Omar Tallab, et. al. International Journal of Engineering Research and Applications
www.ijera.com
ISSN: 2248-9622, Vol. 11, Issue 5, (Series-III) May 2021, pp. 47-53

RESEARCH ARTICLE OPEN ACCESS

Effect of Natural Pozzolana and Sodium Dodecyl Sulfate on Clathrate Hydrate Formation Kinetics with CO2 as a Guest-Gas

Omar Tallab*, Mohammed H. Albeirutty**, Iqbal Ahmed**, Hani A. Abulkhair**, Omar A. Bamaga***

**(Department of Mechanical Engineering, Faculty of Engineering, King Abdulaziz University, P.O. Box 80204, Jeddah 21589, Kingdom of Saudi Arabia*
***(Department of Mechanical Engineering, Faculty of Engineering and Center of Excellence in Desalination Technology, King Abdulaziz University. P.O. Box 80200, Jeddah 21589, Kingdom of Saudi Arabia)*
****(Center of Excellence in Desalination Technology, King Abdulaziz University. P.O. Box 80200, Jeddah 21589, Kingdom of Saudi Arabia)*
Corresponding Author: Omar A. Bamaga, Email: obamaga@kau.edu.sa

ABSTRACT
The scarcity of natural freshwater resources drives research efforts worldwide on developing innovative and energy efficient desalination technologies to fulfill the needs for freshwater. Multistage flash distillation and reverse osmosis desalination are the most applied industrial methods for desalination; however, these two methods are energy intensive. With the trend of the world to go green, the method of clathrate (gas) hydrate desalination is attracting more interest as it is believed to be a low energy use method. In this study, carbon dioxide was used as a guest gas in gas hydrate formation experiments enhanced by the addition of SDS and pozzolana powder having main particle size of 6 μm as kinetic promoters. Stirring can improve the kinetics of the process by breaking the hydrate thin layers formed on top of the solution at the onset of hydrate induction period and also due effect of mixing on improving heat dissipation. Sodium dodecyl sulfate helps increase gas consumption and water recovery. A Synergetic effect on water recovery and the kinetics of the process was observed when both SDS and pozzolana powder were used all together.
Keywords- Clathrate hydrate, Clathrate Hydrate Desalination, CO2 guest gas, Kinetic promoters, Natural pozzolana, SDS

Date of Submission: 01-05-2021 Date of Acceptance: 15-05-2021

I. INTRODUCTION

Saudi Arabia is a country located in the middle eastern hot weather region. The dry weather in this region makes it a country that suffers from scarcity of freshwater resources and excessive depletion of nonrenewable groundwater resources [1]. Most of the freshwater natural sources in Saudi Arabia come from deep ground aquifer water [2], which put Saudi Arabia in front of the freshwater scarcity challenge. To conquer this water scarcity, Saudi Arabia depends on water desalination plants to fulfill its freshwater needs for urban and industrial use. Hence, Saudi Arabia built 30 water desalination plants that are distributed close to the west and east coast of Saudi Arabia makes it the highest country in the production of water desalination [3]. These water desalination plants consumed more than 1.5 million oil barrels in 2013, making an intensive energy process [4].Moreover, the burning of oil produces high carbon dioxide rates and other toxic gases that can affect the inhaled air quality [5]. Desalination removes salts and other impurities from the sea or brackish water to produce fresh or distilled water [6]. Although many desalination processes are used in the country, 99% of desalinated water comes from multistage flash desalination process (MSF) and the reverse osmosis desalination process (RO) [7]. The MSF process costs $ 0.56 to 1.75 per ton of water, while the RO desalination method costs 0.45 to 0.66 per ton of water [8]. The ratio between the produced freshwater and the feed saline water is called water recovery. Noting that the water recovery for the MSF and the RO method can reach up to 20% and 55%, respectively [9,10].

