

Bed Height of Zeolite Affected CO₂ Hydrate Formation Using High Pressure Volumetric Analyzer

A.H. MOHD HAFIZ^{1,*}, C.E. SNAPE² and LEE STEVENS²

¹Faculty of Science and Technology, Islamic Science University of Malaysia (USIM), 71800 Nilai, Negeri Sembilan, Malaysia

²Cleaner Fossil Energy and Carbon Capture Technologies Research Group, Faculty of Engineering, The University of Nottingham, Nottingham NG7 2RD, U.K.

*Corresponding author: Fax: +60 6 7986566; Tel: + 60 11 11069430; E-mail: mhafiz.a.h@usim.edu.my

Received: 3 May 2018;

Accepted: 16 July 2018;

Published online: 31 August 2018;

AJC-19055

The formation of CO₂ hydrate in this work was experimentally investigated using a high pressure volumetric analyzer (HPVA). The investigations in pure CO₂ gas systems (at 275 K and 36 bar) highlighted the effect of bed height on CO₂ hydrate formation by employing standard silica gel and zeolite 13X as porous mediums. The CO₂ uptake of zeolite 13X saturated with 5.6 mol % tetrahydrofuran and 0.01 mol % sodium dodecyl sulfate (zeolite 13X-5) increased from 0 to 0.58 mmol of CO₂ per g of H₂O when the bed height was reduced from 3 to 2 cm.

Keywords: Greenhouse effect, CO₂ hydrate, Driving force, Bed height, Carbon capture and storage.

INTRODUCTION

Carbon dioxide (CO₂) which is a type of 'greenhouse gases (GHG)' absorb warmth from the surroundings and re-radiate some of it back toward earth's surface. Human activities since the Industrial Revolution such as burning coal, natural gas and oil to power machines for manufacturing and transportation have now increased the concentration of CO₂ in the atmosphere from 280 ppm [1] to 400 ppm [2]. The global temperatures are estimated to rise by 2 °C if the concentration of CO₂ in the atmosphere reaches 450 ppm [2]. Thus, the capture of CO₂ needs to be considered where carbon capture and storage (CCS) has been a favourable mitigation against climate change [3,4]. Carbon capture and storage is a 3-step process including CO₂ capture from industrial sources with high CO₂ content, transportation (usually *via* pipe-lines) to the storage site and geological storage in deep saline formations site [4].

Hydrate based gas separation (HBGS) is one of the most promising approaches in CO₂ capture field [5-11] where it relies on the ability of water to form non-stoichiometric crystalline compounds in the presence of CO₂ emitted in the range between 273-290 K at a pressure range of 13-70 bar [12,13]. Numerous parameters have been investigated by previous researchers to improve CO₂ uptake, ease of hydrate formation and operational costs by employing solid adsorbent to make HBGS as the most

preferred method in CCS industry. The stated parameters were type of silicas used, type of promoters used, the concentration of promoters, experimental driving force, bed height and the amount of moisture content for formation of hydrate [14-20].

Adeyemo *et al.* [14] used three different silica gels (gel 1 with a pore size of 30 nm and particle size of 40-75 µm; gel 2 with a pore size of 100 nm and particle size of 40-75 µm; gel 3 with a pore size of 100 nm and particle size of 75-200 µm) and the highest CO₂ composition in hydrate was observed for gel 3 around 92 mol % (CO₂ uptake of 2 mmol of CO₂ per g of H₂O). Park *et al.* [16] studied the hydrate phase equilibria for the fuel gas and water mixtures inside various sizes of silica gel pores and highlighted the relation between small pore sizes (6.0 nm) with capillary effect which decreased activity of water [17] caused by the partial ordering and bonding of water molecules with hydrophilic surfaces of pores.

Metz *et al.* [12] highlighted that silica sand demonstrated better CO₂ capture capability inside fuel gas mixture at the operating temperature of 274.15 K and three different pressures (75, 85, 90 bar) with a 36 mol % conversion of water to hydrate which was almost two-thirds higher than silica gel. Recently, Zheng *et al.* [6] managed to obtain CO₂ uptake of 2.4 mmol of CO₂ per g of H₂O at 283 K and 60 bar by employing 5.56 mol % THF inside a horizontal batch FBR (100 nm silica sand was used as porous media). They also discovered that this horizontal

orientation had 1.5 times higher gas uptake as compared to the common (vertical) orientation. This new finding demonstrates the continuous interest by researchers to ensure that CO₂ hydrate can be used as a promising method for CCS by exploiting the advantages of porous medium in FBR.

