

Feasibility study on hydrate-based carbon capture driven by solar thermal sorption chiller

Fengyuan Zhang, Xiaolin Wang* and Wojciech Lipiński

School of Engineering, The Australian National University, Canberra (Australia)

Abstract

Hydrate-based carbon capture is a promising method for carbon dioxide (CO₂) capture but consumes a large amount of energy in cooling. This paper investigates the feasibility of CO₂ capture from CO₂-N₂ mixtures driven by solar thermal sorption chillers with the addition of thermodynamic promoter tetra-*n*-butylammonium bromide (TBAB) and kinetic promoter sodium dodecyl sulphate (SDS). In the gas mixtures of CO₂-N₂, CO₂ molar fraction varied from 32.3 to 76.0 mol%, which covered a wide range of flue gas compositions. CO₂ gas uptake, CO₂ split fraction and separation factor at temperatures up to 285.45 K and 4.5-MPa feed pressure are studied. The temperature ranges are designed based on the chilled water temperature of an adsorption chiller in Shanghai. The effects of CO₂ fraction in the feed gas and TBAB concentrations on the CO₂ recovery performance are discussed. In addition, the binary effect of TBAB and SDS is disclosed. The results show that the chilled water temperature from solar thermal driven chillers is sufficiently low to trigger CO₂ hydrate formation thermodynamically, and the kinetic performance can be improved by SDS. The combination of TBAB and SDS has the best separation performance under study.

*Keywords: Carbon capture, CO₂ hydrate, Tetra-*n*-butylammonium bromide, Sodium dodecyl sulphate, Separation factor.*

1. Introduction

Carbon capture and storage (CCS) technologies have been recognized as one of the most effective ways to reduce CO₂ emission and mitigate the greenhouse effect (Sun and Zhang, 2016; Zhang et al., 2018). The conventional CO₂ capture technologies include chemical absorption, physical adsorption and membrane separation (Park et al., 2017). Although these technologies have been commercially available for over 50 years, it is shown that such technologies increase the power plant energy requirement by 25–40% (Haszeldine, 2009; Mondal et al., 2012), and may generate a corresponding negative impact on the environment due to the solvent emission (Chazallon and Pirim, 2018). Currently, hydrate-based carbon capture (HBCC) are getting more significant attention as a potential CO₂ capture and storage technology (Wang et al., 2020b; Zhang et al., 2021). Gas hydrates are ice-like solid compounds formed when “guest” molecules of suitable size and shape are incorporated into the well-defined cages in the “host” lattice made up of hydrogen-bonded water molecules (Park et al., 2013). Because each individual gas has different hydrate formation conditions, for example, CO₂ forms hydrate in 1.2 MPa at 273 K and N₂ forms hydrate in 15.9 MPa at 273 K and H₂ hydrate in 200 MPa at 273 K, HBCC technology can separate CO₂ from mixture gases by controlling the pressure of hydrate formation.

However, the application of this new technology is limited. A key reason is the large energy consumption when cooling the materials for gas hydrate formation. Due to the high latent heat of CO₂ hydrates, the cooling capacity required in the formation is up to 507 kJ/kg (Wang et al., 2020a). A good replacement for the conventional electric cooling system is the solar thermal cooling method. The schematic of the configuration of a solar thermal sorption chiller driven hydrate-based carbon capture system is illustrated in Fig. 1. As reported in a previous publication (Zhai et al., 2014), under the weather conditions of Shanghai, the temperature of the chilled water from a 10-kW solar adsorption chiller was in a range from 283 to 288 K at 12:30–15:30 of the day, with an average of 285.3 K. According to CO₂ hydrate phase equilibrium data, this temperature cannot trigger hydrate formation at below 4.5 MPa. However, higher pressure in cooling systems may result in safety issues and high cost. In order to enable CO₂ hydrate formation at reasonable low pressure at temperatures suitable to solar adsorption cooling, thermodynamic promoters can be employed. A large body of literature has discussed the addition of thermodynamic and kinetic promoters to accelerate the rate of hydrate formation (Chen et al., 2017; Kumar et al.,

