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Thermal conductivity enhancement of clathrate hydrate with nanoparticles

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ABSTRACT

The thermal conductivity of a system of tetrahydrofuran clathrate hydrate-nanoparticles (carbon nanotubes and copper nanoparticles) was measured under different temperatures (258.15–270.15 K), different nanoparticle mass fractions (0.1–10 wt%), with and without dispersant (sodium dodecyl sulfate), and different nanoparticle dimensions (25 nm and 50 nm copper nanoparticles). The results indicated that thermal conductivity of the system increases with the increasing mass fractions of nanoparticles. At certain mass fractions, the effect of the thermal conductivity enhancement using carbon nanotubes was more significant than that using copper nanoparticles. The hydrate containing nanoparticles is also a glass-like material. At a certain nanoparticle mass fraction, the rate of the thermal conductivity enhancement increased with increasing temperature. The thermal conductivity of the system without dispersant was lower than that with dispersant, and it increased with decreasing nanoparticle dimension. A model for predicting the thermal conductivity of the hydrate-nanoparticle system was proposed, and it was well fitted with the experimental data. The loading of nanofluids could enhance the heat transformation and promote the formation of the gas hydrate. Furthermore, among the considered factors of influence, microinteraction was considered a main factor.

1. Introduction

Gas hydrates are crystalline compounds formed from water and certain natural gas or volatile liquid compounds. A unit volume of hydrate, i.e., 1 m^3 of methane gas hydrate, when dissociated at atmospheric conditions releases 164 m^3 of methane and 0.8 m^3 of water [1]. The use of the gas hydrate as a new solidifying natural gas technology could be an alternative method for safe natural gas storage and transportation compared to using liquefied natural gas or compressed natural gas technologies, which require either a much lower temperature or much higher pressure than gas hydrate. However, there are several challenges before using the gas hydrate can become a viable technology for the storage and transportation of natural gas [2]. First, the induction time for the methane hydrate formation is relatively high [3]. Next, the amount of gas trapped in methane hydrate crystals is too low, for example, Sun et al. were found that the storage capacity of the methane hydrate is less than 20 V/V within 500 min when the synthetic natural gas hydrate formation experiment was conducted in the absence of surfactants in an acquiescent system [4]. In addition, the requirement of high pressure and low storage temperature is still problematic. Thus, the hydrate formation pressure must be lowered or the formation temperature must be increased using additives, which are typically referred to as promoters. Tetrahydrofuran (THF) is found to be a potential thermodynamic promoter that forms methane hydrate at comparatively lower temperature and pressure conditions suitable for the storage and transportation of natural gas, as well as gas separation, carbon capture, water desalination, etc. [5–7]. Not only can it be a thermodynamic promoter, THF and water can also form Structure II (sII) hydrate without the help of any other gas molecules [8]. Moreover, THF hydrates are one of the cold storage materials currently under study [9–12].

As a type of cool storage medium and hydrate formation promoter, there is no mass transportation in the course of THF hydrate formation, and the formed THF hydrate is very uniform; however, the hydrate sometimes forms slowly [13]. As the formation of gas hydrates is an exothermic process, heat transfer always accompanies hydrate formation or dissociation. The understanding of heat transfer characteristics is critical to the modeling of formation/dis-

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sociation kinetic process of gas hydrates, which favors the best exploitation of natural gas hydrates and the best design of the reactor for hydrate production or decomposer for hydrate dissociation with respect to different types of hydrate application objects. Therefore, it is necessary to study the thermal properties of gas hydrate. Most hydrate heat conductivity data have been obtained using the probe and transient surface heat source method [14,15]. Stoll et al. [16] found that the thermal conductivity of propane hydrate is approximately one-fifth that of ice. Other studies on the thermal conductivities of different hydrates found that gas hydrate has a low thermal conductivity [17–20]. However, studies tend to focus on improving the heat exchanger design [21–23], but studies about enhancing the thermal conductivity of hydrate have hardly been reported. Since the concept of "nanofluid" was suggested by Choi [24] in 1995, many studies about the thermal conductivity of "nanofluids" have been performed. Choi and his co-workers [25–27] measured the thermal conductivity of liquid with a suspension of nanoparticles such as Al_2O_3, Cu, SiO_2, and TiO_2. The results showed that thermal conductivity of the fluid was obviously enhanced by adding nanoparticles. Keblinski et al. [28] and Wang et al. [29] analyzed the mechanism of the thermal conductivity of "nanofluids" and proposed the model. Xing et al. [30] compared the thermal conductivity properties among three types of nanofluids with different carbon nanotubes added to de-ionized water. Their results showed that carbon nanotubes nanofluids exhibit higher thermal conductivities than that of the base fluid, and the thermal conductivities increase with the increase of concentration and temperature. Thus, it has been suggested that the thermal conductivity of hydrates can be enhanced by adding nanoparticles.

