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Comparative Study of Carbon Dioxide Purification Methods

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Considering the several usages of CO_2, it is necessary to find a suitable CO_2 purification method to satisfy each demand with low energy consumption. There are major four methods to separate CO_2 from mixed gas, absorption, adsorption, membrane, and cryogenic separation. These four processes have different characteristics due to their basic separation properties. In this study, the characteristics of those processes were compared based on three performance indexes: CO_2 product purity, recovery ratio, and energy consumption to find a suitable separation process for satisfying various CO_2 demands. As a result, to obtain pure CO_2 with a high recovery ratio and low energy consumption, it was found that vacuum pressure swing adsorption (VPSA) was the most promising among these processes and membrane separation, especially the vacuuming process was a potential candidate for getting low purity of CO_2.

1. Introduction

Japan has set the 2030 greenhouse gas (GHG) emission reduction target at 46 % from that of 2013 levels to net zero by 2050 (JAPAN GOV., 2021). To achieve this ambitious target, the word, “carbon neutrality” has been paid more attention than before. In particular, the enhancement of further energy saving, installation of renewable energy, creation of a recycling system of materials and energies, and prevention of GHG emissions are required. At the same time, the installation of carbon capture and utilization (CCU) into society is necessary due to CO_2 emissions by human activities so far. CO_2 has been inherently helpful for human lives such as a refrigerant (dry ice), a fire extinguisher, and for carbonate drinks and CO_2 arc welding (Kan et al., 2020). However, excess CO_2 emission, in particular from fossil fuel combustion in our history, has contributed to global warming and climate change. To realize carbon neutrality, currently emitting CO_2 must be captured and converted to useful things for human activities as CCU associating with the reduction of CO_2 emission. From this concept, new CO_2 demands such as CO_2-rich agriculture (Saga City, 2020), converting to chemical materials, or fuel (ANRE, 2021) have been proposed.
The required CO_2 properties for each CO_2 utilization ways are not identical, e.g., high concentration CO_2 is suitable for conversion to chemical materials due to chemical reaction kinetics and relatively low concentration CO_2 (<10 %) is suitable for agricultural use. In particular, CO_2 concentration is the most important property, it is necessary to adjust CO_2 concentration from CO_2 source gases to the demand for utilization. Therefore, separation technology is indispensable for the purification of CO_2 to design the CCU process. In fact, there are several CO_2 sources such as exhaust gases from thermal power plants, steel-making plants, and incinerators, and air. There are mainly four methods to separate CO_2 from mixed gas such as chemical/physical absorption and adsorption, and membrane or cryogenic separations. The absorption method using an amine-based solution is the most commonly applied method in industry to condense CO_2 to high concentrations. By the method, quite high purity CO_2 with a high recovery ratio can be obtained. In physical adsorption, CO_2 is adsorbed physically by solid materials such as zeolite. Membrane separation is a method to separate by applying differences in molecular size or diffusivity. The cryogenic method is a method utilizing the sublimation or liquefaction temperature difference of each gas. There are some review papers comparing the above methods. Although one of the studies shows comparing the detailed characteristics of each method (Maniarasu et al., 2021), they did not present concrete values of energy consumption. Therefore, it was impossible to compare in terms of energy performance. Other study shows the characteristics (advantages/disadvantages) of each

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method (Bermeo et al., 2022). Although values of energy consumption were written in the review, feeding CO_2 concentration greatly affected performances; energy consumption, recovery ratio, and CO_2 product purity were not described. Therefore, it was difficult to compare directly and to judge which method is superior.
In this study, those processes were compared in terms of the above three performances with literature reviews and simulations using a commercial process simulator to determine an appropriate method under the same condition (CO_2 concentration in exhausted (=feeding to separation process) stream:15 vol%) in an easy-to-understand way.

2. Result of investigation and simulation

Firstly, the performances such as CO_2 purity, CO_2 recovery ratio (RR), energy consumption (EC), and continuity of four CO_2 separation methods were investigated and summarized. And for the membrane and cryogenic separation, these performances were simulated by process simulator PRO/II (ver. 2020, AVEVA).

