Accepted Manuscript

Recent Advances on Carbon Dioxide Capture through a Hydrate-Based Gas Separation Process

Khalik Mohamad Sabil, Behzad Partoon

Please cite this article as: K.M. Sabil, B. Partoon, Recent Advances on Carbon Dioxide Capture through a Hydrate-Based Gas Separation Process, *Current Opinion in Green and Sustainable Chemistry* (2018), doi: 10.1016/j.cogsc.2018.03.006.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Recent Advances on Carbon Dioxide Capture through a Hydrate-Based Gas Separation Process

Khalik Mohamad Sabil[a,*] and Behzad Partoon[b]

[a] Institute of Petroleum Engineering, School of Energy, Geoscience, Infrastructure and Society, Heriot-Watt University Malaysia, No 1 Jalan Venna P5/2, Precinct 5, 62200 Putrajaya, Federal Territory of Putrajaya, Malaysia.

[b]CO_2 Research Center, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh, 32610, Perak, Malaysia.

[*] Corresponding author. Email: k.msabil@hw.ac.uk, phone: +6012-4211974

Abstract

Hydrate Based Gas Separation (HBGS) process is gaining interest globally as a greener solution for separation of CO_2 from gaseous streams. In this paper, recently published articles on the development of HBGS process as a technique for separation of CO_2 from flue gas, feed gas and high CO_2 natural gas streams are briefly reviewed.

Introduction

Energy intensity of growing economy and carbon intensity associated with the energy system are two main factors that lead to excessive emission of CO_2 [1,2] Conversely, CO_2 sinks are very limited [3]. Carbon Capture and Sequestration (CCS) initiatives are taken globally to dampen the impacts of CO_2 on the global climate. One of the strategies in CCS is to separate CO_2 from feed and flue gases. There are commercially available CO_2 capture technologies that are being used in various industrial applications absorption, adsorption, membrane separation and cryogenic distillation [4]. However, capturing vast amount of CO_2 by conventional technologies requires great amount of CAPEX and OPEX. For example, it was calculated that the deployment of absorption process to eliminate 16 mol% of CO_2 in flue gas, reduces 10% of thermal efficiency of a modern power plant. [4]. Therefore, minimization of energy requirements is one of the highest priorities for the future CCS technology development [5]. There are active and ongoing initiatives targeted to increase the energy efficiency and reduce the costs for the aforementioned technologies [6-14]. In addition, there are also rooms to develop novel and innovative technologies for CCS. Electrochemical pumps, chemical looping and hydrate-based gas separation (HBGS) are few examples of recent technologies being developed for separation of CO_2 [6, 10, 15].

Gas or clathrate hydrates are ice-like crystalline solids, in which small gas/liquid molecules are trapped inside cavities of hydrogen bonded water molecules. These solids are normally stable at moderate to high pressures from few kPa [16] to GPa [17] and low

temperatures from 140 K to 330 K [16]. Formation of gas hydrate is a thermodynamic-driven process. Recently, gas hydrate has been identified as a suitable medium for CO_2 capture, mostly from flue gas streams. [18-20]. Hydrate-based gas separation (HBGS) process is gaining popularity as a carbon capture technology due to its lower energy requirement and it is "greener". [21]. In addition, the selectivity of CO_2 in this process is considerably high [16]. In this work, we attempt to present a brief review of recent studies on CO_2 capture via hydrate-base process.