Other than silicas, zeolites were also being investigated by researchers in the HBGS field [19,20]. Zong *et al.* [19] observed the formation of CH₄ hydrate inside zeolite A-type pores. Zhong *et al.* [20] found that hydrate growth in FBR by employing zeolite 13X was improved as the driving force increased from 25 to 40 bar by employing CO₂/CH₄ gas mixture (40 mol % CO₂ and 60 mol % CH₄) at 277.15 K. However, it obtained lower selectivity towards hydrate formation as compared to stirred-tank reactors (STRs) due to the massive moisture content available inside zeolites pores [17].

Previously, various sample preparation methods were studied and the method with vigorous stirring had the highest moisture content (14.8 wt %) and the greatest water conversion to hydrate (40.5 mol %) at 275 K and 36 bar in a pure CO₂ gas system. High regeneration and repeatability of the results for all samples prepared by this method were expected as less water was occluded inside silica gel pores [21]. Thus, this sample preparation method was preferred to be implemented in this study to overcome the issue of water activity for hydrate formation due to the massive moisture content available inside the adsorbent pores [17]. Additionally, two approaches were used to study the formation of hydrate inside the HPVA: analysis of P-t curves and study of CO₂ dissolution in water [21]. Hence, the focus of this study was to investigate the formation of hydrate inside the HPVA as an alternative to fixed bed reactor (FBR) at various bed heights wherein standard silica gel and zeolite 13X were used as porous mediums to omit the need of stirring process.

EXPERIMENTAL

Standard silica gel (with a mean particle size of 200-500 µm, mean pore size of 5.14 nm, pore volume of 0.64 cm³/g and surface area of 499 m²/g) was purchased from Fisher Scientific. Zeolite 13X (with a mean particle size of 2 µm, mean pore size of 1.50 nm, pore volume of 0.31 cm³/g and surface area of 819 m²/g) was purchased from Sigma-Aldrich. The promoters (supplied by Fisher Scientific) used were THF (99.9 % purity) and SDS (97.5 % purity). CO₂ gas with a purity of 99.99 % (maximum 103 bar), Helium (He) gas with purity of 99.99 % (34.4 bar) for venting or cleaning purposes and nitrogen (N₂) gas/compressed air (5.2 to 5.5 bar) to control the pneumatic valves of the HPVA were supplied by BOC (a member of the Linde Group). Antifreeze was purchased from ASDA.

General procedure: Basically, before the commencement of experiment the system was manually purged with helium gas to clean the line from any impurities. After the operating conditions were pre-defined, the sample cell was charged with wet silica gel and was placed inside water bath. The cell's valve was initially closed. During the experiment, the cell was pressurized to required pressure through a supply vessel containing CO₂ gas (99.99 %) and at the same time the desired operating temperature was established through water bath. After the operating conditions were achieved, the cell's valve was fully

opened. Subsequently, the experiment was left running for 600 min. After the completion of experiment, the pressure was reduced to atmospheric pressure for hydrate decomposition. Then, the system was automatically vented with He gas several times. Subsequently, the cell's valve was fully closed and the sample cell was removed from the HPVA. Finally, the pressure–time (P-t) curve obtained after completion of the experiment was analyzed [21].

Detection method: The HPVA (Fig. 1) consists of water bath (70 vol % water + 30 vol % antifreeze), vacuum pump and degassing unit was manufactured by Micromeritics. It was designed to obtain high-pressure adsorption isotherms by employing the static volumetric method where it consists of introducing (dosing) a known amount of gas (adsorptive) into the chamber containing the sample to be analyzed. It is capable of achieving pressures up to 100 bar. When the sample reaches equilibrium with the adsorbate gas, the final equilibrium pressure is recorded and this process is repeated at given pressure intervals until the maximum pre-selected pressure is reached. These data are then used to calculate the quantity of gas adsorbed by the sample and resulting equilibrium points (volume adsorbed and equilibrium pressure) are then plotted to provide an isotherm. Excellent reproducibility and accuracy are obtained by using separate transducers for dosing the sample and for monitoring the pressure in the sample chamber.