Gas hydration is a process that can be used in water desalination. Gas hydrate is ice-like crystals formed by trapping gas molecules as a guest into cages formed by water molecules as a host under specific pressure and temperature above the freezing temperature. During this process, salt and impurities are extracted from these crystals which formed of %85 of pure water and %15 of gas [11]. The gas is trapped in water cages forms three types of cavity structures. The number of water molecules which form Structure I, Structure II and Structure III is 46, 136 and 34 water molecules, respectively. Structure 1 is formed with small molecules of gasses such as methane and carbon dioxide, while structure 2 is formed with a little bigger molecule of gasses such as propane and iso-butane [12,13]. Gas hydration can be used in gas storage due to its small volume and safe gas storage [14]. Gas hydrate reserves are available in massive amountsin the deep ocean and can be utilized as a source of natural hydrocarbon gasses such as methane, and it is. Also, gas hydration has a beneficial usage in carbon dioxide capturing [5]. Gas hydration was applied for desalination of seawater and brackish water. Since minerals and salts are presented in these water sources, the salt acts as an inhibitor in the gas generation process. It needs a higher pressure and lower temperature above the freezing point to reach the clathrate formation [15]. The gas hydrate can be formed with many gasses, and each gas's formation has its cons and pros. However, to choose a gas for the process of gas hydration, the gas has to be environmentally acceptable, non-flammable, non-poisoned gas at low and high rates [13]. All gasses can be reused after the separation and the disassociation of the gas hydration [16]. The gas hydration process is a stochastic nature process, and it does not follow a specific trend even when the same levels of parameters were maintained under controlled experiments. Since sodium chloride is an inhibitor for gas hydration, it increases the process's stochastic nature. Also, it increases the induction time of the process, which is the time of the pressure and temperature stability until the first nucleation of the gas hydration [17]. There might be multiple nucleation in the gas hydration process, but the first one is the greatest, and the gas uptake after this nucleation is high and then decreases. The occurrence of nucleation is observed in the pressure and temperature diagram over time by a spike in temperature and a drastic drop in pressure [18]. The gas hydration mostly formed on the interface area between the liquid solution and the pressured gas, forming a thin layer of gas hydration formed on the top of the solution that prevents the gas's diffusion into water. Using surfactants such as sodium dodecyl sulfate (SDS) ($C_{12}H_{25}NaO_4S$) and mix it well with the solution will prevent the phenomenon of the top thin layer formation and give the gas a chance the penetration for further gas hydration formation [14]. Adding SDS at a concentration of 500 ppm into the liquid solution can increase the gas hydrate formation rate by 2.25 compared to the non-surfactant process [16]. Mechanical mixing technique can be used for breaking the thin layer formed through the use of stirrer. Using a kinetic promoter or a stirrer at a moderate speed that does not create vortices and bubbles can increase the gas uptake by 2.31. Since the gas hydration process is exothermic, the stirrer also helps heat dissipation and cooling distribution inside the cell [19]. Nanoparticles or absorbents help in the gas hydration process in decreasing the induction time and increasing the gas consumption [20]. Aluminum oxide and silicon dioxide can increase the heat transfer in the solution, leading to increased heat dissipation in the gas hydration and improving the kinetic and gas consumption in the gas hydration process up to 47% when used at 0.3 % wt. [21]. Pozzolanas are used to remove heat from concrete mixes and are found by grinding special rocks into micro-levels. Natural pozzolana consists of 71% wt. of silicon dioxide, 13.7% of wt., aluminum oxide and 1% wt. of ferric oxide ground to the level of 5 micrometers have a high effect on removing heat, and it is easily disposed because it is a non-hazardous material.

In this study, the effect of SDS and pozzolana powder as promoters on gas hydrate formation kinetics was determined for CO_2-distilled water and CO_2-seawater systems under stirring and without stirring. Induction time, water recovery percentage and gas uptake throughout the gas hydration process was calculated and compared using the gas equation of state.

II. MATERIAL AND METHOD

2.1. Materials

The Carbon dioxide gas in this study (99.995 %) is supplied by Abdullah Hashim Industrial Gases and Equipment CO. Ltd.). Pure water was produced in laboratory using an RO lab system (Purelab Option SR-7, Elga Veolia, UK). Pretreated seawater (salinity 3.67% wt.) was obtained from the feed intake of RO desalination plant located on Red Sea coast (Water and Environmental Services Company (WESCO) Plant, Jeddah). SDS of purity 92.5-100.5% was supplied by Sigma-Aldrich. Coarse nano particles of natural pozzolana (Micrasil®) processed by Imerys Minerals Arabia L.L.C., Rabigh, Saudi Arabia were used.