Background

The separation of gases by hydrate formation was first introduced in 1940s when it was suggested for separation of argon from neon by utilization of SO_2 hydrates [22]. Only 60 years later, in 2000, the concept of separation of CO_2 from flue gas through hydrate formation was suggested through the analysis of $CO_2 + N_2$ hydrate phase diagram hydrate [23]. However, the operating pressure for such process is unfavorable as it could be as high as 83.5 bar at 275 K for a flue gas containing 17 mol% CO_2. To overcome the shortcoming, the inclusion of THF as a thermodynamic promoter to reduce the required pressure to 4.75 bar at 275K is suggested. It is shown that a two-step hydrate based separation process is feasible to recover 95 mol% of CO_2 from the studied flue gas [23]. In addition, Seo *et al.* measured phase boundaries of CO_2+N_2 and CO_2+CH_4 hydrate systems at various pressure and composition and their results indicated that separation of CO_2 from these mixtures is thermodynamically feasible. Moreover, they observed CO_2 uptake in the hydrate phase increased with the decrease in the system pressure, suggesting the operating pressure for such separation process should be set as low as possible [24]. Since then, a significant number of work on phase behavior measurement on CO_2+N_2 and CO_2+H_2 systems with or without promoters are published. Comprehensive reviews of these work until 2015 are available in Babu *et al.* [25], Dashti *et al.*[26]*,* and Ma *et al.* [27]. In the following sections, the recent investigations on the development of HBGS process for CO_2 capture in the last 3 years are discussed.

Post-combustion CO$_2$ capture

In recent years, most of the research work related to HBGS are focused on separation of CO_2 from flue gas [28]. This scenario applies to existing conventional power plants or any other facilities dealing with production of energy by burning the fossil fuels. Typically, flue gas is predominantly N_2 with CO_2 concentration ranges from 15 to 20% while O_2 concentration ranges from 5– 9%. Since the flue gas pressure is near atmospheric pressure, a compressor system is normally required to pressurize the gas [29, 30]. In addition, a cooling system is also needed to ensure the temperature of the system goes as low as 2 ^{o}C [31]. A typical schematic diagram for such a process is presented in Figure 1. The high pressure requirement for the system can be significantly reduced by utilization of thermodynamic promoters [25].

[**INSERT FIGURE 1**]

Figure 1. Simplified schematic diagram for post combustion HBGS technology for CO_2 capture

Prior to 2014, most of the reported data on HBGS process is related to batch process. However, Sun *et al.* has reported that continuous HBGS operation of CO_2-CH_4, CH_4-N_2 and CO_2-N_2 is possible by utilizing a new type of reactor and THF as the thermodynamic promoter [32]. They have reported that a recovery of more than 65% of CO_2 in CO_2-N_2 system is possible. More importantly, Sun *et al.* has successfully extended the HBGS study from elementary and exploratory investigation to a more practical condition.

Another important recent advancement in HBGS is the utilization of semi-clathrate hydrate to replace the conventional hydrate system. Kim *et al.* investigated CO_2 capture from flue gas by using the TBAC as the semi-clathrate promoter [33]. Their results indicated that semi-clathrate phase boundary shifted between 13 to 15°C compared to SI hydrate of CO_2+N_2 at the same pressure condition for a 20 mol% of CO_2 in gas mixture. In addition, they showed that the equilibrium temperature is increasing at constant pressure with the increase in CO_2 concentration of the mixture. This observation is extremely important and should be taken into consideration while designing a continuous HBGS process. During a continuous process, the gas phase concentration is changing in the crystallizer due to the enclathration of CO_2 and this will affect the degree of sub-cooling requirement for the system.

Apart for the usage of semi-clathrate for the development of HBGS process, a number of studies are focused on the utilization of new chemicals as hydrate promoters or mixed thermodynamic and kinetic promoters to reduce the pressure requirement for the system. One of the important studies is reported by Kumar *et al.* [34]. They studied the influence of mixed thermodynamic and kinetic hydrate promoter on the hydrate formation of a synthetic flue gas, consisted of CO_2 + N_2 + SO_2. Their results indicated that combining THF and SDS has positive impact on the total gas consumption during the process even though the amount of gas uptake is much lower than that of system with only SDS as promoter. Lee *et al.* investigated CO_2 separation from N_2 by changing the hydrate structure from sI to sH hydrate using neohexene as sH hydrate former [35]. Their results showed an improvement can be achieved for systems with concentration of CO_2 less than 20 mol%. However, increasing the CO_2 concentration leads to the same equilibrium condition regardless of the presence of neohexene due to the formation of sI hydrate as a more stable phase. Methylcyclopentane (MCP) is also studied as the structure sH promoter for CO_2 capture from flue gas with similar trend observed as of the neohexene systems [36]. Moreover, it was reported that the separation efficiency and gas uptake is reducing in the presence of MCP [36]. Lee et al. extended the idea of using sH hydrate for CO_2 sequestration [37]. They demonstrated by injecting flue gas into a sH crystalline network of methane + neohexene, CO_2 molecules replace CH_4 molecules in the crystalline structure and sequestrate while CH_4 molecules are recovered from the system [37].