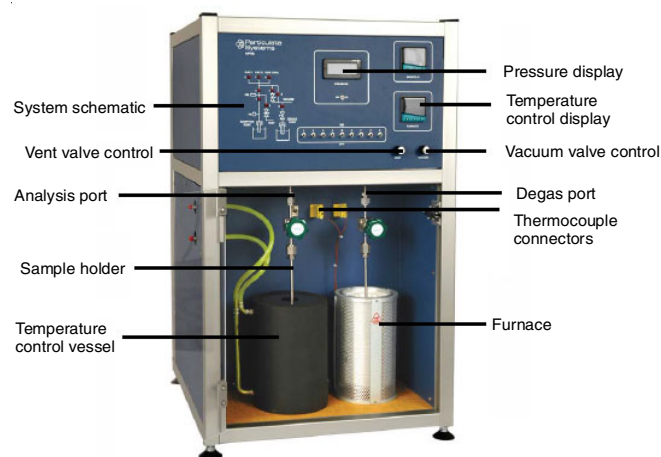


Fig. 1. High pressure volumetric analyzer (HPVA)

RESULTS AND DISCUSSION

Enhancing hydrate formation in zeolite through bed height: In this work the investigation on the implementation of optimum combined-promoter (T1-5; 5.60 mol % THF and 0.01 mol % SDS) [21,22] and the effect of bed height were performed to further study the feasibility of zeolite 13X for hydrate formation in FBR. The bed height was measured by using a vernier calliper.

CO₂ solubility in water: Initially, 0.5 g or 3 cm bed height of zeolite 13X contacted with water (13X-H₂O_3 cm) was used to investigate the formation of hydrate at 275 K and 36 bar inside the HPVA. The study on CO₂ solubility in water showed that no hydrate formation was observed because the total CO₂ consumed after 1200 min was below the red-dashed line as illustrated in Fig. 2. The same result was observed for zeolite

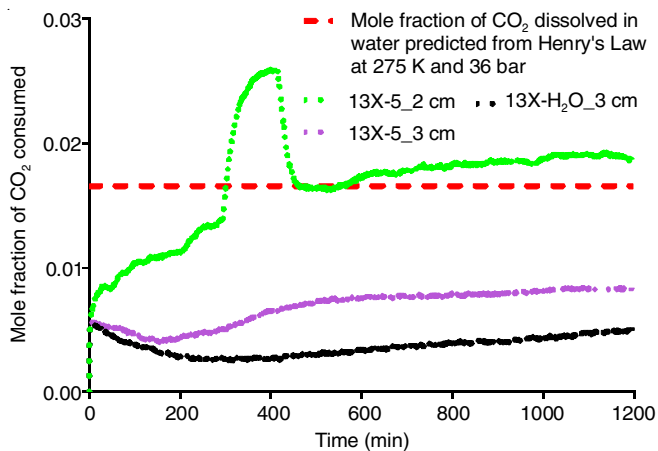


Fig. 2. Mole fraction of CO₂ consumed at the operating conditions of 275 K and 36 bar in 1200 min (*13X-5 = zeolite contacted with 5.6 mol % THF and 0.01 mol % SDS)

13X contacted with 5.6 mol % THF and 0.01 mol % SDS (13X-5_3 cm) when 0.5 g of this sample was employed during the experiment. However, the total CO₂ consumed in 1200 min was slightly higher than the previous sample. Subsequently, the use of 0.3 g of 13X-5 inside the sample cell and reducing the bed height to 2 cm led to the formation of hydrate. The total CO₂ dissolved was above the red-dashed line.

