

Research note

Effect of Single Walled Carbon Nanotubes on Natural Gas Hydrate Formation

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Abstract

Using Co-Mo/MgO catalyst, single walled carbon nanotubes with a diameter of 2nm and a length of 10 μm were produced by chemical vapor deposition process and characterized by XRD, FTIR and SEM. Synthesized single-walled carbon nanotubes were dissolved in water to make a 1w% solution and stabilized by adding sodium dodecyl sulfate surfactant. The synthesized stabilized nanofluid was used in the gaseous hydrate formation at a temperature of 4°C and pressure of 1000 psig. The results were compared with a water/surfactant control solution and it was found that carbon nanotubes have reduced the duration of dissolution process by 58.9% and duration of the induction process by 75.5%. In addition, the amount of gas entrapment and stability of the gas in the hydrate were increased by 13.6% and 18.2%, respectively.

Keywords: *Hydrate, Natural Gas, Single-Walled Carbon Nanotubes, Storage, Induction, Nanofluid*

1. Introduction

During the hydrate formation process, water molecules produce relatively large cages through hydrogen bonding which sequester gas molecules. Van der Waals forces stabilize the gas molecules which occupy these cage hydrate structures. The hydrate crystallographic structure (e.g. cubic) is determined by some factors such as thermodynamic parameters, size of molecules, size and shape of the cages. These structures include a combination of several types of cages and depending on the nature of the entrapped gas molecules, one of the

routine structures of type I, II or H are formed [1].

Gas hydrates could be transferred easily, therefore it could be considered as an appropriate gas transfer method for rough and short distance routes. Also, manufacturing of gas hydrates transport ships is much easier than liquefied natural gas (LNG) transport ships and designing hydrate production facilities are much less complicated than the LNG production plants. On the other hand, the main disadvantages of hydrate formation technology are the slow rate of hydrate formation and its small loading capacity [2]. These matters prohibit

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industrialization of gas loading and transport by NGH. Hydrate formation process is an interfacial phenomenon; factors that could escalate mass and heat transfer through the water and gas interfaces, could increase the hydrate formation rate and the amount of the entrapped gas [3]. A wide range of studies on intensification of mass and heat transfer processes have been carried out to overcome the aforementioned drawbacks.

In recent years application of improver compounds and their effects on hydrate formation (e.g. effect of surfactants on improving the activated compounds) have become of great interest [4]. The effect of sodium dodecyl sulfate on natural gas is investigated and it was found that the best results could be achieved at a concentration of 300 ppm [5]. Sun *et al.* compared the effects of ionic surfactants (e.g. SDS) and non-ionic active materials (e.g. dodecyl polysaccharide glycoside and cyclopentane) on the formation of gas hydrates and they found that ionic surfactants are superior in this respect [6]. By addition of SDS, Link *et al.* experimentally found that, the yield of Methane hydrate formation promotes up to 97% [7]. Zhang *et al.* showed that loading capacity and rate of the natural gas hydrate formation are increased in the presence of alkyl polyglycoside, sodium dodecyl benzene sulfonate and potassium oxalate monohydrate [8].

Application of nanoparticles as a facilitating agent seemed to be a promising idea in gas hydrate formation and accordingly copper nanoparticles were successfully used in the HFC134a hydrate formation [9]. The effect of ternary SiO₂-Ag-TiO₂ nanoparticles was studied in methane hydrate formation and it

was found that the number of used gas molecules was raised to 24% and its induction time reached a low value of 16.7% [10]. The effect of multi-walled carbon nanotubes and its oxidized form on methane hydrate formation was also studied [11].

In this paper, the effect of single-walled carbon nanotubes (SWNT) on natural gas hydrate formation is studied and its effect on dissolution process, induction and loading capacity are discussed.

2. Synthesis of Carbon nanotubes

SWNT was synthesized in accordance with our previous report by chemical vapor deposition (CVD) using Co-Mo/MgO catalyst [12]. Pure sodium dodecyl sulfate (SDS-99%) was purchased from Merck. Deionized water purchased from Bahr-e Zolal-e Tehran Company was used in the hydrate formation. Natural gas containing 92.5% methane in a cylinder under a pressure of 100 bar was purchased from Gas Product Co. and used as the process feed.

3. Structural analyses of Carbon nanotubes

XRD, FTIR and SEM were used to verify the synthesized nanotubes. Fig. 1 shows the XRD pattern of the synthesized carbon nanotubes. The narrow sharp peak at 25.7° corresponded to (002) planes and the broad short peak at 43.6° was assigned to (100) planes of SWNT [13].

