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# Experiment and Evaluation of Natural Gas Hydration in a Spraying Reactor

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## Abstract

1L spraying reactor with a heat exchanger outside was used to investigate the effect of spraying hydration process on storage capacity of methane in hydrate and on a methane storage rate in hydrate to solve a problem of lower gas molecular transfer rate and worse heat transfer rate. Some results showed that ethanol as a promoter had better spraying hydration rate under the liquid spraying pressure 4–5 MPa,  $0.46V_g V_H^{-1} \text{ min}^{-1}$ , which had been approximately 10 times when conventional additive, sodium dodecyl sulfate, was added to reaction system. Others showed that the spraying hydration reactor in advantage had lain in achieving higher hydration rate at lower operational pressure of gas phase compared with semi-continuous stirred tank reactor. Furthermore, evaluation investigation on spraying hydration reaction showed that energy consumption had been 0.41kJ, while methane hydrates containing 1kJ heat were produced, and that the capital efficiency in economy for the hydration process had been 0.41 under perfect competition. Finally, the process evaluation parameter used had become a measure instrument for the prospect of resource utilization efficiency or for venture forecasting of capital investment.

**Keywords:** natural gas hydration, spraying reactor, experiment, evaluation, economics

## 1. Introduction

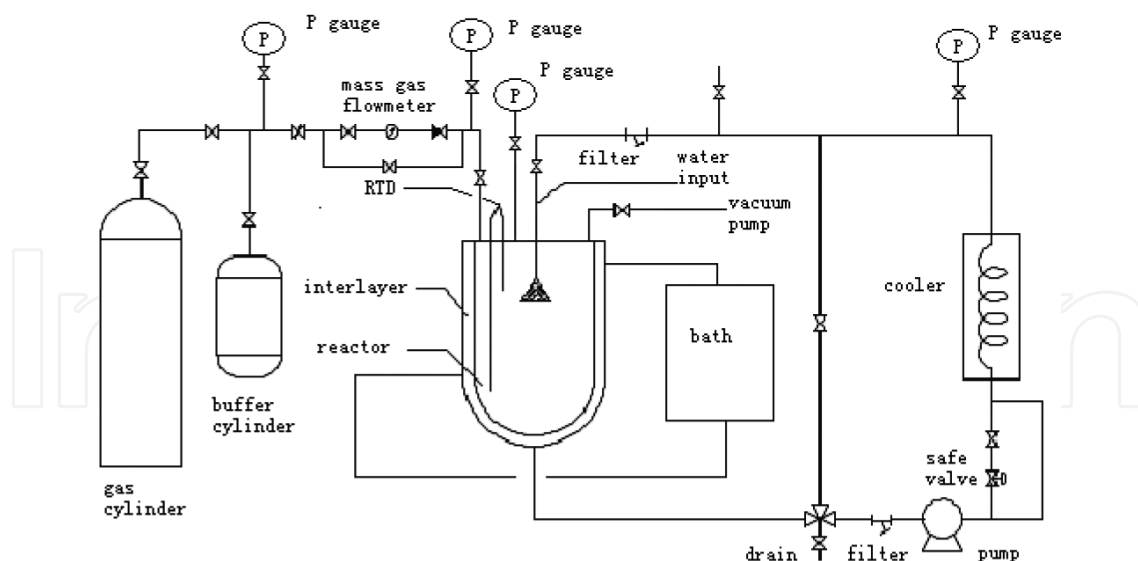
A natural gas hydrate is a crystalline compound in which certain compounds stabilize the cages formed by hydrogen-bonded water molecules under favorable conditions of pressure and temperature [1]. Natural gas hydrates possess exceptional gas storage characteristic, as the hydrates can contain 150–180  $V V^{-1}$  (standard temperature, pressure) natural gas [2, 3]. Utilizing the storage properties of natural gas in hydrates, natural gas storage and transportation

will turn to be more economical than conventional ways such as liquefied natural gas transportation and pipeline transportation in the near future, thus middle- or small-scale natural gas fields also become valuable exploitable resources in the forthcoming times [4]. To improve such a technology and to turn to be a reality as soon as possible, many laboratories have studied the synthesis of natural gas hydrates during recent decades. These studies are mainly divided into two groups: one group consists of fundamental research and the other group consists of applied background research. In fundamental studies, natural gas hydrates are synthesized in gas and liquid reaction systems when the conditions of the reactants or mediums are gases of different compositions [5], liquids of different compositions [6–8], and different combinations of liquid-solid systems [9, 10]. In applied background studies, natural gas hydrate formations and process are evaluated in reactors of varying scales and types [11–15]. In all the above studies, the economic efficiency of natural gas hydrate synthesis is the crucial problem that needed to be solved. At present, the gas capacity in hydrates and the hydrate rate remain the main factors to improve the technical levels. Generally, the mass transfer and heat transfer are enhanced to promote the hydrate process in a reactor. However, none of the endeavors for natural gas hydrate transportation currently show economical advantages over liquefied natural gas transportation and pipeline transportation. These endeavors merely have theoretical significance in a laboratory and are worthless to natural gas fields with middle- or small-scale commercial exploitation. To allow natural gas hydrate transportation to compete with liquefied natural gas transportation and pipeline transportation and promote the effective utilization of natural gas resources, natural gas hydration in a spraying reactor under liquids of different compositions is carried out and experimental results received are compared to other reaction systems in current investigations. Moreover, the hydration process is evaluated to provide an effective way to natural gas hydrate formation in a spraying reactor and to give a reference for optimal resource or capital utilization.

