

Experimental Investigation on Phase Equilibria and Kinetics of Methane Hydrate Formation in Maojian Tea Extracts

Hang Zhou^{1, a}, Qiming Geng^{2, b}, Weilong Zhao^{2, c}, Jun Song^{1, d}, and Ruirui Wang^{1, *}

¹ School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo 454000, China

² School of Civil Engineering, Henan Polytechnic University, Jiaozuo 454000, China

^a18837102254@163.com, ^b2913148600@qq.com, ^c41587787@qq.com,

^d470155226@qq.com, *wangrui2233@126.com

Abstract

The effects of Xinyang Maojian tea extracts on the methane hydrate formation of phase equilibria and kinetics were investigated in this work. Tea extracts at three different concentrations (0.0625wt%, 0.25wt% and 0.625wt%) and two different solution stand time (0 h and 24 h) were performed respectively. The results showed that 0.0625wt% tea extracts have no obvious effect on kinetics of methane hydrate formation; 0.25wt% and 0.625wt% tea extracts increased the gas consumption and hydrate formation rates significantly. The tea extracts have lager gas consumption than the tea extracts standing still for 0h in same concentrations. However, we also found that tea extracts are also thermodynamic promoters and could mitigate the phase equilibrium condition of methane hydrate. This work provides an environmentally friendly and low-cost synthetic hydrate solution, which might promote the development and industrial application of hydrate technology.

Keywords

Tea Extracts; Methane Hydrate; Phase Equilibria; Kinetics.

1. Introduction

The global energy consumption structure is moving towards a green, low-carbon and natural direction. Natural gas is one of the most important clean energy sources and has an important position in the energy field. Natural gas hydrate widely distributed all over the world as an energy resource, the carbon quantity of which is twice more than it of other fossil fuels [1].

Gas hydrate (or clathrate hydrate) is a kind of ice-like nonstoichiometric compound formed by trapping suitable gas molecules physically (such as methane, nitrogen and carbon dioxide) in hydrogen bonded water cages at a certain temperature and pressure condition [2]. The gas molecules are held in the water molecules by Van der Waal forces [3]. Many kinds of substances have been discovered to form hydrates by now, and the thermodynamics theory of hydrates is being well confirmed.

In the beginning, gas hydrate phase equilibria and kinetic experiments were carried out in pure water system [4]. Nowadays, hydrate additives, including promoters and inhibitors, have been widely applied to change the phase equilibria conditions and formation kinetics of hydrates in the experimental study. The conventional thermodynamic promoters of gas hydrates are tetraamylammonium bromide (TAAB), tetraamylammonium chloride (TAAC), tetra-n-butyl ammonium bromide (TBAB), tetra-n-butylammonium chloride (TBAC), tetra-n-butylammonium fluoride (TBAF), Tetrahydrofuran (THF), cyclopentane (CP) [5-25], etc.. The constantly-used

kinetic promoters are ionic surfactant such as sodium dodecyl sulphate (SDS) and sodium dodecyl benzene sulfonate (SDBS), and non-ionic surfactant alkyl polyglucoside (APG) and linear alkyl benzene sulphonate (LABSA) [24-32]. The common hydrate inhibitors include electrolyte aqueous solutions (sodium chloride, magnesium chloride and other inorganic salt solutions), methanol, ethanol, polyvinyl pyrrolidone (PVP) and so on [33-38]. In addition, some special materials were applied to change the phase equilibria conditions and formation kinetics of hydrates in experimental study, for example Tergitol [39], maize starch [40], leucine [41], polyethylene glycol (PEG) [42], bio-additives L-arginine and isoocetyl glucoside [43], bio-surfactants produced by *Bacillus subtilis* and *Pseudomonas aeruginosa* [44], anionic and silicone surfactant [45], metal nanoparticles-grafted carbon nanotubes [46], Ag&SDS-coated nanospheres [47], calcium carbonate [48] and amino acids [49]. The presence of above additives in formation and dissociation of hydrates makes the application of hydrate-based technologies more practicable and convenient in the gas exploitation industrial. However, as the chemical substances, some of them also have obvious disadvantages such as pungent flavor, corrosivity, toxicity, and anti-degradability. These defects are seriously polluting the environment, endangering human health and limiting the application of hydrate technology. Therefore, it is necessary to develop a high safety, mild nature, biodegradable and eco-friendly substance as the hydrate promoter or inhibitor.