2.2. Apparatus

Figure 1 shows a schematic diagram of the apparatus used. The apparatus is equipped with a 143 ml volume reactor that has an internal diameter of 50.8 mm and a height of 69.85 mm. The reactor has two clear polycarbonate windows which allow to view the internal contents of the reactor. The reactor is cooled by a cooling jacket that is connected to an external chiller in order to keep the temperature of the reactor under control. The internal temperature of the reactor is measured by two E-type thermocouples supplied by Omega, one is for the gas that located above the liquid and the other is inserted deep just above the bottom surface of the reactor to measure the liquid temperature. A Rosemount pressure transmitter is used to measure the internal gas pressure during the experiment. Pressure and temperature sensors are connected to data acquisition system and the data are recorded every two seconds.

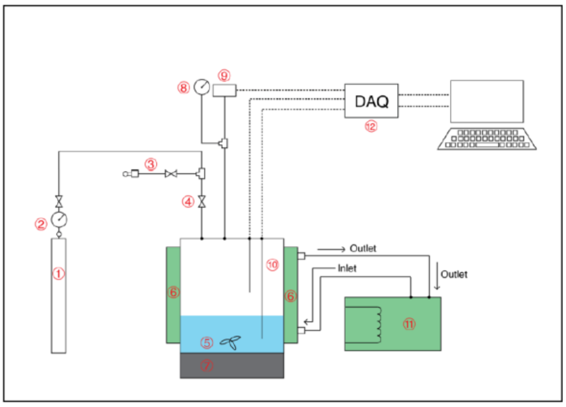

Fig.1 Schematic flow diagram for the apparatus. 1- Gas cylinder. 2- Regulator. 3- Needle valve and release tube. 4- Ball valve. 5- Magnetic stirrer. 6- Cooling jacket. 7- Magnetic stirrer drive. 8- Pressure gauge. 9- Pressure transmitter. 10- Thermocouples. 11- Cooling circulator. 12- Data acquisition system.

2.3. Procedure

1.3.1. Solution preparation

The primary liquids for the experiments are seawater and distilled water. SDS solution is prepared by adding 0.5 g of SDS to 1 liter of seawater or distilled water, thus obtaining solutions with 500 ppm SDS concentration. The solution of o.3 % wt. natural pozzolana with the liquid is prepared by adding 3 g of the natural pozzolana to 1 liter of seawater or distilled water and mixing the product in a blender for at least 2 hours to prevent caking. SDS and pozzolana solution was prepared by mixing equal quantities of already prepared stocks of SDS and pozzolana solutions.

1.3.2. Gas Hydrate Formation Procedure

After preparation of the solution, the reactor was rinsed with the given solution for the experiment, then the reactor was loaded with solution at 40% of its total volume (56 ml solution). Purging the air inside the reactor was done by pressurizing the reactor to 6 bars with carbon dioxide gas and keeping the gas inside for 10 minutes then depressurizing it to reach 2 bar and repeating the same cycle for three times. The reactor was cooled by an external chiller to reach 5 oC, then the system was pressurized to a pressure above the experimental pressure by 1.4 bar this was done to compensate the effects of cooling on parameters of state of the gas. Then, the minimum set temperature of the cooling chiller was adjusted to 1 oC which is below the hydrate stability temperature and the DAQ system was started to record the temperature and the pressure over time at 2 s intervals. When the reactor temperature stabilized at the minimum set temperature the corresponding pressure was noted. Any further drop in the pressure indicates gas consumption due to gas hydrate formation. Once the temperature and the pressure are stabilized and no further pressure decrease was noticed, then the experiment is ended. A quick overview was done over the recorded data by graphing the temperature and the pressure trend. The graph should have at least one temperature spike and a pressure drop after the spike.