## 2. Experimental

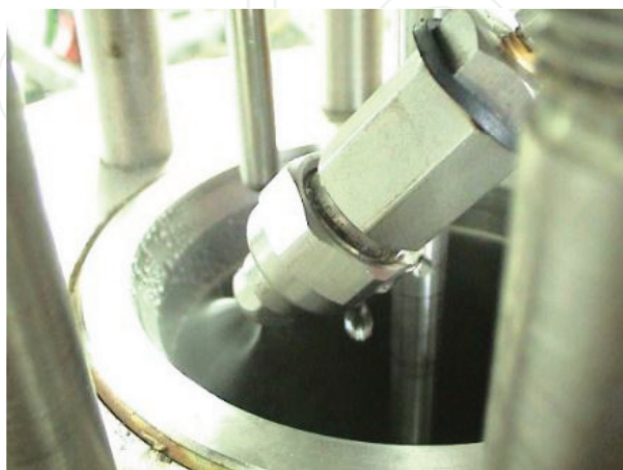
### 2.1. Apparatus and material

An experimental apparatus, as shown in **Figure 1**, is built to investigate the storage capacity of methane hydration and to evaluate the methane gas hydrate process. A cylindrical high-pressure reactor made of stainless steel with available volume 1.072 L is used to generate the gas hydrate. Designing pressure of the hydration reactor is from 0 to 40 MPa with the temperature in the range of 263.15–323.15 K. In order to ensure the stability of the reactor flow and prevent air backflow, a buffer tank is arranged in the experimental device. The pressure regulator is used to retain constant pressure in the reactor when the experiments are carried out. Volume of the buffer tank and maximum working pressure of the buffer tank are 12 L and 15 MPa, respectively. A water bath is used to provide temperature control of the experiments. There is a canella around the exterior of the reactor that circulates a cooling ethylene glycol water solution. A J2-63/7-type piston pump is used as a circulating pump, which drives and cools the liquid in the outer circulation loop by the external water bath DC-2080. At the reactor inlet and piston inlet, two filters are installed to prevent pipe blockage. Besides, a bypass is



**Figure 1.** Liquid spraying experimental apparatus of gas hydrates formation.

used to adjust spraying pressure and liquid flow. External heat exchange pipeline size and length are  $\phi 6 \times 1$  and 2 m, respectively. Spraying water diagram in an idiographic reactor is shown in **Figure 2** when the maximum flow is  $2.5 \text{ L min}^{-1}$ . Moreover, there are two platinum resistance thermometers with an accuracy of  $\pm 0.1 \text{ K}$ . One extends into the bottom of the reactor, which is used to measure temperatures of the reaction liquids, while the other extends into the gas phase at the top, which is used to measure temperatures of the inlet methane gas. A model D07-11 M/ZM mass gas flow meter is used to measure the gas added to reactor during hydrate formation. The flow meter has a capacity of 0–1000 sccm at an accuracy within 2% of full scale and is repeatability of within 0.2% of the flow rate. There is a data collector to record the temperature of the reactor, the gas flow meter and the total gas volume of the consumed gas in the process of hydrate formation as a function of time. An electronic balance with a readability of  $\pm 0.1 \text{ mg}$  and an electronic balance with a readability of  $\pm 0.01 \text{ g}$  are used in weighing. The experimental materials used in this study are provided in **Table 1**.



**Figure 2.** Photograph of water spraying by nozzle.

Component	Purity/composition	Supplier
	(%)	
Methane	≥99.99	Fushan Kede Gas Co.
Sodium dodecyl sulfate	≥98	Guangzhou Chemical Reagent Co.
Ethanol	≥99.9	Guangzhou Chemical Reagent Co.
Water		Distilled

**Table 1.** Experimental material used in this work.

**2.2. Procedure**

*2.2.1. Determination of working conditions*

In order to study the hydration process between methane gas and atomizing liquid sprayed and to ensure hydrate formation mainly in spraying droplet rather than in the main liquid phase, the temperature and pressure of the spraying liquid must meet the phase equilibrium conditions of methane hydrate formation, and the main liquid phase temperature and pressure condition do not meet the conditions of the phase equilibrium of methane, the formation of gas hydrate or seldom hydration occurs in the main body of liquid phase.

By adjusting the temperature of the water bath and the valve, the spray liquid is kept at a state with a low temperature (determined equilibrium pressure) and high pressure. Herein, the outlet pressure nozzle experiment always is higher than the equilibrium pressure of 1–3 MPa, which ensures that the initial impetus is always higher. Then, identify the gas phase pressure, which is slightly lower than the phase equilibrium pressure, to ensure that the hydrate formed mainly in spraying droplet instead of in the main body of liquid phase.

The temperature of the spraying liquid is set at 273.7 K in the experiment while the phase equilibrium pressure is 2.64 MPa for methane hydration at the temperature. Liquid injection pressure and methane gas pressure are from 4 to 5 and 2.4 MPa, respectively. Under these conditions, methane hydrate formation is compared by using pure water, sodium dodecyl sulfate solution, ethanol solution as a spraying liquid to investigate the effect of additive on methane hydrate formation.

