



# The effects of porous medium and temperature on exothermic tetrahydrofuran hydrate formation



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## ABSTRACT

Exothermic energy affects the sustained and rapid formation of hydrates. Therefore, it is necessary to clarify the thermal behaviour during hydrate formation. In this study, tetrahydrofuran (THF) was chosen as the hydrate former component due to its low hydrate equilibrium pressure. Five types of glass beads were used to form a porous medium that was saturated with 19 wt% THF solution. Magnetic resonance imaging (MRI) was used to monitor the distribution of the solution in the vessel. The results showed that the “induction time” of THF hydrate formation is short in the glass beads. The exothermic character of the hydrate formation process was evident in the MRI images. The temperature profile in the porous medium was determined based on the MRI mean intensity and temperature. There were obvious higher temperature regions around the hydrate formation zones. It was found that the hydrate formation rate was slowly at multiple points and aggregated in large glass beads, and that the heat release was homogeneous. The residual MI value is higher than that in the small glass beads. Then, the hydrate began to grow from the vessel wall in the small glass beads. The temperature rose significantly during the hydrate formation. The effect of initial temperature on the experimental results is small. There are two factors that cause the temperature rise that cannot be monitored: if hydrate formation is finished and the exothermic energy has been lost, or if the hydrate does not begin to form abundantly.

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## 1. Introduction

The reformation of natural gas hydrate is an important factor that affects the efficiency. In addition, hydrate-based technology applications require rapid hydrate formation. Therefore, studies of hydrate formation are important for the exploitation of natural gas hydrate and for related hydrate-based technology [1,2]. The temperature is an important factor that controls hydrate formation. Therefore, it is necessary to study the exothermic phenomena and heat transfer that occur during hydrate formation. The heat conduction rate of hydrates is core basic data for the investigation of hydrate heat transfer characteristics. A lot of hydrate heat conductivity data have been obtained using the probe method and the transient surface heat source method [3,4]. Stoll *et al.* found that the thermal conductivity of propane hydrate is about one-fifth that of ice [5,6]. Other researchers measured the thermal conductivities of different hydrates and found that gas hydrate has a

low thermal conductivity [7,8]. Ross *et al.* found that the thermal conductivity of THF hydrate is proportional to temperature and is not obviously affected by pressure [9]. Iida *et al.* studied the heat transfer characteristics at the interface of the hydrate phase and the liquid phase for THF hydrate formation and decomposition [10].

The hydrate heat transfer characteristics in porous media systems and flow systems are also being investigated. The mass transfer characteristics at the (gas + liquid) interface can be improved significantly by adding promoters, and bulk hydrate can be formed without stirring [11–13]. However, common promoters do not improve the heat transfer characteristics of hydrate systems. The pore network in porous media provides a good carrier for hydrate formation. This not only avoids the high energy consumption of stirring but also improves the heat transfer of the system [14]. Experimental measurements of the thermal properties relevant to hydrate formation are scarce, especially for porous media. This is mainly due to the rapidity of hydrate formation and the limitations of measurement technology. Yang *et al.* arranged 16 thermocouples to measure the temperature profile in porous media and found that a temperature increase is obvious during the initial stage of hydrate formation [15]. Zhao *et al.* investigated the heat transfer characteristics of hydrate dissociation in porous media.

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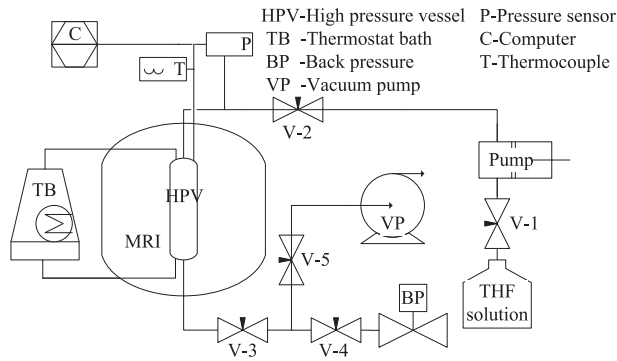


FIGURE 1. Schematic diagram of the apparatus.

They used platinum resistance thermometers to obtain the temperature distribution at multiple points and then analysed the hydrate heat transfer characteristics [16]. It is difficult to obtain accurate temperature profiles using a point by point measurement method. There has been good progress in the development of a heat transfer model for hydrate formation [17–19]. However, further experimental study is necessary to validate the model and to provide some basic data for heat transfer investigation.

Kamath *et al.* tested the heat transfer characteristics under (gas + liquid + solid) three-phase equilibrium. They found that the heat transfer rate during the hydrate decomposition process is a quadratic function of the temperature difference. They believe that the hydrate decomposition is controlled by the heat transfer and that the heat transfer rate depends on the temperature difference between the heating fluid and the hydrate deposit [20]. Because most hydrate former gases are water-insoluble, researchers believe that hydrate forms first at the (gas + liquid) interface [21]. More

researchers have begun to focus on the heat transfer mechanism at the hydrate formation interface. Selim *et al.* have proposed that the heat transfer during hydrate decomposition is an ablation process at the moving interface [22]. Some researchers propose that the formation rate of the hydrate film is controlled by heat transfer. Uchida *et al.* proposed a two-dimensional model for carbon dioxide hydrate formation. They believe that the heat transfer at the interface front is determined by the temperature difference [23,24]. The temperature profile is also a crucial parameter for the investigation of the interfacial heat transfer.

