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Thermodynamic Characteristic of Gases in the Hydrate

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Abstract. Hydrates are solid crystals with ice-like forms composed of gas and water molecules at high pressures and low temperatures. The gas hydrates are also classified as chemical compounds because the hydrate gas is composed of a fixed composition at certain pressures and temperatures depends on the type of gas. The hydrates can be formed due to the attraction of among molecules, so that the water molecules form hydrogen bonds which eventually become frames with cavities. In the cavity among molecules, there are gas molecules that are trapped with various shapes and sizes. It is also depend on the type of gas. Starting from an accidental discovery in the gas distribution industry, some impediments occurs due to the hydrate formation, now researchers have revolutionized the usefulness of the hydrate. One of them as a gas storage substance. In the study, the authors examined the characteristics of different gases filling the water molecules in the hydrate includes their formation rate, stability and storage capacity. The type of gases used are a mixture of propane butane, butane and methane at the same formation pressure and temperature. The initial pressure given for gas formation is 0.2 MPa, the formation temperature is 273 K, and the stability temperature is 268 K. The results show that the fastest formation rate was shown by butane gas, however, methane formation rate presented the slowest one. It was due to the fact that it turns out, only a little of the water molecules-methane mixture could form the gas hydrate due the pressure formation of 0.2 MPa did not meet the occurrence of the clathrate hydrate. However, the stirrer could increase the agitation of water molecules and methane gas. The best stability was also shown by butane, while methane showed an unsatisfactory result.

Keywords : thermodynamic, characteristics, gas, hydrate

1. Introduction

One of the problems of natural gas distribution in oil and gas explorations industries are the formation of hydrates. The natural gas hydrates are solid crystals with ice-like forms composed of natural gas and water formed at high pressures and low temperatures [1], so that the gas will fills the cavity, in the hydrate is called clathrate, when the gas is distributed from refineries gas, especially when the distributed pipe pass under the deep sea.

Initially, the natural gas hydrates were found when it occurs in the distribution pipelines in the petroleum industry, which disrupted the distribution process. However, it also has a beneficial effect, by reversing the situation. In the oil and gas distributions, some people have focused on how to avoid



the hydrates hydrate formations, over time some researchers realize that the hydrate formations have many potential benefits. It can be used to storage the natural gas. It is because the hydrate structures is similar to hollow ice, so that it can be used as a storage substance for practical gas distribution.

As previously explained, the hydrates have cavities formed from hydrogen bonds made up of some water molecules. When it becomes the hydrate, the water molecules will form various structures which can be classified according to the water molecules that form ice crystals [1]. Natural gas hydrates are classified into 3 types according to their crystalline structure, namely cube I (sI), cube II (sII) and hexagonal (sH) structures. In general, this type of structure depends on variations in the type of gas used. It is because, each gas has a different molecular size and composition, which will cause changes in the geometry of the water molecules as a framework of the gas [2]. This phenomena will affects on the pressure and temperature fluctuations during the hydrate formation process. Then, this process will cause the hydrate stability and also give an effect on the storage capacity of the hydrate. It is the reason that we will investigate some different gas in the experimental hydrate to understand the thermodynamics characteristic of the hydrate.

Thermodynamically, the formation of gas hydrate is very dependent on the changes of pressure and temperature, the amount of pressure and temperature given to the system, the amount of the gas moles absorbed by the water molecules, the changes in the thermodynamic states of the gas at STP conditions, and etc. in which it will describe the characteristics of gas when it is formed to be the hydrate. Hence, it is very interesting because the water molecules can store the gas namey the hydrates. It makes some researchers interested in observing the characteristics of the filled gas in the water molecules frameworks. Its characteristics are very important to know in order to exploit the potential of the gas hydrate as a gas storage tools and can also solve the problems caused by gas hydrate itself, such as the prevention of hydrate formation in the gas distribution at a certain pressure and temperature.

