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Methane Gas Hydrate Formation by Using Sodium Dodecyl Sulfate Additives

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Abstract

Gas Hydrates (G. Hyd) such as methane (CH_4) hydrates are forming of water molecules in ice-like crystals (lattice shape) with cavities where the methane gas (gust gas) molecules are engaged in, and this process is conducted in a certain condition, mainly in low temperature and high pressure. The objective of the current work is to study the effect of Sodium Dodecyl Sulfate (SDS) additives on Methane gas hydrate performance. Two solutions were prepared. The first solution consists of distilled water (100 ml), methane gas and SDS additives (0.10 g). The second solution consists of same ingredient with seawater (100 ml) instead of distilled water. A stirred tank with 750 psi has been utilized. The highest recovery ratio was 42.15% for distilled water using SDS additives with a pressure cycle duration of 120 minutes. Significant improvement in the hydrate water recovery ratio can be obtained with distilled water and seawater by about 42 % and 15.6% respectively. Generally, SDS additives improve the recovery rate for water in the presence of methane.

Keywords: Hydrate; Gas hydrate; hydrate additives; Guest Gas CH4; seawater desalination.

1. Introduction

The growth in population and pure water demand forced the researchers to find pure water scarcity worldwide. Generally, water scarcity negatively affects all human sources such as food, industry and energy, which are essential for human living. It is crucial to find proper solutions to overcome the challenges of water shortage. However, several water-based systems have become stressed based on water scarcity.

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In Saudi Arabia, more than 60% for the locale demand is provided through desalination plants with an average production of 10 million m^3/day. The continuous development in the saline water desalination sector is expected to reach 60 million m^3/day by 2050 [1]. Based on some environmental constrains and related regulation. Therefore, few desalination technologies such as membrane distillation (MD) and gas hydrate desalination (G. Hyd) have been interesting to recent researchers. This fact is due to their limited impact on the environment, [2 – 4]. Gas hydrates (clathrate) are crystalline ice-like solids made of the water (host) and the gas molecules (guest) such as methane, carbon dioxide, nitrogen, etc., which are held within water cavities that are composed of hydrogen-bonded water molecules. The gas hydrate process has been applied in various engineering fields, such as gas separation, carbon dioxide sequestration, gas storage and transportation, energy source, refrigeration, and desalination. During gas hydrate formation, water molecules effectively separate themselves from brine solution leaving slats behind. After that, when hydrate crystals are melted, guest gas is released, reused again in the hydrate desalination process. One mole of hydrate consists of about 85% water and 15% guest gas [5]. They are known to occur naturally in the earth. Potential reserves of natural gas hydrates are over 1.5 million tons and are distributed worldwide, in the Arctic on land and offshore. In nature, over 90% of gas hydrate exists in permafrost regions and marine sediments. Figure 1 shows gas hydrate formation in nature.

Figure 1: Gas hydrate formation in nature.