Pre-Combustion

The pre-combustion CO_2 capture is mainly focused on integrated gasification combined cycle (IGCC). In this process, conventional fuels are converted into a syngas mixture consisted of H_2 ($\approx$ 60 mol%) and CO_2 ($\approx$ 40 mol%) with a small trace of H_2O, N_2 and CO. The gas stream is typically at pressure between 2.5 to 5.0 MPa and temperature of approximately 45 °C [20]. A separation of CO_2 from the syngas must be performed before the syngas is fed to a gas turbine or a fuel cell [28]. Based on the pressure condition of gas stream, a HBGS process can be utilized to capture CO_2 directly from the syngas stream although a cooling system is still required to reduce the temperature of the stream.

Most of earlier studies on the CO_2 capture from shifted gas are focused on utilization of proper promoter to enhance the separation and moderate the operational condition of HBGS process. For pre-combustion applications, utilization of structure sII hydrate former, such as THF, propane and cyclopentane, is investigated. In addition, semi-clathrate hydrate formers such as TBAB, TBAF and TBANO$_3$ are frequently studied [25]. In a series of publication, Fukumoto et $al.$ extended the semi-clathrate hydrate research by studying the tetra-n-butyl ammonium chloride (TBAC) and tetra-n-butyl phosphonium bromide (TBPB) systems for CO_2 hydrate, H_2 hydrate, and modeled the phase boundary of $H_2 + CO_2$ hydrate in the presence of tetra-n-alkylammonium/alkylphosphonium salt aqueous solutions [38-40]. Their findings indicate these salts enhance the separation between CO_2 and H_2 and their performance is concentration dependent.

A number of recent studies on pre-combustion HBGS process are focused on the type of reactor coupled with the usage of hydrate promoter. One of the most interesting is reported by Babu et $al.$ [41]. Their experimental work showed that the presence of propane in the syngas mixture leads to an unusual behavior in the system where water molecules are migrating to the surface and form the hydrate on top of the silica sand. Based on this behavior, they proposed a semi-batch process for separation of CO_2 and H_2. In addition, Zheng et $al.$ looked into the impact of a silica sand fixed-bed reactor properties on the kinetics of hydrate formation [42]. The studied properties are reactor orientation, bed temperature, bed volume and saturation. They found out the horizontal bed with higher surface area leads to faster hydrate formation. In addition, they reported water saturation is a critical parameter where low water saturation is preferred as this will give more space for gas to pass through the bed and eventually convert all available water to the hydrate. In addition, the usage of THF, TBAF, TBAB in fixed bed reactors made of silica gels or coal particles are reported although the results of those study are similar to previously reported by earlier studies [43-45].

Miscellaneous

In addition to pre- and post- combustion gas streams, there are few other studies targeting CO_2 separation from CO_2-CH_4 gas mixture to simulate shale gas mixture or natural gas with

high CO2 concentration. The separation of CO_2 from a simulated shale gas mixture with 40 mol% of CO_2 is investigated with pure water , THF as hydrate promoter or TBPB as the semi-clathrate promoter [46, 47, 48]. Interestingly, the results indicate gas hydrates that are produced at lower driving force in pure water could potentially reach to the highest separation efficiency. Recently, Zhou *et al.* investigate the separation of CO_2 from CH_4 in a large-scale stirrer-tank reactor [49]. They mentioned that this process can be utilized for selective separation of CO_2 from CH_4. Unfortunately, when the CO_2 concentration increases in the feed gas, the separation efficiency decreases [49]. Partoon *et al.* introduced a new gas hydrate crystallizer in their attempt to utilize gas hydrate technology for separation of CO_2 from high CO_2 natural gas streams (60-80mol%) [50]. They studied the separation in a series of semi-batch process by using distilled water. Their results indicated that the process is not very feasible, as both gases are tend to form hydrate at experimental condition. Nonetheless, their experimental results showed that the formation rate of gas hydrate can be increased to more than 8 times higher than similar spray reactor, more than 10 times higher from stirrer reactors with SDS as kinetic promoter and more than 50 times higher than bubble reactors [51]. Nonetheless, due to the smaller amount of CH_4 in the gas mixture, they believed that capturing CH_4 can lead to better separation of these gases with the aid of sII hydrate former such as THF and acetone [52, 53].

