



Heriot-Watt University
Research Gateway

Investigating the effect of silver nanoparticles on carbon dioxide hydrates formation

Citation for published version:

Nashed, O, Youssouf, SM, Sabil, KM, Shariff, AM, Sufian, S & Lal, B 2018, 'Investigating the effect of silver nanoparticles on carbon dioxide hydrates formation', *IOP Conference Series: Materials Science and Engineering*, vol. 458, no. 1, 012058. <https://doi.org/10.1088/1757-899X/458/1/012058>

Digital Object Identifier (DOI):

[10.1088/1757-899X/458/1/012058](https://doi.org/10.1088/1757-899X/458/1/012058)

Link:

[Link to publication record in Heriot-Watt Research Portal](#)

Document Version:

Publisher's PDF, also known as Version of record

Published In:

IOP Conference Series: Materials Science and Engineering

General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact open.access@hw.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

PAPER • OPEN ACCESS

Investigating the effect of silver nanoparticles on carbon dioxide hydrates formation

To cite this article: Omar Nashed *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **458** 012058

View the [article online](#) for updates and enhancements.



IOP | ebooksTM

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Investigating the effect of silver nanoparticles on carbon dioxide hydrates formation

Omar Nashed¹, Sadadine Mahamat Youssouf¹, Khalik M. Sabil², Azmi Mohd Shariff¹, Suriati Sufian¹, Bhajan Lal^{1,*}

¹ Chemical Engineering Department Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar Perak, Malaysia.

² Institute of Petroleum Engineering, School of Energy, Geoscience, Infrastructure and Society, 9 Heriot-Watt University Malaysia, No 1 Jalan Venna P5/2, Precinct 5, 62200 Putrajaya, 10 Malaysia

*bhajan.lal@utp.edu.my

Abstract. Gas hydrates have been considered as a promising approach for gas separation, storage, and transportation. Low hydrates formation rate has been identified as a major weakness of this technology. However, introducing hydrate promoter could accelerate the hydrates formation process. In this paper, silver nanofluids are investigated as kinetic CO₂ hydrates promoter by measuring the induction time, the initial rate of CO₂ hydrate formation, and the amount of CO₂ gas consumed at a pressure of 2.7MPa and temperature of 277.15 K. Silver nanofluids are prepared at a concentration range of 0.01 to 0.1 wt% of silver nanoparticles mixed with 0.08 SDS wt%. The experiments are conducted through high pressure reactor hydrate cell. The results show that nanoparticles enhance the initial hydrate formation rate and amount of gas consumption. However, no significant effect is observed on the induction time compared to SDS solution.

1. Introduction

The global emission of Carbon dioxide (CO₂) according to the Emission Database for Global Atmospheric Research has increased by 48% in the past two decades. CO₂ as an essential heat-trapping (greenhouse) gas, is released through human activities and natural processes such as burning fossil fuels, respiration, and deforestation [1]. There are few techniques used to capture CO₂ such as absorption, adsorption, membrane separation, and cryogenic distillation. However, these techniques have some drawbacks such as high cost, equipment faulting, solvent degradation, limited capacity, and high energy consumption [2]. Gas Hydrates or clathrates are referred to crystal structured solid that form from hydrogen-bonded water cages entraps small guest gas molecules such as methane, ethane or carbon dioxide formed at low temperature and high pressure. The guest gases are stabilized by Van der Waals force [3,4]. Gas hydrates cause a blockage in the pipeline so it is known as a serious problem for oil and gas industry [5-7]. Gas hydrates application has received huge attention recently by numerous researchers and scientists for the area of gas separation, storage and transportation. Hydrate based gas separation (HBGS) is a new technique in which CO₂ can be separated from other gases. CO₂ has different phase equilibrium than other gases allowing it to form hydrates crystal easier than other flue gases such as N₂. The advantage of hydrate based CO₂ separation is less energy consumption and the solvent used is water [8]. The solubility limitation of gases in water and the slow formation process of gas hydrates