Some progress has been made with the experimental study of hydrate heat transfer characteristics. The main limitation has been the measurement method for temperature, especially for temperatures in porous media. As mentioned above, several temperature sensors have been arranged to measure the temperature distribution in porous media. It is difficult even then to obtain accurate temperature distributions for heat transfer analysis. In addition, hydrate formation in porous media is a random and complicated process. Therefore, the limited number of temperature sensors makes it difficult to adequately measure the heat transfer characteristics of the hydrate. Magnetic resonance imaging (MRI) is an effective tool for hydrate investigations in porous media because it non-invasively profiles water protons with high space resolution in three dimensions [25–29]. The  $^1\text{H}$  signal obtained by MRI is sensitive to fluid temperature, relaxation time, diffusion coefficient and chemical shifts, and therefore, it can be used to measure the temperature [30–32]. MRI measurement of the temperature distribution can be very useful for the study of hydrate formation in porous media. The key challenge is the development of MRI pulse sequences. Bloembergen *et al.* measured the T1 relaxation time to analyse the temperature and determined that the prediction accuracy was 2 K [33]. MRI thermometry technology has been developing rapidly [34,35]. Hydrate formation and decomposition

TABLE 1  
Properties and suppliers of materials.

Material	Mass fraction purity	Particle size/mm	Porosity (%)	Permeability/ $\mu\text{m}^2$	Supplier
BZ-01	1.00 Soda glass	0.105 to 0.125	36.4	7.8	As-One Co., Ltd., Japan
BZ-02	1.00 Soda glass	0.177 to 0.250	36.8	13.3	As-One Co., Ltd., Japan
BZ-04	1.00 Soda glass	0.350 to 0.500	37.5	38.2	As-One Co., Ltd., Japan
BZ-06	1.00 Soda glass	0.500 to 0.710	38.3	40.6	As-One Co., Ltd., Japan
BZ-1	1.00 Soda glass	0.991 to 1.397	40.0	91.3	As-One Co., Ltd., Japan
THF	$\geq 0.990$				Sinopharm Chemical Reagent Co., Ltd., China

TABLE 2  
Experimental parameters for THF hydrate formation.<sup>a</sup>

Cases No.	$\omega/\text{wt}\%$	T/K	p/MPa	Glass beads	$\Delta t^b/\text{min}$	Residual MI ratio ( $\gamma$ )	Min MI <sup>c</sup>	Mean $\Delta T/\text{K}^d$	Mean row Max. $\Delta T/\text{K}^e$	Mean column Max. $\Delta T/\text{K}^f$
3	19	267.15	0.1	BZ-04	80	0.04	0.0003	1.12	9.11	10.30
5	19	268.15	0.1	BZ-04	30	0.04	0.0003	1.18	10.47	10.22
6	19	266.15	0.1	BZ-04	20	0.04	0.0003	0.74	11.09	6.30
8	19	266.15	0.1	BZ-06	30	0.05	0.0005	0.22	8.79	7.42
9	19	267.15	0.1	BZ-06	20	0.07	0.0005	0.66	11.09	8.83
10	19	268.15	0.1	BZ-06	15	0.06	0.0005	0.90	11.15	10.20
11	19	268.15	0.1	BZ-1	20	0.04	0.0009	0.26	10.62	8.43
12	19	267.15	0.1	BZ-1	20	0.07	0.0009	0.37	10.62	9.07
13	19	266.15	0.1	BZ-1	20	0.08	0.0009	0.44	10.70	9.45
14	19	266.15	0.1	BZ-02	20	0.03	0.0008	0.72	10.95	10.08
15	19	267.15	0.1	BZ-02	25	0.06	0.0008	0.68	9.60	9.76
16	19	268.15	0.1	BZ-02	20	0.07	0.0008	0.22	10.35	6.60
17	19	267.15	0.1	BZ-01	20	0.02	0.0012	0.43	10.78	7.84

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 10$  kPa, and the combined expanded uncertainty  $U_c$  are  $U_c(\omega) = 0.1$  wt%,  $U_c(\gamma) = 0.011$ ,  $U_c(\Delta T) = 0.44$  K with 0.95 level of confidence ( $k = 2$ ).

<sup>b</sup> Hydrate formation “induction time” which is defined as the elapsed time from the start of the cooling process to hydrate formation detected by MRI.

<sup>c</sup> Minimum MI value caused by the exothermic hydrate formation.

<sup>d</sup> Overall mean temperature increase caused by hydrate formation (calculated by MRI data).

<sup>e</sup> Mean value of the maximum temperature increase for each column caused by hydrate formation (calculated by MRI data).

<sup>f</sup> Mean value of the maximum temperature increase for each row caused by hydrate formation (calculated by MRI data).

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