Way forward

The recent studies on the HBGS process for CO_2 capture show that there is still long way to development of this process. The most challenging part of development is the scaling up of the process to continuous/semi-continuous setups. A proper reactor type and design for continuous production of gas hydrate is still a challenge. Once that is fixed, an economic evaluation can lead to a comprehensive comparison of HBGS process with other existing ones.

References

[1]   S. Bachu, "CO2 storage in geological media: Role, means, status and barriers to deployment," *Progress in Energy and Combustion Science,* vol. 34, pp. 254-273, 2008.
[2]   "IPCC, Climate Change The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change,"

Intergovernmental Panel on Climate Change, Cambridge, United Kingdom and New York, NY, USA,2013.

[3] M. I. Hoffert, K. Caldeira, A. K. Jain, E. F. Haites, L. D. D. Harvey, S. D. Potter*, et al.*, "Energy implications of future stabilization of atmosphericCO2 content," *Nature,* vol. 395, pp. 881-885, 1998.

[4] N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson*, et al.*, "An overview of CO2 capture technologies," *Energy & Environmental Science,* vol. 3, pp. 1645-1669, 2010.

[5] K. M. Sabil, G.-J. Witkamp, and C. J. Peters, "Estimations of enthalpies of dissociation of simple and mixed carbon dioxide hydrates from phase equilibrium data," *Fluid Phase Equilibria,* vol. 290, pp. 109-114, 2010.

[6] D. Aaron and C. Tsouris, "Separation of CO2 from Flue Gas: A Review," *Separation Science and Technology,* vol. 40, pp. 321-348, 2005.

[7] C. Gouedard, D. Picq, F. Launay, and P. L. Carrette, "Amine degradation in CO2 capture. I. A review," *International Journal of Greenhouse Gas Control,* vol. 10, pp. 244-270, 2012.

[8] M. K. Mondal, H. K. Balsora, and P. Varshney, "Progress and trends in CO_2 capture/separation technologies: A review," *Energy,* vol. 46, pp. 431-441, 2012.

[9] A. A. Olajire, "CO2 capture and separation technologies for end-of-pipe applications - A review," *Energy,* vol. 35, pp. 2610-2628, 2010.

[10] T. E. Rufford, S. Smart, G. C. Y. Watson, B. F. Graham, J. Boxall, J. C. Diniz da Costa*, et al.*, "The removal of CO2 and N2 from natural gas: A review of conventional and emerging process technologies," *Journal of Petroleum Science and Engineering,* vol. 94-95, pp. 123-154, 2012.

[11] S. Sridhar, B. Smitha, and T. M. Aminabhavi, "Separation of Carbon Dioxide from Natural Gas Mixtures through Polymeric Membranes - A Review," *Separation & Purification Reviews,* vol. 36, pp. 113 - 174, 2007.

[12] H. Yang, Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland*, et al.*, "Progress in carbon dioxide separation and capture: A review," *Journal of Environmental Sciences,* vol. 20, pp. 14-27, 2008.

[13] Z. Yong, V. Mata, and A. E. Rodrigues, "Adsorption of carbon dioxide at high temperature--a review," *Separation and Purification Technology,* vol. 26, pp. 195-205, 2002.

[14] B. Zhao, Y. Su, W. Tao, L. Li, and Y. Peng, "Post-combustion CO2 capture by aqueous ammonia: A state-of-the-art review," *International Journal of Greenhouse Gas Control,* vol. 9, pp. 355-371, 2012.