2.1 Chemical absorption

Chemical absorption is a separate way to absorb CO_2 by an absorbent such as amine-based solutions and metal oxides. In this investigation, monoethanolamine (MEA) was used as a representative amine. Since the amine reacts with CO_2 associated with exothermic heat, it is necessary to supply heat to dissociate CO_2 from carbamate ($R\text{-}NH\text{-}COO^-$) as endothermic heat. EC of the method using MEA solution is reported as approximately 3.8 MJ/kg-CO_2 (Leimbrink et al., 2017). This is because larger heat is required for water evaporation latent heat and endothermic heat for regeneration of the amine solution. Focusing on the point, by amine is supported by a small sensible heat solid absorbent, the proposal of decreasing EC to 1.5 MJ/kg-CO_2 was suggested (Goto et al., 2015). In addition, several absorbents instead of MEA are suggested (Yamada, 2019). The conventional chemical absorption process is shown in Figure 1. The General CO_2 RR of the method is almost 90 %, there is a study that reported that the RR achieved 99.8 % (MHI, 2021). In general, obtained CO_2 purity on the method is quite high, 99.9 % (Iijima et al., 2010), and almost pure CO_2 can be obtained. Exhausted CO_2 streams from several facilities can be treated continuously.

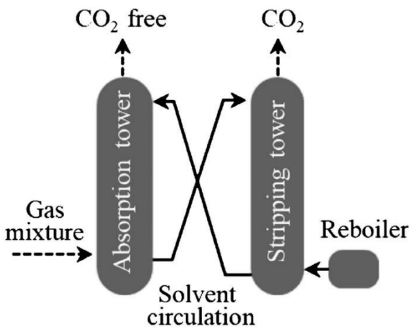

Figure 1: Conventional process of amine absorption (Yamada, 2019)

2.2 Physical adsorption

Physical adsorption is divided into two types; Temperature swing adsorption (TSA) and Pressure swing adsorption (PSA). In addition, PSA is further divided into 2-types; a method called vacuum pressure swing adsorption (VPSA), in which a vacuuming condition is made to remove CO_2 from an adsorbent, and a method in which CO_2 is adsorbed onto an adsorbent under compressed pressure and is desorbed under atmospheric pressure. As compared with vacuum or compress pressure swing adsorption, the required energy for VPSA is theoretically smaller than that for the latter one. However, the process size of the vacuum pressure swing adsorption is inherently larger. Furthermore, temperature and vacuum swing adsorption (TVSA) operating temperature and vacuuming have been studied (Jiang et al., 2020). An instance of the VPSA is shown in Figure 2. A mixed gas containing CO_2 is fed to the adsorption tower setting an adsorbent such as zeolite, the CO_2 molecular is adsorbed selectively. After that, the adsorbed CO_2 is dissociated from the adsorbent by changing a valve and vacuuming the CO_2. For this reason, it is possible to operate in a series of actions by establishing some towers, leading to pseudo-continuous actions.
The CO_2 purity of TSA is relatively high over 91 % (Ntiamoah et al., 2016). In addition, 97.27 % of purity by the TVSA integrated temperature and pressure swings was reported (Jiang et al., 2020). On the other hand, the purity of VPSA was reported as 94.8 % in the study (Krishnamurthy et al. 2014). For RR. of TSA and VPSA, it was relatively high in both cases, there is a study that reported that it was over 90 % (Nikolaidis et al., 2017).

The EC tends to be high in the case of TSA to be essential to add heat, it was reported as 3.22-6.76 MJ/kg-CO_2 (Jiang et. al., 2020). It was reported that the EC of VPSA was 0.79 MJ/kg-CO_2 (Jiang et al., 2020). Therefore, the process is expected to relatively lower energy consumption.
It seems that these values depend on CO_2 concentration in the feed gas, adsorbent type (Zeolite 13X, Activated Carbon (denoted as AC), etc.), and process structure (bed and stage number).

