KINETIC ANALYSIS OF CO_2 GAS HYDRATES BY THE USE OF THREE DIFFERENT IMPELLERS

S.N. Longinos[1,3,*], D.D. Longinou[2], F. Gogus[3], M. Parlaktuna[3]

[1]School of Mining & Geosciences, Nazarbayev University, Astana, Kazakhstan

[2]Economics & Sustainable Development Department, Harokopio University, Athens, Greece

[3]Petroleum & Natural Gas Engineering Department, Middle East Technical University, Ankara, Turkey

(*sotirios.longinos@nu.esu.kz)

ABSTRACT

Gas hydrates are crystalline compounds formed from water and suitable-sized gas molecules. Depending on which gas molecules are present, crystals are divided into three distinct structures. Structure I (sI), structure II (sII), and structure H (sH) are the three gas hydrate structures. Contingent implementation for CO_2 is for gas storage. Hence to apprehend thoroughly the use of CO_2 gas hydrates for gas storage or greenhouse gas sequestration, it is crucial to study the kinetics of CO_2 hydrate formation. The aim of this work is the kinetic analysis of CO_2 gas hydrates by the use of three different flow regimes. This study aims to analyze the CO_2 hydrate formation kinetics by using a novel experimental set-up equipped with a continuous stirred tank reactor (CSTR) having a diameter of 15 cm and a height of 31.2 cm. CO_2 gas hydrates were formed at a constant temperature of 5 °C and pressure between 32.5 and 33 bars. Mixing conditions were changed by using three different types of impellers such as pitched blade turbine-downward trending (PBT-d), Rushton turbine (RT), and marine propeller (MP) with full baffles hence to include three different flow regimes and different numbers of impellers such as single and dual. Kinetic analysis of the six experiments comprises the calculations of rate growth, induction time, driving force, and power consumption. The hydrate formation rate was calculated with an interval of 30 minutes showing that for both single and dual impellers, RT has the highest rate of growth (RT> PBT-d > MP, for single) (RT > PBT-d > MP, for dual). Pitched blade turbines in both single and dual impellers had the highest values in power consumption but they also had the highest amount of water which was converted to hydrates. Induction time for both single and dual impeller experiments was smaller than 2 minutes.

KEYWORDS: Gas hydrates, Kinetics, Carbon dioxide

INTRODUCTION

Gas hydrates are crystalline compounds formed from water and suitable-sized gas molecules. Depending on which gas molecules are present, crystals are divided into three distinct structures. Structure I (sI), structure II (sII), and structure H (sH) are the three gas hydrate structures [1-3]. The structure I hydrate has two types of cavities: a small pentagonal dodecahedral cavity consisting of 12 pentagonal rings of water and a large tetrahedral cavity consisting of 12 pentagonal and two hexagonal rings of water. Structure II hydrate also has two cavity sizes, the pentagonal dodecahedral cavity, and the larger hexakaidecahedral cavity consisting of 12 pentagonal and four hexagonal rings of water, and structure H comprises 34 water molecules per unit cell arranged in three pentagonal dodecahedral voids, 2 irregular dodecahedral voids, and 1 icosahedral void [4-6]. Methane hydrates can contain 150-180 v/v (standard temperature and pressure) hence, researchers became interested in examining the storage, transportation, and kinetics of gas hydrates. Gudmundsson and Parlaktuna firstly and several scientists have reported outcomes in this field [1,7-10]. Hydrates are found both in permafrost areas as well as in oceans and represent huge untapped natural sources

[11-13]. One of the methods for recovering in situ hydrates comprises the displacing of the trapped methane with CO_2 [14,15]. Another contingent implementation for CO_2 is that for gas storage [16]. Hence to apprehend thoroughly the use of CO_2 gas hydrates for gas storage or greenhouse gas sequestration, it is crucial to study the kinetics of CO_2 hydrate formation. The aim of this work is the kinetic analysis of CO_2 gas hydrates by the use of three different flow regimes.