Baek et al. proposed that the appropriate amount of sII cyclopentane (CP) hydrate seeds could significantly improve the kinetic effect of sodium dodecyl sulfate (SDS) solutions on methane hydrate formation [25]. Sun et al. found that the CH₄ bio-hydrate formed by the bio-additives (L-arginine and isoocetyl glucoside) has different thermodynamic and kinetic effects compared with other hydrate [43]. The results showed that L-arginine can be used as hydrate thermodynamic inhibitor and isoocetyl glycosidase is an effective kinetic promoter. Bavoh et al. studied two amino acids (valine and arginine) had the same impact of thermodynamically inhibited but kinetically promoted on methane hydrate phase boundary and formation [49]. Vikash et al. researched the kinetics of methane hydrate formation and dissociation in presence of a non-ionic surfactant Tergitol with different concentrations and the results showed that Tergitol could be used as a thermodynamic and kinetic promoter for methane hydrate formation [39]. Shi et al. discussed the phase equilibrium conditions of double semiclathrate hydrates formed with different mass fractions tetraamylammonium bromide (TAAB) Plus CH₄, CO₂ or N₂ and found that TAAB could improve the phase boundary of CH₄, CO₂ or N₂ hydrates and the phase equilibrium conditions were also enhanced with the mass fraction increased [10]. Mohammadi et al. investigated the phase equilibria of semiclathrate hydrates formed with different mass fractions tetra-n-butylammonium (TBAC) Plus CH₄, CO₂ or N₂ chloride. The data showed the presence of TBAC could improve phase equilibrium conditions and the stabilization effect was also strengthened with the mass fraction increased [16].

Actually, although the kinetic and thermodynamic promotion effects of most chemical additives are better than biological additives, there exist some problems at the same time, such as high price, environmental pollution and poisonous, Due to the requirement for high safety and eco-friendly gas hydrate additives, it is absolutely essential to find green substances as the hydrate promoters or inhibitors.

The chemical components in the Maojian tea extracts are generally derived from the secondary metabolites, mainly natural polyorganisms such as tea polyphenols, tea polysaccharides, proteins, alkaloids, tea pigments, free amino acids, and soap[50]. Organic fiber in tea extracts which the authors observed could promote formation kinetics and mitigate the phase equilibrium condition of methane hydrate. In this work, the formation kinetics and the phase equilibria of methane hydrate in different concentrations tea extracts was investigated, respectively. Additionally, considering that the long standing time of tea extracts may cause some components to be oxidized, thus the properties of its solution were affected. As far as the authors know, no research on tea extracts as the hydrate formation solution has been reported in literatures.

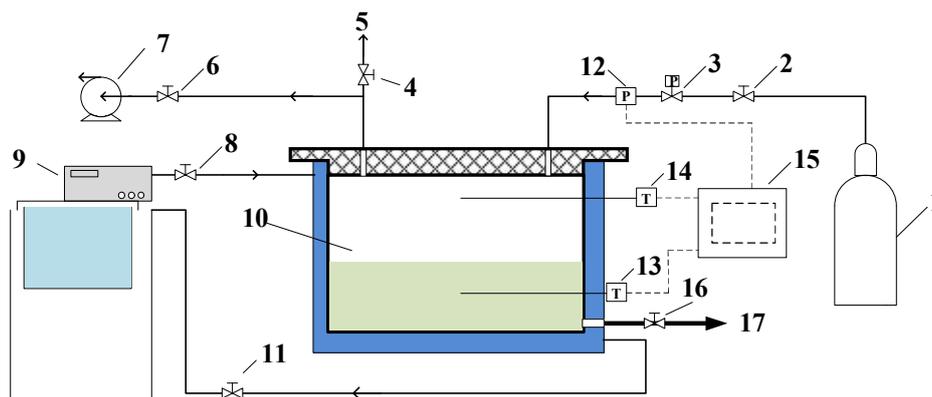


Fig.1. Schematic diagram of the experimental apparatus.

1. Gas cylinder; 2, 4,6,8,11,16. Valves; 3. Pressure regulator; 5. Gas vent; 7. Vacuum pump; 9. Water bath control; 10. Hydrate reactor; 12. Pressure transducer; 13, 14. Resistance thermometer; 15. Computer acquisition system; 17. Liquid inlet/outlet

2. Experimental

2.1 Materials

The information of experimental materials used in this work was listed in Table 1. Pure water was provided by Jiaozuo Xin Bo Long Trading Company. An electronic analytical balance with an accuracy of $\pm 0.001\text{g}$ was used to weigh the mass of the teas and water for the solution preparation. Tea extracts of three mass fractions (0.0625wt%, 0.25wt% and 0.625wt%) were prepared.

Table 1. Specifications of experimental materials.

Materials	Species	Purity	Suppliers
CH ₄	/	99.99mol%	Jiaozuo Xin Bo Long Trading Company
Tea	Xinyang Maojian Tea	/	Xinyang MingZhu Tea Industry
Pure water	/	/	Jiaozuo Xin Bo Long Trading Company

2.2 Apparatus

A detailed schematic diagram of the experimental apparatus was shown in Fig.1. It was mainly composed of the water bath, pressure regulator, hydrate reactor, temperature and pressure measuring probes and computer acquisition system. The water bath keeps a constant temperature for the reactor. The pressure regulator adjusts and controls pressure in the reaction system. The 600 mL reactor is a jacketed stainless steel cell. It could withstand maximum pressures up to 12.5 MPa and was immersed in water bath to maintain the temperature of the equilibrium at setting value. The temperature and pressure are measured by a platinum resistance thermometer (PT100) with the accuracy of 0.1 K and a pressure transducer with accuracy of 0.1 MPa, respectively. The experimental data of temperature and pressure were collected every 5 seconds by a data collector and stored in the computer.

