. Therefore, process simulations using a single-stage membrane system (Fig. 2a) with assumed N_2 permeance (100–1000 GPU) and N_2/CH_4 selectivity (6–50) were conducted for the enrichment of 10,000 m^3/h VAM with a feed methane concentration of 1 vol.% at a feed pressure of 10 bar. A fixed membrane area of 300 m^2 was applied to examine their influences on methane purity and recovery, and the simulation results are presented in Fig. 6. When the

N_2/CH_4 selectivity is lower than 15, increasing gas permeance will not significantly contribute the methane enrichment due to a high methane recovery (>92 %). In order to get much enriched methane in the permeate (e.g., >2 vol.%) of the first-stage membrane unit, an N_2/CH_4 selectivity of greater than 25 is required (see Fig. 6a). However, super-high gas permeance (e.g., >1000 GPU for N_2) is not necessary if a methane recovery of lower than 90 % is acceptable as shown in Fig. 6b. Therefore, further development of highly N_2-selective membranes is still needed to reduce the required membrane stages for the pre-concentration of methane from coal-mining ventilation air. Carbon molecular sieve membranes with the precisely controlled pore size reported in our previous work [21] may provide the great potential for this application, but gas permeance needs to be significantly improved by making composite or asymmetric carbon membranes. Moreover, considering the membrane upscaling for the large-scale processing of VAM, self-supported carbon hollow fiber membranes possess higher packing density and lower cost compared with tubular zeolite membranes (e.g., SAPO-34, AIPO) that are currently only available in the lab-scale. Even though some literature reported to prepare mixed matrix membranes using SAPO-34 nanofillers [23, 39], the obtained membrane performance (especially N_2/CH_4 selectivity) is much lower than those pure SAPO-34 membranes [22, 27, 28]. Therefore, the challenges of bringing down the membrane production cost and addressing the membrane upscaling still hinder the application of zeolite membranes for N_2/CH_4 separation at a large-scale.

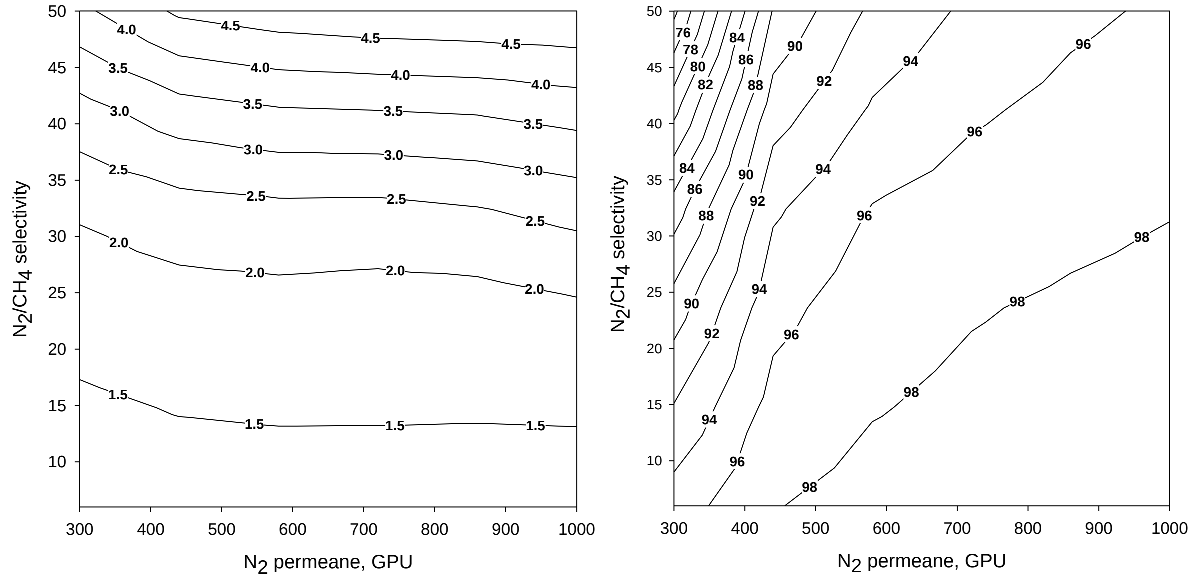

Fig. 6 The influences of membrane materials separation performance on the methane purity and recovery using a single-stage membrane system

