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An Energy-Saving Membrane Process for Carbon Dioxide Purification

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Carbon dioxide capture and utilisation (CCUS) has been gaining attraction for suppressing global warming. This is because CO_2 emissions from human activities have affected environments. For this reason, conventional CO_2 sources such as conventional steelworks are expected to be decreased in the near future. On the other hand, CO_2 is also useful for human lives such as its use as a refrigerant or for medical use. It is indispensable to capture CO_2 from limited sources and supply CO_2 to the demands. Since the characteristics of required CO_2 depend on the use, it is necessary to control the exhausted CO_2 concentration up to the required concentration. An amine absorption method often applied to industrial CO_2 capture consumes a large amount of energy. To overcome this energy issue, some other alternative processes such as physical adsorption and cryogenic have been proposed. Among these processes, membrane separation technology is regarded as an energy-saving process. Although some researchers have estimated membrane process energy performance, complex multi-stage processes were discussed without considering the performance of a simple process. In this study, to obtain high purity CO_2 with less energy consumption by a single-stage membrane process, the membrane separation characteristics were experimentally investigated under several pressure conditions by a single-stage process and simulations using a process simulator. From these investigations, it produces up to 45-70 mol% CO_2 with less energy consumption by the pressure changes.

1. Introduction

Carbon Capture and Storage (CCS) and Carbon Capture and Utilisation (CCU) to suppress global warming have been attracting attention because carbon dioxide (CO_2) causes global warming as a greenhouse gas. On the contrary, CO_2 is an indispensable material for refrigerant, medical use (Ilkben et al, 2021), and welding (Math et al., 2021). Recently, large and high concentration CO_2 sources such as steel-works have been shutting down gradually due to world economics and environmental protections (NIKKEI, 2021). It is required that CO_2 from low concentration CO_2 sources such as thermal power generation plants or garbage incineration plants must be separated to satisfy a variety of CO_2 usage.

There have been some methods such as chemical absorption, physical adsorption, membrane, and cryogenic separation to obtain CO_2 from a gaseous stream. The most commonly used method for CO_2 capture in industries among the above-mentioned methods is a chemical absorption method with amine solutions (Teranishi et al., 2016). In this process, CO_2 in flue gas chemically combines with an amine molecular (R-NH_2) by chemical bonding in an amine absorber and CO_2 is released in the amine regenerator with heat. Although this process produces pure CO_2 and achieves a high CO_2 recovery ratio, it is well-known that the process consumes larger energy to recover CO_2, 4.1 MJ/kg-CO_2 (Kishimoto et al., 2011). It is necessary to develop an alternative technology with low energy consumption (Goto et al., 2015). Membrane separation required less energy compared with other methods such as absorption, physical adsorption, and cryogenic separation (Wang et al., 2016). There are some studies discussing energy consumption of a membrane process to separate CO_2/N_2 for post-combustion. It is reported that the energy consumption was 1.05 MJ/kg-CO_2 for post-combustion CO_2 capture (Alshad et. al., 2015). In addition, there are several reports related to multi-stage membrane sepeartions; e.g. that the energy consumption was 373.6 kWh/t-CO_2 (=1.34 MJ/kg-CO_2) under the multi-stage membrane process (Arias et al., 2016) and that separation performances were compared under several

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operating conditions in the two-stage membrane process (Zhao et al., 2010). To combine membrane separation processes with vacuum pumps, these process only requires 0.4-1 MJ/kg-CO_2. However, they discussed the comparison of the energy required for the integrating processes with multi-stage membrane processes. Therefore, it is difficult to indentify the effect of installation of a simgle-stage membrane process and its elemental avilities such as gas permeances. In the current work, to purify CO_2 from a gas stream containing CO_2 with less energy consumption with single-stage membrane process, the performances such as energy requirement, purity and recovery ratio were examined by varying feed flow rate, permeate area and pressure under high pressure or vacuum conditions. And from the results, it was confirmed that how high the purity could be with the single-stage membrane and compared with other separation methods.