In addition, in order to test the effect of gas phase pressure on the spraying hydration process, spraying hydration formation is also compared when the methane gas pressure is 0.5 and 2.4 MPa.

*2.2.2. Process*

1. The reactor was cleaned by water and experimental gas twice before preparing for an experimental run.
2. Six hundred and fifty grams of 0.001 mol L<sup>-1</sup> sodium dodecyl sulfate solutions were charged into the empty reactor. Afterwards, the constant bath was run and its temperature was maintained at 272.2 K. An external cooler was set in 273.7 K to cool liquid

mixture reacted from piston pump to the reactor. Under the experimental flow rate, as shown in **Figure 2**, cooled liquid temperature could approach external cooler temperature, 273.7 K, after they flowed through the nozzle. The temperature was selected as a hydration temperature.

3. The piston pump was run, and the liquid flow was controlled between 0 and 0.25 L min<sup>-1</sup> reactor by adjusting the liquid pipeline valve while the operating pressure of a reactor was controlled between 4.0 and 5.0 MPa. When the liquid temperature reached 278.2 K, piston pump was closed. Open the gas valve, the gas pressure in the reactor increased to the pressure of 2.4 MPa, and then the piston pump was run again. Afterwards, the data acquisition system was run to record temperatures of liquid and methane gas in the reactor, the gas flow into the reactor, flow velocity, until the piston pump did not run so far because of the pipeline resistance.
4. The experiment of 0.018 mol L<sup>-1</sup> ethanol solution and distilled water was charged into the reactor, and the first, second and third steps were repeated.
5. The experimental gas pressure was dropped to 0.5 MPa, and the first, second and third steps were repeated.

### 2.3. Calculation of storage capacity of methane hydrate

The volume [3] of gas stored in a unit volume of hydrate under the hydrate formation conditions of pressure and temperature is expressed as

$$C = \frac{V_{\text{NG}}}{V_{\text{NGH}}} = \frac{V_{\text{NG}}}{V_L * (1 + \Delta V)} \quad (1)$$

where  $C$  is the volume of gas stored in a unit volume of hydrate,  $V_{\text{NG}}$  is the volume of gas consumed,  $V_{\text{NGH}}$  is the volume of hydrate when the reaction ends,  $V_L$  is the volume of water added and  $\Delta V$  is the molar volume change of water turned into hydrate. Herein  $\Delta V$  of methane hydrate is 4.6 cm<sup>3</sup> mol<sup>-1</sup>.

The hydration rate of hydrate formation can be calculated by the following equation:

$$r = \frac{C}{t} \quad (2)$$

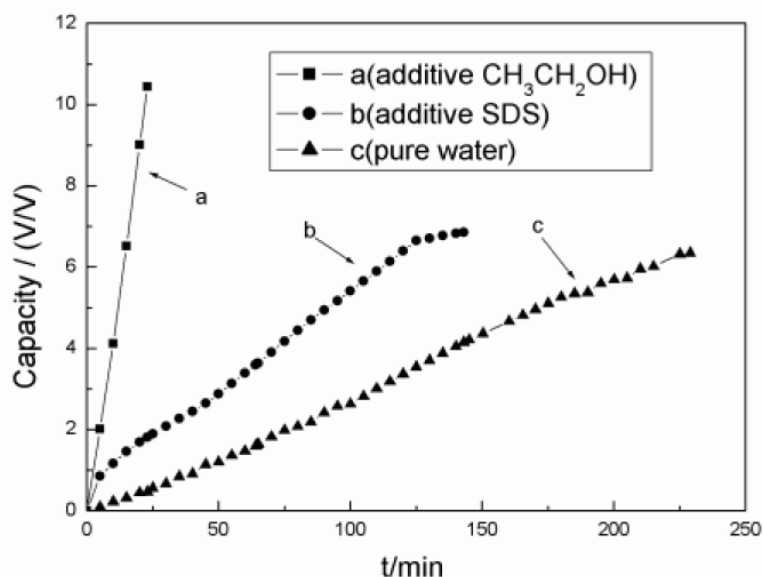
where  $r$ ,  $C$  and  $t$  are hydration rate, gas hydrate capacity and reaction time, respectively.

## 3. Results and discussion

### 3.1. Effect of liquid composition on the hydration process of methane

The capacity and reaction rate of methane hydrate under different liquid compositions are plotted in **Figure 3**. Three results were given at different spraying times. **Figure 3** shows or deduces the following results under gas pressure 2.4 MPa: methane storage capacity, reaction





**Figure 3.** Effect of liquid composition on methane hydrate formation ( $T = 273.7\text{ K}$ ,  $P = 2.4\text{ MPa}$ ).