Some characteristics of the gas hydrate include the hydrate formation rate represented by the number of mole gas bonding to the water molecules due to thermodynamic changes of the system, the hydrate stability in which the gas will decompose from the water molecules when the hydrate is tried to stabilize, and finally, the gas storage capacity when the gas hydrate left in STP condition.

Ganji et al. [3] have examined the characteristics of the hydrates including the formation rates, the stability and the storage capacity of hydrates by using methane gas influenced by anionic surfaces, cations and non-ions. However, in this study, we will compare the thermodynamic conditions of the same hydrate, but it will be applied to in some different gases. In this study, no other molecular effects such as surfactant's effetcs were given, but only it will be influenced by the different gas molecules with slightly lowering the hydrate formation pressure lower than Ganji's research.

The study will examine the effects of different gas types on the characteristics of the gas hydrate. Once, the characteristics of the gas hydrate studied include the formation rate, stability and storage capacity. In the study, it was used methane, butane and butane propane mixture. The hidration process will take duration for a 10-hour in the formation rate and for 5- hour in the stability measurement.

2. Experimental Methods

2.1 Experimental Devices

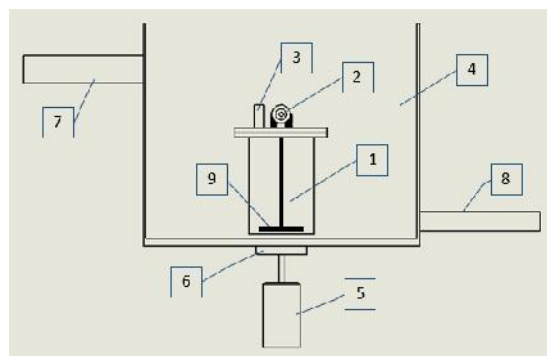


Figure 1. Experimental Devices

The hydrate experimental devices were installed as Fig. 1. They consisted of (1) crystalizer, (2) water and gas valves, (3) pressure sensor and thermocouple, (4) cooling bath, (5) gear box motor, (6) Neodymium magnetic, (7) input water pipe, (8) output water of cooling bath, and the mixer was (9) a stirrer.

The experimental devices used a crystalizer to form the hydrate. Inside the crystalizer, there is a stirrer magnet functioning as a stirrer in the crystalizer. It will give significant influence for heat and mass transfer effects. Then, to maintain the hydrate formation, the temperature of cooling bath was conditioned at constant temperature. Therefore, the refrigerator was used to circulate water by using a pump to pump the cooling water that will be used to reduce and maintain the temperature in the system to be constant. The cooling bath was used as a system to replace the crystallizer functioning to keep constant temperature in hydrate formation and circulating the cooling water. Thermocouple and pressure sensors were used to measure the fluctuated pressure and temperature inside the crystalliser during the hydrate formation. Besides, it used to measure the temperature in cooling bath. Another device, an electric motor was used to rotate the stirrer. The stirrer functions to fold in the water and gas to form the gas hydrate by rotating 200 rpm.

2.2 Materials

We used a demineralized water to mix it with gas to form the gas hydrate. It was hope that the demineralized water contained pure water, so that the gas will be bounded by pure water molecules. In the experiment, there were 3 gas used; butane, propane- butane, and methane. Each gas will be observed its thermodynamics characteristic by measuring the change of pressure and temperature, as well as its amount of gas mol absorbed by water molecules in the hydrate formation process.

Beside it flowed the circulating water from refrigerator to the cooling bath, we also add some ice to make constant temperature in the cooling bath to support the temperature of the cooling bath. It was also to keep the constant temperature when it was conducted the measurement of the hydrate stability process

2.3 Experimental procedures

2.3.1 The hydrate formation process

The experimental procedure of the hydrate formation was conducted almost similar to the previous research [4]. In the beginning, it was kept the crystallizer from other compounds or mixtures. It means, it was cleaned from remaining dirty to avoid another reaction effect between gas and water molecules.