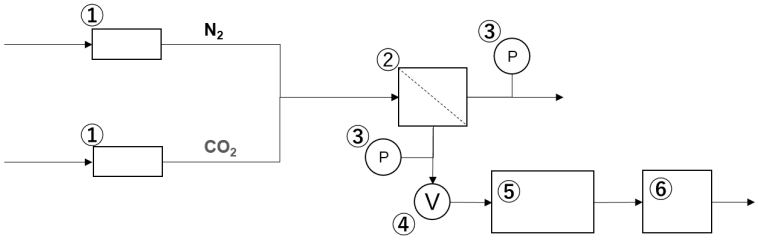
2. Membrane separation performance evaluation

A zeolite membrane separation was selected as an instance of membrane material. The membrane separation performance was experimentally examined, and energy performance was evaluated quantitatively by a commercial process simulator with the experimental results.

2.1 Separation performance of the zeolite membrane

The schematic image of the experimental setup is shown in Figure 3. Two mass flow controllers (Fujikin Inc. FCS-PM1000A-SP) were set to the system to control the flow rate of each gas, CO_2/N_2. Unit number 2 in Figure 1 is a separation unit. A tubular-type membrane (Hitachi Zosen Corporation, inner dia. 12 mm, outer dia. 16 mm, length 30mm) is made of zeolite in this unit. High purity N_2/CO_2 (Suzuki Shokan Co., Ltd., Purity 99.99 %) gases were used.

A needle valve was used to adjust feed pressure. In the steady-state of the gas flow, CO_2 concentration in permeated gas was measured by FI-IR (Thermo Fisher Scientific K.K., Nicolet iS5 iD1 transmission). Flow-meter (Ellutia 7000 series) to check the gas flow rate was set. The membrane performance (permeance, k_m) was calculated from these measured values (flow rate, CO_2 concentration in the non-permeated side, and each pressure gauge). Permeated gas concentration and flow rate were calculated from the material balance of each gas. The calculation equation is shown in Eq(1). Experimental conditions are summarised in Table 1.



① Mass flow controller
② Zeolite membrane in the separation unit
③ Pressure gage
④ Needle valve
⑤ FT-IR
⑥ Flow-meter

Figure 1: Experimental setup

Table 1: Experimental condition for the membrane performance estimation

CO_2 concentration in feed gas	Separation temperature	Differential pressure
10 mol% 30 mol% 50 mol%	30 °C	0.10 MPa

$$N_m = \frac{F_{perm.,m} \cdot x_{perm.,m}}{A} = k_m\left(p_{feed,m} - p_{perm.,m}\right) \quad (1)$$

where, N_m is molar flux of m (m=CO_2 or N_2) [mol s^{-1} m^{-2}], $F_{perm.,m}$ is the flow rate of m in permeate side [mol/s], $x_{perm.,m}$ is the molar fraction of m in the permeate side [-], A is permeate area [m^2], k_m is permeance of m [mol s^{-1} m^{-2} kPa^{-1}], $p_{feed,m}$ is the partial pressure of m in the feed side [kPa], $p_{perm.,m}$ is the partial pressure of m [kPa]. The experimental result of CO_2 and N_2 permeance under 10 mol% CO_2 feeding was 7.9×10^{-5} s^{-1} m^{-2} kPa^{-}

^{1} and 2.0×10^{-6} s^{-1} m^{-2} kPa^{-1}. Other results of 30 mol% and 50 mol% CO_2 feeding were summarised in the previous paper by the authors (Sato et al, 2021).

2.2 Process performances evaluation by simulation

From the experimental results of the permeance of each gas, membrane separation performances such as product CO_2 purity, energy consumption, and recovery ratio was simulated with the commercial process simulator (PRO/II ver.2020, AVEVA). Energy consumption (EC) and Recovery ratio (RR) were calculated by Eq(2) and Eq (3);

$$EC = \frac{E_{compressor}}{F_{perm.,CO_2} \cdot x_{perm.,CO_2} \cdot MW} \tag{2}$$

$$RR = \frac{F_{perm.,CO_2} \cdot x_{perm.,CO_2}}{F_{feed,CO_2} \cdot x_{feed,CO_2}} \times 100 \tag{3}$$

where, $E_{compressor}$ is shaft power of the compressor [kW], $F_{perm.,CO_2}$ is the flow rate of CO_2 in permeate side gas [kmol/s], $x_{perm.,CO_2}$ is molar fraction of CO_2 in permeate side gas [-], MW is molar weight of CO_2 (44.01) [kg/kmol], F_{feed,CO_2} is feed flow rate of CO_2 [kmol/s], x_{feed,CO_2} is the molar fraction of CO_2 in the feed side [-]. Although permeances of gases through the membrane depend on the partial pressure of each gas from a realistic point of view (Kamio et al.,2017), the values of permeance were assumed to be a constant in the simulation due to the small changes. The simulation condition is shown in Table 2. The performances were examined when the initial CO_2 concentration was 10 mol%. The simulated process is shown in Figure 2. The compressor was installed before the membrane unit. Each performance is plotted as a function of the outlet pressure of the compressor (COP) under each average molecular flux (AMF) value in Figure 3. The AFM is defined by the following equations;

$$AMF = \frac{F_{feed}}{A} \tag{4}$$

where F_{feed} is a total feed flow rate and A is a permeate area.