Pellet samples composed of finely milled CNTs diluted with KBr powder were used to obtain FTIR spectra (Fig. 2). The characteristic peak at 1560 cm⁻¹ which was assigned to aromatic C=C bonds, verified the identity of SWNT [14].

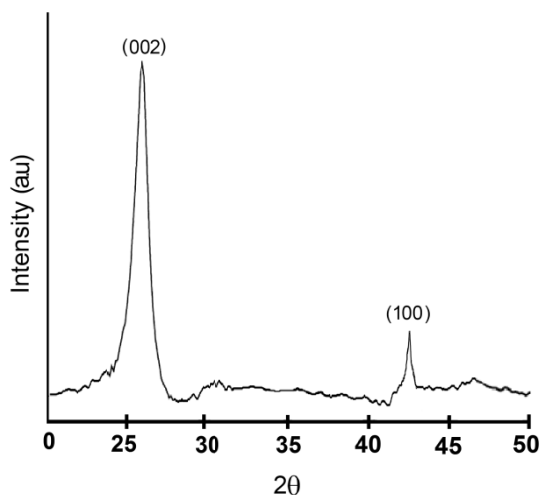


Figure 1. XRD spectrum of CNTs.

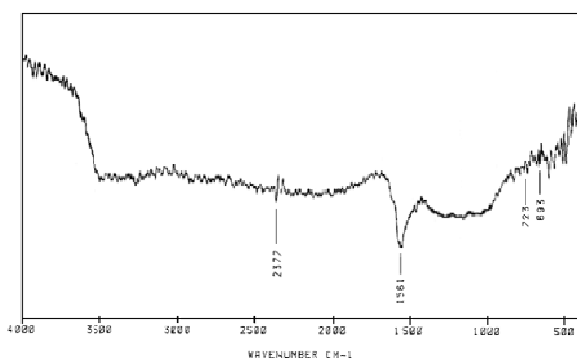


Figure 2. FTIR spectrum of CNTs.

Fig. 3 depicts the SEM image of the SWNT. It was determined that the synthesized CNTs are single walled, having an average diameter of 2nm and average length of 10 μm .

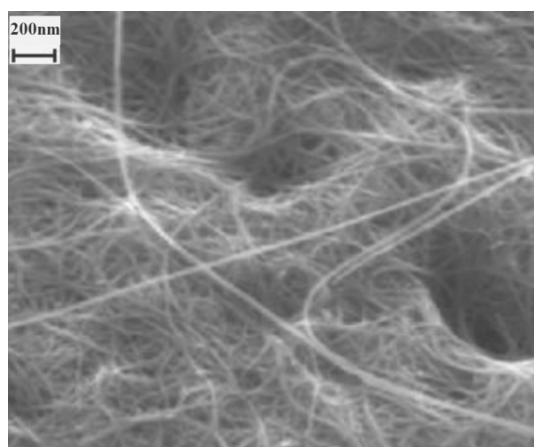


Figure 3. SEM image of SWNT.

4. Preparation of the nanofluid

In order to prepare 1 wt. % of the nanofluid, at the start 1 g of the SWCNT powder was added to 99 g deionized water. Whilst mixing mildly, 1.5 g of SDS was gradually added to stabilize the CNTs. To obtain a uniform dispersion of the SWNT, the mixture was ultrasonicated for 45 min. The stability of the nanofluid was checked after 48 hours; since no precipitate was found the nanofluid was utilized in the hydrate formation process.

The gas hydrate formation was carried out in a 600 ml steel reactor (Parr series 5500 HP). The reactor was put in a Teflon jacket, water/ethylene glycol solution was circulated inside the jacket and around the reactor by circulator (model RE-10, Germany). The reaction temperature could be kept constant with a precision of ± 0.1 K. Two needle valves were installed on the reactor for controlling gas input and output. A 4-blade impeller was located inside the reaction chamber such that the rotation speed could be controlled in the range of 100-1000 rpm. Scheme of the designed system is shown in Fig. 4.

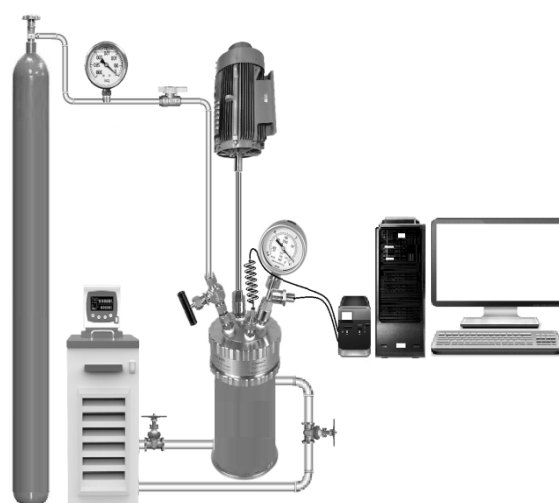


Figure 4. Scheme of the laboratory system designed for the investigation of gas hydrate formation process.

