Effect of The natural Green Materials on Methane Hydrate Formation Kinetics

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Abstract. The kinetic effect of resin (terpene) and ajinomoto (monosodium glutamate) for methane hydrate formation was reported. The induction time of 0.2wt% natural green materials was measured in a sapphire hydrate reactor at 12°C at 9.5MPa. The induction time of all materials were found to be less than pure water. In the presence of resin induction time decreased 20% more than pure water and the initial rate of hydrate formation was enhanced. Resin enhanced the rate of methane hydrate formation 17% more than pure water. However, compared to SDS the rate of hydrate formation by both natural materials was less. Moreover, natural materials consumed more methane during hydrate formation than pure water. In addition, resin promote methane hydrate formation and could act as suitable kinetic promoter for the natural gas separation, transportation and storage.

1. INTRODUCTION

Gas hydrate are crystalline, ice like anomalies, formed in oil and gas transmission lines by the concomitance of hydrogen bonded water molecules and former gases (methane, ethane etc.) at high pressure and low temperature [1, 2]. The formation of gas hydrate disturbs the gas transmission and slows down the production. However, recently natural gas hydrates (NGHs) have been gained much attention as a potential next generation energy source [3-6]. Generally gas hydrate formation take placed by entrapping the former gas molecules within the hydrate cages. The gas molecules form hydrogen bond with water molecules until nuclei of detectable size is formed. This agglomeration of nuclei at water-gas interface results in the formation of thin hydrate film on the surface which severely slow the rate of hydrate formation [3]. In order to improve interfacial interactions between gas and water various chemical additives are used which improves the gas hydrate storage and generation.

Synthetic chemical additives like SDS, sodium tetradecyl sulfate (STS) and sodium hexadecyl sulfate (SHS) are used as kinetic promoters. These additives enhance hydrate formation rate by increasing gas solubility and supporting micelle formation [7-9]. Tetrahydrofuran (THF) and acetone are used as thermodynamic promoter and enhance the hydrate formation by shifting the phase boundary to the right side [10-13]. Undesirably these synthetic surfactants and promoters are toxic in nature and can affect the aquatic life. Studies have been performed to evaluate the performance of natural green materials such as: chitosan [14], tapioca starch [15], amino acids[16] and antifreeze proteins [17]as kinetic hydrate inhibitor (KHI). However, the behaviour of natural materials as kinetic promoters are still unsearched.
Therefore, in order to prevent environmental hazards due to the excessive usage of toxic materials in pipeline, biodegradable and environment friendly chemicals are required to investigate. Consequently the effect of natural green materials such as: ajinomoto, and resin on methane hydrate kinetic is investigated in this work. Ajinomoto is the non-essential amino acid and similar to amino acids have zwitterions behaviour in water. While resin are the highly viscous materials from the pine tree and principally composed of terpenes. The chemical structures of additives are shown in Fig. 1.

| Materials                  | Chemical Structure |
|----------------------------|--------------------|
| Resin (Pine tree, terpenes)| ![Chemical Structure](image1) |
| Ajinomoto (monosodium glutamate) | ![Chemical Structure](image2) |
| Sodium dodecyl sulfate (SDS) | ![Chemical Structure](image3) |

Fig. 1. Chemical structures of studied natural green materials

2. EXPERIMENTAL

2.1. Materials

The chemical structure of the natural green materials, utilized in this work is shown in Fig. 1. These natural materials were used without any refining. Methane gas with purity of 99.995% was supplied by Gas Walker Sdn Bhd, Malaysia. Aqueous samples of additives were prepared using deionised water.

2.2. Apparatus

A hydrate sapphire cell or a rector as illustrated in Fig. 2 was used for kinetic hydrate measurements. The volume of transparent sapphire cell is 29.46ml. The sapphire hydrate reactor setup can operate up to 20 MPa in the temperatures range of 253.15-338.15 K. For temperature and pressure measurement during experiments two Pt100 thermocouples and a GP-M250 Keyence Japan Pressure transducer is used. The sapphire cell is place in a thermo-stated liquid bath that uses ethylene glycol as coolant. The temperature of liquid bath is controlled by Lauda Alpha RA 24 thermostats. The adequate stirring in sapphire is provided by the magnetic torque stirrer. A gas booster compressor is used to introduce methane into the sapphire. The aqueous natural green material solution is pumped into the cell via a manual hand pump. The temperature and pressure in the cell is continuously recorded in every 10sec by a data acquisition system with accuracy of ±0.15 K and ±0.01 MPa respectively.
2.3. Kinetic measurements