These performances depend on the AMF. In other words, if the value becomes larger, the feed flow rate becomes higher for the permeation area. Although RR was improved by increasing COP from Figure 3(a), it decreased in the case of a larger AMF value. The purity was improved up to a certain degree and decreased conversely with COP rising from Figure 3(b). EC decreased with increasing of COP and increased gradually at a certain COP from Figure 3(c). If the treated amount increases, due to EC increase, it is necessary to expand the permeation area (plant scale) for energy-saving operation.

Table 2: Simulation conditions under compressing process

Initial flow gas condition		30 °C, 101.3 kPa
CO_2 Conc. in feeding flow		10 mol%
Feed flow rate		500 1,000 mol s^{-1}
Compressor outlet pressure		101.3-1,091.3 kPa
Permeate area, A		1,000 5,000 10,000 m^2
Compressor adiabatic efficiency		80 %
After cooler of compressor		ON (set to 30 °C)
Separation temp.		30 °C
Permeance	CO_2	7.9×10^{-5} mol s^{-1} m^{-2} kPa^{-1}
	N_2	2.0×10^{-6} mol s^{-1} m^{-2} kPa^{-1}

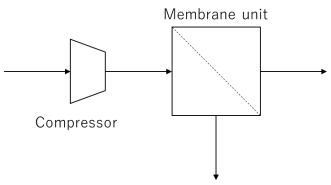


Figure 2: Process of compressing single stage system

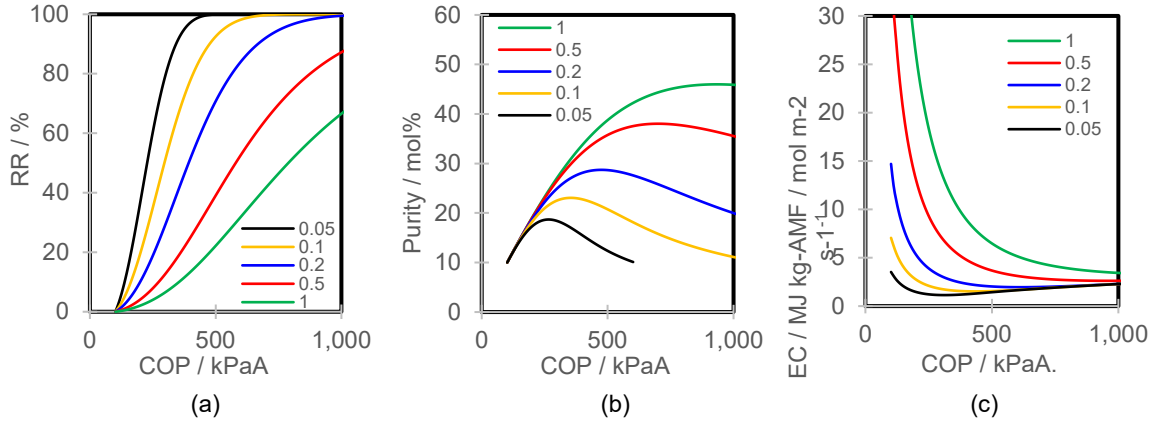


Figure 3: Membrane process performances (a)RR (b)purity (c)EC as a function of compressed pressure under each value of AMF

On the other hand, the performance under vacuum conditions with a single-stage was examined. Permeate side pressure of membrane is set to 5 kPa. The vacuum process is shown in Figure 4. The simulation condition is shown in Table 3. The vacuum pump is connected to permeate side of the membrane unit. The simulation results are shown in Figure 5 as a function of the AMF value.
As the simulation results, the purity was over 70 mol% and saturated around the concentration. Though CO_2 RR decreased, EC was below 0.5 MJ/kg-CO_2. The energy required is quite low as compared with other separation processes. Although purity was improved by increasing vacuum degree, EC increased.

