Measurement of CO2 hydrate phase change heat for renewable energy application of biogas

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Abstract. Biogas is a renewable clean energy produced by decaying organic matter and its main components are methane and CO2, in which CO2 accounts for 25%~40% (volumetric percentage). The storage and transportation of biogas by hydrate method has attracted wide attention at home and abroad. In this paper, the phase equilibrium conditions for the hydrates in CO2, CO2-THF (tetrahydrofuran) and CO2-cyclopentane systems are researched to determine the phase transition heat of the hydrates of corresponding systems. The results illustrate that the phase transition heat of hydrate is related to the structure formed during experiments. Adding THF and cyclopentane into CO2 hydration system both increase the phase transition heat of hydrate. Phase transition heat of the CO2-THF hydration system increases with the increase of the mass concentration of THF, and the phase transition heat of CO2-cyclopentane hydration system is greater than 200kJ/kg. Results in this paper will be helpful for transportation and utilization of biogas as an renewable clean energy.

1. Introduction

Biogas is a kind of combustible gas produced from agricultural wastes under anaerobic conditions and its main components are methane and CO2. It has a high calorific value and can be classified as clean and renewable biomass energy[1]. The hydrate technology can convert gas into solid or slurry hydrate form, which can achieve stable storage and transportation under normal pressure, and it has relatively low requirements for the storage tank materials compared with liquefaction technique or compression technique[2]. Each cubic meter of hydrate can store 150~180 m$^3$ gas under normal pressure, and the hydrate decomposes slowly under proper storage conditions, while it is not liable to leak or explode[3]. It has many characteristics such as high gas storage capacity, high safety, economy and flexibility, etc[4].

The phase change heat of hydrate refers to the heat absorbed or released by the hydrate during the phase change process[5]. Hydrate is a kind of cold storage medium, the value of its phase change heat directly reflects its cold storage capacity. The phase change heat of hydrate is an important parameter when choosing cold storage material. The larger the phase change heat, the less the amount of cold storage materials used, which also contributes to the reduction of the volume of the cold storage tank, thereby further reducing the initial investment cost and floor space of the system, and improving the economics of the hydration system[6]. Therefore, determining the amount of phase change heat of hydrate is of great significance in the selection of cold storage materials and the initial investment cost of the hydration system. There are two kinds of primary measuring methods to determine the phase
change heat of hydrates. One is to directly measure the heat of hydrate phase change, and the other is to use the hydrate phase equilibrium data to calculate by the Clausius-Clapeyron equation[7].

2. Experimental Apparatus and Procedure

2.1. Experimental apparatus and samples

Figure 1 is the schematic diagram of the test devices, which mainly include a high pressure reactor, a low and constant temperature water bath system, a temperature and pressure measuring device, and a stirring device. The high pressure reactor has a volume of 500cm³ with pressure resistance of 20 MPa. One side of the reactor is equipped with glass windows for observing the formation and decomposition process of hydrates. A magnetic stirrer is installed in the high pressure reactor which is used to stir the test fluid and hydrate crystals. The temperature control accuracy of the low and constant temperature water bath is ±0.1°C, the temperature control range is -19.99~99.99°C, and the temperature fluctuation value is ±0.05°C. The temperature in the reactor is measured by a Pt100 platinum resistance with an accuracy of ±0.1°C, and the pressure is measured by an absolute pressure sensor (PTX7517) with an accuracy of ±0.2%. The electronic balance used in the experiment has a measuring range of 220g and an accuracy of ±0.1 mg. The materials used in the experiment were carbon dioxide (provided by Suzhou Hongyun Industrial Gas Co., Ltd., with a purity of 99.99%), THF (purity ≥99%), cyclopentane (purity ≥95%), and the distilled water was made in the laboratory.

![Figure 1. Schematic Diagram of Test Devices](image_url)

2.2. Experimental procedure

In order to explore the influence of THF concentration on CO₂ hydrate formation, mass concentration of THF in the experiments was determined as 7.26wt%, 10.24wt% and 19.05wt% under hydrate formation conditions. Cyclopentane is immiscible with water, and according to the Gibbs phase law, the amount of cyclopentane in the CO₂ hydration system has no effect on its phase equilibrium. In order to ensure that cyclopentane exists under any circumstance during the test, excess cyclopentane was added with a concentration of 24.75wt%.