There are several steps in order to perform kinetic measurements on sapphire hydrate reactor. Prior to experiment the reactor was washed thoroughly and vacuumed for 1 hr. Then reactor was filled with 18 ml of aqueous solution of natural green materials through injection pump. The temperature of reactor was set almost 2-3K, above the equilibrium temperature of methane. Once the system reaches the desired temperature, the reactor was pressurized with 9.5 MPa of pure methane. In order to get stable physical conditions, the system was kept at rest up to 20 min. Then the system temperature was reduced to the experimental temperature with the cooling rate of 4 K/hr for hydrate to form and stirrer was turned on. In sapphire hydrate reactor, the data is acquired by an interface that records the variations in pressure and temperature at every 10 s. In all kinetic experiments the experimental temperature was kept constant at 274.15 K. Kinetic measurement experiments generally take 2-3 hrs to complete. In terms of physical conditions, constant pressure and temperature indicates completion.

Kinetic measurement experiments gave three types of data set which includes induction time, moles of methane consumed and initial rate of hydrate formation. The induction time was delineate as mentioned in previous studies [18]. The real gas equation was used to determine the moles of methane consumed. The compressibility factor (z) in real gas equation was calculated from Peng–Robinson equation of state. The gradient of graph, plotted between moles of methane consumed and time was used to estimate the initial rate of hydrate formation.

3. RESULT AND DISCUSSION

The evaluated kinetic parameters such as induction time, initial rate of hydrate formation and the total moles of methane consumed are determined and used as kinetic inhibition indicators.
To guarantee the reproducibility, the experiments were repeated three times. To evaluate the effect of additives on the methane hydrate nucleation the induction time was determined by the pressure drop. The induction time is the time at which nuclei of detectable size is formed. Fig. 3 shows that in the presence of ajinomoto and resin the induction time was reduced to 14.8 and 13.8 min respectively at the sub-cooling temperature of 12 °C.

![Fig.3 The induction time of methane hydrate in the presence of 0.2wt% concentration of natural green materials and commercial gas hydrate promoter, SDS.](image)

The initial rate of hydrate formation in the presence of ajinomoto and resin is illustrated in Fig.4. Results showed that compared to pure water both additives attractively enhanced the initial rate of hydrate formation. Resin enhances the hydrate formation rate 17% more than pure water while ajinomoto slightly increased the rate of hydrate formation. However, in the presence of commercial kinetic hydrate promoter i.e. SDS the rate of hydrate formation was not much enhanced. As kinetic hydrate inhibition is probabilistic in nature, thus use of induction time and rate of hydrate formation individually be disingenuous. Therefore, the total moles of methane consumed were utilized to examine the effect of ajinomoto and resin on methane hydrate formation. The total methane consumed is taken as a point where the pressure became constant after hydrate formation. It is observed in Fig.5 that compared to pure water presence of ajinomoto significantly increased the total moles of methane consumed. However, compared to SDS both additives consumed less methane. The average methane consumed in the presence of ajinomoto was 4% less than average methane consumed in SDS hydrae formation. Compared to water in the presence of ajinomoto the methane consumed was increased 24%.

The promotional effect of ajinomoto and resin is similar to the adsorption mechanism of surfactants. Ajinomoto and resin hindered the accumulation of hydrate at the liquid interface thus support the displacement of more methane in to the liquid phase. Therefore in the presence
of ajinomoto and resin the mole consumption of methane increased. The similar mechanism of methane hydrate promotion in the presence of arginine was observed by Bavoh et al. [16]

![Initial rate of methane hydrate formation](image1)

![Moles of methane consumed during hydrate formation](image2)

4. CONCLUSIONS

The effect of ajinomoto and resin on the kinetics of methane hydrate formation is studied in sapphire hydrate reactor. It was found that compared to pure water both ajinomoto and resin
decreased the induction time of hydrate formation. Furthermore, both additives enhanced the rate of hydrate formation. It was noticed that in the presence of ajinomoto and resin the total moles of methane consumed are more than pure water. However, in the systems containing ajinomoto and resin, the rate of hydrate formation and moles of methane consumed was dwindled compared to comercial kinetic promotor i.e. SDS. Ajinomoto showed the hightest average methane hydrate promotion impact of about 24%. In addition, resin promote the methane hydrate formation and can act as suitable kinetic promotor for the natural gas separation, transportation and storage.

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