restrain the hydrate applications [8]. Therefore, chemical additives such as surfactants are used as a kinetic promoter to enhance the hydrate formation. However, no definitive solution has been reached for this problem, and more investigations are required. In 2006, Li et al. introduced copper nanoparticles as kinetic hydrates promoters [9]. Even though Nanoparticles do not affect the hydrate dissociation process notably, they reduce the induction time as well as increase the rate at which hydrates grow and storage capacity of the cages [9-12]. This ability is gained by increasing heat and mass transfer increases the solubility of gases in the water, expand contact of gas and liquid area, and supply nucleation sites for hydrate to form. Li et al. (2006), investigated the effect of copper nanoparticles on 1,1,1,2-Tetrafluoroethane used in air conditioning and refrigeration system. They found out that nanocopper have reduced the induction time of the hydrate [9]. Lee et al., studied the methane occupation of hydrates cages in the presence of $\text{TiO}_2\text{-Ag-SiO}_2$ and found out that the formation of methane hydrates rate is double in the presence of 1 wt% $\text{TiO}_2\text{-Ag-SiO}_2$ than that of methane in pure water [10]. Park et al., (2010), studied the effect of multi-walled carbon nanotube (MWCNTs) on the methane hydrate formation at concentration varies from (0.001-0.006 wt%). They reported as well that 0.004 wt.% MWCNT solution consumed the highest amount of methane as much as 300% compared to that in pure water [11]. Arjang et al., employed the silver nanoparticles as kinetic methane hydrate promoters [12]. They found that the induction time decreases by 85% and 73.9% respectively and gas consumption increased by 33.7% and 7.4% respectively. They also reported that SDS still batter than silver nanoparticle. Rahmati-Abkenar et al. also investigated triangular silver nanoparticles for methane hydrate promotion [13]. The results revealed triangular silver nanoparticles reduced the induction time up to 97% in comparison with pure water. Zhou et al. suggested that selected nanoparticles must be acid-resistant to be effective under acidic gas hydrate formation condition [14]. Hence, nanographite as kind of metalloid was studied as CO_2 hydrate promotor. The results showed that the formation of CO_2 hydrate was 80.8% faster in the presence of graphite nanoparticles than in pure water. Meanwhile the CO_2 consumption increased by 12.8%. Liu et al. reported that SDS coated Fe_3O_4 is not only able to shorten the induction periods but also increases the gas storage capacity of hydrates, particularly at low SDS concentrations [15]. They also mention that size of particle showed obvious influence on the promotion of SDS coated Fe_3O_4 to methane hydrate formation.

This paper performs stability study of silver nanoparticles in different SDS concentrations, and evaluate the performance of 0.01 to 1 wt. % silver nanofluid as a kinetic promoter for CO_2 gas hydrate formation by measuring the induction time, rate of CO_2 hydrate formation, and the amount of CO_2 gas consumed. High Pressure Reactor Hydrate Cell is used to run the experiment at temperature 277.15 K and pressure of 2.7MPa.

2. Experimental

2.1. Materials

Silver nanoparticles are supplied by US Research Nanomaterials Inc, with purity 99.9%, and particle size is 30-50nm. Sodium dodecyl sulfate (SDS) used to stabilize the nanofluid supplied by Merck. CO_2 gas with purity 99.9% is supplied by Air Product Sdn. Bhd.

2.2. Apparatus and procedures

To identify the optimum concentration of SDS used to stabilize the nanofluid, visual observation of the suspensions as well as nanoparticle size test using Brooklyn Haven 90 plus particle size analyser are used. High pressure reactor hydrate cell is used to study the kinetic of gas hydrates formation. A schematic representation of the reactor is shown in figure 1.

The High pressure reactor hydrate cell consists of a high-pressure stainless-steel vessel with an internal volume of 412 ml. The maximum working pressure for the vessel is 30 MPa. The vessel is immersed in a water bath to keep the temperature constant at the desired value. The temperature inside the vessel is monitored both in the gas phase and in the liquid phase by two thermocouples with an

accuracy of ± 0.01 °C. To achieve proper mixing in the liquid sample, a magnetic stirrer is placed in the vessel. The pressure inside the cell is measured with a pressure transducer.