Gas Hydrate (G. Hyd) is a crystallization process (non-stoichiometric) which mainly performs based on heat and mass transfer lows. In Natural life, gas hydrate (G. Hyd) is formed in marine sediments at the sides of the continentals and in ice lands such as the Polar Regions. It is a crystalline formation in the solid phase of between molecules of two substances; water and another gas (guest gas) to be inserted in water molecules cavities. The crystalline is performed through hydrogen bonds for both water and the gas under certain pressure and temperature. Several gases can be used in the hydrate formation process, such as methane, carbon dioxide, methane and organic compounds [6]. It is always preferred to conduct the desalination process under atmospheric pressure to minimize the extra cost of energy; however, higher pressure can be performed to obtain faster results to increase the hydrate formation rate. Moreover, vacuum pressure with membrane can provide practical support for salt removals from seawater, such as vacuum distillation technology [7]. Since seawater desalination by gas hydrate is a continuous process, and for using pure water as a thermodynamic inhibitor with salt, the phase equilibrium curve for hydrate formation shifts the operation condition to sever pressure and temperature. High pressure and low temperature are required for the process; therefore, operation conditions need careful attention. An experimental investigation has been conducted for seawater desalination (3.03 wt% seawater) by methane hydrates and silica sand bed at pressure up to 10 MPa and 277 K, and the study showed low hydrate formation rate [8]. It was reported that methane hydrate could increase the storage capacity. A single volume of methane hydrate can store around 180 volumes of methane in the gas phase [9]. Thermodynamic promoters are additives utilized to perform hydrate formation by in easier operation conditions and mainly by low pressure and higher temperature to minimize the operation cost. Therefore, the selection of thermodynamic promoters is subjected to forming hydrate in moderate conditions. Thermodynamic promoters are mainly affecting the phase changes, they fill the large spaces in hydrate structure cages, and the gas fills the small cages. Therefore, they enable the hydrate formed in milder condition and easily achievable; low pressure and high temperature [6]. Cyclopentane can form hydrate with water at atmospheric pressure. However, cyclopentane hydrate (CPH) capability to be formed under mild condition makes potentials to utilize it for seawater desalination. Tetrahydrofuran (THF) has a remarkable influence in hydrate formation kinetics with methane under pressure close to atmospheric pressure and temperature close to $0^{o}C$ [6]. The summary of the previous literature is presented in Table 1. However, as indicated in the table, adding additives enhances the hydrate formation, the process become environmentally friendly and decrease the induction time. Moreover, the storage capacity has been increased by more than 170V/V. In addition, the complete process for hydrate formation become more economically feasible. All these features make the technology more attractive.

Table 1: Summary of using bio-based additives in the previous studies.

Bio-Based Additive Condition	Finding	Reference
Amino acid, 0.5wt% l-lecucine	Increases methane hydrate formation.	[14]
Amino acid, 1wt% l-histidine	Increases methane hydrate formation and showed similar results to SDS with the same ratio.	[15]
Three amino acids (tryptophan, histidine, arginine)	Tryptophan showed higher kinetic promoter with methane	[16]
Bio-based surfactants, Natural oils (coconut, jatropha, castor, palm)	Good performance, economically feasible, low toxicity, environmentally friendly	[17]
Bio-surfactant by-product	Increase in hydrate formation from 96% to 288% and decrease in induction time from 20% to 71%.	[19]
Bio-surfactant, castor oil with a concentration of 9000 ppm	Increases methane hydrate formation. Enhance storage capacity to 172V/V, and decrease in induction time to 12 min.	[20]
Bio-surfactant, methyl ester sulfonate (MES) from palm oil	Low toxicity, good properties and low cost	[21]

Adding Surfactants to methane has been investigated by Ganji [10], to improve the surface tension between methane and water to promote the hydrate formation process. In these experiments, it was observed that the highest hydrate formation limit with the stable rate was obtained by adding sodium dodecyl sulfate (SDS). Others have investigated the relationship between the chain length and hydrate formation [11], and it was concluded that the additives with long alkyl chain length have low solubility for gas which led to limited changes in the rate of hydrate formation. Others have investigated adding SDS to methane [12]. It was reported that adding 650 ppm form SDS increases the storage capacity up to 170 volume per one methane volume. Moreover, others [13] reveled that adding 770 ppm form SDS increases hydrate formation capacity. However, Surfactants has been reported to have some negative impacts on the environmental. Others have proposed using bio-based additives such as Amino acids and bio-based surfactants to overcome the environmental concerns from pure surfactants. The amino acid has shown promising results with methane hydrates formation [14]. In quiescent water, it showed flexibility to induce methane expansion in the solution, which eventually enhances the hydrate formation rate. In addition, amino acid prevents foam existence during the recovery process of the gas. Linga [22] indicated that significantly higher formation rates for the gas mixtures containing a pressure up to 46 bar could be performed. Babu [23] reveled a significantly higher rate of hydrate formation can be attributed due to the presence of propane. Deugd and his colleagues [24] reported that a higher rate of formation could be obtained at 50 bar in the case of using methane gas mixture. In the current work, an experimental study will be implemented in Center of Excellence in Desalination Technology (CEDT) in King Abdulaziz University (KAU) which equipped with lab prototype system and the required equipment to perform the experimental works. However, this work investigates some options for improving the gas hydrate formation rate during seawater desalination. The main research objectives are to assess the performance of gas hydrate formation SDS additives.