3.2.4. Permeate pressure influence

Different operation modes of using feed compression, permeate vacuum suction and their combination were reported to investigate the influences on the system performance and specific CO_2 capture cost in the previous work [40]. Thus, by keeping a constant pressure ratio of 10, varying both feed and permeate pressures was conducted for the enrichment of 10,000 m^3/h VAM with a feed methane concentration of 1 vol.%. The membrane performance of scenario 2 was used to achieve a 70 % methane recovery by adjusting membrane area using a single-stage membrane system. Fig. 7 shows the dependence of the required membrane area and compressor power on the permeate pressure. It can be seen that the specific methane enrichment cost has no significant difference with the permeate pressures of higher than 30 kPa. Therefore, the permeate pressure of 1 bar is recommended considering the benefit of the compressed retentate stream for the purification of the enriched methane further.

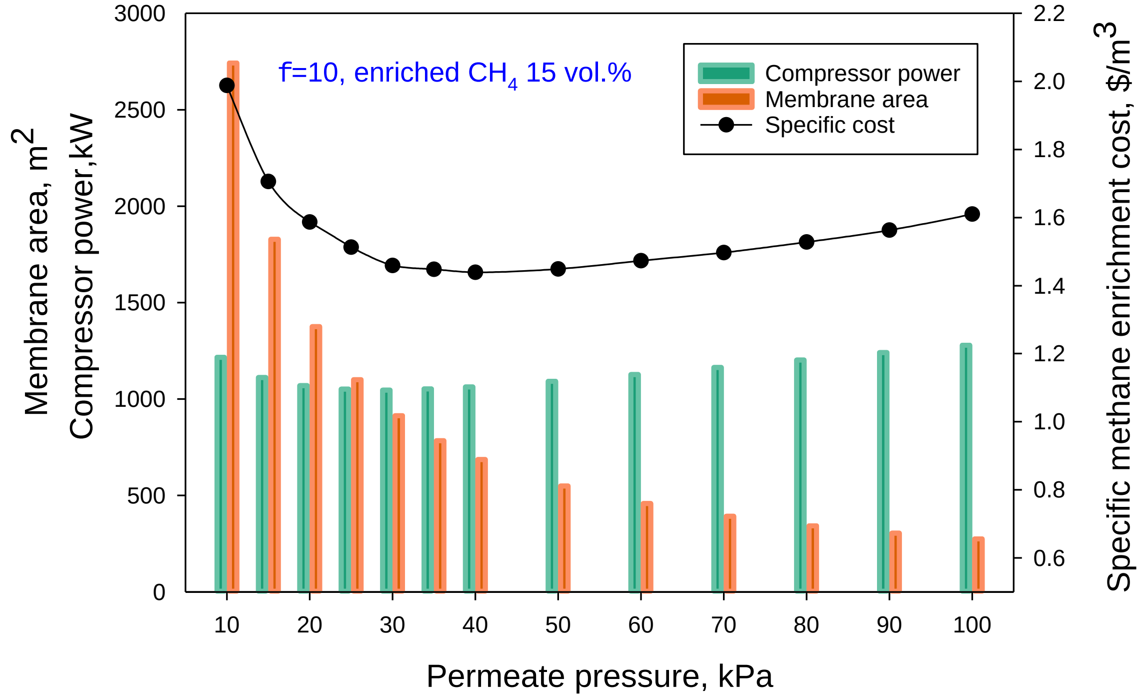

Fig. 7 Dependence of required membrane area, power demand and specific cost on the permeate pressure at a constant pressure ratio of 10