Before the test, interior of the high pressure reactor was rinsed with distilled water for 3 times. After drying, the pipeline was purged with test gas for 3 times and finally vacuumed. Then, the test reagent was sucked into the reactor, and CO₂ gas is introduced from the sample transfer kettle into the reactor until the pressure reached the set value. The reactor was immersed in the constant temperature water bath which contained ethylene glycol and water, and the temperature of test fluid in the reactor was lowered, so as to form hydrate.
When a large amount of hydrate was generated and observed from the glass window, the test fluid was heated, so as to decompose the hydrate. The amplitude of each time of heating increase is 0.1 °C and it was kept stable for 3~5 hours. Before the hydrate was completely decomposed, the pressure in the reactor can be observed to rise every time the temperature is raised due to the decomposition of hydrate and the release of CO₂ gas. Once the hydrate in the reactor is completely decomposed, a slight increase in pressure can be observed. According to the pressure and temperature parameters in the reactor in the hydrate decomposition process, the P-T curve is drawn, and the hydrate phase equilibrium point is the point where the slope of the P-T curve changes sharply.

2.3. Calculation of phase change heat

The hydrate phase change heat is composed of two parts: the enthalpy difference caused by the transformation of water from the hydrate phase to the liquid phase and the enthalpy difference caused by the transformation of the gas hydrate phase to the gas phase. The phase change heat of hydrate can be calculated by Clausius-Clapeyron equation:

$$\frac{d\ln P_{eq}}{d(1/T_{eq})} = \frac{\Delta H_d}{Z R}$$

Wherein, $P_{eq}$ and $T_{eq}$ are the equilibrium pressure and temperature for the hydrate phase; $\Delta H_d$ is the hydrate phase change heat; $Z$ is the compression factor; $R$ is the universal gas constant.

The compression factor $Z$ can be calculated by the PT equation shown as:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+c(V-b)}$$

In this equation, $a(T)$ represent the function of temperature.

$$a(T) = \frac{\Omega_c R^2 T^2}{p_c} \cdot \alpha(T) \quad b = \frac{\Omega_b RT_c}{p_c} \quad c = \frac{\Omega_b RT_c}{p_c}$$

$$\alpha(T) = [1 + F(1-T_r^{0.5})]^2$$

Wherein, subscript $c$ and $r$ represent the critical parameter and comparison parameter respectively.

The calculation method of $\Omega_a$, $\Omega_b$ and $\Omega_c$ are as follows:

$$\Omega_c = 1 - 3\xi_c \quad \Omega_a = 3\xi_c^2 + 3(1-2\xi_c)\Omega_b + \Omega_b^2 + \Omega_c$$

And $\Omega_b$ is the smallest positive root in the following formula:

$$\Omega_b^4 + (2-3\xi_c)\Omega_b^3 + 3\xi_c^2\Omega_b - \xi_c^3 = 0$$

$\xi_c$ and $F$ in the above formulas are two empirical parameters, which are calculated from the saturation properties of pure substances, and can also be calculated according to the following two formulas:

$$F = 0.452413 + 1.30982\omega - 0.295937\omega^2$$

$$\xi_c = 0.329032 - 0.076799\omega + 0.0211947\omega^2$$

In this equation, $\omega$ is the eccentricity factor.

The cubic expansion of the compression factor of the PT equation is:

$$Z^3 - (1-C)Z^2 + (A - B - C - 2BC - B^2)Z - (AB - BC - B^2C) = 0$$

Wherein:

$$A = \frac{ap}{R^2 T^2} \quad B = \frac{bp}{RT} \quad C = \frac{cp}{RT}$$

3. Results and Discussion

3.1. Condition for hydrate formation

According to the hydrate phase equilibrium conditions of the three systems of CO₂, CO₂-THF and CO₂-cyclopentane, the slope of the reciprocal curve of the logarithm of the hydrate phase equilibrium
pressure on the left side of the formula (1) and the phase equilibrium temperature can be obtained, as shown in Figure 1.

**Table 1.** The slope of the fitted line for hydrate formation conditions

| Guest molecule | CO₂ | CO₂-THF (wt=0.0726) | CO₂-THF (wt=0.1024) | CO₂-THF (wt=0.1905) | CO₂-Cyclopentane (wt=0.2475) |
|----------------|-----|---------------------|---------------------|---------------------|-----------------------------|
| Straight line slope | -10404 | -19938 | -19113 | -22059 | -23652 |

Table 1 lists the slopes of the fitted straight lines in the above figure. Compared with pure CO₂ hydrate, the absolute value of the linear slope after the addition of low-pressure hydration medium is significantly increased, indicating that the phase equilibrium pressure is significantly reduced. This is because the CO₂-water system forms structure type I hydrate. In contrast, the addition of low-pressure hydration media changes the hydrate structure (from type I to type II), resulting in a drop in phase equilibrium pressure.