EXPERIMENTAL SECTION

A new reactor with an internal volume of 5.7 l has been designed and built to carry out studies on the scale-up of gas hydrate formation. It consists of a high-pressure cylindrical AISI 316 L stainless steel vessel with an internal diameter of 15cm and an internal length of 312mm. To avoid friction heat due to the rotational speed of impellers, cooling water is circulated in the shaft of the motor. The flow rate of a refrigerated cooling bath (WCL-P12) is 12 l/min. The temperature of the Refrigerated Cooling Bath was measured by a thermocouple inside of the bath. The five ports (3 on the flange and two on the body of the reactor) are used for supplying gas and measuring temperature and pressure. Gas is supplied by gas bottles through a pressure-reducing valve that provides adjustment of the pressure to the gas injection line. Mixing is supplied by a servomotor type of High Inertia (permanent-magnet synchronous motor Siemens model SIMOTICS S-1FL6. Voltage signals from pressure transducers, temperature sensors, and torque values for every second are collected by a PLC unit (software) for data acquisition on a personal computer. Figure 1 shows the carbon dioxide hydrate formation reactor with the control unit and cooling bath.

Figure 1. *Carbon dioxide hydrate formation reactor connected with control unit (left) and cooling bath (right)*

The experimental process is as follows: the gas (carbon dioxide) is injected through a steel tube into the reactor which is already filled with distilled water. The volume of water is 2.65 l for single impellers and 3.8 l for dual impellers, respectively. Water is put into the reactor when the room temperature is around 14-15 ^oC and the gas is fed around 34-35 bars. Then the cooler of the room is set to a temperature of -5 ^oC. During this cooling process due to the high solubility of carbon dioxide, a considerable decrease in pressure is observed. Therefore, CO_2 is injected a few times to stabilize the reactor pressure at 34 bars. When the reactor temperature is at 5 ^oC, the reactor pressure is adjusted to 32.5–33 bars, and rotation is started. The rotational speed is kept at 500 rpm for all experiments for a period of 3 hours.

The impellers that are used are Pitched Blade Turbine downward trending (PBT-d) with mixed flow, Rushton Turbine (RT) with radial flow, and Marine Propeller (MP) with axial flow. The diameters of the impellers are 7.5 cm and in dual impellers the distance between them is 5 cm. The height of water in the reactor reaches 15 cm for single impellers (equal to the inside diameter of the tank) while in dual impellers the water height reaches 22.5 cm (1.5 times the inside diameter of the tank). Furthermore, full baffles are also used with a width of 1cm and a sparger with a 1 cm height for better gas-liquid contact for mass transfer and/or reaction. The bottom of clearance (distance between the bottom of the reactor and impeller) is 5cm. Figure 2 shows the three different impellers and figure 3 shows the sparger and the full baffle.