2013). Thermodynamic promoters are small molecules that take part in the hydrate cages formation together with gas molecules. The most investigated thermodynamic promoters include tetrahydrofuran (THF), cyclopentane (CP), propane (C_3H_8) and tetra-n-butyl ammonium bromide (TBAB), among which THF, CP and C_3H_8 form hydrate crystals without changing the structure of the water cavity (Dashti et al., 2015), while TBAB takes part in the process through the formation of a semi-clathrate structure by breaking the water cage (Eslamimanesh et al., 2012; Wang and Dennis, 2016). With the addition of thermodynamic promoters, the phase equilibrium temperature of hydrate formation can be raised under a certain pressure (Ma et al., 2016). Kinetic promoters increase the rate of gas hydrate formation without taking part in the gas hydrate formation itself. Commonly used surfactants, as kinetic promoters in gas hydrate forming systems, include sodium dodecyl sulphate (SDS), Tween-80 (T-80) and dodecyl-trimethyl-ammonium chloride (DTAC) (Li et al., 2010). In recent years, the effects of CO_2 capture from mixture gases in the presence of promoters have been widely studied; however, few of them focused on the binary effect of two types of promoters, and most of them only investigated gas mixtures with CO_2 molar fraction of 17–20% (Adeyemo et al., 2010; Yang et al., 2017).

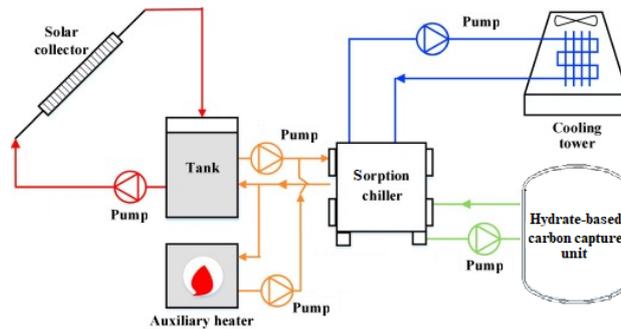


Fig. 1: Schematic of a solar thermal sorption chiller driven hydrate-based carbon capture system

In this work, low- CO_2 fraction, medium- CO_2 fraction and high- CO_2 fraction CO_2 - N_2 gas mixtures are studied. TBAB and SDS are chosen as the thermodynamic and kinetic promoters, respectively. The effects of feed CO_2 molar fraction, TBAB concentration, and the combined effect of TBAB and SDS are studied. CO_2 uptake, pressure drop, split fraction and separation factor are used as performance metrics to evaluate the performance and feasibility of CO_2 capture based on hydrate formation chilled by solar absorption chillers.

2. Experimental section

2.1 Apparatus and materials

The apparatus mainly consisted of a 635-mL steel cylindrical reactor (CR, maximum pressure 30 MPa) with a mechanical stirrer on the top cover, a low-temperature thermostatic bath, a water tank, a vacuum pump, as well as a data acquisition system, shown in Fig. 2. The gas analyzer used in this study was QMS 100 Series Gas Analyser from Stanford Research Systems to measure the gas components. The pressure and temperature change inside the reactor were recorded by a pressure transmitter and a digital temperature sensor with the accuracy of ± 0.01 MPa and $\pm 0.1^\circ C$, respectively.

The gases were supplied by BOC Limited, Australia. The dry molar (%) gas fraction of the binary gases was determined by gas analyzer as follows: CO_2 (76.0%)– N_2 (24.0%), CO_2 (54.1%)– N_2 (45.9%), CO_2 (32.3%)– N_2 (67.7%), corresponding to the high-fraction, medium-fraction and low-fraction CO_2 gas mixtures. TBAB and SDS were supplied by Sigma-Aldrich with 99% purity. Deionized water was used to prepare the TBAB and SDS solution. More details of apparatus and materials are shown in Tab. 1.