3.3. Technology comparison of membrane materials

To compare the technology advances of different membrane systems with the state-of-the-art cryogenic distillation for the methane enrichment/recovery, process simulations of carbon hollow fiber membranes and SAPO-34 membranes were conducted at a 10,000 m^3/h VAM with a feed methane concentration of 1.5 vol.% at a feed pressure of 15 bar. The separation target was set at a methane purity of 96 vol.% for vehicle fuels. The results are shown in Table 5. It can be found the specific cost of the carbon membrane system has no significant difference compared with the SAPO-34 membranes for the purification of methane from 1.5 to 15 vol.% even though the latter has a N_2 permeance of 130 times higher than the former, which aligns with the statistical analysis results that N_2 permeance has no significant influence on the specific cost. It is worth noting that further purification of methane from 15 to 96 vol.% dramatically increases the specific cost of membrane system, which is 10 times higher compared to the cost for the enrichment from 1.5 to 15 vol.%. Thus, a hybrid system of using membranes for the crude enrichment together with cryogenic distillation for the ultimate purification may bring down the overall cost compared to a stand-alone membrane system. It should be noted that the specific cost of different membrane systems is very much dependent on the membrane material cost. Thus, the sensitivity analysis of membrane cost was further conducted to document the potential of carbon membranes compared to inorganic zeolite membranes, and the results are shown in Fig. 8. It can be found that carbon membrane cost has a significant influence on the specific methane enrichment cost. However, for the highly permeable SAPO-34 membranes, the membrane material cost has a minor influence on the overall cost due to the required much smaller membrane area. Therefore, future research on bringing down the carbon membrane production cost will be more significant to enhance the competitiveness of membrane technology for methane recovery. For zeolite membranes, the improvement of membrane performance (especially N_2/CH_4 selectivity) is more crucial to reduce the operating cost related to the requirement of high pressure-ratio to complete a specific separation task. Moreover, compared with the literature reported zeolite membranes and cryogenic distillation for the N_2 removal from natural gas, the specific cost obtained in this work is much higher which is caused by: 1) a lower feed flow rate of 31 m^3/h (15 vol.% methane) compared with 1177 m^3/h reported by Li et al. [27], 2) the higher membrane module cost, and, 3) probably different cost models applied.

Table 5 Comparison of different technologies for the enrichment of VAM

Technology	Membrane performance	C^S (\$/m^3 enriched methane)		Reference
		Membrane enrichment from 1.5 to 15 vol.%	Methane purification from 15 to 96 vol.%	
SAPO-34 membranes	P_{N2}=1300 GPU $S_{N2/CH4}$=10	0.154	1.94	This work
Carbon hollow fiber membranes*	P_{N2}=10 GPU $S_{N2/CH4}$=10	0.231	3.03	This work

SAPO-34 membranes#	P_{N2}=500 GPU $S_{N2/CH4}$=8	-	0.04	[27]
Cryogenic distillation		-	0.085	[27]

*: membrane performance based on [21] and membrane cost $100/m^2, #: membrane cost $ 400/m^2

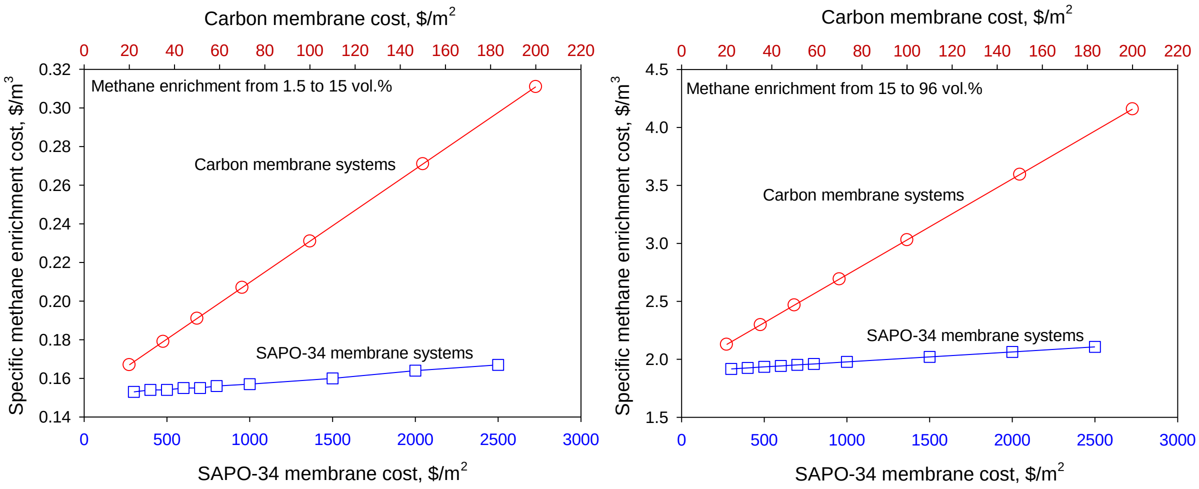

Fig. 8 The dependence of the specific methane enrichment cost on the membrane cost.