Water conversion and maximum gas uptake: Performance comparison of zeolite and standard silica for CO₂ hydrate formation was performed as illustrated in Fig. 3. In this analysis, the best result of standard silica (T1-5_3 cm; 5.6 mol % THF and 0.01 mol % SDS) at 275 K and 36 bar was chosen together with baseline experiment (SiG-H₂O_3 cm) with both samples weighing 0.5 g. The equilibrium moisture content for 13X-5 at 0.5 g was around 20 wt % as illustrated in Fig. 3(a) which was more than 30 % higher than the baseline experiment and T1-5. 3 (b) and Table-1 demonstrate that the maximum gas uptake of 13X-5_2 cm was the lowest around 0.6 mmol of CO₂ per g of H₂O and was almost 5.5 and 3.5 mmol of CO₂ per g of H₂O lower than T1-5_3 cm and baseline experiment respectively. At this bed height, the amount of equilibrium moisture content of 13X-5 was reduced from 5.7 to 3.5 mmol of H₂O, which was almost comparable to T1-5 and baseline experiment. However, at this comparable amount of moisture content, standard silica was found to have better CO₂ capture capability where the total CO₂ molecules consumed was 10 times higher than

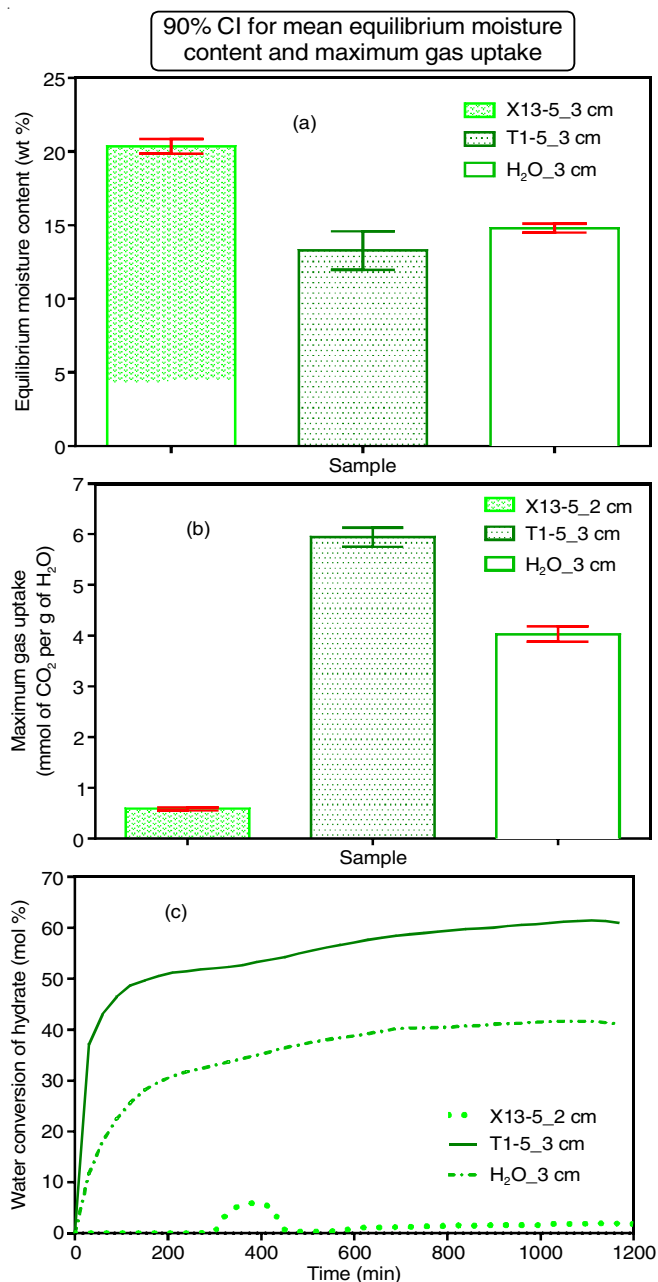


Fig. 3. Comparison of (a) equilibrium moisture content at 3 cm bed height, (b) maximum gas uptake and (c) water conversion to hydrate for 13X-5_2 cm, T1-5_3 cm and baseline experiment at 275 K and 36 bar in 1200 min