[15] E. J. Granite and T. O'Brien, "Review of novel methods for carbon dioxide separation from flue and fuel gases," *Fuel Processing Technology,* vol. 86, pp. 1423-1434, 2005.

[16] E. D. Sloan and C. Koh, *Clathrate hydrates of natural gases*, 3rd ed. New York, USA: CRC Press-Taylor & Francis Group, 2008.

[17] T. Iitaka and T. Ebisuzaki, "Methane hydrate under high pressure," *Physical Review B,* vol. 68, p. 172105, 2003.

[18] S. M. Kim, J. D. Lee, H. J. Lee, E. K. Lee, and Y. Kim, "Gas hydrate formation method to capture the carbon dioxide for pre-combustion process in IGCC plant," *International journal of hydrogen energy,* vol. 36, pp. 1115-1121, 2011.

[19] C.-G. Xu, X.-S. Li, Q.-N. Lv, Z.-Y. Chen, and J. Cai, "Hydrate-based CO2 (carbon dioxide) capture from IGCC (integrated gasification combined cycle) synthesis gas using bubble method with a set of visual equipment," *Energy,* vol. 44, pp. 358-366, 2012.

[20] A. Skorek-Osikowska, K. Janusz-Szymańska, and J. Kotowicz, "Modeling and analysis of selected carbon dioxide capture methods in IGCC systems," *Energy,* vol. 45, pp. 92-100, 2012.

[21] X.-S. Li, C.-G. Xu, Z.-Y. Chen, and H.-J. Wu, "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,* vol. 35, pp. 3902-3908, 2010.

[22] B. A. Nikitin, "Chemical Properties of the Rare Gases," *Nature,* vol. 140, p. 643, 1937.

*[23] S. P. Kang and H. Lee, "Recovery of CO2 from flue gas using gas hydrate: Thermodynamic verification through phase equilibrium measurements," *Environmental Science & Technology,* vol. 34, pp. 4397-4400, 2000.
[Among the first article to report on conceptual HBGS process]

[24] Y.-T. Seo, S.-P. Kang, H. Lee, C.-S. Lee, and W.-M. Sung, "Hydrate Phase Equilibria for Gas Mixtures Containing Carbon Dioxide: A Proof-of-Concept to Carbon Dioxide Recovery from Multicomponent Gas Stream," *Korean Journal of Chemical Engineering,* vol. 17, pp. 659-667, 2000.

**[25] P. Babu, P. Linga, R. Kumar, and P. Englezos, "A review of the hydrate based gas separation (HBGS) process for carbon dioxide pre-combustion capture," *Energy,* vol. 85, pp. 261-279, 2015.
[A comprehensive review of HBGS process prior to 2015]

**[26] Z. W. Ma, P. Zhang, H. S. Bao, and S. Deng, "Review of fundamental properties of CO_2 hydrates and CO_2 capture and separation using hydration method," *Renewable and Sustainable Energy Reviews,* vol. 53, pp. 1273-1302, 2016.
[A comprehensive review of properties of CO_2 hydrate and hydrate formation as separation technique]

**[27] H. Dashti, L. Zhehao Yew, and X. Lou, "Recent advances in gas hydrate-based CO_2 capture," *Journal of Natural Gas Science and Engineering,* vol. 23, pp. 195-207, 2015.
[A comprehensive review of HBGS process prior to 2015]

[28] T. F. Wall, "Combustion processes for carbon capture," *Proceedings of the Combustion Institute,* vol. 31, pp. 31-47, 2007/01/01/ 2007.

[29] P. Linga, A. Adeyemo, and P. Englezos, "Medium-Pressure Clathrate Hydrate/Membrane Hybrid Process for Postcombustion Capture of Carbon Dioxide," *Environmental Science and Technology,* vol. 42, pp. 315-320, 2008.

[30] P. J. Herslund, K. Thomsen, J. Abildskov, and N. von Solms, "Modelling of tetrahydrofuran promoted gas hydrate systems for carbon dioxide capture processes," *Fluid Phase Equilibria,* vol. 375, pp. 45-65, 2014.

