



Promotion effect of graphite on cyclopentane hydrate based desalination

Feng Li, Zhijie Chen, Hongsheng Dong, Changrui Shi, Bohao Wang, Lei Yang, Zheng Ling*

Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, School of Energy & Power Engineering, Dalian University of Technology, Dalian 116024, China



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ABSTRACT

Desalination via hydrate processes is promising in producing freshwater at low energy cost. However, it is a great challenge to instantaneously produce and form large amount of hydrates in short time, particularly with salts presence. In this study, we used cheap and easily separated graphite particles to promote hydrate based desalination. The added graphite can promote the formation of hydrate, greatly shortening the induction time. The desalination efficiency was also enhanced due to the introduced graphite. Combined graphite and stirring, both the desalination efficiency and water conversion ratio were boosted. The impact of particle sizes of graphite on hydrate formation was found to be different at static state and stirring. The proposed hydrate based desalination is almost independent on treated volume. Additionally, this method can use the nature chilling, which is potential in further reducing the energy cost of desalination via hydrate. The findings in this study would help rationally choose and design promoting agents and hydrate processes for facilitating hydrate formation and desalination via hydrates.

1. Introduction

Water shortage is one of the most pressing global problems that human being are facing. About 80% of the population worldwide is under the high level threat of water security [1]. Seawater is the largest water resource on Earth [2], however, the high content of salt makes seawater unusable for people's daily life. Therefore, desalination technologies are highly desired for producing freshwater from seawater [3]. Desalination processes can generally be categorized as thermal-based and membrane-based technologies, with various alternative methods having been proposed [3]. It is highly demanded to improve desalting efficiency and reduce the cost of desalination processes. Recently, the application of gas hydrate technology has been investigated as an economical process for desalination [4].

Gas hydrate formation is a novel freezing desalination technology [5]. Desalination via freezing has attracted increasing attention [6], because the energy costed for inducing the phase change during freezing (6.02 kJ/mol) is much lower compared to that of liquid water to vapor during distillation (40.70 kJ/mol) [2] which is used by the traditional approaches, such as multistage flash and multi-effect distillation. The heat of hydrate formation is as low as 4.84 kJ/mol for cyclopentane hydrate [14], thus the energy consumption could be reduced further, comparing to the enthalpies of the phase change of water [2]. Another advantage of desalination via freezing is that the process is

conducted at relatively low temperature, so the corrosion problem would be less, compared with the processes forming water vapor. So desalination via freezing processes, especially the ones forming hydrate, is superior in terms of energy and cost.

Desalination via gas hydrate formation has been studied over the past 50 years [3,7–9]. The hydrate solids form at suitable temperature and pressure [10,11], and are separated from concentrated solutions, then dissociated by breaking the temperature or pressure [2,12–14]. The freshwater is produced during the dissociation process, while the hydrate guest chemicals can be collected and recycled. Various hydrate guests and formation technologies have been proposed and investigated to boost hydrate formation kinetics and conversion. Gases, such as light hydrocarbons and CO₂, are preferred guests to form hydrates for desalination due to their easy separation from produced freshwater [15–18]. However, high pressure is required for the hydrate formation, which inevitably requires more energy and expensive equipment, increasing the cost of hydrate desalination. Therefore, it is highly desired for hydrate formers to react with water at atmospheric pressure.

Cyclopentane is an ideal hydrate former since it has low solubility in water and is immiscible with water, so it is easy to separate from produced freshwater [2,19,20]. Most importantly, cyclopentane can form hydrate with water at atmospheric pressure above the ice point [21]. Conventional processes for producing gas hydrate take hours or days due to the long induction time, stochastic nucleation, and limited

* Corresponding author.

E-mail address: zling@dlut.edu.cn (Z. Ling).

mass transfer. It is ideal but challenging to instantaneously create hydrate and form large amount of hydrate in short time. Therefore, plenty of work has been devoted to promote hydrate formation.

Nanoparticles, particularly carbon materials including graphene and carbon nanotubes, were confirmed to be effective promoters to enhance gas hydrate formation [22–25]. The most significant effect was dramatically reduced induction time. However, little work has been reported using particles to enhance the formation hydrate in salty solution system with cyclopentane as guest. It is widely known that salts can make hydrate and ice formation more difficult, due to the thermodynamic limitation [26,27]. It requires larger degree of supercooling or pressure to drive the gas hydrate formation, which is far from energy conservation. Additionally, using nanoparticles will inevitably increase the cost of the hydrate formation process due to their large cost. Due to the strong interaction among the nanoparticles, surfactants are indispensable to assist the dispersion of the used nanoparticles. The surfactants would contaminate the produced fresh water because it is very difficult to separate them from water. Separation of nanoparticles is also a time and energy consuming process which would increase the cost. Another issue is that nanoparticles usually have nonstoichiometric composition, such as graphene oxides [28], or contain impurity [29], such as the metal residue derived from the catalysts in carbon nanotubes [30]. The undefined composition and impurity make it difficult to pin down what contributes to the enhanced performance. So it is highly desired to find cheap and well-defined materials with comparable or superior performance for promoting hydrate formation.