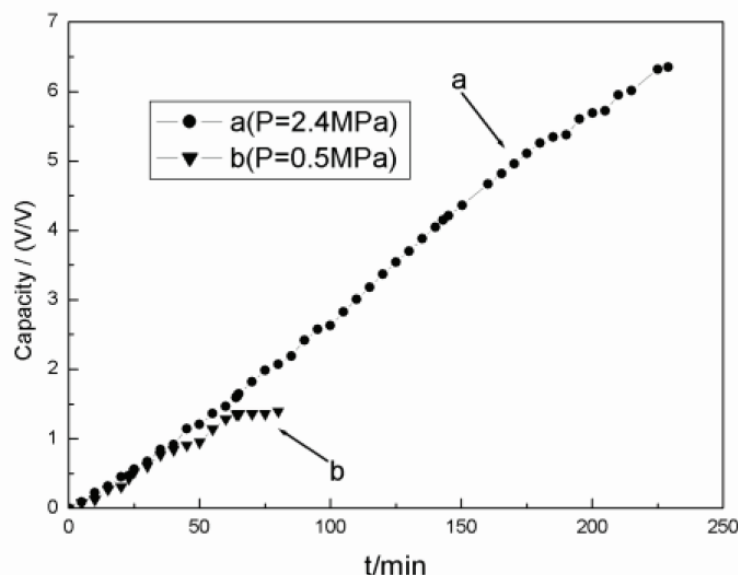
time, and the average hydration rate were  $6.4\text{ V}_g\text{ V}_H^{-1}$ ,  $229\text{ min}$ , and  $0.028\text{ V}_g\text{ V}_H^{-1}\text{ min}^{-1}$ , respectively, when reaction liquid did not have any additives; methane storage capacity, reaction time, and the average hydration rate were  $6.9\text{ V}_g\text{ V}_H^{-1}$ ,  $143\text{ min}$ , and  $0.048\text{ V}_g\text{ V}_H^{-1}\text{ min}^{-1}$ , respectively, when  $0.001\text{ mol L}^{-1}$  sodium dodecyl sulfate solutions were reaction liquid; methane storage capacity, reaction time, and the average hydration rate were  $10.5\text{ V}_g\text{ V}_H^{-1}$ ,  $23\text{ min}$ , and  $0.46\text{ V}_g\text{ V}_H^{-1}\text{ min}^{-1}$ , respectively, when  $0.018\text{ mol L}^{-1}$  ethanol solutions were reaction liquid.

By analysis **Figure 3**, the following deductions could have been drawn:

1. Liquid spraying with a higher pressure and lower temperature could increase the driving force of the hydration reaction, which had reduced the pressure of the gas phase.
2. The additive would affect the hydration reaction rate: without additives, hydration rate was slower and operation time was also longer; if additive was used, hydration rate and operation time were shortened obviously. In the experiments, sodium dodecyl sulfate and ethanol as additives on the hydration rate increase were given. Ethanol as an additive, hydration rate reaches  $0.46\text{ V}_g\text{ V}_H^{-1}\text{ min}^{-1}$ , which was about 10 times sodium dodecyl sulfate as an additive.
3. Because the spraying system was a closed circuit device, the hydrate particles were apt to block the reaction device. As a result, the gas hydrate slurry had a lower gas storage capacity under this state. Thus, this device still had greater space to be improved.

### 3.2. Effect of gas pressure on the hydration process of methane

Effects of gas pressure on methane hydrate formation in a spraying reactor with a closed loop are given in **Figure 4**. The capacity and reaction rate of methane hydrate under two different



**Figure 4.** Effect of pressure of gas phase on methane hydrate formation ( $T = 273.7\text{ K}$ ).

gas pressures were compared. On the one hand, when methane gas pressure was 0.5 MPa, and there were no additives in liquid reagent, gas storage capacity in hydrate, operation time, and hydration rate were  $1.4\text{ V}_g\text{ V}_H^{-1}$ , 80 min, and  $0.0175\text{ V}_g\text{ V}_H^{-1}\text{ min}^{-1}$ , respectively. On the other hand, when methane gas pressure was 2.4 MPa, and there were no additives in liquid reagent, gas storage capacity in hydrate, operation time, and hydration rate were  $6.4\text{ V}_g\text{ V}_H^{-1}$ , 229 min, and  $0.028\text{ V}_g\text{ V}_H^{-1}\text{ min}^{-1}$ , respectively.

Analysis of **Figure 4** showed that the hydration rate had depended not only on the liquid pressure and temperature, but also on the gas pressure as an important factor. If a higher hydration rate needed to be kept, an appropriate gas pressure must have been maintained.

### 3.3. Comparison of a hydration rate between two kinds of reactors

In order to show the characteristics of methane hydration process in the spraying reactor, the methane hydration rate in the spray reactor was compared with that of the semi-continuous stirred tank reactor, and the results obtained are shown in **Table 2**.

Reactor type	Gas pressure	Spraying pressure (MPa)	Additive	Hydrate rate
	(MPa)			( $\text{V}_g\text{ V}_H^{-1}\text{ min}^{-1}$ )
Semi-CSTR	5.0		Sodium dodecyl sulfate	0.43
Spraying reactor	2.4	4–5	Ethanol	0.46

**Table 2.** Comparison of two kinds of reactors on hydration rate.



The methane hydrate rate was  $0.43 V_g V_H^{-1} \text{ min}^{-1}$  in a semi-continuous stirred tank reactor at 5.0 MPa and sodium dodecyl sulfate being additives. However, the methane spraying hydration rate reached  $0.46 V_g V_H^{-1} \text{ min}^{-1}$  at 2.4 MPa and under liquid spraying pressure 4–5 MPa with the assistance of ethanol as additives. The compared results showed that the advantages of methane hydration process in a spraying reactor had lain in lower gas pressure and higher hydration rate could have been obtained.