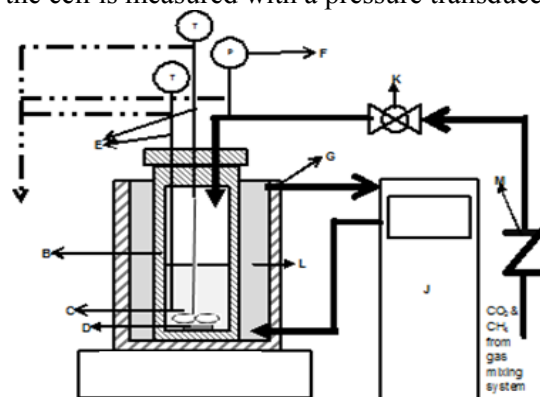


Figure 1. Pressure reactor hydrate cell schematics

Approximately 100 ml of sample is inserted into the vessel (high pressure reactor). The system then vacuumed, and the reactor is purged with gas twice to remove excess air inside of the reactor. Afterward, the reactor is submerged inside the cooling bath. The reactor is allowed to cool down to the temperature of 279.65 K that is 2 K higher than the hydrate equilibrium temperature. Finally, sufficient CO₂ is introduced to the reactor up to 2.7 MPa. After that, the system is cooled down up to 277.15 K without stirring during the cooling period. The decrease in pressure is observed due to the dissolution of gas into the liquid mixture. When pressure regains stability and temperature of the system reached to 277.15 K, the stirrer is turned on. When hydrate formation occurs, the sudden pressure drop in the system is observed. The change in pressure and temperature is recorded every 10 seconds by data acquisition system. When the pressure of the system remains unchanged for 2 to 3 hours, this indicates that hydrate formation is completed, and the experiment is ended.

Three kinetic indexes are calculated to evaluate the silver nanoparticles as promoters. First, the induction time is taken from the starting moment of cooling up to hydrate formation indicated by the sudden drop in pressure. Secondly, the gas consumption rate is calculated using Eq (1).

$$r(t) = \frac{n_{g,i-1} - n_{g,i+1}}{(t_{i+1} - t_{i-1})} \quad (1)$$

where $n_{g,i-1}$ and $n_{g,i+1}$ are the mole number of gas in the gas phase at t_{i-1} and t_{i+1} , respectively. The amount of gas consumption is calculated using Eq (2).

$$\Delta n_{gas} = \frac{P_0 V_0}{Z_0 R T_0} - \frac{P_t V_t}{Z_t R T_t} \quad (2)$$

where P and T are the cell pressure and temperature, respectively. V is the volume of the gas inside the cell; R is the universal gas constant, and subscripts 0 is for the initial time and t is for a time equal to t . Z is the compressibility factor calculated by the Peng Robinson equation of state.

3. Results and Discussion

3.1. Stability study

The nanofluids are prepared by adding the silver and SDS to the water. Afterward, vigorous mixing applied for an hour using magnetic stirrer. Then, the nanofluid is placed in the ultrasonic bath for 60 minutes. For stability study, 0.1 wt% of silver nanoparticles are prepared with different SDS concentrations 0.03, 0.05, 0.08, and 1 wt%. At the initial state where time equal to zero all the samples look similar and no change was recorded until after two days (figure 2). The settlement increases and

after seven days is shown clear that silver nanoparticle with 0.08 wt% SDS concentration is the most stable.

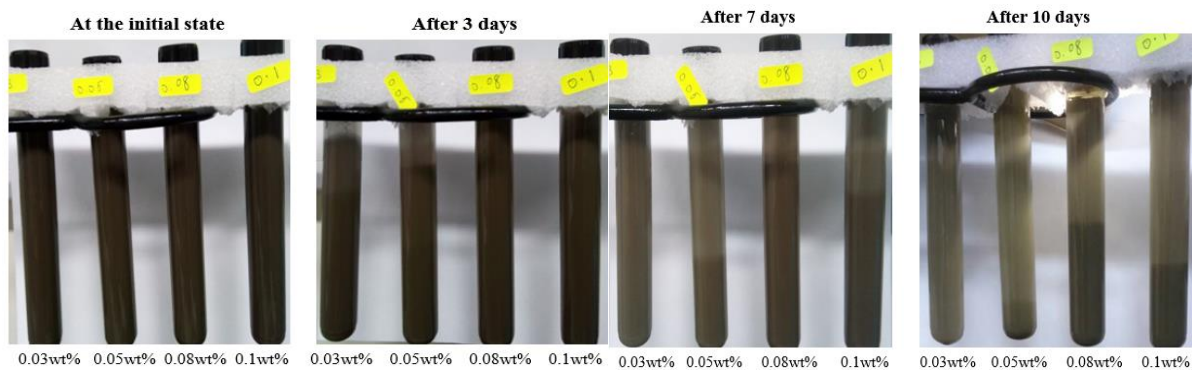


Figure 2. Stability of 0.1 wt. % Silver nanoparticles in different SDS concentrations.

Table 1. Particle Size of silver particles in different SDS concentration.

SAMPLE	Eff. Diam. (nm)
0.03SDS +0.1Ag	198.10
0.05SDS +0.1Ag	125.89
0.08SDS +0.1Ag	73.16
0.1SDS +0.1Ag	102.82

The particles size test also shows that the silver nanoparticles size is smallest at SDS concentration of 0.08 wt %. It indicates that, the nanoparticles tend to distribute better in the suspension and they do not aggregate, which results in better stability. Particle size for all different SDS concentration is shown in table 1 [14].