1.3.3. Calculation method of hydrate formation parameters

Gas consumed in moles during the experiment due the gas hydrate formation is calculated by the general law of gasses using Equation (1) as follow:

$$m_t = \left(\frac{PV}{zRT}\right)_0 - \left(\frac{PV}{zRT}\right)_t \qquad (1)$$

Wherem_t is gas consumption, P is the reactor's pressure, V is volume, Z is the compressibility factor, R is the gas constant and T is the temperature of the gas [16]. The indices 0 and t represent, respectively, the conditions of the cell at t = 0 and t.
Volume of water converted to hydrate can be found by Equation (2):

$$V_{Water\ to\ hydrate} = m_t * HN * 18\ cm^3 \quad (2)$$

Where HN is the hydration number for the gas used which was taken as 6.0 for the pure carbon dioxide [22].
Water recovery measures the volumetric efficiency of the gas hydration process as a desalination method [16] and can be calculated as follow:

$$Water\ recovery = \frac{V_{water\ converted\ \ to\ hydrate}}{V_{prepeared\ \ feed\ solution}} \qquad (3)$$

III. RESULTS AND DISCUSSION

Eight carbon dioxide gas hydrate formation experiments were conducted according to the conditions shown in Table 1. The gas hydrate formation temperature for experiments was found in the range 1 to 1.5 oC.The results of induction time, gas consumption, volume of water converted to hydrate and water recovery are also shown in Table.1.

Table 1 Experimental conditions and results (

Exp #	Solution	Promoter type	P (Psi)	T_{in} (min)	M_{gc}, mol	V H2O to Hyd (ml) *	Water Recovery (%)*
1	SW	NA	20	20.6	0.0001	0.0160	0.02%
2	DI	NA	20	18.3	0.0021	0.2264	0.37%
3	SW	NA	30	15	0.0115	1.2470	2.18%
4	SW	Poz.	20	6	0.0157	1.6965	2.97%
5	SW	SDS	20	18.3	0.0175	1.8863	3.30%
6	SW	Stir.	20	9	0.0215	2.3227	4.06%
7	SW	SDS + Poz.	20	10.1	0.0232	2.5050	4.37%
8	SW	SDS + Poz.+ Stir	20	8.3	0.0331	4.8964	8.58%

Abbreviation: SW: seawater, DI: distilled water, Poz.: Pozzolana , Stir.: Stirring, P: initial pressure of gas in reactor, T_{in} : induction time, M_{gc}: gas consumption

*All values were calculated after 1.5 hour from induction time.

Minimum reactor temperature range 1.0 +/- 0.5^{0}C

3.1 Effect of water salinity

The presence of sodium chloride highly affects the thermodynamics phase equilibrium pressure and temperature negatively as well as the kinetic of the process. The patterns of water recovery and gas consumption with the change of feed salinity and additives type are demonstrated in Fig. 2 and Fig. 3, respectively.At a gas pressure of 20 bar in experiment 1 and 2, the gas consumption is reduced from 0.0021 mol in the distilled water to 0.0001 in the seawater. This reduction is explained only by the higher concentration of salt in seawater. Also, the water recovery in the distilled water is 18.5 times the water recovery in the seawater experiment.