## 4. Evaluation of hydration process in a spraying reactor

### 4.1. Mechanism of spraying hydration process

In order to explain and evaluate the hydration formation in the spraying reactor, the following procedures were assumed:

1. Methane gas molecules with a certain pressure quickly diffused to spraying and atomization liquid droplet surface with a higher pressure and lower temperature from the nozzle afterwards were dissolved in it. The temperature condition was less than phase equilibrium temperature at the given pressure and had a greater degree of super-cooling.
2. Methane gas molecules around spherical droplets diffused toward the internal liquid droplets and formed an unstable cluster. Afterwards, they began to nucleate and to form a collective cluster. After that collective clusters had reached a critical size and they began to grow rapidly and formed a stable crystal releasing the heat of reaction. At the same time, the liquid pressure drops and liquid droplets temperature increased. When gas pressure was too low, because driving force from methane gas molecules to liquid droplet diffusion was insufficient, the hydration reaction process had occurred only on the droplet surface and had stayed in the nucleation stage.
3. With the decrease of the reaction degree of super-cooling, crystal growth rate declined. When the droplet temperature was higher than the equilibrium temperature, crystal growth ceased and crystal was suspended in the liquid under the action of gravity and of buoyant force.
4. During the hydration process, the hydrate particles in the liquid increased rapidly and the viscosity of hydrate slurry increased gradually. Moreover, the resistance from the gas hydrate slurry that inhaled into the circulating pipeline was gradually increased until the piston pump could not be continued to run.

In the experiment, an additive as a hydration promoter reduced the surface tension of solution and had some functions such as wetting, penetration, emulsification, and solubilization; thus, the surface gas-liquid mass transfer rate was improved, accelerating the implementation of the above process. Moreover, the phase equilibrium conditions of methane gas and water were only considered in the experimental design, neglecting the effects of the additives on the phase equilibrium change. The understanding of the mechanism still had limitations, which could not fully have explained the spraying hydration process. Thus, phase equilibrium data from different components of the hydration system still needed to have been added and other pieces of evidence had also been needed.

## 4.2. Evaluation of the reactor performance evaluation

The production capacity and energy consumption for the spraying reactor would have become key points as a basis for the reactor amplification in this section. The daily production capacity and daily energy consumption of the reactor were calculated for evaluating the reactor efficiency.

### 4.2.1. Mass balance

For this experiment, 4.32 g methane gas was stored when 650 g solution or pure water was added to the reactor for a batch operation. Process reaction time was 0.5 h and supplementary time was 0.5 h, allowing 20 runs per day.

Throughput calculation was the first step of a mass balance. The mass of methane hydrates produced during the hydration process, which consisted of mass of water solution and mass of methane gas reacted, was calculated. The mass balance equation for the produced methane hydrate slurry could thus have been expressed as

$$m = m_w + m_{\text{CH}_4} \quad (3)$$

where  $m$ ,  $m_w$ , and  $m_{\text{CH}_4}$  are mass of hydrates formed, mass of water solution added, and mass of methane gas reacted, respectively, during a run.

If the run time of the reactor was  $\tau$ , then the mass of methane hydrates slurry produced could have been written as follows:

$$m_t = m \cdot \tau \quad (4)$$

where  $m_t$  is the mass of hydrates formed and  $\tau$  is the daily run time.

The methane gas fraction of the methane hydrates slurry might have been expressed as

$$\theta = \frac{m_{\text{CH}_4}}{m} \times 100\% \quad (5)$$

where  $\theta$  is the methane gas mass fraction of the methane hydrates slurry.

In terms of these equations, a mass balance was calculated and is shown in **Table 3**.

### 4.2.2. Energy balance

For convenience in calculation, the temperature changes of the inlet gas and the inlet water could have been considered to have a negligible effect on their consumption of the hydration

Parameter	$m_w$ (g)	$m_{\text{CH}_4}$ (g)	$m$ (g)	$\tau$	$m_t$ (kg)	$\theta$ (%)
Value	650	4.32	654.32	20	13.09	0.66

**Table 3.** Throughput and methane gas fraction of methane hydrates.

process, or else their temperature could have been controlled. Then, the total energy consumption during a run could have been expressed, including energy consumption of the compression process, energy consumption of the cooling process, and the power for driving the plunger pump. In each run the equation for the total energy consumption could have been written as

$$Q^* = (1 + \zeta) \times (Q_{cp} + W_r + W) \tag{6}$$

where  $Q^*$ ,  $Q_{cp}$ ,  $W_r$ ,  $W$  and  $\zeta$  are the total energy consumption, energy consumption of the compression process, energy consumption of the refrigeration unit, work for driving the plunger pump, and an coefficient of other auxiliary operation energy consumption to operation process energy consumption, respectively. Here  $\zeta$  value was 0.01 when the calculation of the total energy consumption was carried out implemented.