3.2. Kinetic promotion

After the most stable SDS concentration is determined, it used with three different silver nanoparticle concentration 0.01-0.1 wt%. The results obtained are illustrated in figures 3, 4 and 5.

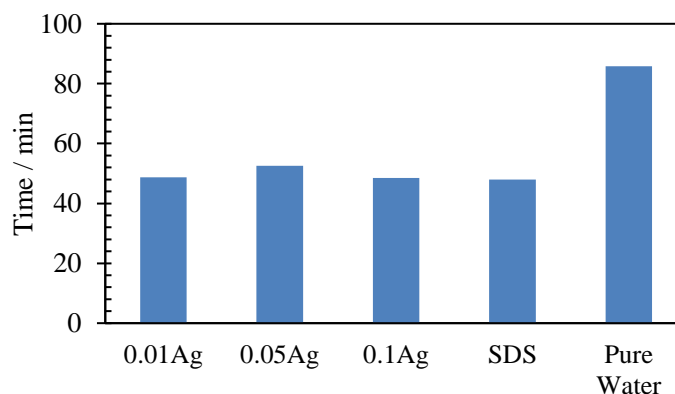


Figure 3. Induction time for 4°C Sub-cooling for pure water, 0.08 wt% SDS, and nanofluids.

Figure 3 illustrates the induction time, for pure water, 0.08 wt% SDS, and three different concentration of silver nanoparticle. It can be observed that all studied concentration have a promotional effect. In addition, there is no appreciable difference in the induction time between SDS solution and

silver nanoparticles for average three experiment tests, with enhancement rate of 44% compared with water.

The initial rate of CO₂ gas consumption is plotted in figure 4. It shows that the pure water has the lowest consumption rate. 0.01 wt% Ag can enhance the initial rate by 417.4% and 15% compared with pure water and 0.08 wt% SDS, respectively. Then, it followed by SDS, 0.05 and 0.1 wt% as it shown in figure 4.

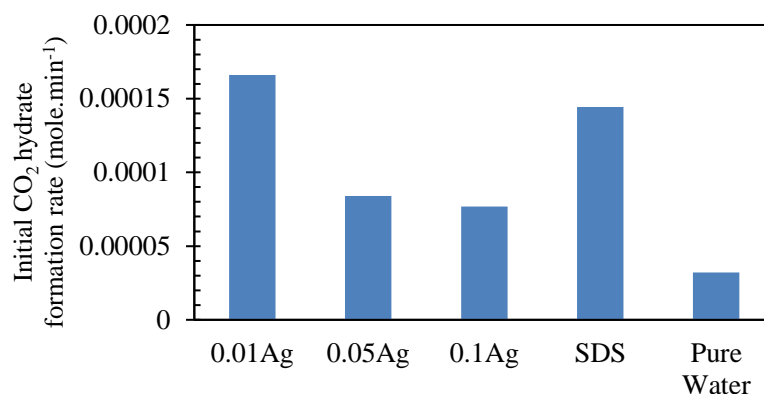


Figure 4. Initial CO₂ hydrate formation rate for pure water, 0.08 wt% SDS, and nanofluids.

The amount of CO₂ consumed is found to be the highest at a concentration of 0.1 wt% Ag. The experimental results show that the presence of Ag increased about 9.7, 1.8, and 11.4% in the amount of CO₂ consumption for a period of 180 min for 0.01, 0.05, 0.1 wt%, respectively. The presence of a mixture of Ag + 0.08 wt% SDS enhance the CO₂ consumption compared to 0.08 wt % SDS about 3.3 % and 5.1 % for 0.01 and 0.1 wt%, respectively.

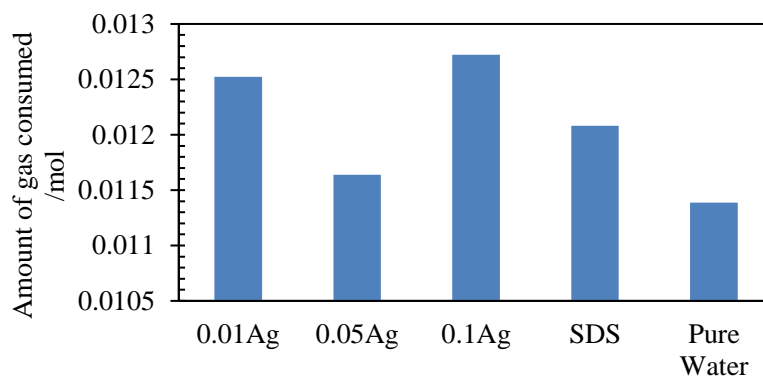


Figure 5. Amount of CO₂ Gas consumed at 180 minutes for pure water, 0.08 wt% SDS, and nanofluids.