2. Materials and Method

2.1 Materials

A 1760 ml stainless-steel reactor was used in the current investigation and consisted of acrylic glass windows to allow visual observation while conducting the experiments. A gas pipeline was installed from gas cylinder to (gas inlet) the reactor. 0.10 g of SDS additive was utilized and mixt with the solution. Methane (CH4), distilled water and seawater (38000 mg/l) was used. Figure 2 shows a photo of the experimental setup.

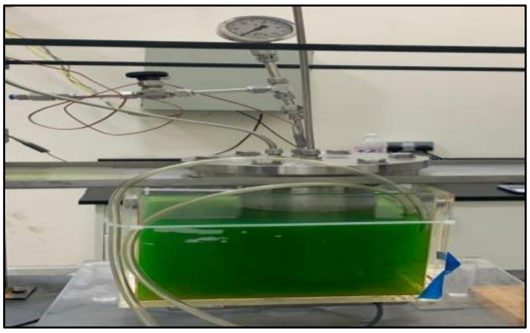


Figure 2: Experimental setup.

2.1 Experimental parameters

The below table illustrates the parameters of the experimental investigations.

Table 2: Parameters of the study

Parameters	**Name**
Solutions	• Distilled Water • Sea Water
Gas	Methane CH_4
Durations	2 (Hr)
Gas Pressures	750 (PSI)
Additives	• (SDS) sodium dodecyl sulfate
Stirring	600 (RPM)
Temperature	2 (^oC)

A total of 4 experimental runs have planned to determine the effect of pressurization step period, concentration and type of additives and water sample type on the amount of hydrate formed. The number of moles of methane gas released from hydrate dissociation can be found by using the following formula [25].

$$(\Delta n_{H\uparrow}) = V_R\left(\frac{P}{zRT}\right)_t - V_R\left(\frac{P}{zRT}\right)_0 \quad \text{moles} \qquad (1)$$

Where $\Delta n_{H\uparrow}$ amount of methane gas consumed, V_R reactor volume, P and T are the pressure and temperature of the reactor at any time, z is the compressibility factor calculated by Pitzer's correlations, and R is the universal gas constant. Hydrate Water recovery ratio (Hydrate yield) was calculated by Eq (2) [26].

$$\text{Hydrate Water recovery (\%)} = \frac{\Delta n_{H\uparrow} \times \text{Hydrate Rate}}{\Delta n_{H2O}} \times 100 \qquad (2)$$

3. Results and Discussions

The stirred tank (600 RPM) was set up to investigate the effect of SDS additive on Methane hydrate formation. Table 4 summarizes the experiments and presents the induction time for hydrate formation, the gas uptake, the volume of water to hydrate, the percentage of water recovery and the final gas consumption which are the indicator of hydrate growth. The SDS additive was added to freshwater samples by 1% of the total volume. As shown in the table, the induction times were between 9.4 and 28.20 min. Distilled water samples have almost typical induction time (between 9.4 and 9.9 min). However, the induction time has been improved by 1% with SDS additive. Seawater samples showed similar improvement in terms of induction time with additives. The induction time was enhanced by 73% with SDS. The gas uptake has been increased with additives. Figure 3 shows the changes in gas uptakes for 120 min for all experiments.

Table 4: Summary of the experiments

Exp. No.	System	Sample State	Driving Force (PSI)	Pressure (PSI)	Induction Time (min)	Gas Uptake (mol)	Volume H2O to Hyd (ml)	Water Recovery (%)	Final Gas Consumption (mol of Gas / mol of H2O)
1	Distilled Water	Fresh	25	750	9.90	0.4492	48.55	37.27 %	0.0622
2	Distilled water with SDS 0.10 g	Fresh	25	750	9.40	0.5079	54.90	42.15 %	0.0703
3	Seawater	Fresh	25	750	28.20	0.0462	5.25	4.01%	0.0064
4	Seawater with SDS 0.10 g	Fresh	25	750	16.30	0.1782	20.22	15.63 %	0.0247