Table 3: Simulation conditions under the vacuuming process

Initial flow gas condition	30 °C, 101.3 kPa	Compressor adiabatic efficiency	80 %	
CO_2 Conc. in feeding flow	10 mol%	After cooler	ON (set to 30 °C)	
Feed rate	0.1~10 kmol/s	Separation temp.	30 °C	
Membrane outlet pressure	5 kPa	Permeance	N_2	2.0×10^{-6}
Permeate area	1,000 5,000 10,000 m^2	[s^{-1} m^{-2} kPa^{-1}]	CO_2	7.9×10^{-5}

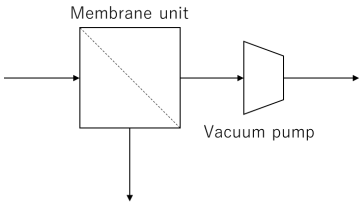


Figure 4: Process of vacuuming single stage system

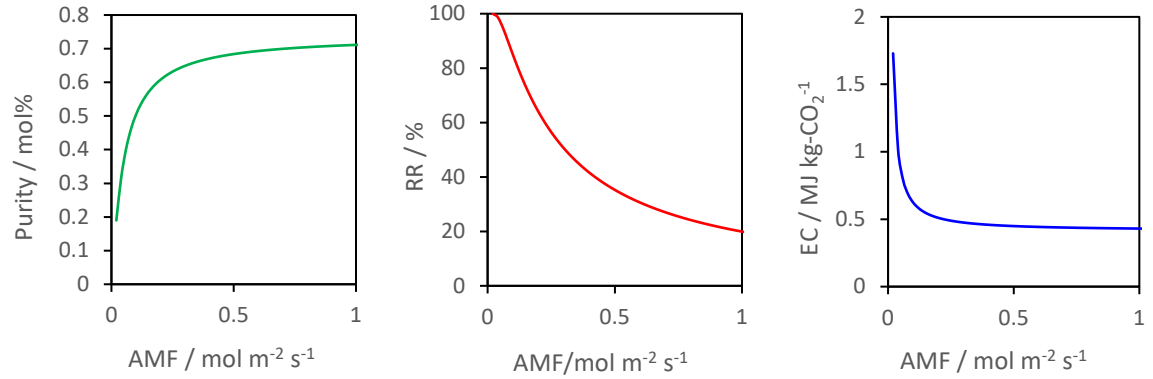


Figure 5: Membrane process performances (a) Purity (b) RR (c)EC under vacuuming single-stage process

3. Result and discussion

From the results of the compressing process, the purity became high with the increase of the outlet pressure of the compressor. Concretely, it was possible to condense up to 45 mol% under 960 kPa of COP in the case of AMF=1 from Figure 3 (b). The energy consumption was 3.5 MJ/kg-CO_2 at the condition. Maximum purity and minimum energy consumption points were shown in Figure 6 (a) and (c). These values were plotted as a function of AMF in Figure 6. The relationship between each performance and AMF is useful for building and operating. Permeate area and approximate operation condition (compressing pressure) were determined from the relationship between performance and AMF, amount of gas to be treated and required CO_2 concentration. The value of minimum EC can be obtained at the same time. For concrete instance, in the case of 1,000 mol/s feeding and 40 mol% CO_2 is required, AMF value was obtained as 0.611 from relation equation (RE) 1 in Figure 6 (a). Secondly, permeate area could be obtained as 1,637 (=1,000/0.611) m^2. Simultaneously EC of 2.78 MJ/kg-CO_2 was obtained from the AMF value and RE 3 in Figure 6 (c). In addition, the approximate proper operation pressure of the compressor in terms of energy consumption was 1,078 MPa from the AMF value and RE 2 in Figure 6 (b).

The purity and the energy consumption have a trade-off relationship, it is necessary to pay attention to the point of the purification. However, it is a promising method for designing a consistent process where high purity (over 90 mol%) is unnecessary such as algae cultivation (Sato et. al., 2021).