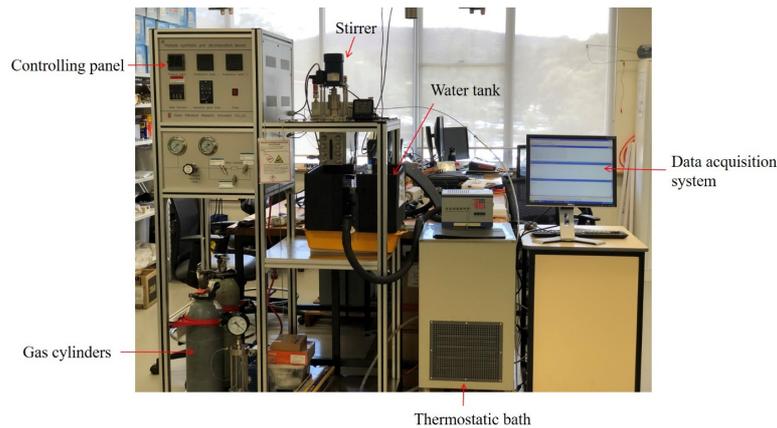


Fig. 2. Experimental apparatus for gas uptake measurements.

2.2 Experimental procedures

The CO₂ capture experiments were conducted under the condition of constant temperature and volume. The CR was first washed and rinsed with deionized water for at least three times. The amount of TBAB or SDS solution used in each experiment was 100 mL. After the solution was charged into the CR, the reactor was sealed tightly and evacuated by a vacuum pump to ensure no air in CR. Then the reactor was cooled by the thermostatic bath. When the CR was cooled and remained stable at the desired temperature, the CR was pressured by CO₂-N₂ mixture gases to 4.5 MPa in this study. At this point, the data acquisition system started to record the pressure and temperature of CR every 10 seconds. As soon as the formed hydrate crystals were observed through the visual windows, the remaining gas composition in the CR was detected by the gas analyzer every 30 minutes. The effect of gas loss on the system by using the gas analyzer, normally 0.3–0.5 mL, was ignored. The QMS series gas analyzer had a fast response time of less than 0.5 seconds. Each experiment was run for 4 hours after crystal formation to compare the amount of CO₂ captured. The constant temperature is maintained at the desired value shown in Tab. 2 to emulate different chilled water temperatures from a solar thermal driven chiller. These temperature sets can also prevent the formation of TBAB hydrate in the absence of gas, based on the concentration of TBAB solutions (Oyama et al., 2005).

Tab. 1: Apparatus and materials properties

Apparatus/materials	Model	Technical index	Supplier
Cylindrical reactor	316L steel	635 mL, 30 MPa	Hai'an Scientific Research Apparatus Co., Ltd, China
Speed motor	MY-358	200 W	Hai'an Scientific Research Apparatus Co., Ltd, China
Thermostatic bath	HX-1030	From -10 to 99.99°C, 30 L, 16 L/min	TOPTION Group Co., Ltd, China
Vacuum pump	2XZ-2	-0.1 MPa	Hai'an Scientific Research Apparatus Co., Ltd, China
Pressure transmitter	PS2-8	40 MPa ± 0.01 MPa	Hongrun Research Co., Ltd, China
Temperature sensor	KS390	From -20 to 100°C, ±0.1°C	Yudian Electronic Co., Ltd, China
CO ₂	–	Purity 99.99%	BOC Limited, Australia
N ₂	–	Purity 99.99%	BOC Limited, Australia
TBAB	–	Purity 99%	Sigma-Aldrich, Australia
SDS	–	Purity 99%	Sigma-Aldrich, Australia

2.3 Performance metrics

The performance of studied recipes was quantified and evaluated based on different parameters. The pressure drop and CO₂ uptake were calculated for each experiment. According to Linga et al. (Linga et al., 2007), two metrics, split fraction (S.Fr.) and separation factor (S.F.) were calculated by the following equations.

CO₂ recovery or split fraction (S.Fr.)

$$\text{S.Fr.} = \frac{n_{\text{CO}_2}^{\text{H}}}{n_{\text{CO}_2,0}} \quad (\text{eq. 1})$$

where $n_{\text{CO}_2,0}$ is defined as the number of moles of CO₂ in feed gas and $n_{\text{CO}_2}^{\text{H}}$ is the number of moles of CO₂ in hydrate phase at the end of the experiment.

Separation factor (S.F.)

$$\text{S.F.} = \frac{n_{\text{CO}_2}^{\text{H}} \cdot n_{\text{N}_2}^{\text{gas}}}{n_{\text{N}_2}^{\text{H}} \cdot n_{\text{CO}_2}^{\text{gas}}} \quad (\text{eq. 2})$$

where $n_{\text{X}}^{\text{gas}}$ is the number of moles of X in the gas phase at the end of the experiment, and n_{X}^{H} is the number of moles of X in the hydrate phase.