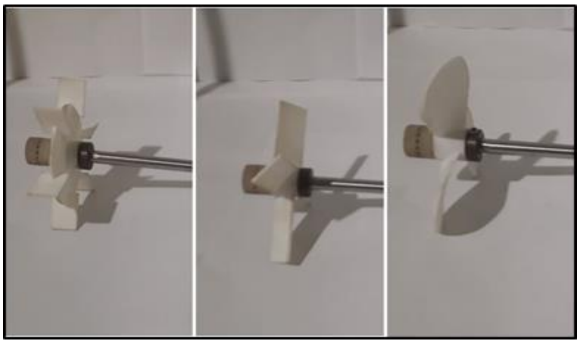


Figure 2. *RT (left). PBT-d (middle) and MP (right)*

Figure 3. *Full baffle (left) and sparger (right)*

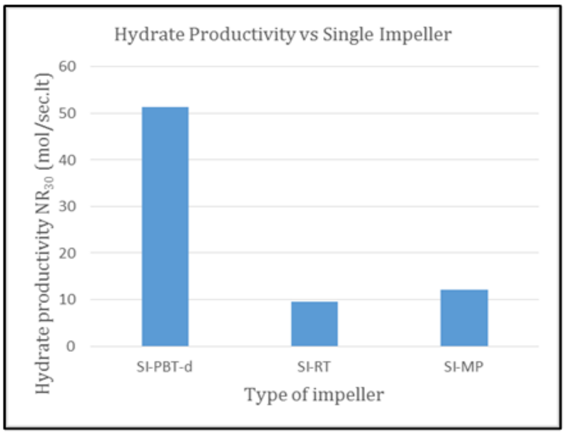
RESULTS AND DISCUSSION

Table 1 presents the relevant experimental conditions, the induction time for hydrate formation, the water conversion to hydrate (hydrate yield), and the power consumption. As seen in Table 1 the water conversion to hydrates for single impellers follows the specific order: from 0.81 % which is the highest value for pitched blade turbine in downward trending, then to the marine propeller with 0.51 % and last comes the Rushton turbine with the value of 0.31 %. The same order is also followed in the dual impellers such as pitched blade turbine downward trending have the value of 0.0089 %, then follows marine propeller with 0.0043 % and last comes the Rushton turbine with 0.0039 %. Another factor that is examined is the power consumption of every different impeller single and dual from the start stirring until the end of the experiment (3 hours after induction time). In single impellers, the power consumption is approximately the same for both pitched blade turbines and Rushton turbines (Rushton turbines consume a little more compared to pitched blade turbines, which is less than 0.02) while is less for marine propellers. The difference in percentage between the two first impellers compared to the marine propeller is approximately more power consumption around 14 %. On the other hand, in dual impellers, the marine propellers consume less energy compared to pitched blade turbines and Rushton turbines 32.87 % and 30.56 % respectively.

Table 1 *Summary of experimental conditions and percent conversion to hydrates together with the power consumption*

Design	V_{water} (l)	Induction time (min)	Hydrate Yield mol%	Power Consumption ($Kg*m^2/s^3$)
SI-PBT-d	2.65	<1	0.945132075	36.46541125
SI-RT	2.65	<1	0.362769057	36.64237292
SI-MP	2.65	<1	0.598224797	30.79206434
DI-PBT-d	3.8	<1	1.101348684	42.77516745
DI-RT	3.8	<1	0.569586261	41.35666148
DI-MP	3.8	<1	0.496062936	28.71803463

Another factor that is calculated is the hydrate productivity for both single and dual impellers and they are presented in Figures 4 and 5, respectively. In single impellers pitched blade turbine has the highest value (51.32 mol/s*l), then follows the marine propeller (12.03 mol/s*l), and last comes the Rushton turbine (9.54 mol/s*l). On the other hand, in dual impellers the Rushton turbines have the highest value (41.31 mol/s*l), then followed pitched blade turbine (31.84 mol/s*l) and the smallest value belongs to the marine propeller (8.31 mol/s*l).



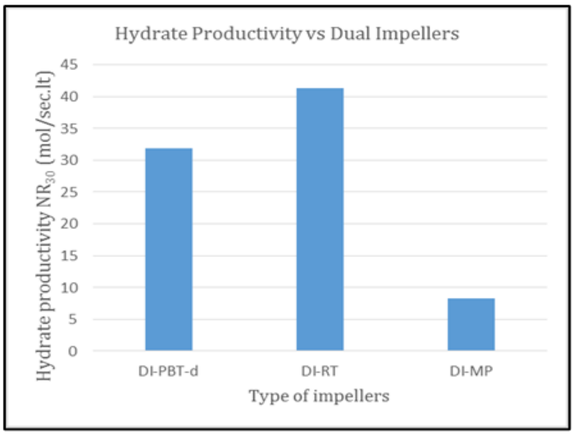


Figure 4. *Hydrate Productivity of single impellers* ***Figure 5.*** *Hydrate Productivity of dual impellers*