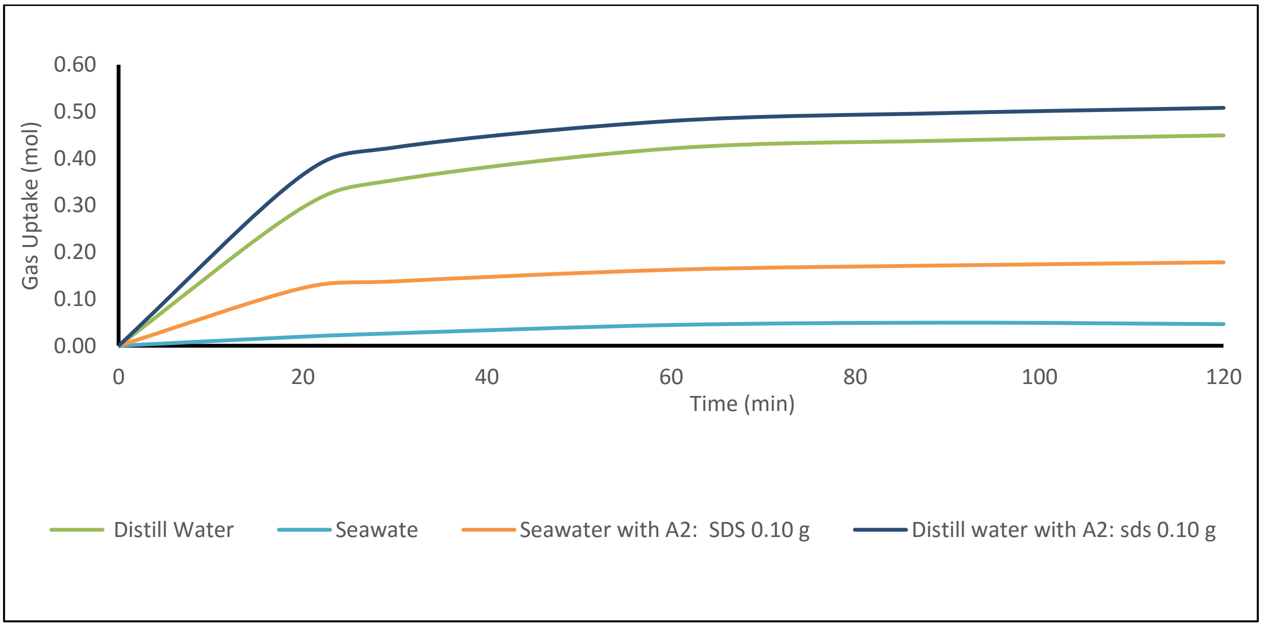
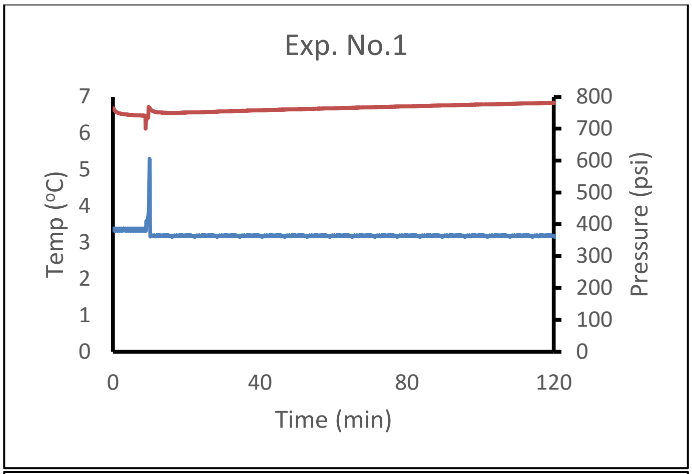
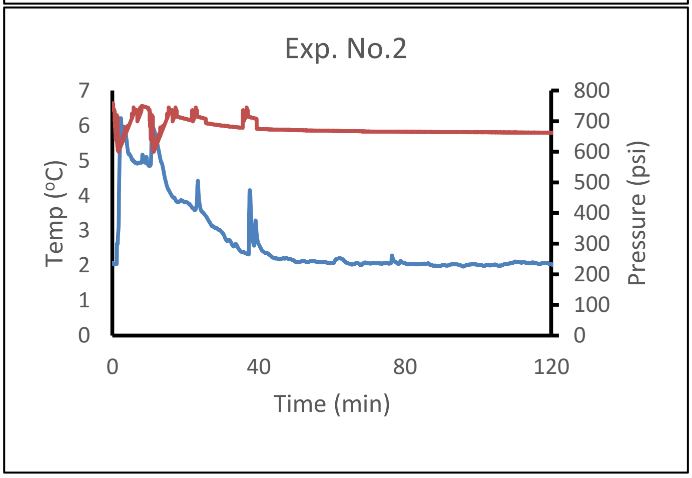