1. Compression of methane gas

Here, a general assumption and conventional calculation were used [16]. Assume that the initial pressure of the feed gas was set to be  $P_1$  and the initial temperature was set to be  $T_1$ . The feed gas was pressurized to the hydrate operation pressure  $P_2$  by an adiabatic compression process with efficiency factor  $\eta_{ad}$ . The final temperature  $T_2$  after compression could have been calculated from the initial temperature using the following equation:

$$T_2 = \left( \frac{1 + \phi^{(\lambda-1/\lambda)} - 1}{\eta_{ad}} \right) T_1 \tag{7}$$

where  $\lambda$  is the ratio of the heat capacity at constant pressure to the heat capacity at constant volume, expressed as

$$\lambda = c_p/c_v, \tag{8}$$

where  $c_p$  is the heat capacity at constant pressure and  $c_v$  is the heat capacity at constant volume.

$\phi$ , the ratio of the final pressure  $P_2$  to the initial pressure  $P_1$  of the compression process, could have been expressed as

$$\phi = P_2/P_1. \tag{9}$$

The temperature of the compression process was calculated from the above equation. Results for the model parameters are given in **Table 4**.

Assuming that the work performed on methane gas was  $W_{cp}$ , the compression process energy consumption  $Q_{cp}$  could have been expressed as

Parameter	$T_1$ (K)	(MPa)	(MPa)	$\eta_{ad}$	$\phi$	$\lambda$	$T_2$ (K)
Value	298	0.1	7	0.8	70	1.29	894

**Table 4.** Calculation of final temperature of compress process.

$$W_{cp} = Q_{cp} \eta_{ad} \quad (10)$$

where  $\eta_{ad}$  is the efficiency factor under adiabatic conditions.

One was that the internal energy change  $\Delta U$  could have been expressed as

$$\Delta U = Q_{cp} - W_{cp} = (1 - \eta_{ad}) Q_{cp}. \quad (11)$$

That was:

$$Q_{cp} = \frac{\Delta U}{1 - \eta_{ad}}. \quad (12)$$

The other was that the internal energy change  $\Delta U$  could also have been expressed as

$$\Delta U = n \int_{T_1}^{T_2} C_v dT \quad (13)$$

where  $n$  is the molecular number of the methane gas.

The heat capacity at constant volume  $c_v$  could have been expressed using the heat capacity at constant pressure  $c_p$ , which in turn was related to absolute temperature  $T$ . So, the heat capacity at constant volume  $c_v$  was related to absolute temperature  $T$ . The relationship between the heat capacity at constant pressure and absolute temperature could have been expressed as follows:

$$c_p = a + bT + cT^2, \quad (14)$$

where  $a$ ,  $b$ , and  $c$  are the parameters of heat capacity at constant pressure.

But the relationship between the heat capacity at constant volume and the heat capacity at constant pressure was

$$c_v = c_p - R, \quad (15)$$

where  $R$  is the gas constant.

Therefore, substituting Eqs. (14) and (15) into Eq. (13),  $\Delta U$  became

$$\Delta U = n \int_{T_1}^{T_2} (a + bT + cT^2 - R) dT \quad (16)$$

Integrating the right-hand side of Eq. (16), the internal energy change  $\Delta U$  became

$$\Delta U = n \left[ (a - R)(T_2 - T_1) + \frac{b}{2} (T_2^2 - T_1^2) + \frac{c}{3} (T_2^3 - T_1^3) \right]. \quad (17)$$

In Eq. (17), values of  $T_1$  and  $T_2$  are presented in **Table 4**, and values of  $a$ ,  $b$ ,  $c$  and  $R$  are presented in **Table 5**.

Parameter	$a \text{ (J mol}^{-1} \text{ K}^{-1})$	$b \times 10^3 \text{ (J mol}^{-1} \text{ K}^{-2})$	$c \times 10^6 \text{ (J mol}^{-1} \text{ K}^{-3})$	$R \text{ (J mol}^{-1} \text{ K}^{-1})$
Methane	14.15	75.496	-17.99	8.314

**Table 5.** Parameter of heat capacity at constant pressure and gas constant [17].

Substituting these data into Eq. (17), the internal energy change  $\Delta U$  was written simply as

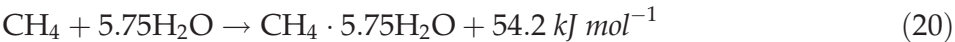
$$\Delta U = 26.17n, \quad (18)$$

Substituting Eq. (18) into Eq. (11) or Eq. (12), the compression process energy consumption  $Q_{cp}$  became

$$Q_{cp} = 130.85n \quad (19)$$

## 2. Cooling of the methane hydration process

In the methane hydration process, substantial heat of the reaction,  $54.2 \text{ kJ mol}^{-1}$  [18], was released by a chemical reaction, which could have been expressed as



Therefore, the heat of reaction released could have been expressed as

$$Q_{rh} = 54.2n \quad (21)$$

where  $Q_{rh}$  is the heat of reaction released and  $n$  is the molecular number of the methane gas.

According to principle of heat balance, heat exchanged in the cooling system was equal to the heat of reaction released that was,

$$Q_e = 54.2n \quad (22)$$

where  $Q_e$  is the heat exchanged in the cooling system.