2.3 Procedure

Tea extracts were prepared before all experiments. The Maojian tea was weighed by the electronic balance. Pure water was added to immerse in a water bath twice at a constant temperature of 353.15 K for 20 mins each time. Finally, the tea extracts were mixed with pure water to specific volume (100ml for kinetic study or 300ml for thermodynamic study). If needed, the tea extracts would stand for 24 h. All the kinetic study experiments conducted were of batch type and conducted at 6.05 MPa, 274.15K without stirring. Prior to the experiments, the reactor was cleaned with pure water and dried three times. Then 100 ml tea extracts of specific concentration were put into the reactor. After the liquid was cooled to setting temperature, the reactor was pressurized to 0.35 MPa and evacuated with

a vacuum pump about 5min for three times in order to remove the air initially. Then the reactor was inflated to 6.05 MPa with CH₄. Temperature and pressure data were recorded continuously for every 5s from the start of the experiment.

During hydrate formation process, the initially gas dissolution in tea extracts results in pressure drop in the reactor before saturation. The pressure remained stable till the formation of first hydrate crystal. After nucleation, the pressure reduces due to the gas occupying and stabilizing hydrate cages. The pressure drop is accompanied by a marked temperature rise due to the exothermic nature of hydrate formation. Gas hydrate formation continues till no further pressure drop.

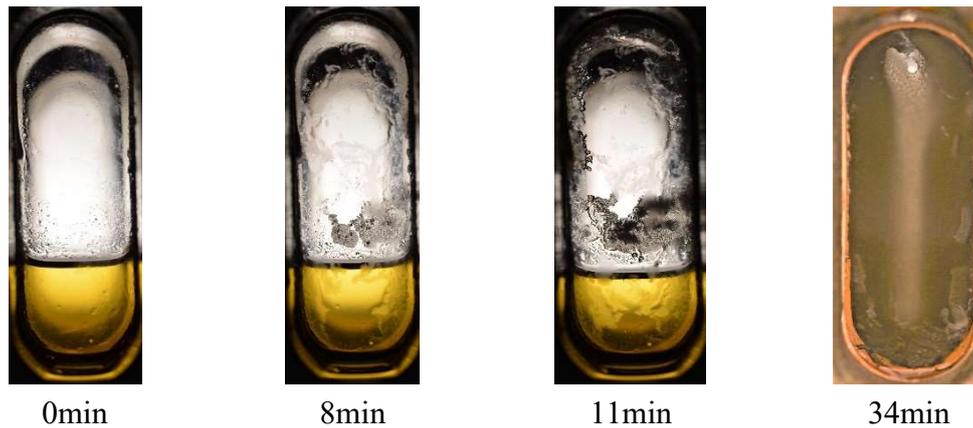


Fig.2. CH₄ hydrate formation process in 0.25wt% tea extracts (24h) at 274.55 K, 4.84 MPa. (without stirring).

The equilibrium data of CH₄ hydrate were measured by using an isochoric pressure-search method described in detail by Du et al. [51, 52]. All experiments were operated in 300 mL tea extracts of different concentration. After the hydrate formed completely or the pressure kept stable, the system temperature was beginning to be increased by steps of 0.1 K. At each step, the temperature was kept constant for at least 3h to guarantee entire system equilibrium. During the experiment, both the temperature and pressure were recorded and plotted. Eventually, by repeating the procedure, the P–T diagram for hydrate formation and dissociation was plotted. In this way, the hydrate dissociation point was determined at which the P–T curve slope changed sharply. The reliability and reproducibility of the data reported through this procedure has been previously demonstrated [53-59].

Fig.2 shows the CH₄ hydrate formation process in 0.25wt% tea extracts (24h) at 274.55 K, 4.84 MPa (without stirring). Four stages of gas hydrate formation were described by a, b, c, d. Initially, due to the lower temperature of inner steel wall, methane hydrate formed upward adhering the inner wall, and the liquid level decreased. It was remarkable that during hydrate formation process, no ice-like layer covered on the gas-liquid surface.

2.4 Calculation of the Methane Consumption

Base on values of the temperature and pressure of the experiments, the number of moles of methane forming hydrate crystals in tea extracts was calculated by Eq. 1.

$$\begin{aligned} \Delta n_c &= n_{g,0} - n_{g,t} \\ &= [(PV)/(ZRT)]_0 - [(PV)/(ZRT)]_t \end{aligned} \quad (1)$$

Where n_g is the number of moles of methane in the reactor at time 0 and time t, P is the pressure in the reactor, T is the temperature of gas phase, V is the volume of gas phase, R is universal gas constant

and Z is the compression factor calculated by the Pitzer’s correlation for the second Virial coefficient (Eq. 2) [60].

$$Z = 1 + (B^0 P_r) / T_r + (\omega B^1 P_r) / T_r \tag{2}$$

Where the equations of Abbott were used for B0 and B1.