[31] F. Li, L. Duanmu, L. Fu, and X. l. Zhao, "Research and Application of Flue Gas Waste Heat Recovery in Co-generation Based on Absorption Heat-exchange," *Procedia Engineering,* vol. 146, pp. 594-603, 2016.

**[32] Q. Sun, G. Chen, X. Guo, and A. Liu, "Experiments on the continuous separation of gas mixtures via dissolution and hydrate formation in the presence of THF," *Fluid Phase Equilibria,* vol. 361, pp. 250-256, 2014.
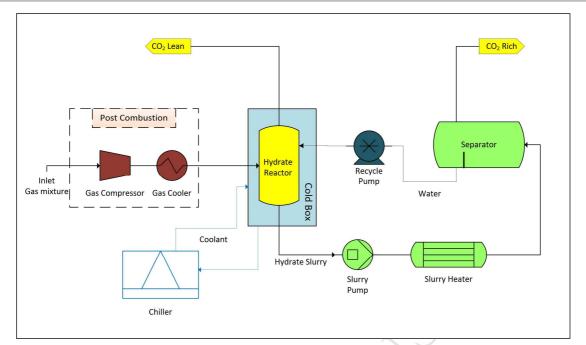**[The highlight of this article is on the success of its continuous HBGSprocess]**

[33] S. Kim, S.-P. Kang, and Y. Seo, "Semiclathrate-based CO2 capture from flue gas in the presence of tetra-n-butyl ammonium chloride (TBAC)," *Chemical Engineering Journal,* vol. 276, pp. 205-212, 2015.

[34] A. Kumar, G. Bhattacharjee, V. Barmecha, S. Diwan, and O. S. Kushwaha, "Influence of kinetic and thermodynamic promoters on post-combustion carbon dioxide capture through gas hydrate crystallization," *Journal of Environmental Chemical Engineering,* vol. 4, pp. 1955-1961, 2016.

[35] Y. Lee, D. Lee, J.-W. Lee, and Y. Seo, "Enclathration of CO_2 as a co-guest of structure H hydrates and its implications for CO_2 capture and sequestration," *Applied Energy,* vol. 163, pp. 51-59, 2016.

[36] D. Lee, Y. Lee, J. Lim, and Y. Seo, "Guest enclathration and structural transition in CO_2 + N_2 + methylcyclopentane hydrates and their significance for CO_2 capture and sequestration," *Chemical Engineering Journal,* vol. 320, pp. 43-49, 2017.

[37] Y. Lee, Y.-j. Seo, T. Ahn, J. Lee, J. Y. Lee, S.-J. Kim*, et al.*, "CH_4 – Flue gas replacement occurring in sH hydrates and its significance for CH_4 recovery and CO_2 sequestration," *Chemical Engineering Journal,* vol. 308, pp. 50-58, 2017.

[38] A. Fukumoto, P. Paricaud, D. Dalmazzone, W. Bouchafaa, T. T.-S. Ho, and W. Fürst, "Modeling the Dissociation Conditions of Carbon Dioxide + TBAB, TBAC, TBAF, and TBPB Semiclathrate Hydrates," *Journal of Chemical & Engineering Data,* vol. 59, pp. 3193-3204, 2014.

[39]   A. Fukumoto, D. Dalmazzone, P. Paricaud, and W. Fürst, "Experimental Measurements and Modeling of the Dissociation Conditions of Tetrabutylammonium Chloride Semiclathrate Hydrates in the Presence of Hydrogen," *Journal of Chemical & Engineering Data,* vol. 60, pp. 343-350, 2015.

[40]   A. Fukumoto, L. P. Sales Silva, P. Paricaud, D. Dalmazzone, and W. Fürst, "Modeling of the dissociation conditions of H 2 + CO 2 semiclathrate hydrate formed with TBAB, TBAC, TBAF, TBPB, and TBNO 3 salts. Application to CO 2 capture from syngas," *International Journal of Hydrogen Energy,* vol. 40, pp. 9254-9266, 2015.