Figure 3: Gas uptake for all Experiments

The hydrate behavior and growth can be explained by temperature and pressure profile as shown in Figure 4. The temperature and pressure profile were detected by using thermocouple and pressure sensors respectively. As shown in the figure for Exp. No.1 for distilled water, a peak was observed at 9.90 min, and the temperature was increased up to 5.2°C. However, the temperature spike has been performed due to hydrate nucleation and releasing exothermic heat. The pressure drops to 705 PSI at this point, and then the set experimental temperature was reached after 10 min. The temperature profile for SDS (Exp. No.2) illustrates several peaks during the first quarter of the period, indicating the system is releasing more exothermic heat, which can be validated with the gas uptake calculation for this system (0.579 mol). In Exp. No. 3, the first peak was observed at 28.20 min, the temperature was increased up to 4.4°C. The pressure drops to 600 PSI at this point, and then the set experimental temperature was reached after 30 min. In Exp. No. 4 with SDS additive, the first peak was observed at 16.30 min, which was slower than isopentane. The temperature was increased up to 3.8°C, and the pressure drops to 739 PSI at this point, then the set experimental temperature was reached after 51 min. The water recovery and final gas consumption reached 15.63% and 0.0.0247 mol respectively. The highest was 42.15% from Exp. No.2 for distilled water using SDS additives with a pressure cycle duration of 120 minutes. Therefore, adding SDS additives, significant improvement in the hydrate water recovery ratio can be obtained with distilled and seawater by about 42 % and 15.6% respectively, and higher hydrate yields can be observed.