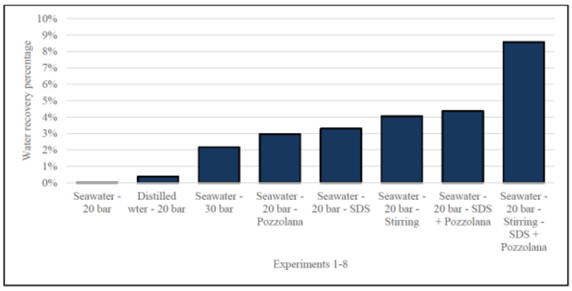

Fig. 2 Water recovery percentage for eachexperiment

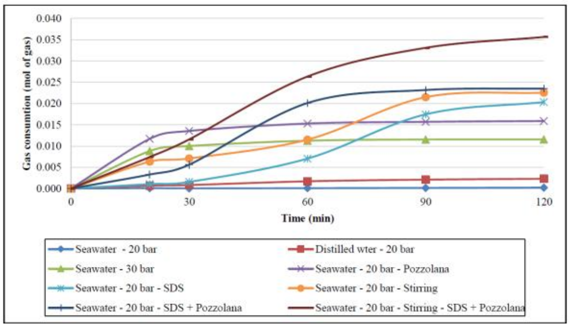

Fig. 3 Pattern of gas consumption during two hours after induction time

3.2 Effect of gas pressure

Gas pressure and temperature are the main thermodynamics parameters which induce gas hydrate formation in the water gas system. Enhancing the thermodynamics phase equilibrium by increasing the pressure will improve the efficiency of the gas hydration process. Experiments 1 and 3 were conducted with the same parameters except for increasing the pressure from 20 to 30 bar. Increasing the pressure reduced the induction time of the process by 25% as well as it improves the gas consumption of the gas hydrate formation from 0.0001 to 0.0115 mol of gas. Even though the increase in pressure highly improves the gas hydrate parameters, however the cost of the gas hydrate formation system will increase due to requirements of high rigidity of the system and more energy use for compressing the gas to a higher pressure.

3.3 Effect of additives (heat absorbents and surfactants)

When no hydrate promoter additive is used, as in experiment 1, a solid layer of gas hydrate was formed on the top surface of the solution which prevents the direct contact between gas and water liquid phase thus no more hydrate formation can occur. The characteristic pressure and temperature profilesfor this case show only a single hydrate nucleation (Fig. 4).

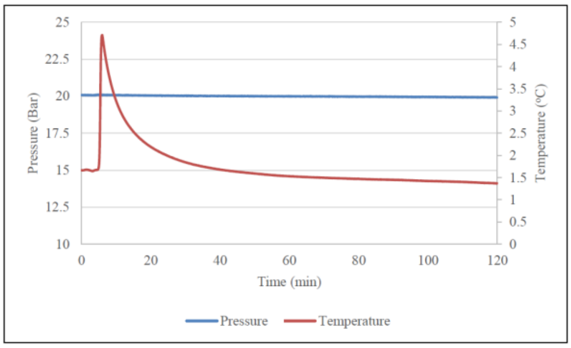

Fig4. Pressure and temperature profile for a single hydrate nucleation in experiment 1

However, the presence of additives in the solution brings about changes in the kinetics and thermodynamics features of the hydrate formation process. The cooling distribution from the reactor wall to the bulk of solution and the dissipation of the gas hydration exothermic heat are directly related to the gas hydration formation process. Adding the natural pozzolana that contains 71% wt. silicon dioxide, 13.7% wt. Aluminum oxide and 1% wt. of ferric oxide to seawater (Exp. 4) increased the gas hydration by 156 times compared to experiment 1. As indicated in Fig. 5, the gas hydrate formation in the presence of natural pozzolana happened in multiple nucleates due to breaking the thin gas hydrate layer that formed on the gas-solution surface contact area. It has been observed visually that gas hydrate formed took the shape of non-identical crystals within the bulk of solution and a thin gas hydrate layer on the top surface of the solution that could not be broken due to weak action of the magnetic bar.

The thin gas hydrate layer can be weakened and easily removed by surfactants such as SDS. SDS gives the liquid solution the texture of bubbly and soapy solution. The bubbles help in increasing the contact surface area between the gas and the liquid. Gas consumption in experiment 1 and 5 were 0.0001 and 0.0175. All parameters in these experiments were the same except for the presence of SDS in experiment 5. SDS can improved by 174 times compared to the gas hydrate formation in the absence of the surfactant. The fact that formed gas hydrate layer is a significant barrier to further development of gas hydrate process is reported by many researchers [16].