The reaction temperature was monitored by a temperature sensor with a precision of ± 0.01 K. Software received electrical pulses from a temperature recorder system. To monitor reaction chamber pressure, BD sensors 26.600 operable within 0-400 bar at accuracy of ± 0.005 of the full scale output was used.

To start hydrate formation process, reactor interior was washed, cleaned and perfectly dried. The reactor was loaded with 100 g water/SWCNT, and then natural gas was injected to de-air the reaction chamber. The outlet valve was closed and with the injection of natural gas the chamber was pressurized to 1000 psig. Simultaneously the cooling system gently decreased the internal temperature to 4°C . Reaching 1000 psig, the inlet valve was closed and the clock started.

The initial amount of the gas was calculated by equation 1.

$$PV = znR \quad (1)$$

where z is the gas compressibility factor that could be obtained by Peng-Robinson state equation. 1.66 moles was the initial calculated amount of the gas. System software was monitored and pressure changes of the reaction course were recorded. Sequestration of gas by nanofluid, formation of hydrate crystals and their growth were sources of pressure drop during the reaction progress. After a while the rate of change of pressure became minimal which showed the completion of gaseous hydrate formation.

Hydrate storage capacity is one of the main factors which determines the pertinence of a hydrate for gas storage and transfer. Usually this factor is defined as the ratio of the volume of the gas stored in the hydrate at

standard conditions to the unit volume of the hydrate. Replacing values of the constants and the standard values of $p=1$ atm and $T=15^{\circ}\text{C}$ in eq. 1 resulted in $V = 23.643 n$. Since $n = m/M_w$ and $\rho = m/V$:

$$\frac{V_{(gas)}}{V_{(hyd)}} = 23.643 \frac{\rho c}{M_w} \quad (2)$$

Where $V_{(gas)}$: volume of the gas, $V_{(hyd)}$: volume of the hydrate, ρ : hydrate density, c : mole fraction of the trapped gas in the hydrate and M_w is the molecular weight of the hydrate. Methane has the maximum storage capacity; since it makes the best type, I hydrate structure. By replacing $\rho=913$ kg/m^3 $M_w=17.74$ and $c=14.1$ mol% in equation 2, 171.6 was obtained as the maximum storage capacity in Methane hydrate formation. Hydrate stability is an important parameter. Hydrate should be cooled to -10°C to remain stable at atmospheric conditions [15]. The stability of the hydrate was studied by reduction of hydrate temperature to -10°C after 12 hours equilibration. The pressure changes were monitored during this period and the amount of the released gas due to hydrate dissociation was calculated using eq. 1. The result was reported as the percentage of dissociated hydrate.

5. Results and discussion

5-1. Hydrate formation process in the presence of water/SWNT

Prior to the application of nanofluid, control sample was tested for gas hydrate formation. The control sample was composed of a 1.5 wt. % SDS solution in deionized water. Then the results of the control sample were used in

the hydrate formation in the presence of SWCNT nanofluid. Pressure and temperature changes of the reaction vessel versus time for water/SWCNT are shown in Fig 5.

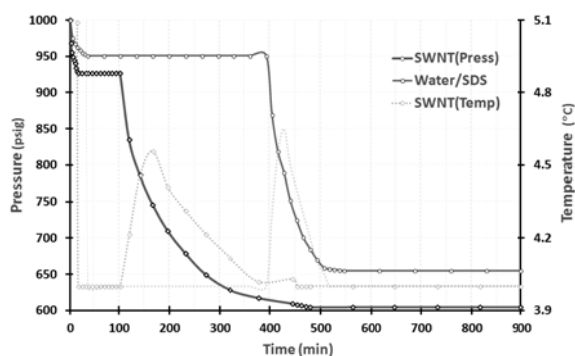


Figure 5. Pressure and temperature changes of the hydrate formation process versus time for water/SWCNT.

Fig 5. showed that the maximum pressure changes have occurred in the first 15 min and the pressure has dropped to 927 psig, this could be attributed to the natural gas dissolution in nanofluid. As a result, 1.51 mole of gas remained in the reaction vessel; therefore, 0.145 mole of the natural gas was dissolved in the nanofluid to take part in nucleation process. On the other hand, after 102 min another pressure drop was observed and at the same time due to the nucleation of natural gas hydrate and its consumption, reaction vessel temperature was increased. The induction time of the water/SWCNT sample (t_i) was calculated as: $t_{i(\text{water/SWCNT})} = 102 - 15 = 87$ min.