The demineralized water was flowed as 50 cm³ into the crystallizer and then it was closed. Next, the gas was inputed to the crsytallizer by arranging the valve in the crystallizer until the pressure formation reaches 0.2 MPa. After closing the crystallizer at 0.2 MPa, the crystallizer was inserted into the cooling bath in which the tempareture of cooling bath was controlled at 273 K using circulating water from chiller to the cooling bath. Afterwards, for the hydrate fromation process, it will be started by adjusting the rotation of the magnetic stirrer at 200 rpm. Some data retrieval was carried out for temperature and pressure during 10 hours. The change of temperature and pressure during the process was observed by recording it every 15 minutes. After we found the data of the temperature and pressure, it was able to calculate the amount of consumed gas by using the equation:

$$n = \frac{P_{hydrate}V}{ZRT} \quad (1)$$

in which P is gas pressure inside the hydrate or the water molecules (Mpa), V represents gas volume (m³), T is gas temperature (K), Z reflects compressibility factor [5].

For calculating the consumed gas absorbed by the water molecules, it will be used :

$$P_{hydrate}(t) = P_{initial hydrate formation} - P_{hydrate}(t + \Delta t) \quad (2)$$

In which $P_{initial hydrate formation}$ is 0.2 Mpa.

2.3.2 The stability process

After conducting the hydrate formation during 10 hours experiment, then, it was measured the hydrate stability. After accomplishing the hydrate formation process, the gas valve on the crystallizer was opened to remove the remaining gas that did not bond among the water molecules to be the hydrate. Next, it has been removed from the crystallizer, at that time, the valve was closed again. The crystallizer was inserted in the cooling bath before the cooling bath temperature was decreased to around 268 K. Later, the crystallizer was put back into the cooling bath and kept it during 5 hours. Similar to the hydrate formation process, every 15 minutes stability process, the pressure and temperature were recorded.

The pressure and temperature were used to calculated the decomposed gas, also, by using equation 1. The decomposed gas (mol) represented the amount of gas that did not bind again with the water molecules due to gas-water conditions were unstable. Consequently, they were easily broken down.

2.3.3 The storage capacity measurement

The storage capacity measurement was begun after the hydrate stability process was accomplished. The crystallizer was detached from the cooling bath and kept at room temperature (300 K). As a result, the gas inside the hydrate would decompose and release out the hydrate. After temperature inside the crystallizer reached the room temperature, the pressure inside one was recorded. The volume of the trapped gas would be calculated by comparing the gas volume in the crystallizer to the volume at standard conditions.

3. Results and discussions

3.1 The hydrate formation rate

Figure 2 shows the hydrate formation pressure during the hydrate formation process begins with a formation pressure of 0.2 Mpa for all gas types. Along with the pressure, the hydrate formation temperature is also illustrated in the graph during the hydrate formation process. In the hydrate formation process, there are 2 processes, namely the induction process and the hydrate formation process until the pressure reaches equilibrium state. The induction process is the condition of hydrate as long as the pressure and temperature decrease sharply that represents the gas go into the water molecules until the equilibrium phase of pressure and temperature until the is formed hydrate, so the time in this phase. It is also called by the hydrate time. Meanwhile, the hydrate formation process is characterized by a slightly decreasing of pressure and temperature. Then, the gas-water molecules begins to form the hydrate. It is shown when the pressure has begun to be constant. The hydrate time reaches peak at $t = 50$ minutes, after that, it is begun with the hydrate formation.