Kinetic analysis continues with the calculations of rate growth. The rate growth for single is presented in Figure 6. The best performance has the pitched blade turbine (downward trending) which has mixed flow with a value of $144*10^{-8}$ mol/s, second comes marine which has axial flow with a value of $31.9*10^{-8}$ mol/s, and last comes the Rushton turbine with a radial flow and value $25.3*10^{-8}$ mol/s. Furthermore, only the pitched blade turbine and marine propeller continue to form hydrates after the first 30 minutes. For the three hours after induction time (first hydrate particle), we took measurements to calculate the values in Table 1 only the marine propeller continued to form hydrates while in the pitched blade turbine there was a stabilization in hydrate formation (no more hydrate formation) after 1.5 hours after its induction time and a small hydrate dissociation. As far as it concerns the Rushton turbine impeller, there is hydrate formation for only the first 30 minutes, then a small period of stabilization of hydrate formation and continues with hydrate dissociation (losing the amount of hydrate formation). The above descriptions are all presented in Figure 7 which also shows that in hydrate formation there is a decrease in pressure and an increase in temperature due to the reaction being exothermic.

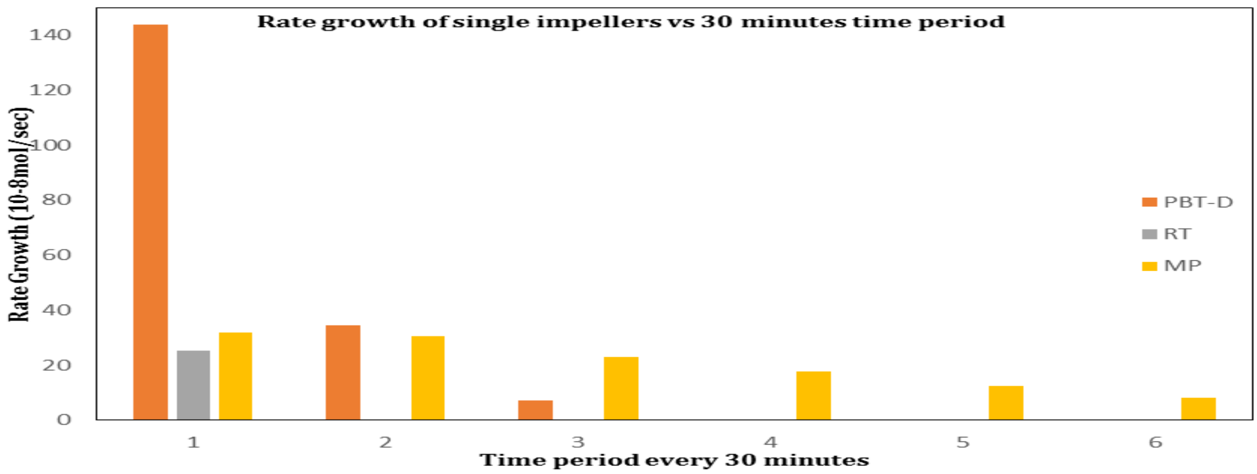


Figure 6. *Rate growth of single impeller every 30 minutes*

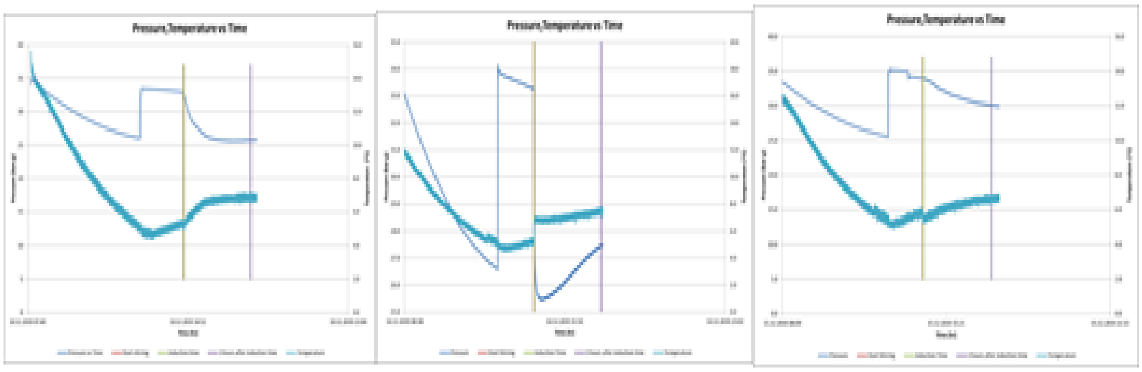


Figure 7. *Pressure and Temperature vs Time for three different impellers (left is pitched blade turbine, middle is Rushton turbine and right is marine propeller)*