4. Conclusion

The N_2-selective inorganic membranes were investigated for the methane enrichment from coal-mining ventilation air. The techno-economic feasibility analysis indicates that the feed methane concentration in VAM and gas permeance have great effects on the specific methane enrichment cost and the specific power demand, while feed pressure in the range of 5–15 bar has a minor influence on the overall specific cost as the reduced membrane cost can largely offset the increased OPEX. It was also found that higher gas permeances may result in higher OPEX if the membranes have an N_2/CH_4 selectivity of > 6. The specific cost increases with the increase of methane purity at a given recovery, and the optimal methane recovery of ca. 70 % is identified to achieve a higher methane purity at the same cost. Therefore, for a stand-alone membrane system, pursuing a very high methane purity increases the cost dramatically, and vacuum operation in the permeate is not preferred at a constant pressure ratio. Moreover, the specific methane enrichment cost decreases with increasing plant capacity, and membrane systems can be readily scaled up and down to accommodate the variety of the ventilation air capacity in coal mining. Even though the literature reported SAPO-34 membranes is technologically feasible for the enrichment of VAM, the development of highly N_2-selective membranes is still needed to reduce the required membrane stages and the operation complexity. Seeking alternative carbon hollow fiber membranes with high packing density and easier module-making may address the high production cost and upscaling challenges that hinder the application of the flat-sheet or tubular zeolite membranes for N_2/CH_4 separation at a large-scale. Moreover, bringing down the carbon membrane production cost may significantly contribute to reduce the specific cost and enhance the competitiveness of membrane technology for the enrichment of VAM. Finally, process design with membrane-cryogenics hybrid systems may provide a more cost-effective solution for this application.

Credit authorship contribution statement

Xuezhong He: Methodology, Investigation, Manuscript writing, review and editing, Project administration. Linfeng Lei: Investigation, Manuscript review and editing.

Conflict of interest

The authors declare that there is no conflict of interest in this work.

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References

[1] O. Boucher, G.A. Folberth, New Directions: Atmospheric methane removal as a way to mitigate climate change?, Atmos Environ, 44 (2010) 3343-3345.