3. Results and Discussion

3.1 Examination of the Reliability and Accuracy of the Experimental System

In order to verify the reliability and accuracy of the apparatus and the isochoric equilibrium step-heating pressure search method in this work, the phase equilibrium data of CH4 hydrate in pure water were compared with the experimental data given by Gayet et al.[61], Mohammadi et al.[16] and Qing et al.[12].

Table 2. Three phase equilibrium conditions of CH4 hydrate in pure water.a

T/K	P/MPa
275.25	3.23
276.35	3.62
277.15	3.91
278.55	4.55
279.15	4.74

aUncertainties u are u(T) = ± 0.15 K, u(P) = ± 0.01 MPa.

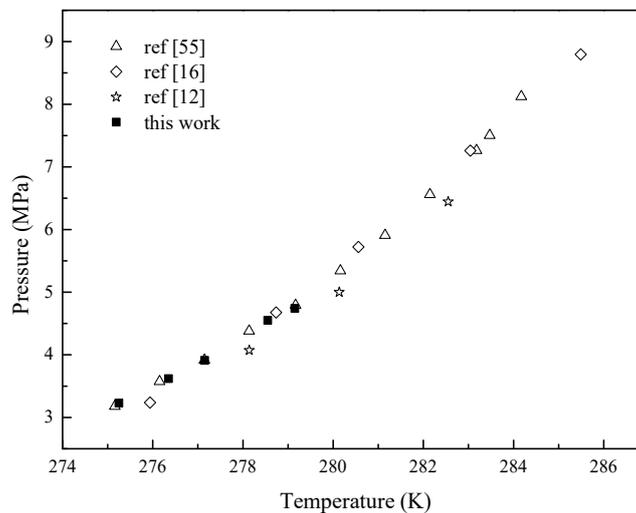


Fig.3. The rate phase equilibrium data for CH4+ H2O system in this work.

The phase equilibrium data for CH4 hydrate in pure water measured in this work were presented in Table 2 and Fig.3, together with data reported by Gayet et al.[61], Mohammadi et al.[16] and Qing et al.[12]. As shown in Fig.3, the results of this work have been compared with literatures data and show good agreement with literature data [12, 16, 61].

3.2 Formation Kinetics of CH₄ Hydrate in Maojian Tea Extracts (0h and 24h)

The temperature and gas uptake curves of 0h tea extracts with 0.625wt% and 0.25wt% mass fraction obtained at 274.15 K, 6.05 MPa are given in Fig.4 and Fig.5, respectively. The induction time is identified by a sudden temperature rise, and is 18 mins for 0.625wt%, and 10 mins for 0.25wt%. The gas uptake is the number of moles of the methane captured by the gas hydrate formed in the tea extracts, which was obtained using Eq (1). As shown in Fig.5, the gas uptake increases rapidly to about 0.577mol at 62 mins and then decreases, plateauing at 0.599 mol at about 150 mins. The gas uptake trend in Fig.4 turns out to be the same as Fig.5, but the gas uptake is smaller than Fig.4.

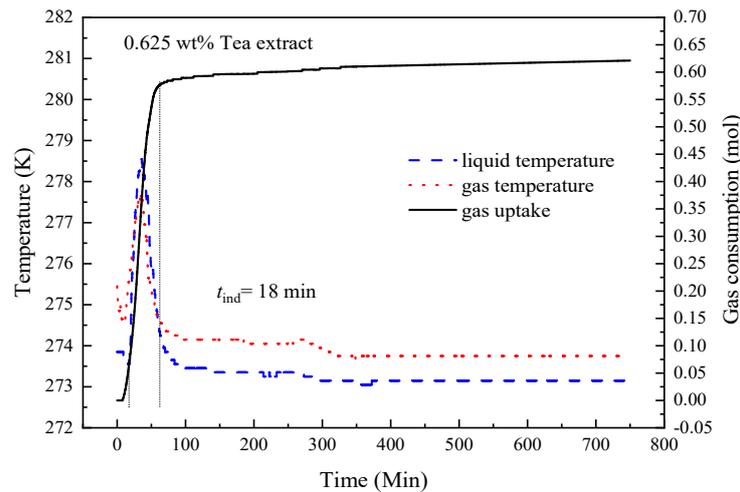


Fig.4. Temperature and gas uptake in 0.625wt% tea extracts (0h) at 274.15 K, 6.05 MPa. (without stirring)