Tab. 2: Summary of experiments conditions

Exp. No.	Gas composition	Solutions	P _{exp} (MPa)	T _{exp} (K)
1	CO ₂ (76.0)/N ₂ (24.0)	TBAB 16 wt%, 100 mL	4.50	283.15
2	CO ₂ (76.0)/N ₂ (24.0)	TBAB 32 wt%, 100 mL	4.50	285.15
3	CO ₂ (54.1%)/N ₂ (45.9%)	TBAB 32 wt%, 100 mL	4.50	285.15
4	CO ₂ (32.3%)/N ₂ (67.7%)	TBAB 32 wt%, 100 mL	4.50	285.15
5	CO ₂ (76.0)/N ₂ (24.0)	TBAB 40 wt%, 100 mL	4.50	286.65
6	CO ₂ (76.0)/N ₂ (24.0)	SDS 1000 ppm, 100 mL	4.50	276.35
7	CO ₂ (76.0)/N ₂ (24.0)	TBAB 32 wt%+ SDS 1000 ppm, 100 mL	4.50	285.15

3. Results and discussion

3.1 Effect of TBAB concentration on pressure drop

Fig. 3 shows a comparison of pressure drop during the experiments in three different TBAB concentrations under the same feed CO₂ molar fraction of 76.0%. The experimental temperatures were maintained at 10, 12 and 13.5°C to emulate various chilled water temperatures from a solar thermal driven chiller.

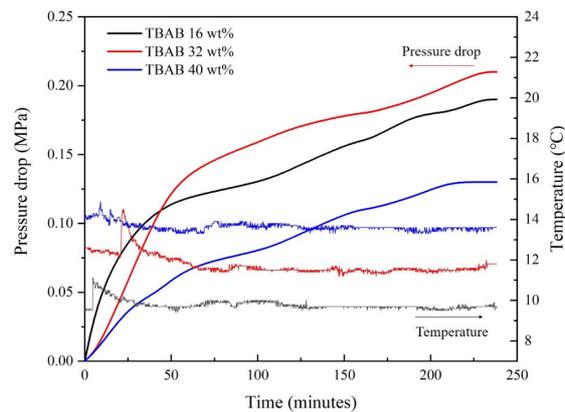


Fig. 3: Effects of TBAB concentration on pressure drop at the same feed CO₂ gas molar fraction of 76.0%.

Compared with 16-wt% and 40-wt% TBAB, 32-wt% TBAB had the highest gas uptake in this study, indicated by the largest pressure drop. Based on the phase equilibrium conditions (Ye and Zhang, 2012), 32-wt% TBAB had higher equilibrium temperature than 16-wt% TBAB and 40-wt% TBAB. TBAB takes part in the process through the formation of a semi-clathrate structure by breaking the water cage. For a polar ionic promoter such as

TBAB, it can easily result in low gas uptake due to the high mass transfer resistance caused by dense hydrate layer (Li et al., 2010). So if the concentration of TBAB is too high, it will be difficult for gas molecules to enter the hydrate cages.

3.2 Effect of TBAB and SDS on the kinetic performance

SDS is a kind of surfactant used as a kinetic promoter in hydrate formation. Kinetic promoters can speed up the rate of hydrate formation without taking part in the hydrate formation itself. To study the combined effect of TBAB and SDS, 32 wt% TBAB with 1000 ppm SDS solution were used in Exp. 7. Meanwhile, 1000 ppm SDS solution in the absence of TBAB were used as a reference. All the lines show in Fig. 4 and Fig. 5 were under the same initial CO₂ molar fraction of 76.0%. It can be found from Fig. 4 and Fig. 5 that with the addition of SDS, CO₂ uptake rate was greatly improved. Figs. 4 and 5 also show that within 4 hours, both the CO₂ uptake amount and uptake rate were the largest in SDS solution among all the experiments. This is because that SDS can enhance the mass transfer between gas phase and water phase, so that the kinetics of reaction was greatly improved in the beginning, which however kept dropping as formed hydrate blocked further gas–water mass transfer. Without SDS, TBAB in hydrate formation showed an increase at first, followed by a drop. The peaks happened after 60 min for TBAB 16 wt% and 40 wt%; and for 32 wt% it was 150 min. The average formation rates in other runs were obviously smaller than that in Exp. 6 due to the lowest experimental temperature adopted (lower by 8.75 °C in average). Overall, without SDS, the formation kinetics in the presence of TBAB had a stochastic nature, although TBAB effects in formation thermodynamics are predictable. Moreover, the increase of TBAB did not increase the amount of CO₂ captured necessarily.