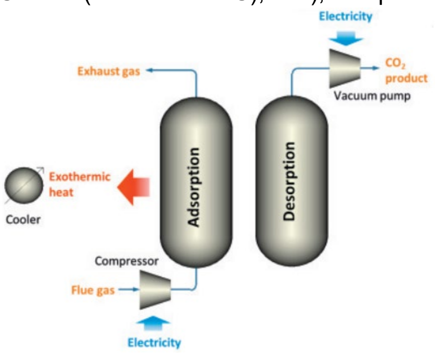

Figure 2: Physical adsorption (VPSA) process (Song et al., 2014)

2.3 Membrane separation

Membrane separation is a method to separate CO_2 with membrane material consisting of metal, polymer, ceramic, etc. Until now, authors have estimated membrane separation performances through experiments and simulations. (Sato et al., 2022). Zeolite was adapted as a membrane material, and the permeance of the membrane was experimentally acquired. The acquired permeance was applied to the simulation. Membrane performances such as purity, RR, and EC were obtained from the simulations under the condition that the initial concentration of CO_2 was 10 vol%, the feed flow rate was 100 mol/s, CO_2 selectivity comparing nitrogen gas of the membrane was 41, the separation temperature was 30 °C. More detailed conditions, experimental methods (Sato et al., 2021) and simulation process flow (Sato et al., 2022) were written in the previous studies.
Obtained performances in relation to compressing/vacuuming single-stage membrane process are shown in Figure 3 as a function of RR. The vacuuming process was more promising in terms of purification than the compressing process. However, the size of the vacuuming process becomes larger than that of the same as the compressed type of adsorption method. Therefore, the building cost is larger inevitably. The relation between EC and RR was a trade-off. And the relation between product CO_2 purity and RR was also a trade-off. These mean that it is impossible to manage two things at the same time. For continuity of the method, it is possible to treat continuously as well as chemical absorption.

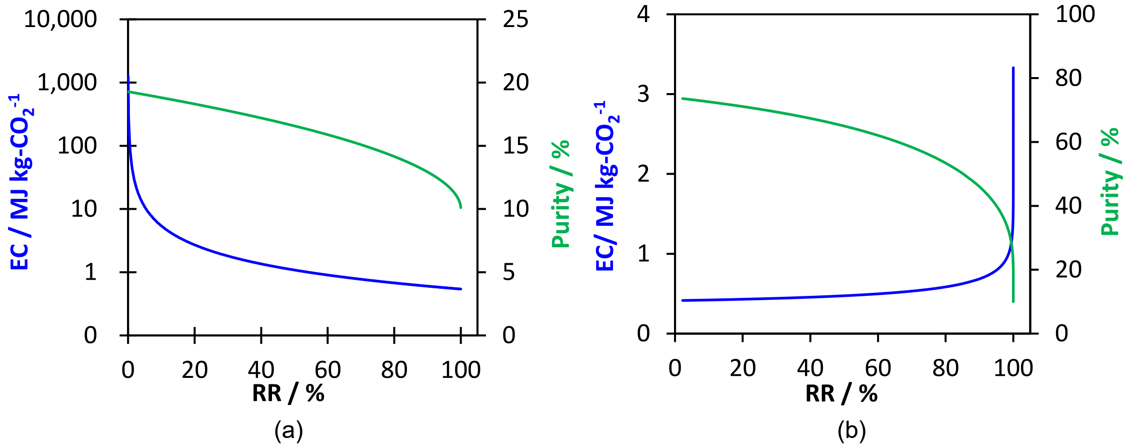

Figure 3: Membrane process performances (a) under compressing single-stage process (b) under vacuuming single-stage process

2.4 Cryogenic separation

The cryogenic method is a method to separate by utilizing the sublimation or liquefaction temperature difference of gases. The cryogenic process is shown in Figure 4. Mix gas (S1) is compressed by the compressor (C1) and

the high pressure is released at the release valve (RV1). At this moment, the mixed gas is cooled by adiabatic expansion cooling called the "Joule-Thomson effect". Almost only CO_2 sublimates to the solid phase and accumulates at the bottom of the tower (F1). On the other hand, lower billing temperature N_2 goes up to the top side of the tower with keeping the gas phase. The performances of the process were estimated by the simulator. The results are shown in Figure 5. From Figure 5(a), EC was decreasing rapidly and increasing gradually with increasing compressing pressure. In other words, each curve has a minimum point of EC. Then, the minimum point was plotted as a function of the initial CO_2 concentration in the feed gas (Figure 5(b)). From the result, the initial CO_2 concentration has a large effect on the EC to condense CO_2. In this process simulation, energy recovery was not conducted. Therefore, more energy saving will be promising in the future. The product CO_2 purity of this method was quite high, over 99.0 % under a wide range of compressing pressure.
And, because CO_2 sublimates to the solid phase at the tower, it is generally difficult to recover CO_2 continuously. Then, some researchers proposed a continuous recovery cryogenic process using some towers and coolers (Xu et al., 2014). Considering the pure CO_2 phase diagram, it may be possible to recover CO_2 continuously as a liquid by controlling pressure and cooling temperature. However, it will be difficult to make a pump enduring for extremely low temperatures in this case.