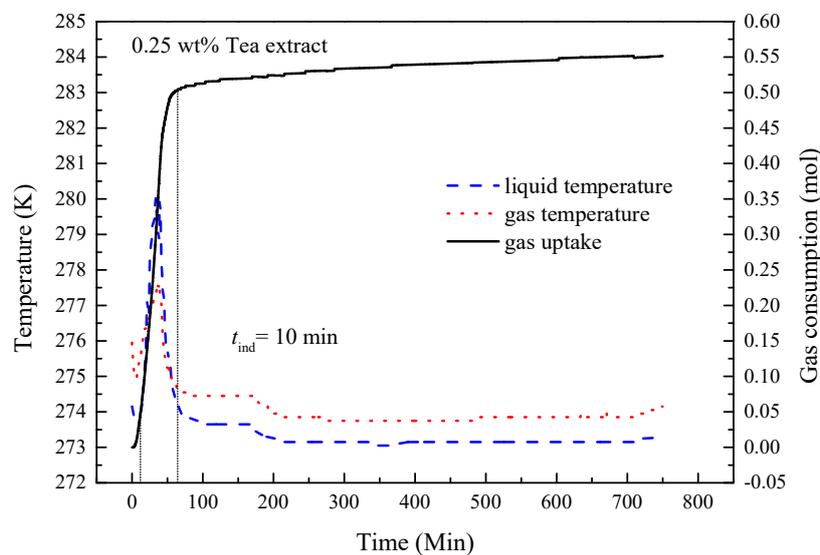


Fig.5. Temperature and gas uptake in 0.25wt% tea extracts (0h) at 274.15 K, 6.05 MPa. (without stirring)

The temperature and gas uptake curves of 24h tea extracts with 0.625wt% and 0.25wt% mass fraction obtained at 274.15 K, 6.05 MPa are given in Fig.6 and Fig.7, respectively. The induction time is 10 mins for 0.625wt%, and 15 mins for 0.25wt%. In Fig.6, the gas uptake increases rapidly to about 0.64 mol at 70 mins and then decreases, plateauing at 0.657 mol at about 150 mins. The gas uptake trend in Fig.7 turns out to be the same as Fig.6, but the gas uptake is smaller than Fig.6.

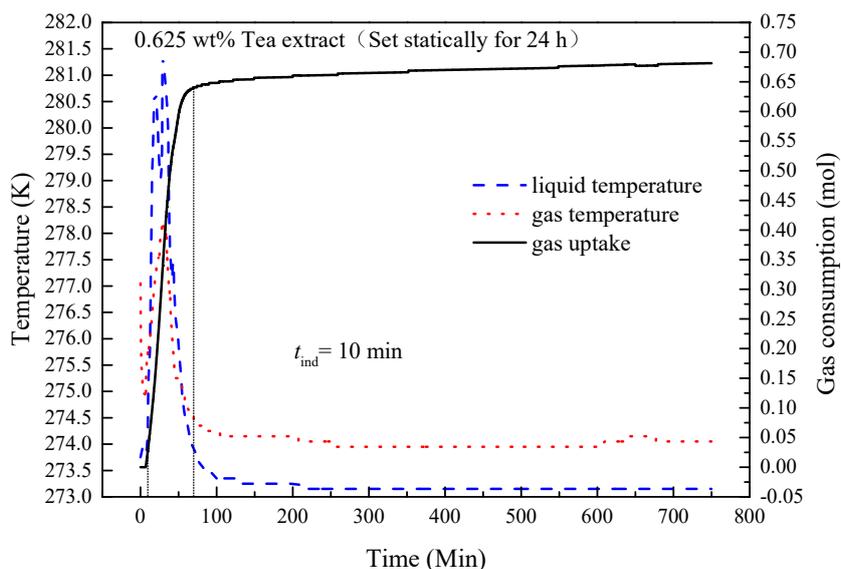


Fig.6. Temperature and gas uptake in 0.625wt% tea extracts (24h) at 274.15 K, 6.05 MPa. (without stirring)

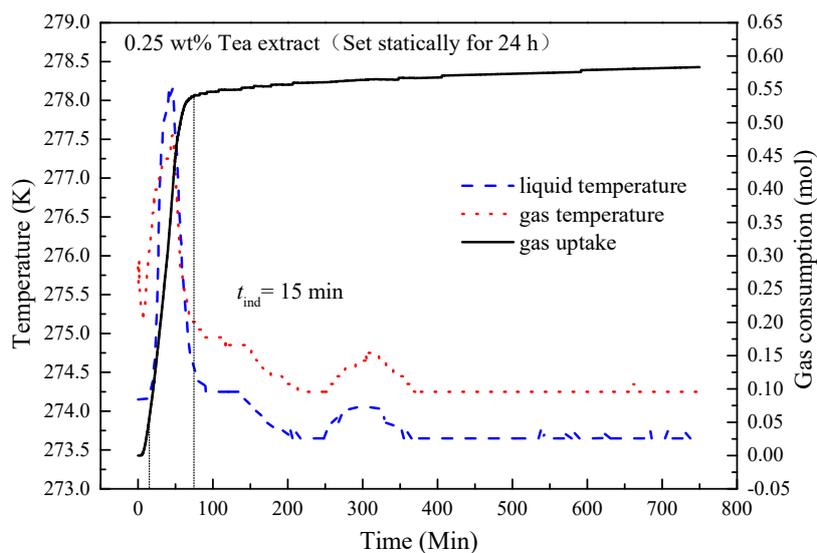


Fig.7. Temperature and gas uptake in 0.25wt% tea extracts (24h) at 274.15 K, 6.05 MPa. (without stirring)

The kinetic experiments of tea extracts set statically for 0h and 24h were also conducted. The gas uptake and temperature of 24h tea extracts are both higher than 0h tea extracts. It is clearly that methane hydrate forms violently in 24h tea extracts. The reason might be that there are some organic matters created in 24h tea extracts, which deserve further study.