On the other hand, on dual impellers, our results differ. For dual impellers, the highest rate growth has the Rushton turbine impellers ($157*10^{-8}$ mol/s), then followed by the pitched blade turbines ($121*10^{-8}$ mol/s) and finally comes the marine propeller ($31.6*10^{-8}$ mol/s). As can be seen in Figure 8 pitched blade turbines and Rushton turbines form hydrates for only 1 hour and after this the dissociation of hydrates. Marine propeller form hydrates for all three hours with an almost constant value for the first hour ($31.6*10^{-8}$ mol/s for the first 30 minutes and $30.2*10^{-8}$ mol/s for the second 30 minutes) while the decrease in hydrate growth between the first half hour and the last is less than 50 % ($16.6*10^{-8}$ mol/s).

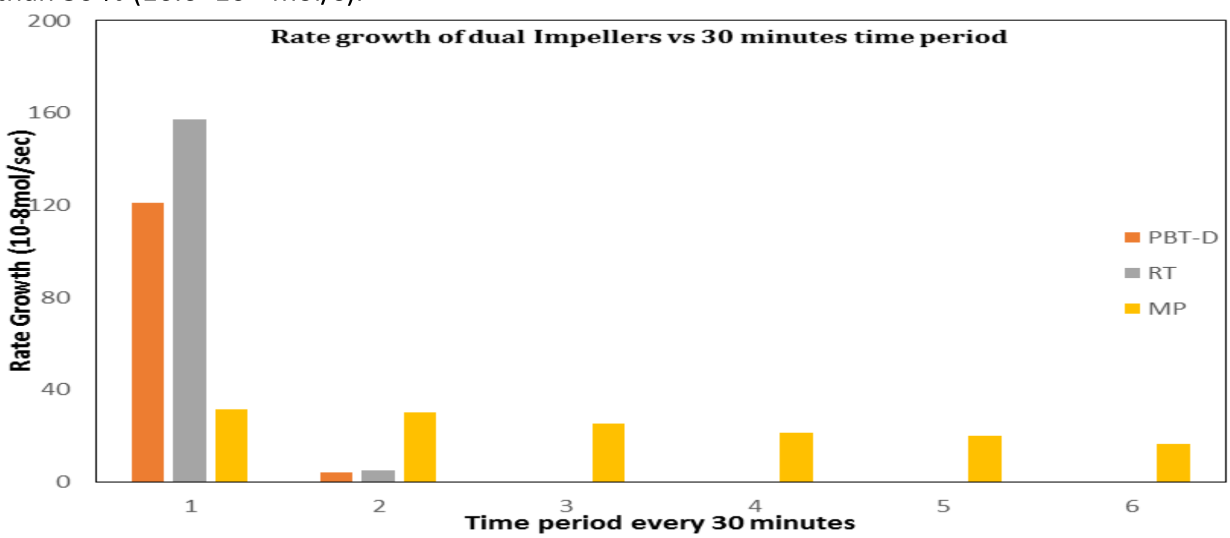


Figure 8. *Rate growth of dual impellers every 30 minutes*

CONCLUSIONS

This work aimed to compare CO_2 hydrate formation experiments carried out at constant temperature 5 ^{O}C and pressure 32.5-33 bars with three different impellers in both single and dual designs. The kinetic analysis was compared among the three different impellers with their different flows. In a single design of impellers, the better performance of rate growth had the Rushton turbine with the radial flow while the less good performance had the marine propeller with the axial flow. In dual impellers, the best performance in hydrate growth had the Rushton turbines, then pitched blade turbines followed and last were the marine propellers. Pitched blade turbines in both single and dual had the highest values in power consumption but they also had the highest amount of water which was converted to hydrates.