### 3.2. Phase change heat of hydrate

**Table 2.** Phase transition heat of pure CO₂ hydrate

| P<sub>eq</sub>/kPa | T<sub>eq</sub>/K | Z     | △H<sub>Δ</sub>/kJ/mol |
|-------------------|----------------|-------|-----------------------|
| 1805              | 276.45         | 0.6974| 60.31                 |
| 2252              | 278.15         | 0.7248| 62.67                 |
| 2506              | 279.05         | 0.7573| 65.49                 |
| 2940              | 280.25         | 0.7789| 67.36                 |
| 3193              | 280.85         | 0.8142| 70.41                 |
| 3550              | 281.55         | 0.8338| 72.11                 |
| 3830              | 282.05         | 0.8676| 75.02                 |

Table 2 states the calculation results of phase change heat of pure CO₂ hydrate under various phase equilibrium conditions. From the Table 2, P<sub>eq</sub> and T<sub>eq</sub> are the equilibrium pressure and temperature of the hydrate phase, respectively, and H<sub>Δ</sub> is the heat of phase change. It can be seen from Table 2 that in the range of 1.805 ~ 3.830MPa, when the minimum pressure is 1.805MPa, the compressibility factor is 0.6974 and the phase change heat is 60.31kJ/mol. When the maximum pressure is 3.830MPa, the compressibility factor is 0.8676. The heat of phase change is 75.02kJ/mol, and the compressibility has changed by 0.1702, which affects the calculated value of heat of phase change. This is because CO₂ gas is highly compressible, which means the compressibility of CO₂ gas changes greatly in the high-pressure range. In order to reduce the influence of compressibility factor on phase change heat, this paper selects the compressibility factor corresponding to the average pressure which is the compressibility factor Z<sub>mid</sub> corresponding to the arithmetic average value P<sub>mid</sub> of the maximum pressure and the minimum pressure. Using the calculated arithmetic mean value of 2.818MPa, Z<sub>mid</sub>=0.78886 is obtained, thereby obtaining the phase change heat of CO₂ hydrate H<sub>eq</sub>=68.22kJ/mol. Kang<sup>[12]</sup> measured the phase transition heat of CO₂ hydrate to be about 65.22kJ/mol and the difference between the two results is 4.6%, demonstrating that the method is feasible.

Table 3 shows the hydrate phase change heat calculated according to the above-mentioned method. The calculation results indicate that as the mass concentration of THF increases, the phase transition heat of CO₂-THF hydrate also increases. Delahaye<sup>[13]</sup> found that the phase transition heat of CO₂-THF hydrate is about two times of pure CO₂ hydrate system, which is similar to the calculated results; the phase transition heat of CO₂ hydrate is as high as 232.93kJ/mol, and the phase change heat of CO₂-cyclopentane hydrate is close to that of CO₂ hydrate, which is 248.27kJ/mol. At present, the hydrate phase change heat data of these two systems are missing, and it is necessary to use differential scanning calorimeters and other equipment for experimental measurement.
Table 3. Calculation results of hydrate phase change heat

| Guest molecule | CO₂     | CO₂-THF (wt=0.0726) | CO₂-THF (wt=0.1024) | CO₂-THF (wt=0.1905) | CO₂-Cyclopentane (wt=0.2475) |
|---------------|---------|----------------------|----------------------|----------------------|-------------------------------|
| Pressure range/kPa | 1805~3830 | 114~1870              | 121~1851              | 104~1870              | 149~1924                      |
| Temperature range/K | 276.45~  | 276.45~               | 277.15~               | 278.85~               | 281.55~                       |
| Z             | 0.78886 | 0.9360               | 0.9863                | 0.9377                | 1.2625                        |
| ΔH_d/(kJ/mol) | 68.22   | 155.15               | 156.73                | 171.98                | 248.27                        |

4. Conclusions
The hydrate phase equilibrium conditions of CO₂, CO₂-THF and CO₂-cyclopentane hydration system are measured and used to determine the phase transition heat of the corresponding hydrate, and the following conclusions were drawn: (1) Using the P-T equation and the average pressure to calculate the corresponding compression factor, the phase transition heat of pure CO₂ hydrate is different from the value measured in the literature by 4.6%. (2) Compared with pure CO₂ hydrate, the addition of low-pressure hydration medium changes the hydrate structure and reduces the phase equilibrium pressure. (3) As the mass concentration of THF increases, the phase change heat of CO₂-THF hydrate also increases; the phase change heat of CO₂-water and CO₂-cyclopentane systems are both greater than 200kJ/mol.

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