[2] E. Dlugokencky, Trends in Atmospheric Methane, https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4/, in: NOAA/GML (Ed.), 2020.
[3] L. Höglund-Isaksson, A. Gómez-Sanabria, Z. Klimont, P. Rafaj, W. Schöpp, Technical potentials and costs for reducing global anthropogenic methane emissions in the 2050 timeframe –results from the GAINS model, Environ. Res. Commun., 2 (2020) 025004.
[4] W. Wang, J. Ren, X. Li, H. Li, D. Li, H. Li, Y. Song, Enrichment experiment of ventilation air methane (0.5%) by the mechanical tower, Scientific Reports, 10 (2020) 7276.
[5] W. Wang, H. Wang, H. Li, D. Li, H. Li, Z. Li, Experimental Enrichment of Low-Concentration Ventilation Air Methane in Free Diffusion Conditions, Energies, 11 (2018).
[6] E. Díaz, J. Fernández, S. Ordóñez, N. Canto, A. González, Carbon and ecological footprints as tools for evaluating the environmental impact of coal mine ventilation air, Ecological Indicators, 18 (2012) 126-130.
[7] H. Limbri, C. Gunawan, T. Thomas, A. Smith, J. Scott, B. Rosche, Coal-Packed Methane Biofilter for Mitigation of Green House Gas Emissions from Coal Mine Ventilation Air, PLOS ONE, 9 (2014) e94641.
[8] Q. Li, B. Lin, D. Yuan, G. Chen, Demonstration and its validation for ventilation air methane (VAM) thermal oxidation and energy recovery project, Appl Therm Eng, 90 (2015) 75-85.
[9] Y. Zhang, E. Doroodchi, B. Moghtaderi, Utilization of ventilation air methane as an oxidizing agent in chemical looping combustion, Energy Conversion and Management, 85 (2014) 839-847.
[10] B. Lan, Y.-R. Li, X.-S. Zhao, J.-D. Kang, Industrial-Scale Experimental Study on the Thermal Oxidation of Ventilation Air Methane and the Heat Recovery in a Multibed Thermal Flow-Reversal Reactor, Energies, 11 (2018) 1578.
[11] K. Baris, Assessing ventilation air methane (VAM) mitigation and utilization opportunities: A case study at Kozlu Mine, Turkey, Energy for Sustainable Development, 17 (2013) 13-23.
[12] H.R. Sant Anna, A.G. Barreto, F.W. Tavares, J.F. do Nascimento, Methane/nitrogen separation through pressure swing adsorption process from nitrogen-rich streams, Chemical Engineering and Processing: Process Intensification, 103 (2016) 70-79.
[13] Z.-Y. Han, R. Xing, D.-H. Zhang, Y.-H. Shen, Q. Fu, Z.-Y. Ding, C.-X. Tian, Vacuum pressure swing adsorption system for N_2/CH_4 separation under uncertainty, Chemical Engineering Research and Design, 142 (2019) 245-256.
[14] J. Yang, H. Bai, H. Shang, J. Wang, J. Li, S. Deng, Experimental and simulation study on efficient CH_4/N_2 separation by pressure swing adsorption on silicalite-1 pellets, Chem Eng J, 388 (2020) 124222.
[15] Y. Chen, H. Wu, Y. Yuan, D. Lv, Z. Qiao, D. An, X. Wu, H. Liang, Z. Li, Q. Xia, Highly rapid mechanochemical synthesis of a pillar-layer metal-organic framework for efficient CH_4/N_2 separation, Chem Eng J, 385 (2020) 123836.
[16] D.-l. Zhong, Y. Ye, C. Yang, Y. Bian, K. Ding, Experimental Investigation of Methane Separation from Low-Concentration Coal Mine Gas ($CH_4/N_2/O_2$) by Tetra-n-butyl Ammonium Bromide Semiclathrate Hydrate Crystallization, Ind Eng Chem Res, 51 (2012) 14806-14813.
[17] D.-L. Zhong, N. Daraboina, P. Englezos, Recovery of CH_4 from coal mine model gas mixture (CH_4/N_2) by hydrate crystallization in the presence of cyclopentane, Fuel, 106 (2013) 425-430.
[18] S. Su, A. Beath, H. Guo, C. Mallett, An assessment of mine methane mitigation and utilisation technologies, Prog Energ Combust, 31 (2005) 123-170.