Although the gas uptake curves in Fig. 4-7 were obtained at two different concentrations (0.625wt% and 0.25wt%) and two different stand time (0h and 24h), the shape of the gas uptake curves are almost the same. This indicates that the process of methane captured by gas hydrate in tea extracts experienced three stages of the hydrate induction stage (~18 min), rapid growth stage (~62 min), and the final stage (~750 min). In Fig. 4-7, the gas uptakes of the final stage are similar. It is due to the surface of the aqueous covered with a thin ice film, which blocked gas molecules going into liquid to form hydrate. The rise of temperature curves in Fig.7 might because the thin ice film broke at 250mins.

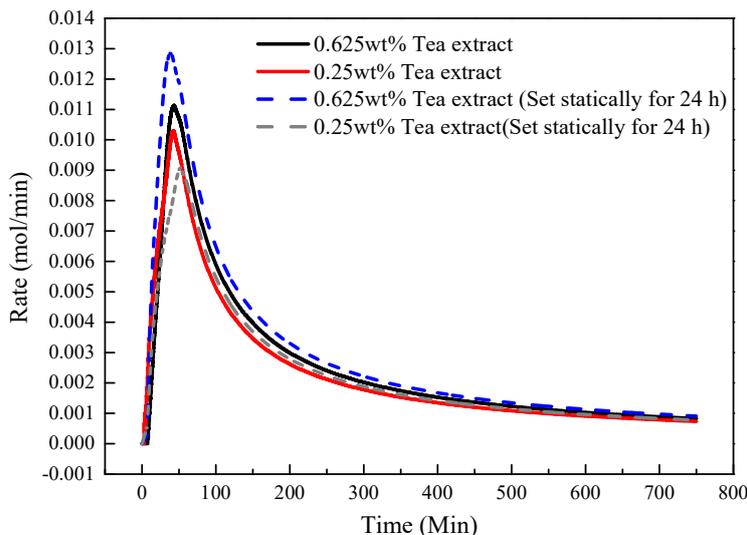


Fig.8. Hydrate growth rate in two different tea extracts concentration (0.625wt% and 0.25wt%) and solution stand time (0h and 24h). (without stirring).

Fig.8 shows the growth rates of methane hydrate in 0h and 24h, 0.625wt% and 0.25wt% tea extracts. It can be observed that the rate of hydrate growth at a fixed temperature is magnified with the increment of tea extracts concentration. For example, under 274.15 K, the growth rates (assessed over the 25 min after the nucleation point) obtained in 0.625wt% and 0.25wt% tea extracts were 0.0111 and 0.0103 mol/min, respectively. The growth rates obtained in 0.625wt% and 0.25wt% tea extracts (24h) were 0.0129 and 0.00909 mol/min under the same condition, respectively. However, the effect of solution stand time is probably not in order for the hydrate growth rate, the reason of which is that the thin ice film limits the gas molecules being mixed with the liquid. In certain time, only limited gas molecules can go into liquid to form hydrate.