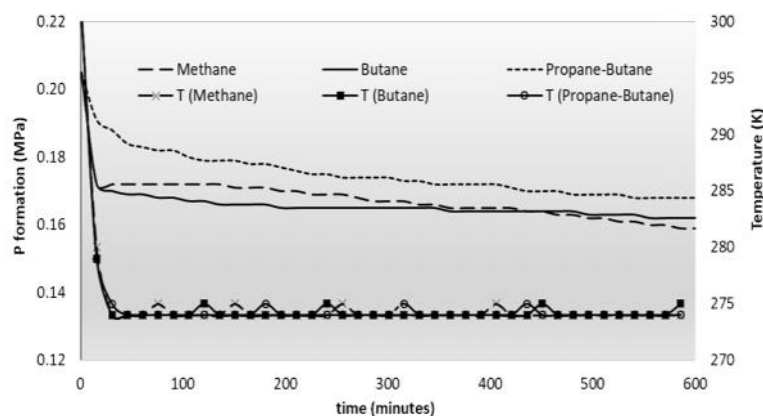


Figure 2. Hydrate formation pressure and temperature in elapsed time

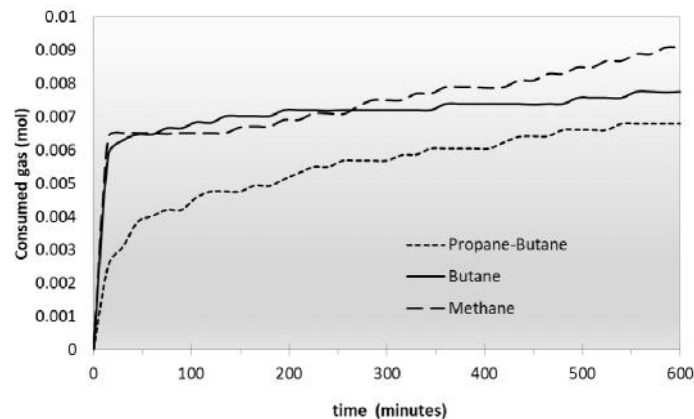


Figure 3. Consumed gas by water molecules in elapsed time

The hydrate formation rate represents by occurring the pressure drop as long as the hydrate formation process. The fastest one is taken place by butane, conversly, the slowest one is propane-butane. However, it is strange for methane. If butane and propane-butane show the equilibrium state at the hydrate fromation process, it does not happen for methane. The hydrate formation pressure for methane continues to fall and does not reach constant pressure. It seems that the hydrate is not formed. Theoritically, based on the phase diagram [3], the pressure needed to form the hydrate for methane is about 20 MPa. Actually, it is tried to give the a stirrer tank to make excellent mixing among methane gas and water molecules, to increase mass transfer in the hydrate formation. By agitating gas and water, it will increase the consumed gas in the process. Eventhough it is not enough to form the methane hydrate by using 0.2 MPa pressure, it can be improved by the stirrer. If it is connected to Figure 4, theoritically methane does not form the hydrate, however, the figure shows that the hydrate is able to absorbed methane. It is represented by the capabilities of hydrate to release methane gas. It means that, eventhough, 0.2 MPa pressure does not be enough to form the hydrate, but the hydrate can be formed by the agitation of the stirrer tank. For other gases, it can be seen that butane reached the fastest stability condition, followed by a mixture of butane-propane.

By using the hydrate formation pressure and temperature, at Figure 2, the consumed gas can be calculated by equation 1, Then, the calculated consumption gas can be plotted at Figure 3. The consumed gas shows an opposite trend with the hydrate formation pressure, because it was used the pressure inside the hydrate, inside the water molecules. It was not the decreasing pressure at Figure 2, so that the calculation of the consumed gas is determined by using equation 1 and equation 2. It can be corralated between Figure 2 and Figure 3, if the hydrate formation pressure increase, so the consumed gas will increase. Eventhough it has just a calcuation results, but the validation of the results can be matched with another experiment [6] and another future work.

3.2 The hydrate stability

In the hydrate stability, the bond strength is determined by the difficulty of release gas from the hydrate. As stronger the bonds of gas hydrate, as more difficult the gas to release. It is represented by the low release gas stated by mol release gas. The lower release gas affects a slower the hydrate decomposition rate. Hydrate stability explains the ability of the hydrate to maintain its shape and bonds, so that the stability of the hydrate is inversely proportional to its gas decompositions.

Figure 4 shows the hydrate decomposition rate at temperature 268 K. It is illustrated by the changes of the decomposition gas from the hydrate in elapsed time. In this study, the duration of 5- hours time is sufficient to test whether the gas is easy or difficult to decompose on the hydrate. In the decomposition, it can be seen that the decomposition occurs the fastest in methane and the slowest in butane. From the graph, it can be confirmed that the highest stability of the hydrate is butane, while

the weakest one or easily gas to decompose is propane-butane mixture. Something interesting happens in methane.