The enchantment of gas hydrate formation by adding silver nanoparticles is attributed to its high thermal conductivity. Gas hydrates formation is an exothermic process that leads to increasing in the temperature, thus decreasing the driving force for hydrate formation. Therefore, the heat of formation can be removed from the system more effectively and much faster by using a higher thermal conductivity fluid. This will provide a more suitable temperature profile that is required for better nucleation. In addition, the presence of solid particles in the system, offer the nucleation sites for easier heterogeneous nucleation [13-15].

4. Conclusion

The silver nanofluid shows the best stability and smallest particle size at 0.08 wt % SDS. The kinetic study revealed that adding kinetic promoters shorten the induction time. However, no significant effect

has been observed for Silver Nanoparticles. The initial rate of hydrates formation and amount of gas consumption are enhanced by adding silver nanoparticles. 0.01 wt% Ag enhance the initial rate by 417.4% and 15% compared with pure water and 0.08 wt% SDS. Meanwhile, 0.1 wt% show the highest gas consumption enhancement rate by 5.1 wt.

Acknowledgment

The authors thank Universiti Teknologi PETRONAS and CO₂ Research Centre for providing the facilities.

References

- [1] Le Quéré C, Raupach M R, Canadell J G, Marland G, Bopp L, Ciais P, Conway TJ, Doney SC, Feely RA, Foster P and Friedlingstein P 2009 Trends in the sources and sinks of carbon dioxide *NAT GEOSCI* **2** pp 831–36
- [2] Leung D Y, Caramanna G and Maroto-Valer MM 2014 An overview of current status of carbon dioxide capture and storage technologies *Renew Sust Energ Rev* **39** pp 426–43
- [3] 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 237–57
- [4] Sloan E D and Koh C 2008 Clathrate Hydrates of Natural Gases 3rd Ed. New York Marcel Dekker CRC press p 119
- [5] Nashed O, Sabil K M, Ismail L, Japper-Jaafar A and Lal B, 2018 Mean induction time and isothermal kinetic analysis of methane hydrate formation in water and imidazolium based ionic liquid solutions *J Chem Thermodyn* **117** pp 147–54
- [6] Nashed O, Dadebayev D, Khan M S, Bavoh C B, Lal B and Shariff A M 2018 Experimental and modelling studies on thermodynamic methane hydrate inhibition in the presence of ionic liquids. *J. Mol. Liq* **249** pp 886–91
- [7] Bavoh C B, Nashed O, Khan M S, Partoon B, Lal B and Sharif A M 2018 The impact of amino acids on methane hydrate phase boundary and formation kinetics *J Chem Thermodyn* **117** pp 48–53
- [8] Babu P, Linga P, Kumar R and Englezos P 2015 A review of the hydrate based gas separation (HBGS) process for carbon dioxide pre-combustion capture *Energy* **85** pp 261–79
- [9] Li J, Liang D, Guo K, Wang R and Fan S 2006 Formation and dissociation of HFC134a gas hydrate in nano-copper suspension *Energ Convers Manage* **47** pp 201–10
- [10] Lee J D, Kim H C, Kim Y S, Kim Y D and Lee M S 2007 Synthesis of nanosized TiO₂-Ag-SiO₂ sols by modified sol-gel method and their application for methane hydrate formation *In solid state phenomena* **124** pp 1059–62
- [11] Park S S, Lee S B and Kim N J 2010 Effect of multi-walled carbon nanotubes on methane hydrate formation. *J. Ind. Eng. Chem.*, **16** (4) pp 551-55
- [12] Arjang S, Manteghian M and Mohammadi A 2013 Effect of synthesized silver nanoparticles in promoting methane hydrate formation at 4.7 MPa and 5.7 MPa *Chem. Eng. Res. Des.* **91** pp 1050–54
- [13] Rahmati-Abkenar M, Manteghian M and Pahlavanzadeh H 2017 Experimental and theoretical investigation of methane hydrate induction time in the presence of triangular silver nanoparticles *Chem. Eng. Res. Des.* **120** pp 325–32
- [14] Zhou S d, Yu Y S, Zhao M M., Wang S L and Zhang G Z 2014 Effect of graphite nanoparticles on promoting CO₂ hydrate formation *Energy & Fuels* **28** pp 4694–98
- [15] Liu, G Q, Wang F, Luo S-J, Xu D Y and Guo R-B 2017 Enhanced methane hydrate formation with SDS-coated Fe₃O₄ nanoparticles as promoters *J. Mol. Liq* **230** pp 315–321