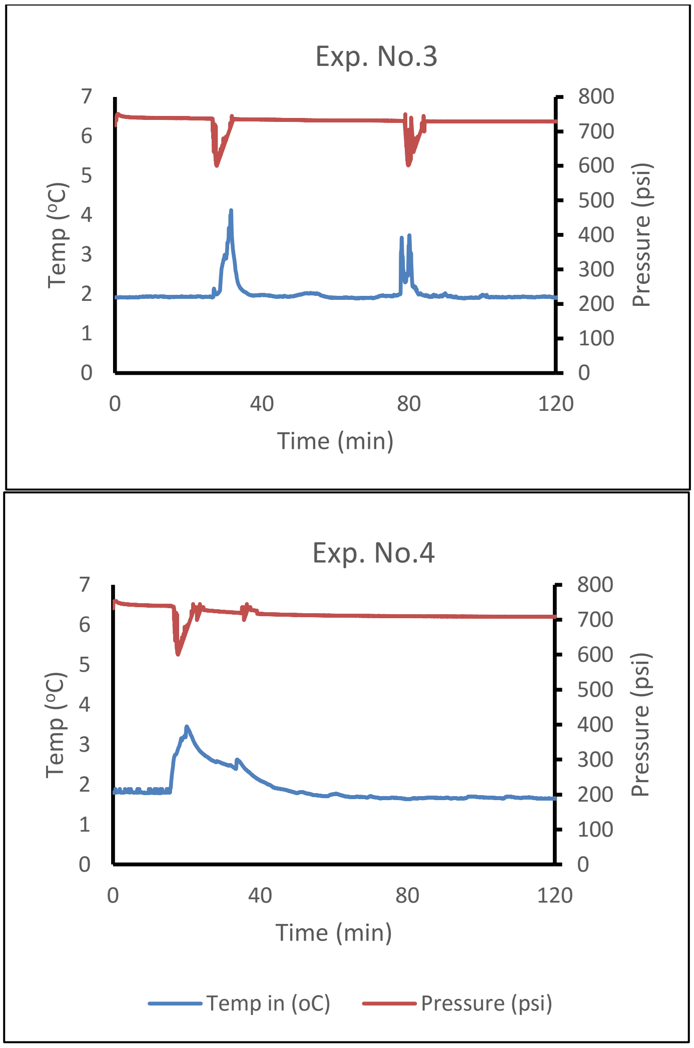


Figure 4: Temperature and pressure profiles.

4. Conclusion

This work investigates some options for improving the gas hydrate formation rate. The main research objectives are to investigate the performance of SDS additives in a stirred tank. It was concluded that SDS additives improve the recovery rate for water in the presence of methane, thus enhance the hydrate formation process.

5. Recommendation

Additional factors can be considered to enhance the hydrate formation process such as improving the heat and mass transfer mechanism and overcomes the thermal resistance through modifying the reactor tank design. Also the process cycle needs to be demonstrated on large scale and employing a series of fixed reactors.

6. Nomenclature

Symbol	Description
$\Delta n_{H\uparrow}$	The amount of methane gas consumed
V_R	The reactor volume
P	The pressure of the reactor at any time
T	The temperature of the reactor at any time
z	The compressibility factor
R	The universal gas constant.
ρ	The density of the gas

References

[1]. U. Caldera, D. Bogdanov, S. Afanasyeva, C. Breyer, Role of Seawater Desalination in the Management of an Integrated Water and 100% Renewable Energy Based Power Sector in Saudi Arabia, Water. 10 (2017) 3, https://doi.org/10.3390/ w10010003.

[2]. Bartolomé Ortega-Delgado, Matteo Cornali, Patricia Palenzuela, Diego C. Alarcón-Padilla. Operational analysis of the coupling between a multi-effect distillation unit with thermal vapor compression and a Rankine cycle power block using variable nozzle thermocompressors. Applied Energy 204 (2017) 690–701.

[3]. Chong Wei Ong, Cheng-Liang Chen. Technical and economic evaluation of seawater freezing desalination using liquefied natural gas. Energy 181 (2019) 429-439.

[4]. Syed M. Zubair, Mohamed A. Antar, Samih M. Elmutasim, Dahiru U. Lawal. Performance evaluation of humidification-dehumidification (HDH) desalination systems with and without heat recovery options: An experimental and theoretical investigation. Desalination 436 (2018) 161–175.

[5]. Abhishek Nambiar, Ponnivalavan Babu, Praveen Linga. Improved Kinetics and Water Recovery with Propane as Co-Guest Gas on the Hydrate-Based Desalination (HyDesal) Process. ChemEngineering 2019, 3, 31; doi:10.3390/chem engineering 3010031.

[6]. Veluswamy HP, Kumar S, Kumar R, Rangsunvigit P, Linga P. Enhanced clathrate hydrate formation kinetics at near ambient temperatures and moderate pressures: application to natural gas storage. Fuel 2016;182:907–19.

[7]. T.J. Itsuno, K.H. Amabe, Vacuum distillation system aiming to use solar-heat for desalination, J. Arid L. Stud. 155 (2012) 153–155.

[8]. Mekala P, Babu P, Sangwai JS, Linga P. Formation and dissociation kinetics of methane hydrates in seawater and silica sand. Energy Fuels 2014;28:2708–16.

[9]. Sloan Jr. ED. Fundamental principles and applications of natural gas hydrates. Nature 2003;426:353.

[10]. Ganji, H., Manteghian, M., Sadaghiani Zadeh, K., Omidkhah, M.R., Rahimi Mofrad, H., 2007. Effect of different surfactants on methane hydrate formation rate, stability and storage capacity. Fuel 86, 434–441.

