
Completion Time of CH₄ Hydrate Formation in the Presence of Copper NanoFluid

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Abstract

Research design on the toxicity of Sodium Dodecyl Urea (SDU) and Sodium Dodecyl Sulphides (SDS) copper nanofluid on kinetics of methane hydrate formation was studied. The experiments were done using stainless steel stirred reactor at 5.1 MPa pressure and 274.15 K temperature. Completion time was reported to describe overall formation kinetic. The consequences exposed that SDS and nanofluid reduced the completion time significantly. Among all samples 0.05wt% copper nanoparticles suspended in The 0.03 weight percent SDS solution achieved the average formation of methane hydrate in shortest time. Nanofluid contains 0.01wt% and 0.1wt% copper nanoparticles do not enhance the hydrate formation in compare to 0.03 wt% SDS solution.

Keywords: methane hydrate, copper nanoparticle, hydrates formation, completion time, Sodium Dodecyl Sulphides

1 Introduction

Inclusion compounds comprised of light guest molecules trapped in water cavities are clathrate hydrates [1]. Gas hydrates formation requires relatively low temperature and high pressure [1]. Comparable Clathrate structures include different cage size could be formed. However, the most studied

structures are structure H hexagonal, structure I cubic, and structure I cubic II [2]. In 1934, it has been reported by Hammerschmidt that gas hydrates plug the natural gas pipelines [3]. This attracted the researchers to investigate experimentally and numerically the gas hydrates formation, intensively [4]–[7][8]. In 1960, natural gas hydrates were discovered in Siberia by Makogon[9]. This motivated the researchers to deal with gas hydrates as an advantage that could be used as technology [10]–[12]. The storage capacity of gas hydrates at standard circumstances are 150-180 m³ of gas volume and can be stable at relatively mild conditions [13]. Therefore, gas hydrate could be an alternative, safe, and feasible technology for gas separation, transportation, and storage. Carbon dioxide capture and sequestration (CCS) is one of the potential applications that could achieved by gas hydrate technology. The main challenge to utilize gas hydrate technology in the industrial application is to perform fast hydrate formation rate with high gas storage capacity [10], [14]–[15].

Many published reports investigated the chemical additives that could promote hydrate formation [16]–[20]. Surfactants have been investigated as kinetic hydrate promoters (KHPs) [21]. It has been found that sodium dodecyl chloride (SDS) is the most effective KHP [21]. However, using surfactants in the industrial applications is unfavorable due to the foam creation [18]. In order to find an effective KHP, Li et al. proposed Cu nanoparticles as hydrate promoter [22]. They reported that, the elevated thermal conductivity of copper during hydrate formation, it could remove the heat released as it is exothermic process. Hence, the temperature profile is kept appropriate for further hydrates formation. Afterward, carbon nanotubes, silver, metallic oxides, and silica nanoparticles were used to promote gas hydrates [23]–[27]. The nanofluid were prepared by suspending the nanoparticles either in water or in surfactant solution. The nanofluid showed an efficient enhancement rate in comparison with pure water sample or surfactant. The nanofluid can efficiently enhance the hydrates formation mainly because nanoparticles have high thermal conductivity, provide nucleation sites, and reduce the surface tension [18].

In this study, completion duration of the formation of CO₂ hydrates in the presence of suspended nano particles of copper in 0.03 wt% SDS aqueous solution was reported. Completion time represent the time required to perform 100 % gas hydrates formation.

2 Methodology

2.1 Materials

Methane was obtained from Air Product Sdn. Bhd. Copper nanoparticles with diameter of 40 nm was purchased from Research Nanomaterials Inc US. Sodium dodecyl sulfate was supplied by Merk and used to stabilize nanofluid as well as for comparison. Ultra-Pure water system was used to obtain deionized water needed to prepare nanofluids. Copper nanoparticles loading in the range of 0.005-0.1 wt maximum concentrated in an aqueous solution of

0.03 wt percent SDS. To prepare the samples, an electronic approximation with an error of ± 0.0001 g was used.

2.2 Apparatus and Procedure

Stainless-Steel Reactor stirred with internal volume of 423.9 ml were used to run the kinetic experiments. The reactor was located in water/glycol bath and equipped with all necessary thermocouples and pressure transducer. More details of the equipment specifications were reported in our previous work [23].

Water-based nanofluids samples are prepared by dispersing copper nanoparticles in component SDS aqueous solution of 0.03 wt. The concentrations of copper powder are 0.01, 0.05, and 0.1 wt%. To ensure a stable nanofluid, vigorous magnetic stirring was applied for 1 hr followed by one hour sonication in ultrasonic bath. 100 ml of injected into the reactor was a sample of liquid. The procedure was then vacuumed and purged inside the reactor with 40 days or as much with water discharge of extra air.