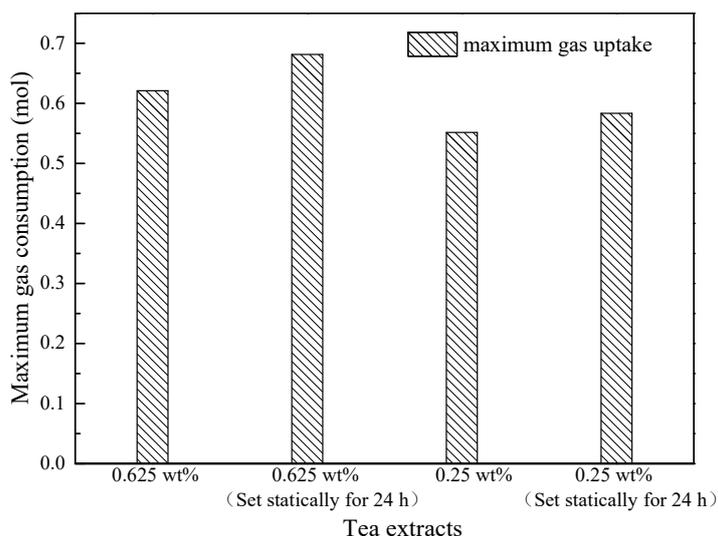


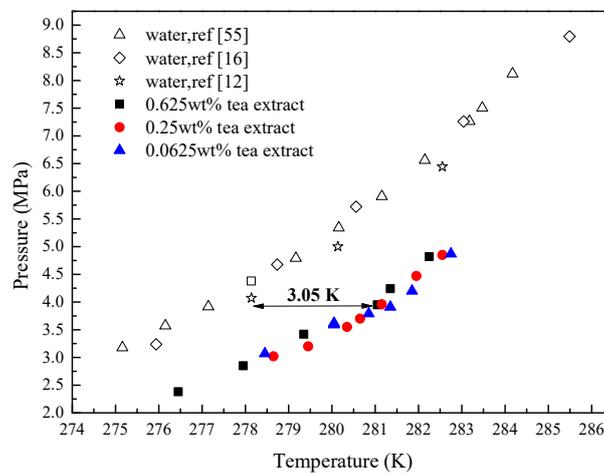
Fig.9. Maximum gas consumption of two different tea extracts (0.625wt% and 0.25wt%) and two stand time (0 and 24h).

Fig.9 presents maximum gas consumption at two different tea extracts concentrations of 0.625wt% and 0.25wt% and two stand time of 0h and 24h. Maximum gas consumption is enlarged with increasing tea extracts concentration and settling time. This should be attributed to the organic fiber substance in the tea extracts, which reduces the gas-liquid interfacial tension and accordingly increases the solubility of CH₄ in liquid. As a result, the more CH₄ forms hydrate, the fewer gas

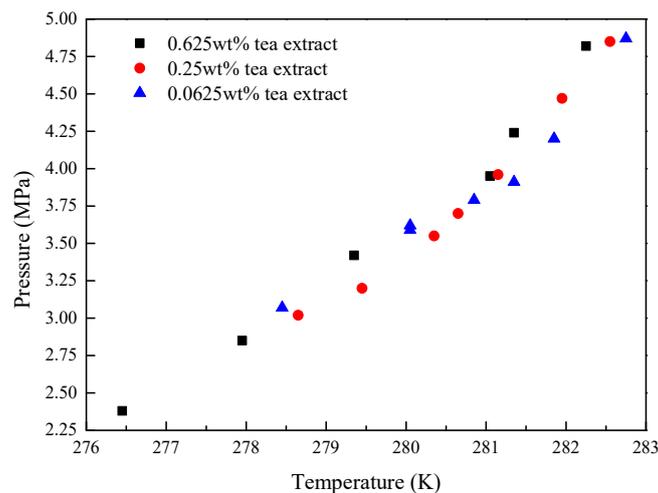
consumptions in reactor decreases. The higher concentration and longer settling time cause more organic fiber substance and greater maximum gas consumption.

3.3 Phase Equilibria of CH₄ Hydrate in Maojian Tea Extracts

Fig.10 sketches the experimental hydrate phase equilibrium conditions (P-T data) for the tea extracts (0.0625wt%, 0.25wt% and 0.625 wt%) and methane system. The results were compared with literatures [12, 16, 61]. It depicts that the phase equilibrium conditions are shifted to the high temperature region in tea extracts contrasted with pure water system at same pressure. By changing the tea extracts concentration, the promotion effect increases inconspicuously. As detailed in Fig.10, by increasing the tea extracts concentration from 0 wt% to 0.625wt%, at 3.9 MPa, the methane hydrate dissociation temperature increases by 3.05K, while the dissociation temperature difference for 0.625wt% to 0.25wt% and 0.25wt% to 0.0625wt% is 0.1K and 0.2K, respectively, at the same pressure (3.9 MPa). Although the promotion effect of the three different concentrations tea extracts has no significant difference, it suggests that the tea extracts thermodynamically promote hydrate formation and stable.



(a)



(b)

Fig.10. (a) The difference of phase equilibrium condition between tea extracts and pure water. (b) Phase equilibrium data of methane hydrate in three different tea extracts concentration (0.0625wt%, 0.25wt% and 0.625wt%).

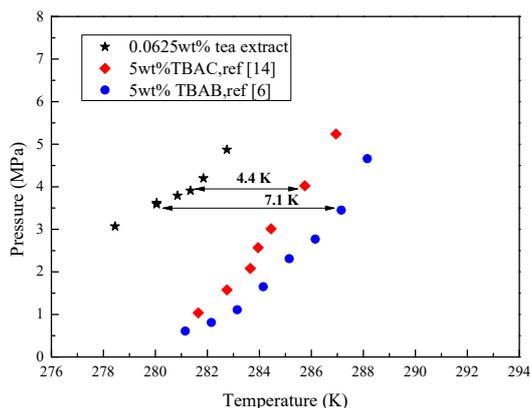


Fig.11. Phase equilibrium conditions of methane hydrate in 0.0625wt% tea extracts, 5wt% TBAC [14], and 5wt% TBAB [6].