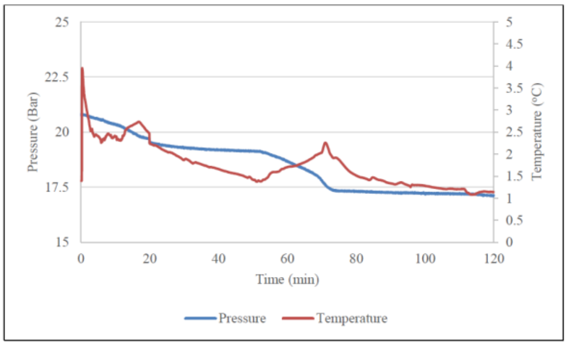

Fig. 5 Pressure and temperature profile for multinucleation in the presence of pozzolana in experiment 4

3.4 Effect of stirring

The negative effect of the formed thin hydrate layer on the top of the solution can be avoided by stirring the liquid solution inside the reactor by a magnetic bar that rotates at 600 rpm which prevents the development and breaks the gas hydrate layer. Also, stirring the liquid solution helps in cooling distribution inside the reactor. Comparing experiment 1 (no stirring) with experiment 6 (with stirring), the gas consumption increased from 0.0001 to 0.0215 mol, respectively due to the stirring alone.

3.5 Synergetic effect of promoters

When SDS and the natural pozzolana were added altogether in one run (Experiment 8) a synergetic effect was observed. As expected, the combination of the two promoters resulted in better water recovery percentage and gas consumption compared to cases when they were used alone. The stirring of the mixed promoters in experiment 8 resulted in a water recovery of around 9%. This value is the highest water recovery percentage comparing to all other experiments.

IV. CONCLUSION

In this study, the gas hydrate formation process efficiency was evaluated using carbon dioxide as guest gas and kinetic promoters. The formation of the gas hydrate without promoters with the carbon dioxide gas was found fragile and it results in insignificant water recovery. By the addition of natural pozzolana nanoparticles in seawater solution enhanced gas consumption by improving the cooling distribution and heat dissipation. Natural pozzolana can be easily separated from the produced water, and it is non-hazardous material. Sodium dodecyl sulfate (SDS) had a significant increase in the water recovery by more than 116 times compared with non SDS experiments. Stirring leads to breakage the thin hydrate layers formed at the solution surface and improves the heat dissipation in the gas hydrate formation. Besides, stirring is a very efficient method compared to kinetic additives since gas hydrate produced with stirring is free of additives and will not need further separation process. With the combination of natural pozzolana and SDS in a stirred reactor a value of 9% water recovery was obtained. Natural pozzolana is a low-cost promoter that can be used to enhance gas hydrate formation process significantly. Since the natural pozzolana minerals are not similar in its chemical properties, further studies should be conducted to compare the effects of different natural pozzolanas as a kinetic promoter and evaluate suitable methods for separation of the natural pozzolana from the produced fresh water.

ACKNOWLEDGMENT

This project was funded by the National Plan for Science, Technology and Innovation (MAARIFAH) – King Abdulaziz City for Science and Technology – the Kingdom of Saudi Arabia –

award number (11-WAT2007-03). The authors also thank Science and Technology Unit, King Abdulaziz University for technical support.

REFERENCES

[1] M. Rasheeduddin, W. A. Abderrahman, and J. W. Lloyd,Management of Groundwater Resources in Eastern Saudi Arabia, *International Journal of Water Resources Development, 17(2)*, 2001, 185–210, 2001.

[2] A. A. Ghanim, Water Resources Crisis in Saudi Arabia, Challenges and Possible Management Options: An Analytic Review, *International Scholarly and Scientific Research & Innovation 13(2)*, 2019, 51-56.

[3] K.A. Rambo, D. M. Warsinger, S.J. Shanbhogue, V.J.H. Lienhard and A.F. Ghoniem, Water-Energy Nexus in Saudi Arabia. *Energy Procedia, 105*, 2017, 3837–3843.

[4] B. D. Negewo, Renewable energy desalination: an emerging solution to close the water gap in the Middle East and North Africa. Washington, DC: World Bank, 2012.

[5] A. Demirbas, A. A. Hashem and A. A. Bakhsh, The cost analysis of electric power generation in Saudi Arabia, *Energy Sources, Part B: Economics, Planning, and Policy, 12(6)*, 2017, 591-596

[6] P. Mekala, P. Babu, J. S. Sangwai, and P. Linga, Formation and Dissociation Kinetics of Methane Hydrates in Seawater and Silica Sand, Energy & *Fuels, 28(4)*, 2014, 2708–2716.