Work consumption of the refrigeration unit  $W_r$  could have been expressed as

$$W_r = \frac{54.2n}{\text{CO}_p}, \quad (23)$$

where  $W_r$  is the work consumption of the refrigeration unit and  $\text{CO}_p$  is the coefficient of performance.

## 3. Power for driving the plunger pump

The power for driving the plunger pump in terms of experimental determination was expressed as

$$W = (P_o - P_i)Vt \quad (24)$$

where  $W$ ,  $P_i$ ,  $P_o$ ,  $V$ , and  $t$  are the power for driving the plunger pump, inlet pressure of plunger pump, outlet pressure of plunger pump, liquid volume flow rate, and operation time, respectively.

During a run, power for driving the plunger pump was calculated and is shown in **Table 6**.

#### 4. Total energy consumption of the methane hydration process

Total energy consumption per day for the methane hydration process could have been calculated from Eq. (6). The total energy consumption per day for the methane hydration process  $Q_t$  was expressed as

$$Q_t = Q^* \cdot \tau Q^*, \quad (25)$$

where  $Q_t$  is the total energy consumption per day and  $\tau$  is the run time per day.

Since the total mass of methane hydrate slurry produced per day was  $m_t$ , the energy consumption for each 1 kg methane hydrate slurry produced could have been written as

$$Q_0 = \frac{Q_t}{m_t}, \quad (26)$$

where  $Q_0$  is the energy consumption per 1 kg methane hydrate produced, and  $m_t$  is the total mass of methane hydrates produced in a day.

The parameter values for the methane hydration process are given in **Table 7**.

#### 4.2.3. Resource efficiency for utilization in a spraying reactor

In order to evaluate the resource efficiency for utilization of the methane hydration process in a spray reactor, introducing a dimensionless parameter  $\Omega$ , energy consumption evaluation parameter [11], which was expressed as the ratio between the energy consumption per 1 kg methane hydrate slurry produced to heat value of the 1 kg methane hydrate slurry.

Parameter	$P_i$ (MPa)	$P_o$ (MPa)	$V$ (L·h <sup>-1</sup> )	$t$ (h)	$W$ (kJ)
Value	2.4	7.0	15	0.5	34.5

**Table 6.** Power calculation for driving the plunger pump.

Parameter	Value	Parameter	Value
$m_{CH_4}$ (g)	4.32	$Q^*$ (kJ)	88.81
$CO_p$	3	$\tau$	20
$Q_{cp}$ (kJ)	35.33	$Q_t$ (kJ)	1776.2
$W$ (kJ)	34.5	$m_t$ (kg)	13.09
$W_r$ (kJ)	18.1	$Q_0$ (kJ kg <sup>-1</sup> )	135.69

**Table 7.** Energy consumption calculation for hydration process in a spraying reactor.



The expression was

$$\Omega = Q_0/Q_c, \tag{27}$$

where  $Q_0$  is the energy consumption per 1 kg methane hydrate produced, and  $Q_c$  is the heat value of 1 kg methane hydrate slurry.

The heat value of 1 kg methane hydrate slurry was expressed as

$$Q_c = 1 \times \theta \times q, \tag{28}$$

where  $q$  is the combustion heat of methane [19].

The dependent data of heat value of methane hydrate slurry and energy consumption of hydration process are given in **Table 8**.

According to the thoughts of the energy consumption evaluation parameter, assessment of the parameter could have been used as reference data to evaluate the process quality. The size of its value depends on the complexity of the process, energy consumption level of the auxiliary process, and specific factors of the level of science and technology.

For the methane hydration process in a spraying reactor, if experimental gas directly came from a small-scale natural gas field, then the energy consumption of methane gas compression could have been neglected. Thus, the total energy consumption in such a run could have been replaced by the energy consumption of the cooling process and the power of driving plunger pump. Calculated results are given in **Table 9**.

As shown in **Table 9**, the energy consumption evaluation parameter had a value of 0.246. Compared to the process for hydration of compressed methane gas, the energy consumption decrease was 39%. If the management level was improved or the auxiliary energy consumption  $\zeta$  was reduced to 0.005, the energy consumption evaluation parameter would have continued to decline, the calculation results are shown in **Table 10**. As shown in **Table 10**, the process evaluation parameter had a value of 0.245. Compared to spraying hydration of this laboratory scale, the decrease was 40%. If further decrease of the process evaluation parameter needed to be done, then specific aspects of the scientific and technological levels, such as a reactor with a superior performance, optimal operation condition, and production with a large scale should have been excavated. Under current states, the parameter value still was at a high level

Parameter	$q$ (kJ kg <sup>-1</sup> )	$\theta$	$Q_c$ (kJ kg <sup>-1</sup> )	$Q_0$ (kJ kg <sup>-1</sup> )	$\Omega$
Value	50010	0.0066	330.07	135.69	0.41

**Table 8.** Heat value of the hydrate slurry and evaluation for the hydration process.

Parameter	$Q^*$ (kJ)	$Q_t$ (kJ)	$Q_c$ (kJ kg <sup>-1</sup> )	$Q_0$ (kJ kg <sup>-1</sup> )	$\Omega$
Value	53.1	1062	330.07	81.1	0.246

**Table 9.** Data of the process evaluation after process simplification.

Parameter	$Q^*$ (kJ)	$Q_t$ (kJ)	$Q_c$ (kJ kg <sup>-1</sup> )	$Q_0$ (kJ kg <sup>-1</sup> )	$\Omega$
Value	52.9	1058	330.07	80.8	0.245

**Table 10.** Data of the process evaluation with smaller auxiliary energy consumption.

compared with references data reported [4–14]. Therefore, the investigation still would have had a long way to go if this technology could have been applied to industrial production. Only when the energy consumption parameter has been controlled into an appropriate level and has had some advantages compared to the operational mode, the technology would have had possibility to implement practice in industry.