In this study, we chose graphite particles as the promoters to enhance cyclopentane hydrate formation in artificial and real seawater. The used graphite has high purity and is very cheap and easy to separate. It turned out that graphite can promote the nucleation and formation of hydrate and enhance desalination efficiency. The particle size was found to play a critical role in conversion ratio of salty water into hydrate. The proposed hydrate process is independent in the treated volume for desalination. The findings in this study would help rationally choose and design promoting agents for facilitating hydrate formation and desalination via hydrates.

2. Experimental section

2.1. Materials and characterization

The deionized water with a specific resistance of 18 MΩ was produced using Aquapro2S via reverse osmosis. Cyclopentane was bought from Aladdin Industrial Corporation. Graphite powders with average sizes of 80 mesh, 750 mesh, 2000 mesh and 8000 mesh, (corresponding to average size of 150 μm, 18 μm, 6.5 μm, and 1.6 μm) and purity over 99.95%, were purchased from Shanghai Macklin Biochemical Co., Ltd. NaCl was bought from Sinopharm Chemical. All the chemical agents were analytical pure and used without any further process.

NaCl aqueous solution with a concentration of 3.5 wt% was used as the artificial seawater in this study. The real seawater was also used to study the feasibility of hydrate desalination. The seawater was obtained from the Yellow Sea, Dalian coast, China (38°52′53″ North, 121°30′34″ East). The seawater was filtrated before using to remove particles. The filter membrane has an average pore size of 20 nm.

The morphology was studied using field emission scanning electron microscopy (FESEM, FEI NanoSEM 450). Graphite was studied using a powder X-ray diffractometer (XRD, D/MAX-2400 Japan) using Cu-Kα radiation generated at 40 kV and 100 mA. The composition of graphite was analyzed via the thermogravimetric analysis (TGA, STA 449 F3). The TGA was conducted in air at a heating rate of 10 °C/min from room temperature to 1000 °C. The micro-differential scanning calorimetry (DSC, Micro DSC7) was used to study the impact of graphite on the formation of ice and hydrate. The temperature was cooled down to −30 °C from 20 °C, then heated back to 20 °C at 0.5 °C/min. The ratio of cyclopentane to salt solution and graphite was identical to the ones

used for desalination tests.

2.2. Hydrate formation and desalination test

The cyclopentane hydrate formation was conducted at 2 °C under atmospheric pressure. Cyclopentane was mixed with NaCl solution or real seawater at a volume ratio of 1:3 with a total volume of 60 mL. Graphite was added into the cyclopentane/NaCl solution mixture at a loading of 50 mg graphite/60 mL mixture. (For the study of graphite loading effect, the loading of 0, 10, 30, 50, 70 mg was used.) Then the mixture was subjected to tip sonication for 10 min, in order to enhance the dispersion of graphite particles. Glass bottles were used as the reactors. The bottles were sealed during the whole reaction process. It was reported that it is very hard to form cyclopentane in the static state without adding ice, particularly in salt solutions. So we froze the mixtures at −15 °C for 3 h to nucleate, then conducted the reactions at 2 °C. After reaction for 50 h, the produced hydrates were separated via vacuum filtration for 30 s, then centrifuged at −5 °C at a speed of 4000 rpm for 3 min to remove the residual salt solution further. The obtained hydrates were dissociated at room temperature. Immiscible two-phase liquids consisting of cyclopentane and produced freshwater were separated carefully by decanting, with graphite locating in cyclopentane. The conductivity of the produced water was tested using an ion conductivity meter (ET915, eDAQ TECH, Australia). The concentrations of produced water and original solution were calculated using a calibration curve according to the conductivity profiles.

The reaction conducted under stirring needs no pre-freezing. The reaction agents and graphite were identical to the ones used in the static state. The reactions were directly conducted at 2 °C under stirring of 600 rpm. The same separation processes were used. In order to study the volume-dependent performance, a total volume of 600 mL reaction agents was used. We also conducted the hydrate formation outdoors with identical conditions except using no cryostat to provide low temperature. The reaction was conducted in the winter when the temperature is −10 °C.

The desalting efficiency was calculated using the Eq. (1)

$$\text{Desalting efficiency} = \frac{C_0 - C_f}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of the feeding synthetic seawater, C_f is the concentration of produced freshwater from the dissociated cyclopentane hydrate.

The water conversion rate was calculated using the Eq. (2)

$$\text{Conversion rate} = \frac{V_f}{V_0} \times 100\% \quad (2)$$

where V_0 is the volume of the feeding synthetic seawater, V_f is the volume of the produced freshwater from the dissociated cyclopentane hydrate.

3. Results and discussions

3.1. Characterization of graphite particles and their impact on hydrate nucleation in artificial seawater

The used graphite particles have a narrow size distribution with an average size of 6.5 μm as shown in Fig. 1a and b. The morphologies of other particles with different average sizes can be found in the supporting information (SI, Fig. S1). The particles with larger sizes over 1 μm can be easily separated via filtration or centrifugation. So the as-used graphite compared with the reported nanoparticles would be superior in easy separation from water without risk of residual. The XRD pattern shows two distinct peaks locating at 26° and 54° (see Fig. 1c) corresponding to graphite [31]. The XRD result suggests there is no impurity except graphite. The TGA conducted in air shows there is no ash left (see Fig. 1d), this also confirms no impurity in the used

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