[7] D. Khawaji, I. K. Kutubkhanah, and J.-M. Wie, Advances in seawater desalination technologies, *Desalination, 221(1-3)*, 2008, 47–69.

[8] Al-Karaghouli and L. L. Kazmerski, Energy consumption and water production cost of conventional and renewable-energy-powered desalination processes, *Renewable and Sustainable Energy Reviews, 24*, 2013, 343–356.

[9] M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas, and A. M. Mayes, Science and technology for water purification in the coming decades, *Nature, 452(7185)*, 2008.

[10] E. T. Igunnu and G. Z. Chen, Produced water treatment technologies, *International Journal of Low-Carbon Technologies, 9(3)*, 2012, 157–177.

[11] K. C. Kang, S. Y. Hong, S. J. Cho, D. H. Kim, and J. D. Lee, Evaluation of Desalination by Nanostructured Hydrate Formation and Pellet Production Process, *Journal of Nanoscience and Nanotechnology, 17(6)*, 2017, 4059–4062.

[12] E. D. Sloan and C. A. Koh, Clathrate hydrates of natural gases. Boca Raton, FL: CRC, 2008.

[13] T. He, S. K. Nair, P. Babu, P. Linga, and I. A. Karimi, A novel conceptual design of hydrate based desalination (HyDesal) process by utilizing LNG cold energy, *Applied Energy, (222)*, 2018,13–24.

[14] H. Hashemi, S. Babaee, K. Tumba, A. H. Mohammadi, P. Naidoo, and D. Ramjugernath, Experimental study and modeling of the kinetics of gas hydrate formation for acetylene, ethylene, propane and propylene in the presence and absence of SDS, *Petroleum Science and Technology, 37(5)*, 2019, 506–512.

[15] P. Babu, T. Yang, H. P. Veluswamy, R. Kumar, and P. Linga, Hydrate phase equilibrium of ternary gas mixtures containing carbon dioxide, hydrogen and propane,*The Journal of Chemical Thermodynamics, 61*, 2013, 58–63.

[16] Nambiar, P. Babu, and P. Linga, Improved Kinetics and Water Recovery with Propane as Co-Guest Gas on the Hydrate-Based Desalination (HyDesal) Process, *ChemEngineering, 3(1)*, 2019, 31.

[17] S. H. Yang, P. Babu, S. F. Chua, and P. Linga, Carbon dioxide hydrate kinetics in porous media with and without salts, *Applied Energy, 162*, 2016, 1131–1140.

[18] 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, 35*, 2016, 1499–1510.

[19] P. Thoutam, S. Rezaei Gomari, A. Chapoy, F. Ahmad, and M. Islam, Study on CO2 hydrate formation kinetics in saline water in the presence of low concentrations of CH4, *ACS Omega, 4(19)*, 2019, 18210–18218.

[20] J. Tang, D. Zeng, C. Wang, Y. Chen, L. He, and N. Cai, Study on the influence of SDS and THF on hydrate-based gas separation performance, *Chemical Engineering Research and Design, 91(9)*, 2013, 1777–1782.

[21] S. Said, V. Govindaraj, J.-M. Herri, Y. Ouabbas, M. Khodja, M. Belloum, J. S. Sangwai, and R. Nagarajan, A study on the influence of nanofluids on gas hydrate formation kinetics and their potential: Application to the CO 2 capture process, *Journal of Natural Gas Science and Engineering, 32*, 2016, 95–108.

[22] T. Uchida, Physical property measurements on CO2 clathrate hydrates. Review of crystallography, hydration number, and mechanical properties, *Waste Management*, *17(5-6)*, 1998, 343–352.

Omar Tallab, et. al. "Effect of Natural Pozzolana and Sodium Dodecyl Sulfate on Clathrate Hydrate Formation Kinetics with CO2 as a Guest-Gas." *International Journal of Engineering Research and Applications (IJERA)*, vol.11 (5), 2021, pp 47-53.