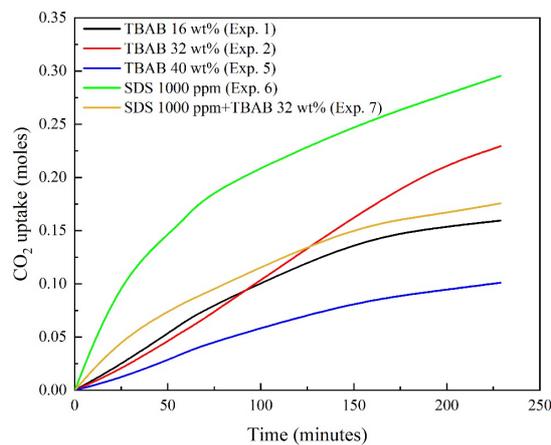


Fig. 4: CO₂ uptake during the experiments.

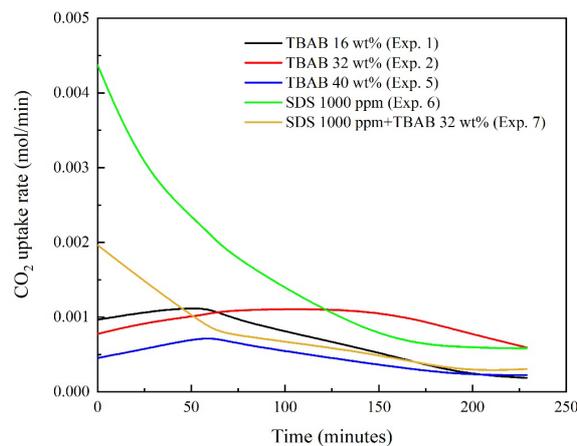


Fig. 5: CO₂ uptake rate during the experiments.

Fig. 6 shows the moles of CO₂ and N₂ in each experiment in the beginning and at the end of experiments. The gas uptake in solution with SDS at 1000 ppm was the highest among all the experiments, and Exp. 4 (32.3% CO₂ and 32-wt% TBAB) had the lowest gas uptake due to the lowest CO₂ proportion in the feed gas. Besides, although

pure N₂ can hardly form hydrate in such pressure, N₂ in gas mixture can form a small amount of N₂ hydrate which was, however, non-negligible. This is obvious in Exp. 4 in which the fraction of N₂ is higher than that of CO₂. In Exp. 4, the final CO₂ uptake was 0.041 moles and the final N₂ uptake was 0.038 moles. The solubility of CO₂ in water is much higher than N₂, resulting in more formed CO₂ hydrate in theory. However, the kinetic diameter of CO₂ and N₂ molecules are 0.33 nm and 0.36 nm, respectively (Cui et al., 2004), so the potential of being trapped in cages is similar. Thus, at high N₂ fractions, CO₂ hydrate cages tend to provide favorable conditions for N₂ uptake.

Fig. 7 summarised the split fraction and separation factor for each experiment. Comparing Exp. 2 and Exp. 7, it can be concluded that the combination of TBAB and SDS greatly improved the separation factor by 147.3%. The presence of SDS was helpful for the separation of CO₂ and N₂ in the solutions of TBAB. Comparing Exp. 6 and Exp. 7, the presence of TBAB, although moderated the phase equilibrium conditions and increased the separation factor, reduced the split fraction of CO₂ at the same time. Comparing Exp. 1, Exp. 2 and Exp. 5, the increment in TBAB concentration reduced CO₂ separation factor, and TBAB at 32 wt% achieved the highest CO₂ split fraction as it is the stoichiometric fraction of the hydrate. Comparing Exp. 2, Exp. 3 and Exp. 4, a drop in CO₂ mole fraction led to a lower CO₂ split fraction.