[11]. Okutani, K., Kuwabara, Y., Mori, Y.H., 2008. Surfactant effects on hydrate formation in an unstirred gas/liquid system: an experimental study using methane and sodium alkyl sulfates. Chem. Eng. Sci. 63,

183–194.

[12]. Lin, W., Chen, G.J., Sun, C.Y., Guo, X.Q., Wu, Z.K., Liang, M.Y., Chen, L.T., Yang, L.Y., 2004. Effect of surfactant on the formation and dissociation kinetic behavior of methane hydrate. Chem. Eng. Sci. 59, 4449–4455.

[13]. Zhang, J.S., Lee, S., Lee, J.W., 2007. Does SDS micellize under methane hydrate-forming conditions below the normal Krafft point? J. Colloid Interface Sci. 315, 313–318.

[14]. Liu, Y., Chen, B., Chen, Y., Zhang, S., Guo, W., Cai, Y., Tan, B., Wang, W., 2015. Methane storage in a hydrated form as promoted by leucines for possible application to natural gas transportation and storage. Energy Technol. 3, 815–819.

[15]. Bhattacharjee, G., Choudhary, N., Kumar, A., Chakrabarty, S., Kumar, R., 2016. Effect of the amino acid l-histidine on methane hydrate growth kinetics. J. Nat. Gas Sci. Eng. 35, 1453–1462.

[16]. Veluswamy, H.P., Lee, P.Y., Premasinghe, K., Linga, P., 2017. Effect of biofriendly amino acids on the kinetics of methane hydrate formation and dissociation. Ind. Eng. Chem. Res. 56, 6145–6154.

[17]. Babu, K., Maurya, N., Mandal, A., Saxena, V., 2015. Synthesis and characterization of sodium methyl ester sulfonate for chemically-enhanced oil recovery. Braz. J. Chem. Eng. 32, 795–803.

[18]. Kumar, S., Kumar, A., Mandal, A., 2017. Characterizations of surfactant synthesized from Jatropha oil and its application in enhanced oil recovery. AIChE J. 63, 2731–2741.

[19]. Rogers, R.E., Kothapalli, C., Lee, M.S., Woolsey, J.R., 2003. Catalysis of gas hydrates by biosurfactants in seawater-saturated sand/clay. Can. J. Chem. Eng. 81, 973–980.

[20]. Chaturvedi, E., Prasad, N., Mandal, A., 2018. Enhanced formation of methane hydrate using a novel synthesized anionic surfactant for application in storage and transportation of natural gas. J. Nat. Gas Sci. Eng. 56, 246–257.

[21]. Tobori, N., Kakui, T., 2019. Chapter 9 - methyl ester sulfonate. In: Hayes, D.G., Solaiman, D.K.Y., Ashby, R.D. (Eds.), Biobased Surfactants, second ed. AOCS Press, pp. 303–324.

[22]. Linga, P.,Daraboina,N.,Ripmeester,J.A.,Englezos,P.,2012.Enhancedrateofgas hydrate formation in a fixed bed column filled with sand compared to a stirred vessel. Chem.Eng.Sci.68,617–623.

[23]. Babu Pa., RajnishKumar, PraveenLinga Unusual behavior of propane as a co-guest during hydrate formation in silica sand: Potential application to seawater desalination and carbon dioxide capture /ChemicalEngineeringScience117(2014)342–351.

[24]. R. De Deugd, M. Jager, J. de Swaan Arons, Mixed hydrates of methane and water-soluble hydrocarbons modeling of empirical results, AIChE J. 47 (2001) 693–704.

[25]. Babu, P., Kumar R., Linga, P. ,2013. Medium pressure hydrate based gas separation (HBGS) process for pre-combustion capture of carbon dioxide employing a novel fixedbedreactor.Int.J.Greenh.GasControl17,206–214.

[26]. Veluswamy HP, Kumar S, Kumar R, Rangsunvigit P, Linga P. Enhanced clathrate hydrate formation kinetics at near ambient temperatures and moderate pressures: application to natural gas storage. Fuel 2016;182:907–19.