TABLE-1
COMPARISON OF GAS UPTAKE OF 13X-5_2 cm, 13X-5_3 cm, 13X-H₂O_3 cm, T1-5_3 cm AND BASELINE EXPERIMENT AT 36 bar AND 275 K IN 1200 min

| Sample | Bed height (cm) | Exp. No. | No. of moles of water (mmol) | CO ₂ formed in hydrate (mmol) | Mean CO ₂ formed in hydrate (mmol) | CO ₂ uptake (mmol of CO ₂ /g of H ₂ O) | Mean CO ₂ uptake (mmol of CO ₂ /g of H ₂ O) (90 % CI) | SD |
|----------------------|-----------------|----------|------------------------------|--|---|---|--|------|
| 13X-5 | 2 | 1 | 3.40 | 0.03 | 0.04 | 0.56 | 0.58 ± 0.03 | 0.03 |
| | | 2 | 3.50 | 0.04 | — | 0.60 | — | — |
| 13X-5 | 3 | 1 | 5.70 | — | — | — | — | — |
| | | 2 | 5.70 | — | — | — | — | — |
| 13X-H ₂ O | 3 | 1 | 5.90 | — | — | — | — | — |
| | | 2 | 5.90 | — | — | — | — | — |
| T1-5 | 3 | 1 | 3.70 | 0.39 | 0.40 | 5.82 | 5.95 ± 0.21 | 0.18 |
| | | 2 | 3.70 | 0.41 | — | 6.08 | — | — |
| H ₂ O | 3 | 1 | 4.10 | 0.29 | 0.31 | 3.93 | 4.04 ± 0.17 | 0.15 |
| | | 2 | 4.30 | 0.32 | — | 4.14 | — | — |

zeolite. Fig. 3(c) shows that the highest water conversion to hydrate observed for 13X-5_2cm was almost 10 mol % in the first 400 min. However, after 400 min, the CO₂ hydrate was found to dissociate before it started to increase again at 600 min. This indicated that the CO₂ hydrate formed during the experiment was not stable and also requires future investigation if zeolite is going to be implemented for CO₂ capture with hydrate formation. In contrast, the CO₂ hydrate formed by implementing standard silica was stable throughout the experiment, which is necessary for CO₂ transport and storage purposes.

Rate of hydrate formation: Fig. 4 illustrates that the kinetics of standard silica was extensively higher than zeolite. The initial kinetics of 13X-5_2 cm was really slow wherein it indicated that the induction time for hydrate growth was longer than T1-5_3 cm and the baseline experiment.

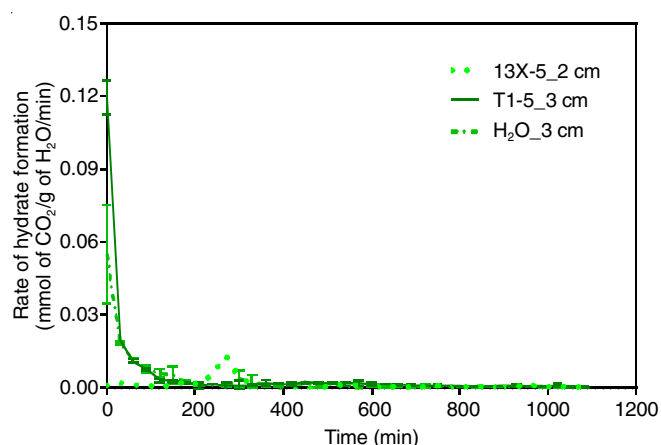


Fig. 4. Rate of hydrate formation at 275 K and 36 bar for 1200 min and inset for the first 400 min (13X-5_2 cm, T1-5_3 cm and baseline experiment)

Conclusion

Generally, the effect of employing a combined-promoter inside zeolite pores did not really enhance hydrate formation and is considered a disadvantage of employing zeolite for CO₂ capture with hydrate formation. Only when the bed height was reduced from 3 to 2 cm, then the rate of hydrate formation was improved. In conclusion, the effect of bed height on hydrate formation was more significant as compared to the implementation of combined-promoter.