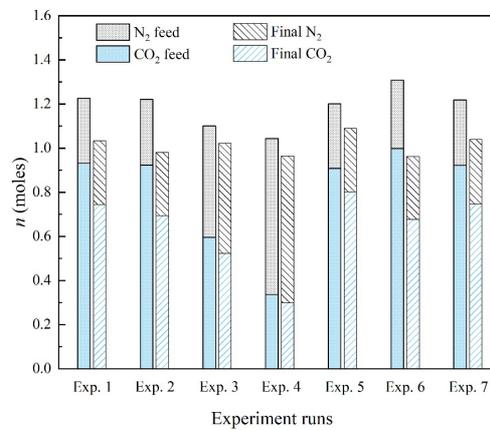


Fig. 6: Moles of CO₂ and N₂ in the beginning and at the end of experiments.

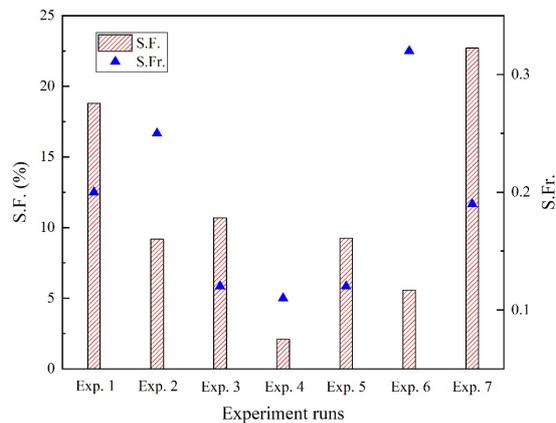


Fig. 7: Split fraction and separation factor for each experiment.

4. Summary and conclusions

In this study, CO₂ capture performance through the hydrate method from CO₂-N₂ mixtures in the presence of tetra-n-butylammonium bromide (TBAB) and sodium dodecyl sulphate (SDS) were studied to evaluate the feasibility of solar thermal driven hydrate-based carbon capture. The CO₂ gas hydrate formation experiments were carried out in a cylindrical reactor with a certain amount of solution at a constant temperature. It was found that under the same initial pressure and TBAB concentration, the higher the CO₂ molar fraction in the feed gas mixture

the greater the split fraction. At a certain gaseous CO₂ molar fraction, 32-wt% TBAB resulted in the highest CO₂ uptake compared with 16-wt% and 40-wt% TBAB. The addition of 1000-ppm SDS sped up the hydrate formation. The combination of TBAB and SDS showed the highest separation factor among all the studied experiments. Overall, the temperature of chilled water from solar thermal driven chillers can be sufficiently low to trigger CO₂ hydrate formation thermodynamically, and the kinetic performance can be improved by SDS. Future studies is suggested to look at the performance of such systems at fluctuating chilled water temperature as most solar thermal driven chillers are periodic.