For further understanding, in Fig.11, hydrate phase equilibrium data (0.0625wt% tea extracts) obtained were contrasted with those for TBAC/TBAB + CH₄ + H₂O systems at different mass fractions [6, 14]. As shown, the TBAC mass fraction of 5wt%, at p = 4.0 MPa comparing the tea extracts concentration of 0.0625wt% at same condition, the methane hydrate dissociation temperature increases by 4.4 K. Furthermore, the TBAB concentration at 5wt%, at 3.5 MPa comparing the tea extracts concentration at the same condition, the methane hydrate dissociation temperature increases by 7.1 K. It shows that the tea extracts have the weakest stabilization effect. However, tea extracts are not as effective as chemical additives, but for industrial applications, lower cost means higher economics. As listed in Table 3, the cost of Maojian tea, TBAB and TBAC was contrasted. In future work, the influence of tea extracts mixed with promoters on phase equilibrium conditions and kinetic effects will be investigated. The data generated in this study could be beneficial for the development of CH₄ storage based on gas hydrates technology.

Table 3. Comparison of the cost of Maojian tea, TBAB and TBAC

Materials	Maojian (crushed tea)	TBAB	TBAC
Unit price (¥/100g)	3	60	80
Purity	/	99%	99%
Mass fraction	0.0625%	5%	5%
Dosage (g)	0.5	15.789	5.263
Cost(¥/100g)	0.015	9.47	4.21

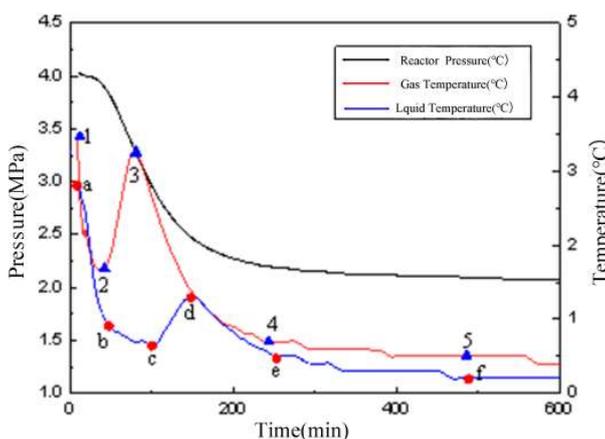


Fig.12. Temperature and pressure curve in the reactor changed with time.

The concentration of maojian tea was 2g/800ml, The solution volume was 300ml, The inlet pressure is 4.03MPa, The solution temperature is 0.7 °C, Figure.12 is the temperature and pressure curve in the reactor, As shown in the figure, the change of gas temperature curve can be divided into four parts, Part 1: 1~2, Gas and reactor wall heat transfer and the temperature gradually decreases; Part 2: 2~3, Because of the temperature drop, The degree of subcooling required for hydrate formation, Methane hydrate begins to form at the gas-liquid contact surface, The reaction gives off a lot of heat. Gas has smaller heat capacity, Make the gas temperature rise; Part 3: 3~4, After the hydrate is formed on the gas-liquid surface, Methane gas enters the liquid along the capillary structure of the hydrate , The heat transfer of gas and hydrate decreases, The temperature of the gas begins to decrease, Part 4: 4~5, With the end of hydrate formation, The gas temperature in the reactor is further reduced, And stabilize.

As shown in Figure.12, There are six parts to the temperature change of the solution, Part 1: a~b, Heat transfer between the solution and the reactor wall surface, and the temperature decreases; Part 2: b~c, It can be seen from figure 1 that the solution cooling decreases, It means that hydrate is formed and exothermic reaction occurs, Heat production reduces the cooling range of the solution. Part 3: c~d, Gases enter the solution to hydrate and emit a lot of heat. which makes the temperature of the whole solution rise. Part 4: d~e, Hydrate formation decreases, heat release is less than wall heat conduction, and solution temperature decreases. Part 5: e~f, With the end of hydrate formation, the solution temperature in the reactor decreases and tends to be stable.

After hydrate formation, the phase equilibrium points are found to be 3.8 MPa and 5.6°C, and the supercooling degree is 5.1°C, by gradually increasing the temperature.

4. Conclusion

In this work, the Maojian tea extracts were employed to form methane hydrate, and the phase equilibrium and kinetic data were reported. The effect of different tea extracts concentration and solution stand time on the gas consumption and hydrate growth rate were elucidated. It was found that the optimal formation condition for methane hydrate was 0.625wt% tea extracts (24h) among all experiments in present work. The phase equilibrium conditions indicated that the tea extract is a cheap thermodynamic promoter of methane hydrate. Maximum gas consumption and hydrate growth rates of 0.0625wt% tea extracts set statically for 24h are the largest, which could be used in the promotion of hydrate formation. However, further studies are needed to determine which chemical constituents in the Maojian tea extracts have the best effect in promoting hydrate formation and ameliorating phase equilibrium condition for methane hydrate.

Acknowledgments

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