A blank sample, 0.03 level artificial immune recognition percent, has been injected into in the reactor or nanofluid and the temperature is set at 281.65 K. Then, up to 5.1 MPa was compressed into the reactor by CH₄ steam. The stirrer is then turned on and left to enter the stable state of the system. Then, at the cooling stage, the inlet pressure valve was closed and the machine cooled down to 274.15 K without agitation. A change in friction is found as the temperature falls. Once the system pressure reached a steady state the ignition source is turned on after 60 rpm at a constant rate of 274.15 K with speed of 300 rpm. hydrate growth is defined by a sudden decrease in pressure and a spike in system temperature. The change in pressure and temperature is documented every 10 min by the data acquisition system. This measurement of completed hydrate formation is used when the system pressure become constant for 2 to 3 hours.

3 Results and Discussions

The completion time of CH₄ hydrates formation are measured for pure water, 0.03 wt% SDS, and nanofluid (0.03 wt% SDS+0.01-0.1 wt% Cu). Since the slow kinetic of hydrate formation hampered gas hydrates application, it is crucial to study the induction time and gas hydrate growth rate. The time of induction means the time of appearance of the first hydrate crystal. Some chemicals, however, can reduce induction time and slow growth rate that make evaluating the promoter's performance complicated. Therefore, the the completion time affects the entire phase of kinetic construction. The experimental results indicate that the completion time of pure water sample hydrate formation is 2794 min. This is necessary for better water solubility of methane. in the presence of 1.5 Weight percent SDSS, the completion interval is diminished to 199 mins. This is due to lower surface tension between the liquid and gas phase caused by adding a surfactant. In

addition, a porous hydrate structure is formed continuously along with sidewall due to the capillary effect, which maintain high liquid/gas interfacial area.

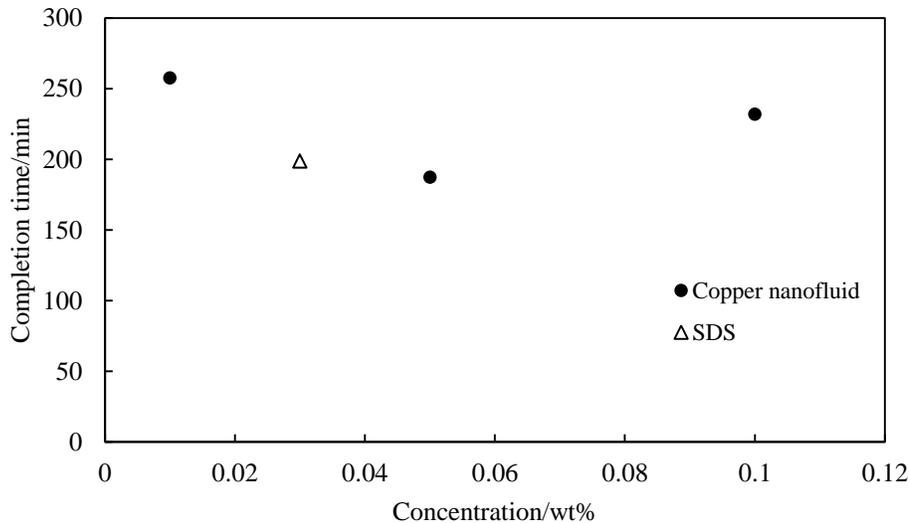


Figure 1: In the presence of 0.03 at% SDS and nanofluid (0.03 wt percent SDS+ (0.01 -0.1 on off) Cu nanoparticles), methane hydrate completion level.

The presence of copper nanofluid show appreciable reduction in the completion time in comparison to the water. That could be ascribed to the SDS effect along with presence of copper nanoparticles. SDS contains both hydrophobic and hydrophilic component that could improve methane solubility in liquid phase. The presence of copper could be nucleation sites to initiate hydrate formation earlier than other pure water or SDS samples. Additionally, copper could has higher especially in comparison to water, thermal conductivity ($401 \text{ W.m}^{-1}\text{.K}^{-1}$) finally, the presence of Cu nanoparticles could maintain the favorable hydrate formation condition by removing the heat released during exothermic hydrate formation. Figure 1 show that (0.03 wt SDS degree +0.05 wt Cu basis points) is the most effective promoter compared to water as well as 0.03 wt% SDS. However, the completion time in the existence of 0.01 wt% and 0.1 wt% of copper is higher than 0.03 wt% SDS. This is could be either insufficient concentration at 0.01 wt% or very fast hydrate formation on the liquid surface. Hydrates formation at liquid/gas interfacial could slightly slow further mass transfer.

4 Conclusion

This study presents the effect of the copper nanofluid on methane hydrate formation completion time. The results show that the kinetic of methane formation can be boosted by 0.03 weight percent SDS and nanofluid significantly. In addition, nanofluid consist of 0.03 wt% SDS + 0.05 wt% Cu complete methane hydrate formation process in shorter time compared to other samples including 0.03 wt% SDS. The consequences are attributed to the reduced surface tension, availability of nucleation sites, and fast evacuate of the heat free during hydrate formation.

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