5. References

- Adeyemo, A., Kumar, R., Linga, P., Ripmeester, J., Englezos, P., 2010. Capture of carbon dioxide from flue or fuel gas mixtures by clathrate crystallization in a silica gel column. *International Journal of Greenhouse Gas Control* 4(3), 478–485.
- Chazallon, B., Pirim, C., 2018. Selectivity and CO₂ capture efficiency in CO₂-N₂ clathrate hydrates investigated by in-situ Raman spectroscopy. *Chemical Engineering Journal* 342, 171–183.
- Chen, Z.-Y., Chen, C., Zhang, Y., Xia, Z.-M., Yan, K.-F., Li, X.-S., 2017. Carbon dioxide and sulfur dioxide capture from flue gas by gas hydrate based process. *Energy Procedia* 142, 3454–3459.
- Cui, X., Bustin, R.M., Dipple, G., 2004. Selective transport of CO₂, CH₄, and N₂ in coals: insights from modeling of experimental gas adsorption data. *Fuel* 83(3), 293–303.
- Dashti, H., Zhehao Yew, L., Lou, X., 2015. Recent advances in gas hydrate-based CO₂ capture. *Journal of Natural Gas Science and Engineering* 23, 195–207.
- Eslamimanesh, A., Mohammadi, A.H., Richon, D., Naidoo, P., Ramjugernath, D., 2012. Application of gas hydrate formation in separation processes: A review of experimental studies. *The Journal of Chemical Thermodynamics* 46, 62–71.
- Haszeldine, R.S., 2009. Carbon Capture and Storage: How Green Can Black Be? *Science* 325(5948), 1647–1652.
- Kumar, A., Sakpal, T., Linga, P., Kumar, R., 2013. Influence of contact medium and surfactants on carbon dioxide clathrate hydrate kinetics. *Fuel* 105, 664–671.
- Li, X.-S., Xu, C.-G., Chen, Z.-Y., Wu, H.-J., 2010. Tetra-n-butyl ammonium bromide semi-clathrate hydrate process for post-combustion capture of carbon dioxide in the presence of dodecyl trimethyl ammonium chloride. *Energy* 35(9), 3902–3908.
- Linga, P., Kumar, R., Englezos, P., 2007. The clathrate hydrate process for post and pre-combustion capture of carbon dioxide. *J Hazard Mater* 149(3), 625–629.
- Ma, Z.W., Zhang, P., Bao, H.S., Deng, S., 2016. Review of fundamental properties of CO₂ hydrates and CO₂ capture and separation using hydration method. *Renewable and Sustainable Energy Reviews* 53, 1273–1302.
- Mondal, M.K., Balsora, H.K., Varshney, P., 2012. Progress and trends in CO₂ capture/separation technologies: A review. *Energy* 46(1), 431–441.
- Oyama, H., Shimada, W., Ebinuma, T., Kamata, Y., Takeya, S., Uchida, T., Nagao, J., Narita, H., 2005. Phase diagram, latent heat, and specific heat of TBAB semiclathrate hydrate crystals. *Fluid Phase Equilibria* 234(1), 131–135.
- Park, H.B., Kamcev, J., Robeson, L.M., Elimelech, M., Freeman, B.D., 2017. Maximizing the right stuff: The trade-off between membrane permeability and selectivity. *Science* 356(6343), eaab0530.
- Park, S., Lee, S., Lee, Y., Lee, Y., Seo, Y., 2013. Hydrate-based pre-combustion capture of carbon dioxide in the presence of a thermodynamic promoter and porous silica gels. *International Journal of Greenhouse Gas Control* 14, 193–199.
- Sun, W., Zhang, F., 2016. Design and thermodynamic analysis of a flash power system driven by process heat of continuous casting grade steel billet. *Energy* 116, 94–101.
- Wang, X., Dennis, M., 2016. Phase equilibrium and formation behaviour of CO₂-TBAB semi-clathrate hydrate at

low pressures for cold storage air conditioning applications. *Chemical Engineering Science* 155, 294–305.

Wang, X., Zhang, F., Lipiński, W., 2020a. Carbon dioxide hydrates for cold thermal energy storage: A review. *Solar Energy* 211, 11–30.

Wang, X., Zhang, F., Lipiński, W., 2020b. Research progress and challenges in hydrate-based carbon dioxide capture applications. *Applied Energy* 269, 114928.

Yang, M., Zhou, H., Wang, P., Li, N., Song, Y., 2017. Hydrate-based CO₂ capture from flue gas in constant pressure process with the presence of THF. *Energy Procedia* 142, 3939–3943.

Ye, N., Zhang, P., 2012. Equilibrium data and morphology of tetra-n-butyl ammonium bromide semiclathrate hydrate with carbon dioxide. *Journal of Chemical & Engineering Data* 57(5), 1557–1562.

Zhai, X., Wang, X., Wang, C., Wang, R., 2014. Experimental investigation of a novel phase change cold storage used for a solar air-conditioning system. *HVAC&R Research* 20(3), 302–310.

Zhang, F., Wang, X., Lou, X., Lipiński, W., 2021. The effect of sodium dodecyl sulfate and dodecyltrimethylammonium chloride on the kinetics of CO₂ hydrate formation in the presence of tetra-n-butyl ammonium bromide for carbon capture applications. *Energy* 227, 120424.

Zhang, F., Zhou, Y., Sun, W., Hou, S., Yu, L., 2018. CO₂ capture from reheating furnace based on the sensible heat of continuous casting slabs. *International Journal of Energy Research* 42(6), 2273–2283.