**[41]   P. Babu, R. Kumar, and P. Linga, "Unusual behavior of propane as a co-guest during hydrate formation in silica sand: Potential application to seawater desalination and carbon dioxide capture," *Chemical Engineering Science,* vol. 117, pp. 342-351, 2014.
[**This article reporting on the unusual behaviour of water movement in silica gel with the presence of propane during hydrate formation**]

**[42]   J. Zheng, Y. K. Lee, P. Babu, P. Zhang, and P. Linga, "Impact of fixed bed reactor orientation, liquid saturation, bed volume and temperature on the clathrate hydrate process for pre-combustion carbon capture," *Journal of Natural Gas Science and Engineering,* vol. 35, pp. 1499-1510, 2016.
[**A thorough discussion on the effects of reactor parameters on the HBGS process is presented in this article**]

[43]   P. Babu, H. W. N. Ong, and P. Linga, "A systematic kinetic study to evaluate the effect of tetrahydrofuran on the clathrate process for pre-combustion capture of carbon dioxide," *Energy,* vol. 94, pp. 431-442, 2016.

[44]   J. Zheng, P. Zhang, and P. Linga, "Semiclathrate hydrate process for pre-combustion capture of CO_2 at near ambient temperatures," *Applied Energy,* vol. 194, pp. 267-278, 2017.

[45]   J. Yan, Y.-Y. Lu, J.-L. Wang, S.-L. Qing, and Y.-R. Wang, "Experimental Investigation of Precombustion CO2Capture Using a Fixed Bed of Coal Particles in the Presence of Tetrahydrofuran," *Energy & Fuels,* vol. 30, pp. 6570-6577, 2016.

[46]   D.-L. Zhong, Z. Li, Y.-Y. Lu, J.-L. Wang, and J. Yan, "Evaluation of CO 2 removal from a CO 2 + CH 4 gas mixture using gas hydrate formation in liquid water and THF solutions," *Applied Energy,* vol. 158, pp. 133-141, 2015.

[47]   Z. Li, D.-L. Zhong, Y.-Y. Lu, J. Yan, and Z.-L. Zou, "Preferential enclathration of CO 2 into tetra- n -butyl phosphonium bromide semiclathrate hydrate in moderate operating conditions: Application for CO 2 capture from shale gas," *Applied Energy,* vol. 199, pp. 370-381, 2017.

[48]   Z. Li, D.-L. Zhong, Y.-Y. Lu, and J. Yan, "Efficient CO 2 Capture from a Simulated Shale Gas using Tetra- n -butylphosphonium Bromide Semiclathrate Hydrate," *Energy Procedia,* vol. 105, pp. 4904-4908, 2017.

[49]   X. Zhou, D. Liang, and L. Yi, "Experimental study of mixed CH4/CO2hydrate formation kinetics and modeling," *Asia-Pacific Journal of Chemical Engineering,* vol. 9, pp. 886-894, 2014.

[50]   B. Partoon, K. M. Sabil, and L. K. Keong, "Capturing Carbon Dioxide through a Gas Hydrate-Based Process," *Chemical Engineering Transactions,* vol. 45, pp. 1867-1872, 2015.

[51]   B. Partoon, "Separation of Carbon Dioxide and Methane via Hydrate Formation with Utilization of Modified Spray Reactor and Thermodynamic Promoters," PhD, Chemical Engineering Department, Universiti Teknologi PETRONAS, Perak, Malaysia, 2017.

[52]   B. Partoon, O. Nashed, Z. Kassim, K. M. Sabil, J. Sangwai, and B. Lal, "Gas Hydrate Equilibrium Measurement of Methane + Carbon Dioxide + Tetrahydrofuran+ Water System at High CO2 Concentrations," *Procedia Engineering,* vol. 148, pp. 1220-1224, 2016.

[53]   B. Partoon, K. M. Sabil, H. Roslan, B. Lal, and L. K. Keong, "Impact of acetone on phase boundary of methane and carbon dioxide mixed hydrates," *Fluid Phase Equilibria,* vol. 412, pp. 51-56, 2016.