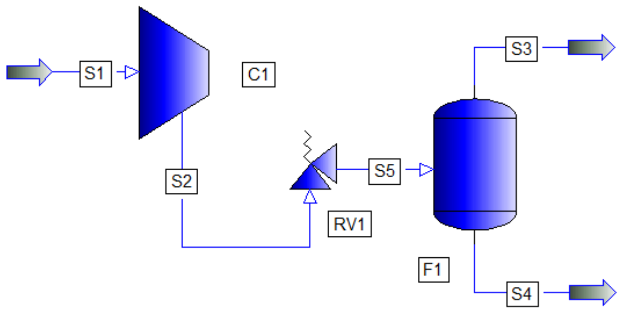

Figure 4: Cryogenic separation method by adiabatic expansion cooling

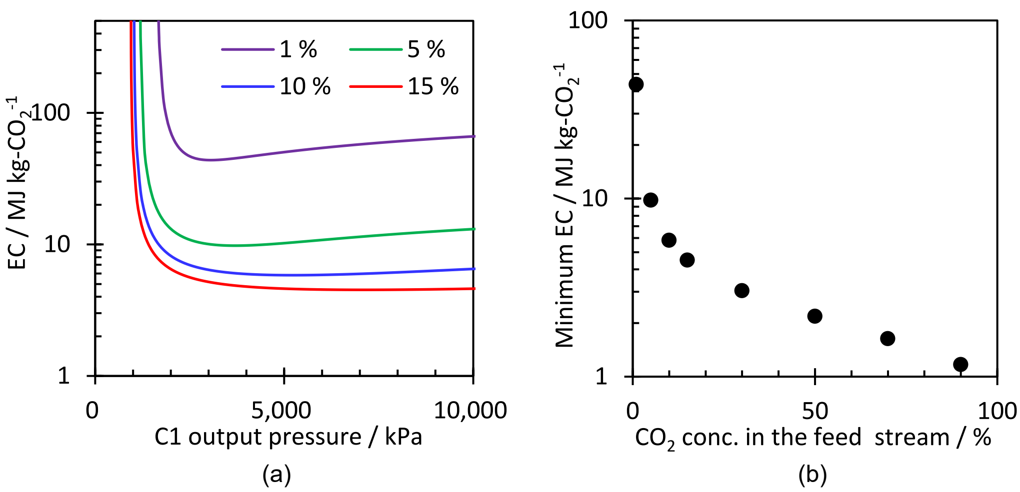

Figure 5: Energy consumption of the cryogenic method as a function of (a) compressing pressure under each initial concentration of CO_2 and (b) minimum EC as a function of CO_2 concentration in the feed stream

3. Discussion

As above mentioned, the characteristics of each separation method could be obtained by investigations and simulations. The performances of each method are summarized in Table 1. From the table, in the case of utilization such as chemical synthesis required high purity, chemical absorption or cryogenic were suitable as the CO_2 separation method in terms of purity. On the other hand, in a lower CO_2 required case such as algae cultivation, and CO_2-rich agriculture, the membrane method was suitable. In the chemical absorption and cryogenic method, EC was higher. On the other hand, in the physical adsorption and membrane method, EC was lower. In terms of continuity, it was possible to process by three methods except cryogenic. Therefore, these methods are appropriate for large amounts of CO_2 production. Considering the performances comprehensively, PVSA or membrane (vacuuming) was promising.