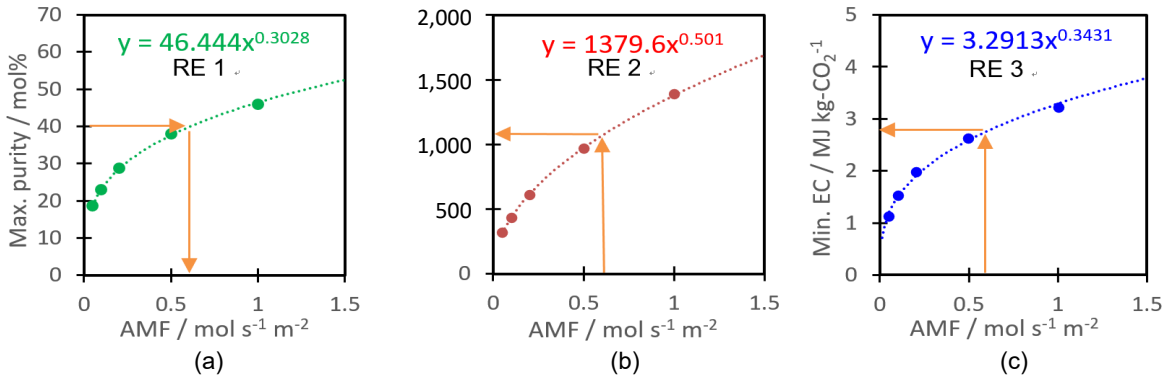


Figure 6: Membrane process performances (a)Max purity (b)COP (c)Min. EC under vacuuming process

If high pressure emitted gas stream from a source such as IGCC (Integrated Gasification Combined Cycle) can be applied to the membrane unit, it is possible to separate without any additional energy to compress the gaseous stream. The integrated process from emissions to separation is promising in terms of energy saving. Some researchers reported that a membrane separation method is an alternative solution for separating CO_2 from the off-gas of an IGCC (Basile et al.2010).

Under vacuum process, CO_2 purity became high with decreasing of energy consumption different from compressing process. Though the recovery ratio is low, the CO_2 concentration achieved over 70 mol% with energy consumption of 0.4-0.5 MJ/kg-CO_2 without recovering energy. Vacuum membrane system will be more energy-saving with recovering energy. These values are quite low compared to other separation methods such as chemical absorption (4.1 MJ/kg-CO_2 (Kishimoto et al., 2011)), temperature swing adsorption (3.22 MJ/kg-CO_2 (Jiang et al., 2020)), and cryogenic method (5.8 MJ/kg-CO_2, by our simulations with PRO/II). In the case of applying the membrane system to low pressure emitted gas stream, the vacuum process is promising in terms of energy saving.

In any case, it was difficult to purify up to over 90 mol% with a single-stage membrane process under current selectivity.

4. Conclusions

In this study, performances such as energy consumption, purity, and recovery ratio were estimated experimentally and simulated by a process simulator for the purification from 10 mol% CO_2 included gas stream with single-stage membrane separation.

In the compressed gas feeding cases, the maximum product CO_2 purity was 45 mol% and the energy consumption was 3.5 MJ/kg-CO_2. Although the product purity could be improved with a higher compression ratio for feeding, the energy consumption becomes too large. So, it was not realistic for industrial use. In vacuum conditions, it is difficult to increase the recovery ratio. However, the purity of the product CO_2 reaches over 70 mol% with 0.4-0.5 MJ/kg-CO_2 of energy consumption.

In any case, it was impossible to purify up to 90 mol% under a single-stage membrane process, which often requires CO_2 purification depending on some applications in terms of energy saving. For example, in the case of applying high-pressure CO_2 included gas stream for algae cultivation, compressing single-stage membrane process is recommended in the future.

Nomenclature

AMF – average molecular flux on membrane, mol s^{-1} m^{-2}
COP – compressor outlet pressure, kPaA.
EC – energy consumption, MJ kg-CO_2^{-1}
MW – molar weight, g mol^{-1}
RE – relation equation, -
RR – recovery ratio, %
N_m – molar flux of m (m = CO_2 or N_2), mol s^{-1}
$F_{perm.,m}$ – flow rate of m in permeate side, mol s^{-1}
$x_{perm.,m}$ – molar fraction of m in permeate side, -
A – permeate area, m^2
k_m – permeance of m, mol s^{-1} m^{-2} kPa^{-1}
F_{feed} – total feeding flow rate
$p_{feed,m}$ – partial pressure of m in feed side, Pa
$p_{perm,m}$ – partial pressure of m in permeate side, Pa
$E_{compressor}$ – actual work of compressor, MJ
$x_{perm.,m}$ – molar fraction of m in feed side, -

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