.

REFERENCES

[1] Gudmundsson, J.S., Parlaktuna, M. and Khokhar, A.A., 1994. Storage of natural gas as frozen hydrate. SPE Production & Facilities, 9(01), pp.69-73
[2] Sloan Jr, E.D. and Koh, C.A., 2007. Clathrate hydrates of natural gases. CRC press.
[3] Longinos, S.N., Longinou, D.D. and Achinas, S., 2020. Natural gas hydrates: Possible environmental issues. Contemporary environmental issues and challenges in era of climate change, pp.277-293.
[4] Sloan Jr, E.D., 2003. Fundamental principles and applications of natural gas hydrates. Nature, 426(6964), pp.353-359.
[5] Koh, C.A., Sum, A.K. and Sloan, E.D., 2009. Gas hydrates: Unlocking the energy from icy cages. Journal of applied physics, 106(6).
[6] Koh, C.A., Sloan, E.D., Sum, A.K. and Wu, D.T., 2011. Fundamentals and applications of gas hydrates. Annual review of chemical and biomolecular engineering, 2, pp.237-257.
[7] Gudmundson, J.S. and Borrehaug, A., 1996. Natural gas hydrate-an alternative to liquefied natural gas?. Petroleum Review, 50.
[8] Shirota, H., Aya, I., Namie, S., Bollavaram, P., Turner, D. and Sloan, E.D., 2002, May. Measurement of methane hydrate dissociation for application to natural gas storage and transportation. In Proceedings of the 4th international conference on gas hydrates, Yokohama, Japan (pp. 972-977).
[9] Hao, W., Wang, J., Fan, S. and Hao, W., 2008. Evaluation and analysis method for natural gas hydrate storage and transportation processes. Energy conversion and management, 49(10), pp.2546-2553.
[10] Mimachi, H., Takeya, S., Yoneyama, A., Hyodo, K., Takeda, T., Gotoh, Y. and Murayama, T., 2014. Natural gas storage and transportation within gas hydrate of smaller particle: Size dependence of self-preservation phenomenon of natural gas hydrate. Chemical Engineering Science, 118, pp.208-213.
[11] Merey, Ş. and Longinos, S., 2019. The gas hydrate potential of the Eastern Mediterranean basin. Bulletin of the Mineral Research and Exploration, 160.
[12] Longinos, S.N. and Parlaktuna, M., 2020. The effect of experimental conditions on methane (95%)–propane (5%) hydrate formation. Energies, 13(24), p.6710.
[13] Longinos, S.N. and Parlaktuna, M., 2021. Kinetic study of the effect of amino acids on methane (95%)—propane (5%) hydrate formation. Reaction Kinetics, Mechanisms and Catalysis, 133(2), pp.753-763.
[14] Komai, T., Yamamoto, Y., Haneda, H., Kang, S.P., Kawamura, T. and Ohga, K., 2002, May. Fundamental study on gas hydrate recovery from marine sediments. In ISOPE International Ocean and Polar Engineering Conference (pp. ISOPE-I). ISOPE.
[15] Longinos, S.N. and Parlaktuna, M., 2021. Kinetic analysis of CO2 hydrate formation by the use of different impellers. Reaction Kinetics, Mechanisms and Catalysis, 133(1), pp.85-100.
[16] Englezos, P. and Lee, J.D., 2005. Gas hydrates: A cleaner source of energy and opportunity for innovative technologies. Korean Journal of Chemical Engineering, 22, pp.671-681.