Table 1: The characteristics of each separation method

Method	Purity	RR	EC	Continuity
Chemical absorption	High	High	High	Possible
Physical adsorption(PVSA)	Mid.-High	Mid.-High	Low	Impossible
Physical adsorption(TSA)	Mid.-High	Mid.-High	Mid.-High	Possible
Membrane(compressing)	Low	Mid.	Mid.	Possible
Membrane(vacuuming)	Mid.	Mid.	Low	Possible
Cryogenic	High	High	High	Impossible

Furthermore, to clarify more which method can process pure CO_2 with high RR and low EC, the performances were compared quantitatively under the same condition (15 vol% CO_2). Figure 6 shows the results of EC and RR. They were plotted as a function of product CO_2 purity in the graph. From Figure 6(a), membrane separation and adsorption (especially VPSA) required less energy (under 1 MJ/kg-CO_2) as compared with other methods. From Figure 6(b), it seemed that it is possible to recover with high RR (over 90 %) in all methods depending on the required CO_2 concentration under the utilization. In addition, the product purities through absorption, adsorption, and cryogenic methods were relatively high (over 90 %). Therefore, these above methods are expected in some utilizations such as EOR (Enhanced Oil Recovery), CCS (Carbon dioxide Capture and Storage), chemical synthesis, etc. (Hashizaki, 2018). According to our investigation, it might be concluded that the most promising method was "VPSA" considering the three properties; purity, RR, and EC. In addition, "the vacuuming membrane process" was also a candidate for some utilization ways that required low CO_2 concentration in terms of energy performance.

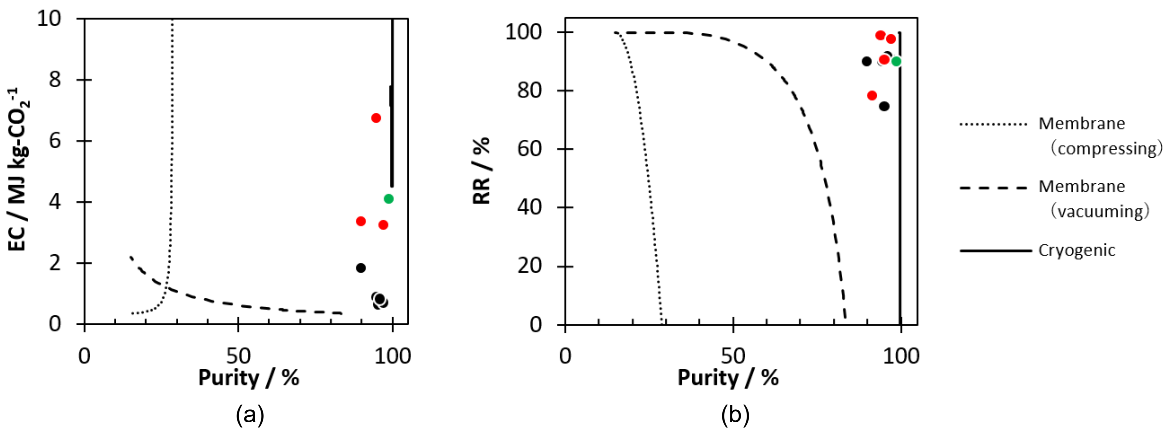

Figure 6: Relationship between product CO_2 purity and (a) Energy consumption (b) Recovery ratio (●) Conventional amine absorption, surveyed (●)TSA, (●)PVSA using zeolite 13X or AC.

4. Conclusions

For designing a CCU process utilizing CO_2 exhausted from a thermal generation plant, etc., characteristics (product CO_2 purity, recovery ratio, energy consumption, continuity) of four separation methods (absorption, adsorption, membrane, cryogenic) were investigated by literature review and simulations. And they were compared under the same feeding CO_2 concentration (15 vol%). As a result, VPSA was the most promising CO_2 separation method to obtain pure CO_2 (>90 %) at a high recovery ratio (>90 %) with low energy consumption (<1 MJ/kg-CO_2). And vacuuming membrane process was also expected for some utilization ways required a low CO_2 concentration in terms of its energy performance. Unfortunately, since technical progress and energy recovery were not considered in this study, we continue to investigate and simulate them as future works. To conclude the finding ways for suitable CO_2 separation for designing a CCU process, firstly we should decide how the level of concentration is required. Secondly, a more energy-saving method with a high recovery ratio as possible should be selected among the candidates as condensation technology in the CCU process.

Nomenclature

AC – Activated carbon
CCS – Carbon dioxide capture and storage
CCU – Carbon dioxide capture and utilization
EC – Energy consumption, MJ kg-CO_2^{-1}
EOR – Enhanced Oil Recovery
MEA – Mono ethanol amine
RR – Recovery ratio, %
TSA – Temperature swing adsorption
TVSA – Temperature vacuum swing adsorption
VPSA – vacuum pressure swing adsorption

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