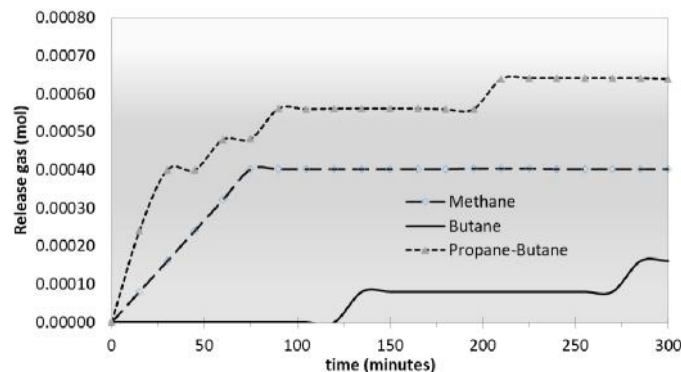


Figure 4. The hydrate decomposition rate in elapsed time at 268 K

As mentioned in the previous hydrate formation process, in fact that methane was found to be able to inject the gas to the hydrate and made a few hydrate molecules, even though theoretically it could not form due to too low the hydrate formation pressure. However, because of the stirrer, the methane hydrate is slightly formed, and it is an extraordinary results that must be observed in the next work. It can be emphasized that the bonding capacity between methane and water is very high. It can be proved by comparing the decomposition abilities between methane and propane-butane mixture. Methane hydrate is much more stable than propane-butane hydrate. Whereas, in the gas consumption, propane-butane have much higher consumed gas than methane.

3.3 The storage capacity

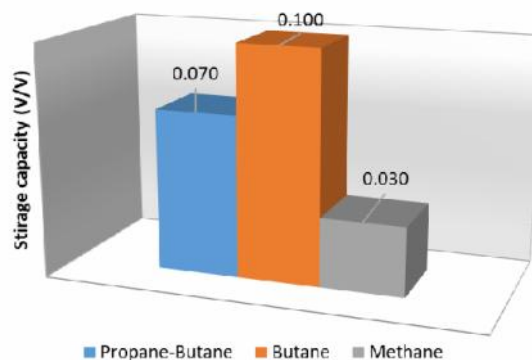


Figure 5 The hydrate storage capacity

After investigating the hydrate stability, another important parameter is how hydrates can store gas in atmospheric conditions. It is important that the gas hydrate as a medium of storing the natural gas in which it concerns the purpose of this study.

The storage capacity of the hydrates for 3 types of gases can be seen in Figure 5. By comparing the measured gas volume at the crystallizer in the final conditions. The gas volume was calculated by using equation 1 after the pressure reaches equilibrium condition. Then, it is compared to the gas volume at STP condition. It is the reason why

the unity of the hydrate storage capacity is V/V. The gas storage capacity of the hydrate is illustrated in Figure 5. Butane has the biggest capacity followed by propane butane and methane. Accordance to the hypothesis that the storage capacity is directly proportional to the size of gas molecules. It is known that the molecules size of butane is bigger than propane, and also bigger than methane [2].

4. Conclusions

Thermodynamic characteristics of gases in the hydrate were experimentally investigated. The results and the hydrate characteristic included the hydrate formation rate, stability, and storage capacity were discussed. The conclusion obtained in the present study are summarized as follows :

1. The fastest hydrate formation rate was taken place by butane, conversly, the slowest one is propane-butane.
2. Eventhough it is needed about 20 MPa to form methane hydrate. However, it can be improved by using the stirrer to agitate the mixing between gas and water molecules to increase the mass transfer process.
3. The highest stability of the hydrate is butane, while the weakest one is propane-butane mixture.
4. The methane hydrate is slightly formed, however, the bonding capacity between methane and water is very strong.
5. Butane has the biggest capacity followed by propane butane and methane.

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