ACKNOWLEDGEMENTS

One of the authors, A.M. Mohd Hafiz expresses his gratitude to Universiti Sains Islam Malaysia (USIM; Project Code PPP-FST-12118-00) and Ministry of Higher Education (MoHE) for this research funding.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. K. Caitlyn, Climate Change: Atmospheric Carbon Dioxide (2014); <https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide>. [Access online 20 January 2015].
2. D. Biello, 400 ppm: Carbon Dioxide in the Atmosphere Reaches Prehistoric Levels (2013); <http://blogs.scientificamerican.com/observations/2013/05/09/>. [Access online 20 January 2015].
3. C. Kunze and H. Spliethoff, *Appl. Energy*, **94**, 109 (2012); <https://doi.org/10.1016/j.apenergy.2012.01.013>.
4. IEA, Energy Technology Essentials; OECD/IEA 2006, ETE01 (2006).
5. D.M. D'Alessandro, B. Smit and J.R. Long, *Angew. Chem. Int. Ed.*, **49**, 6058 (2010); <https://doi.org/10.1002/anie.201000431>.
6. J. Zheng, Y.K. Lee, P. Babu, P. Zhang and P. Linga, *J. Natural Gas Sci. Eng.*, **35**, 1499 (2016); <https://doi.org/10.1016/j.jngse.2016.03.100>.
7. P. Babu, C.Y. Ho, R. Kumar and P. Linga, *Energy*, **70**, 664 (2014); <https://doi.org/10.1016/j.energy.2014.04.053>.
8. P. Linga, R. Kumar and P. Englezos, *Chem. Eng. Sci.*, **62**, 4268 (2007); <https://doi.org/10.1016/j.ces.2007.04.033>.
9. S.D. McCallum, D.E. Riestenberg, O.Y. Zatsepina and T.J. Phelps, *J. Petrol. Sci. Eng.*, **56**, 54 (2007); <https://doi.org/10.1016/j.petrol.2005.08.004>.
10. IEA Clean Coal Centre, Pre-Combustion Capture of CO₂ in IGCC Plants No. 11/14, London: pp.11-14 (2011).
11. P. Babu, R. Kumar and P. Linga, *Energy*, **50**, 364 (2013); <https://doi.org/10.1016/j.energy.2012.10.046>.
12. B. Metz, O. Davidson, H.D. Coninck, M. Loos and L. Meyer, IPCC Special Report on Carbon Dioxide Capture and Storage. Intergovernmental Panel on Climate Change, New York, pp. 109-110 (2005).
13. J. Carroll, Natural Gas Hydrates: A Guide for Engineers, Elsevier Inc.: Burlington, edn 2, pp. 1-15 (2009).
14. A. Adeyemo, R. Kumar, P. Linga, J. Ripmeester and P. Englezos, *Int. J. Greenh. Gas Control*, **4**, 478 (2010); <https://doi.org/10.1016/j.ijggc.2009.11.011>.
15. A. Kumar, T. Sakpal, P. Linga and R. Kumar, *Fuel*, **105**, 664 (2013); <https://doi.org/10.1016/j.fuel.2012.10.031>.
16. S. Park, S. Lee, Y. Lee, Y. Lee and Y. Seo, *Int. J. Greenh. Gas Control*, **14**, 193 (2013); <https://doi.org/10.1016/j.ijggc.2013.01.026>.
17. S.P. Kang, J. Lee and Y. Seo, *Chem. Eng. J.*, **218**, 126 (2013); <https://doi.org/10.1016/j.cej.2012.11.131>.
18. P. Mekala, M. Busch, D. Mech, R.S. Patel and J.S. Sangwai, *J. Petrol. Sci. Eng.*, **122**, 1 (2014); <https://doi.org/10.1016/j.petrol.2014.08.017>.
19. X. Zang, J. Du, D. Liang, S. Fan and C. Tang, *Chin. J. Chem. Eng.*, **17**, 854 (2009); [https://doi.org/10.1016/S1004-9541\(08\)60287-6](https://doi.org/10.1016/S1004-9541(08)60287-6).
20. D.L. Zhong, Z. Li, Y.Y. Lu, J.L. Wang, J. Yan and S.L. Qing, *Ind. Eng. Chem. Res.*, **55**, 7973 (2016); <https://doi.org/10.1021/acs.iecr.5b03989>.
21. A.H. Mohd Hafiz, C.E. Snape and L. Stevens, Enhance CO₂ Hydrate Formation Inside the HPVA by Vigorous Stirring During Sample Preparation, Proceeding of Postgraduate Seminar on Science and Technology, 7th November 2016, Nilai, Malaysia (2017).
22. A.H. Mohd Hafiz, C.E. Snape and L. Stevens, *AIP Conf. Proc.*, **1972**, 030019 (2018); <https://doi.org/10.1063/1.5041240>.