A nanofluid is a multiphase system. There are many different models for evaluating the effective thermal conductivity of a multi-phase system, such as the Maxwell model [31], Hamilton–Crosser model [32], Krupiczka model [33], and Wooside model [34]. It is too complicated to consider all factors for measuring effective thermal conductivity, and therefore, every model has certain applicable conditions. For example, the Maxwell model is strictly applicable only when solid spheres are sufficiently far apart such that they do not mutually interact. Therefore, in this study, a model based on the microinteraction between the hydrate and the nanoparticles was established to predict the effective thermal conductivity of a hydrate–nanoparticle system.

Zhong et al. found that the surfactant sodium dodecyl sulfate (SDS) could improve the gas hydrate formation ratio and reduce formation time [35]. On adding 284 ppm SDS to the water phase, ethane hydrates formed at a rate that exceeded the rate obtained with pure water by a factor of 700 times. Thus, the 280 ppm SDS aqueous solution would be used in this study. Huang et al. [36] found that the thermal conductivities of the THF-SDS hydrate only showed a ±1.5% deviation from that of the pure THF hydrate by measuring and comparing the thermal conductivity of the THF hydrate formed under different SDS concentrations (100 ppm, 500 ppm, and 1000 ppm). Thus, the deviation in the thermal conductivity result of the hydrate formed from a 280 ppm SDS solution in the experiments was acceptable. In this study, the thermal conductivity of the THF hydrate containing nanoparticles was measured under different temperatures (258.15–270.15 K), different nanoparticle mass fractions (0.1–10 wt%), with and without dispersant (SDS), and different nanoparticle dimensions (25 nm and 50 nm).

2. Experimental

2.1. Apparatus

The primary measurement apparatus consisted of a hydrate formation system and a thermal conductivity test system, as shown in Fig. 1. The device allowed hydrate formation and subsequent direct thermal conductivity testing. The hydrate formation system included a cell immersed in an alcohol bath. The plastic cell had a volume of 80 cm^3. The temperature range controlled by the alcohol bath was from 228.15 K–313.15 K, and its precision was ±0.1 K. To measure the temperature change in the hydration process, a Pt100 Resistance Temperature Detector (RTD) with a precision of ±0.01 K was placed in the solution in the cell. A hot disk thermal constant analyzer system (Sweden Hot Disk AB Company) was used to measure the thermal conductivities of the samples. The thermal constant analyzer system allowed measurements over the temperature range from 10–500 K, and the standard uncertainty of the measured thermal conductivity was 0.002 $W \cdot m^{-1} \cdot K^{-1}$. The temperature data were collected using an Agilent 34,970 Data Acquisition/Switch Unit and logged with an Agilent BenchLink Data Logger program.

2.2. Materials

The SDS surfactant was obtained from Guangzhou Chemical Reagent Factory with purity greater than 98 wt%; THF was obtained from the Huankai Experimental Technology Corporation in Guangzhou, and its purity was above 99 wt%. In this study, multiwall carbon nanotubes (95 wt% purity) were obtained from Shenzhen Nanotech Port Co., Ltd. Copper nanoparticles (99.9 wt% purity) were obtained from Shenzhen Junye Nano Material Co., Ltd.; they had a spherical shape and dimensions of 25 nm and 50 nm. The properties of nanoparticles used in our experiment are listed in Table 1.

2.3. Procedure

2.3.1. Preparation of the THF aqueous solution

THF is miscible in water and forms a sII hydrate with water at a composition of 1:17 molar ratio or 19% by weight [37]. Therefore, the mass ratio of THF and water (SDS aqueous solution) was 19:81 (mole ratio of 1:17) in the experiments.

2.3.2. Preparation of the nanofluids

After preparing the THF aqueous solution, the nanoparticles need to be uniformly and stably dispersed in the solution. Several dispersion methods such as the mechanical, ultrasonic, high-energy, and chemical methods are commonly used to mix the suspension. In this study, a method combining ultrasonic and mechanical dispersion was used (when the SDS aqueous solution was used, SDS acted as dispersant). First, nanoparticles were added to the THF aqueous solution, and then, they were mixed by an agitator for 15 min. Second, ultrasonic waves were used to disperse the nanoparticles in the solution. Finally, the solution was again mixed by the agitator for 15 min.

During the formation of the THF hydrate, SDS acted as not only a dispersant but also a promoter [38]. Because THF was easy to volatilize in the ultrasonic process, the volatilized fraction was compensated according to the loss of mass to ensure that the mass ratio of THF and water remains stable after the process.

2.3.3. Hydrate formation

The initial temperature of the alcohol bath was set at 258.15 K, and the pressure in these experiments was atmospheric pressure. The prepared nanofluids (volume = 60 ml) were placed in the cell and the hydrate reaction process was started. To avoid THF volatilization, the cell was usually sealed after the nanofluids were loaded. When the hydrate reaction process started, the reactor was still and unstirred to make sure the system was quiescent. Once the hydrate began to form, the temperature increased. The hydrate reaction completion was determined by a shift of the sample