Moreover, an energy consumption evaluation parameter was converted into a process evaluation parameter to represent another meaning in application. Here, it meant that social resource in economy was used to produce new resources from nature or other areas, holding efficiency for a capital utilization process in economy [11]. The capital efficiency for utilization in economy was 0.41 in terms of principle of process evaluation in this experimental work. In other words, 0.41 United States dollar must be consumed when 1 United States dollar was produced under perfect competition. It was thus clear that the parameter was a measure for the prospect of capital economic analysis and of venture forecasting [20–23].

## 5. Conclusions

Through the methane hydration experiment in a spraying reactor and analysis of the result received, the following conclusions were drawn:

1. Liquid spraying hydration experiment with higher pressure and lower temperature enhanced the mass transfer and heat transfer, increasing the hydration rate and reducing the pressure of the gas phase.
2. Additives had an obvious effect on enhancing spraying hydration. When ethanol was used as an additive, a hydration rate reached up to  $0.46 V_g V_H^{-1} \text{ min}^{-1}$ , which was about 10 times higher than that sodium dodecyl sulfate as an additive. Compared with the semi-continuous stirring tank reactor, advantages of methane hydration were that the higher rate of hydration could have been obtained at lower gas phase pressure.
3. Hydrate slurry throughput of the spraying hydration reactor was found to be  $13.09 \text{ kg d}^{-1}$ , and the product contained 0.66% methane gas. Energy consumption was 0.41 kJ when methane hydrates containing 1 kJ heat were produced.
4. Process evaluation parameters could have been used to evaluate the resource efficiency for utilization in economy when methane spraying hydration investigation was performed. The parameter analysis showed that the simplified process, the integrated process, or better management level could effectively reduce the resource consumption and could further improve the resource output level. Assume that the experimental natural gas directly came from natural gas field and the better management mode was adopted in a scaled up reactor, the energy consumption of the spraying hydration process was 0.245 kJ when methane

hydrate slurry with 1 kJ heat was produced in this work. The derivative result only was equal to 40% of this experimental apparatus. If the natural gas was from natural gas and the better management mode was used, then the energy consumption was 0.245 kJ when methane hydrate slurry production with 1 kJ heat value, whose decrease was 40% compared to the experimental scale.

5. The efficiency for capital utilization in economy was 0.41 in this work. Compared to data reported, the capital efficiency for utilization in economy still was at lower level. The spraying hydration process still had larger space to be improved.

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## Nomenclature

$a$	Parameters of heat capacity at constant pressure ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$b$	Parameters of heat capacity at constant pressure ( $\text{J mol}^{-1} \text{K}^{-2}$ )
$c$	Parameters of heat capacity at constant pressure ( $\text{J mol}^{-1} \text{K}^{-3}$ )
$CO_p$	Coefficient of performance ( $\text{W W}^{-1}$ )
$C$	Volume of gas stored in a unit volume of hydrate ( $\text{V V}^{-1}$ )
$C$	Heat capacity at constant volume or pressure ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$n$	Molecular number of the methane gas (mol)
$P$	Pressure or power (MPa) (W)
$Q$	Energy consumption, heat or heat value (kJ) ( $\text{kJ kg}^{-1}$ )
$q$	Combustion heat of methane hydrates ( $\text{kJ kg}^{-1}$ )
$R$	Gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$r$	Hydration rate ( $\text{V V}^{-1} \text{s}^{-1}$ )
$T$	Absolute temperature (K)
$t$	Time (s)
$U$	Internal energy (kJ)
$V$	Volume or volume velocity ( $\text{m}^3$ )
$W$	Work or work consumption (kJ)
Special characters	
$\Delta$	Change value of a parameter (–)
$\eta$	Efficiency factor (–)

$\zeta$	Coefficient of other auxiliary operation energy consumption to operation process energy consumption (–)
$\vartheta$	Methane gas mass fraction of methane hydrates (–)
$\lambda$	the Ratio of the heat capacity at constant pressure to the heat capacity at constant volume (–)
$\tau$	Run times in a day (–)
$\varphi$	Pressure ratio of the gas compression process or load coefficient (–)
$\Omega$	A parameter of process evaluation or a parameter of energy consumption evaluation (–)
Superscript	
*	Mark
Subscript	
1,2	Initial state and final state
<i>ad</i>	Adiabatic compression process
<i>cp</i>	Compress process
<i>e</i>	Exchange
<i>h</i>	Heat
<i>i</i>	Input
<i>NG</i>	Natural gas
<i>NGH</i>	Natural gas hydrate
<i>o</i>	Output
<i>p</i>	Pressure
<i>r</i>	Refrigerator or reaction
<i>t</i>	Total
<i>v</i>	Volume
<i>w</i>	Water
0	Reference value

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