[19] W. Wang, H. Wang, H. Li, D. Li, H. Li, Z. Li, Experimental Enrichment of Low-Concentration Ventilation Air Methane in Free Diffusion Conditions, Energies, 11 (2018) 428.
[20] X. Ning, W.J. Koros, Carbon molecular sieve membranes derived from Matrimid® polyimide for nitrogen/methane separation, Carbon, 66 (2014) 511-522.
[21] L. Lei, A. Lindbråthen, X. Zhang, E.P. Favvas, M. Sandru, M. Hillestad, X. He, Preparation of carbon molecular sieve membranes with remarkable CO_2/CH_4 selectivity for high-pressure natural gas sweetening, J Membr Sci, 614 (2020) DOI:0.1016/j.memsci.2020.118529.
[22] Z. Zong, X. Feng, Y. Huang, Z. Song, R. Zhou, S.J. Zhou, M.A. Carreon, M. Yu, S. Li, Highly permeable N_2/CH_4 separation SAPO-34 membranes synthesized by diluted gels and increased crystallization temperature, Micropor Mesopor Mat, 224 (2016) 36-42.
[23] G. Sodeifian, M. Raji, M. Asghari, M. Rezakazemi, A. Dashti, Polyurethane-SAPO-34 mixed matrix membrane for CO_2/CH_4 and CO_2/N_2 separation, Chinese J Chem Eng, 27 (2019) 322-334.
[24] D.F. Sanders, Z.P. Smith, C.P. Ribeiro, R. Guo, J.E. McGrath, D.R. Paul, B.D. Freeman, Gas permeability, diffusivity, and free volume of thermally rearranged polymers based on 3,3′-dihydroxy-4,4′-diamino-biphenyl (HAB) and 2,2′-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), J Membr Sci, 409-410 (2012) 232-241.
[25] D.F. Sanders, Z.P. Smith, R. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B.D. Freeman, Energy-efficient polymeric gas separation membranes for a sustainable future: A review, Polymer, 54 (2013) 4729-4761.
[26] H.B. Park, S.H. Han, C.H. Jung, Y.M. Lee, A.J. Hill, Thermally rearranged (TR) polymer membranes for CO_2 separation, J Membr Sci, 359 (2010) 11-24.
[27] S. Li, Z. Zong, S.J. Zhou, Y. Huang, Z. Song, X. Feng, R. Zhou, H.S. Meyer, M. Yu, M.A. Carreon, SAPO-34 Membranes for N_2/CH_4 separation: Preparation, characterization, separation performance and economic evaluation, J Membr Sci, 487 (2015) 141-151.
[28] Z. Zong, M.A. Carreon, Thin SAPO-34 membranes synthesized in stainless steel autoclaves for N_2/CH_4 separation, J Membr Sci, 524 (2017) 117-123.
[29] Z. Zong, S.K. Elsaidi, P.K. Thallapally, M.A. Carreon, Highly Permeable AlPO-18 Membranes for N_2/CH_4 Separation, Ind Eng Chem Res, 56 (2017) 4113-4118.
[30] P. Marín, Z. Yang, Y. Xia, S. Ordóñez, Concentration of unconventional methane resources using microporous membranes: Process assessment and scale-up, Journal of Natural Gas Science and Engineering, 81 (2020) 103420.
[31] D. Grainger, M.-B. Hägg, The recovery by carbon molecular sieve membranes of hydrogen transmitted in natural gas networks, Int J Hydrogen Energ, 33 (2008) 2379-2388.
[32] X. He, M.-B. Hägg, Hollow fiber carbon membranes: From material to application, Chem Eng J, 215–216 (2013) 440-448.
[33] X. He, Techno-economic feasibility analysis on carbon membranes for hydrogen purification, Sep Purif Technol, 186 (2017) 117-124.
[34] R. Turton, R.C. Bailie, W.B. Whiting, J.A. Shaeiwitz, D. Bhattacharyya, Analysis, synthesis, and design of chemical processes, Fourth Edition, Pearson Education, Upper Saddle River, NJ, 2013.
[35] Y. Chu, X. He, Process Simulation and Cost Evaluation of Carbon Membranes for CO_2 Removal from High-Pressure Natural Gas, Membranes, 8 (2018) 118.
[36] X. He, Y. Chu, A. Lindbråthen, M. Hillestad, M.-B. Hägg, Carbon molecular sieve membranes for biogas upgrading: Techno-economic feasibility analysis, Journal of Cleaner Production, 194 (2018) 584-593.

[37] X. He, I. Kumakiri, M. Hillestad, Conceptual process design and simulation of membrane systems for integrated natural gas dehydration and sweetening, Sep Purif Technol, 247 (2020) 116993.
[38] L. Lei, A. Lindbråthen, M. Hillestad, M. Sandru, E.P. Favvas, X. He, Screening Cellulose Spinning Parameters for Fabrication of Novel Carbon Hollow Fiber Membranes for Gas Separation, Ind Eng Chem Res, 58 (2019) 13330-13339.
[39] D. Zhao, J. Ren, H. Li, K. Hua, M. Deng, Poly(amide-6-b-ethylene oxide)/SAPO-34 mixed matrix membrane for CO_2 separation, Journal of Energy Chemistry, 23 (2014) 227-234.
[40] X. He, M.-B. Hägg, T.-J. Kim, Hybrid FSC membrane for CO_2 removal from natural gas: Experimental, process simulation, and economic feasibility analysis, AIChE Journal, 60 (2014) 4174-4184.