Thus, the reaction vessel pressure was constant for 87 min and its temperature was kept constant at 4°C. This induction time was 75.5% less than the induction time of the control sample. Induction time for methane hydrate was reduced by 73.9% in the presence of silver nanoparticles under

(827 psi) 5.7 Mpa [16]. The second pressure drop to 609 psig lasted 342 min and afterwards pressure changes were trivial; such that during the last 34 min the pressure drop was only 5 psig, which is negligible. Therefore, 445 min was needed for completion of the hydrate formation process and the reaction vessel equilibrium pressure was 609 psig. At this pressure, 0.972 mole of the gas remained in the reaction vessel.

5-2. Hydrate storage capacity and stability studies

Replacing 17.8 kg/kmol for Mw and 910.41 kg/m³ for ρ in equation 2 resulted in $V_{(\text{gas})}/V_{(\text{hyd})} = 1209c$. The calculated hydrate storage capacities in the presence of SWCNT are summarized in Table 1.

Table 1. Loading capacity of SWCNT.

Nanostructure	Water/SDS	SWCNT
Equilibrium pressure (psig)	655.1	604.2
Moles remained	1.007	0.918
Hydrate moles	0.652	0.741
Gas mole percent within hydrate	0.118	0.134
Storage capacity	142.3	161.7
Storage growth (%)	---	13.6

Table 1 showed that hydrate storage capacity has increased 13.6% in the presence of 1 wt.% of SWCNT. The storage capacity of methane in hydrate was increased by silver nano particles about 7.4% in (827 psi) 5.7 Mpa [16]. The cause of this increase was the rise in the amount of the dissolved gas during dissolution and induction processes. Moreover, SWCNT caused the growth process to proceed with more nuclei, thus more gas could be sequestered by hydrate crystals. For investigation of hydrate stability, after

completion of hydrate formation, first, the reaction temperature was decreased from 4°C to -10°C, and then excess gas was sent to the ambient. Then the clock was started and during 10 hours, the relative pressure of reaction vessel was recorded hourly. Based on the relative pressure of each stage, mole numbers of the released gas were calculated and subtracted from the initial mole number at maximum storage capacity. Fig. 6 compares the calculated dissociation percentage in the presence and absence of SWNT.

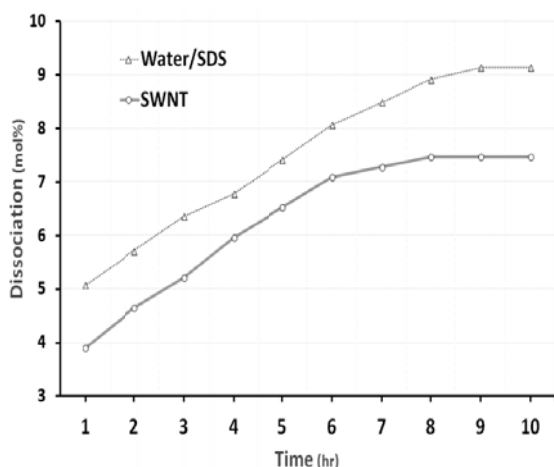


Figure 6. Natural gas hydrate dissociation rate in water/SWNT ($p=1$ atm; $T=263$ K).

Maximum hydrate dissociation in 10 hours was 7.1% for SWCNT nanofluid. The first 6 hours showed a high rate of hydrate dissociation such that 94.5% of total dissociation occurred in this period. The same trend with the same quality was observed for control sample, as well. Hydrate dissociation in the presence of SWCNT almost stopped after the 6th hour, whereas it continued for the control sample. Therefore, it could be concluded that the reasonable stability of gas hydrate originated from the

networking of SWNT within the nanofluid that produced a more stable hydrate structure. Therefore, the dissociation resistance of the formed hydrate would be reinforced. In other words, the strong framework produced by carbon networking amplified the stability of the hydrate structure.

6. Conclusions

Considering 13.6% enhancement of storage capacity by SWNT against water and smaller amount of framing water in SWCNT hydrate versus control sample, it might be inferred that because of the reduced amount of water, SWCNT hydrate has a lower self-storing resistivity. However, it was observed that hydrate dissociation was not intensified and it was even smaller than the control sample's. Therefore, besides a positive effect on the storage capacity, CNTs have protected the hydrate and created a dissociation resistive layer, as well.

Furthermore, in gas storage, it was observed that SWNT acted the same as surfactants. Nonetheless, while the former have increased the hydrate stability, the latter lowered it and increased the dissociation rate. SWNT could make an appropriate replacement for surfactants, since in every aspect they were superior for hydrate formation and eventually produced a more stable product.

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