

ACCUMULATION OF HIGH-POTENTIAL CHEMICAL ENERGY OF METHANE TO HYDRATES

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Abstract: For countries with limited access to conventional hydrocarbon gases, methane hydrates appear as a possible source of energy or as a strategic concern for the creation of alternative natural gas reserves. Currently, natural gas hydrates are beginning to be included in the considerations of gas supply for the next decades. From a perspective point of view, the accumulation of natural gas in the form of hydrate structures and subsequent release, if necessary, proves to be very advantageous. Storing gas in such a form creates an energy-efficient interest in developing and innovating technology in this area.

1 Introduction

In general, a hydrate is defined as a substance containing water and hydrocarbons (or other gases) [1]. It is commonly found in the world in solid form, which accounts for about 85% of water and 15% of gas [2]. From a chemical point of view, hydrates belong to a group of compounds known as clathrates (from the Latin word “clatratus”, grated) [3]. The amount of hydrocarbon molecules captured depends on the shape of the crystal lattice because methane is not chemically bound but only “trapped” in the crystal lattice. To put it simply, the natural gas hydrate is a clathrate formed by water molecules, where a molecule of one of the natural gas hydrocarbons is trapped in the cavity. The hydrocarbon gas molecule is surrounded by water molecules [4].

Due to the formation and retention of hydrate structures, the gas concentration is critically dependent on a sufficient amount of water molecules surrounding them. Since they are ice-like compounds, hydrates at room temperature and pressure are unstable. The stability of hydrocarbon gas hydrates is mainly related to the structure of these substances and the interaction of several factors that interact with each other under certain physical conditions [1]. The formation of hydrates predominantly determines the presence of water and hydrocarbon gases in a concentration allowing the formation of clathrate

structures (Figure 1), at the temperature and pressure at which the hydrates normally occur. It is clear from the foregoing that the occurrence of hydrates is limited to two types of geological area, namely permafrost in the polar continental shelves (Figure 2) and in sediments under the seabed [5].

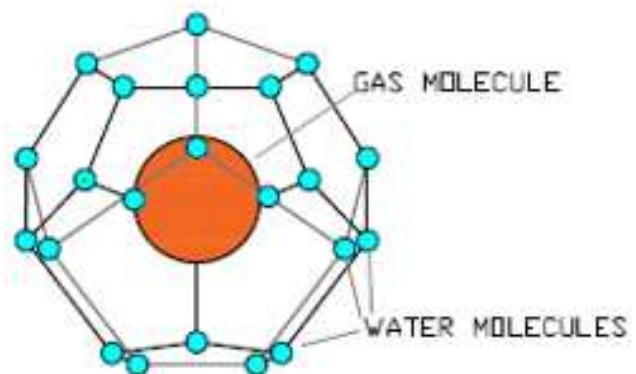


Figure 1 Typical hydrate structure with water molecules

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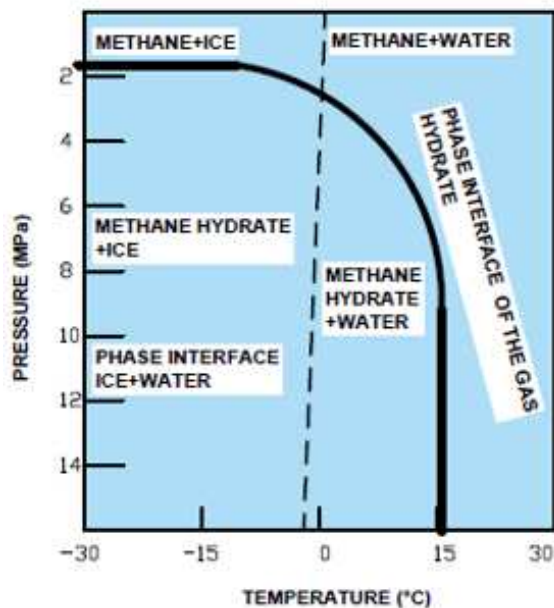


Figure 2 Phase diagram of methane hydrate formation

2 Natural gas hydrates

Natural gas is a mixture of gaseous hydrocarbons whose main component is methane. The formation of natural gas can be partly attributed to the thermal decompositions of organic matter and therefore very often occurs in deposits along with oil or coal. It can occur in various form and one of them is CNG (Compressed Natural Gas) is compressed natural gas to a pressure of about 20 MPa. The second form is LNG (Liquefied Natural Gas), is a liquefied natural gas at -162 °C. It consists predominantly of methane and higher hydrocarbons with little inert gas. However, hydrates have been considered as a potential source of energy for decades, especially for countries with limited access to conventional hydrocarbons or for the strategic interest in creating alternative natural gas reserves. From a perspective, the accumulation of standard natural gas in the form of synthetically generated hydrates appears to be very advantageous. The storage of natural gas in hydrates appears to be particularly beneficial in terms of safety. Because natural gas hydrates can be stored at higher temperatures and lower pressures compared to other storage technologies, for example liquefaction or compression [6].

Saving energy in a convenient form for safe storage and its subsequent release is a challenge in processes where energy is needed to accumulate. At present, a high emphasis is placed on the overall efficiency of these processes, in terms of energy use, energy efficiency and energy storage (Figure 3, Table 1). Hydrates have the potential to provide peak coverage in cogeneration of electricity and heat by natural gas released from hydrates [2].

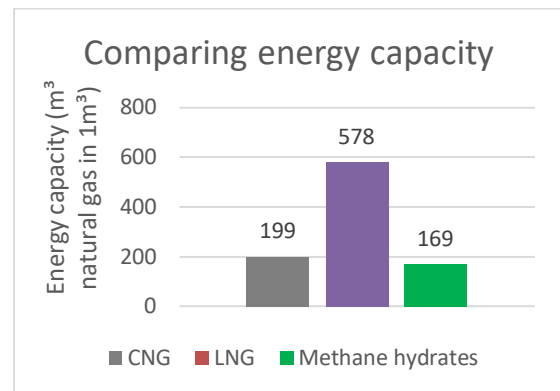


Figure 3 Comparing energy capacity

Table 1 Parameters of individual accumulation methods

	Energy capacity (m ³)	Specific energy (MJkg ⁻¹)	Energy density (MJm ⁻³)	Energy input (kJkg ⁻¹)
CNG	199	49	6914	2430
LNG	578	49	20093	908
Methane hydrates	169	7	5880	416

3 Quantification of hydrate generation

For the calculation of hydrate formation, we can proceed with two basic methods, manual or computerized calculation method [7].

3.1 Manual calculation method

These methods are based on the equilibrium of the three phases, namely liquid water - hydrate - water vapour. When designing processes involving hydrates, it is a problem to predict the pressure and temperature conditions at which the hydrates will be formed. The advantage of manual calculation methods is e.g. a quick estimate of the hydrate formation conditions but the disadvantage is their inaccuracy. However, these methods are still popular. Manual calculation methods include e.g. gas gravity method and K-factor method.

The gas gravity method is simple, including only one graph (Figure 4) from which temperature and pressure can be read, with gas density being the third parameter. The disadvantage of this method is some inaccuracy with respect to experimental results [7].

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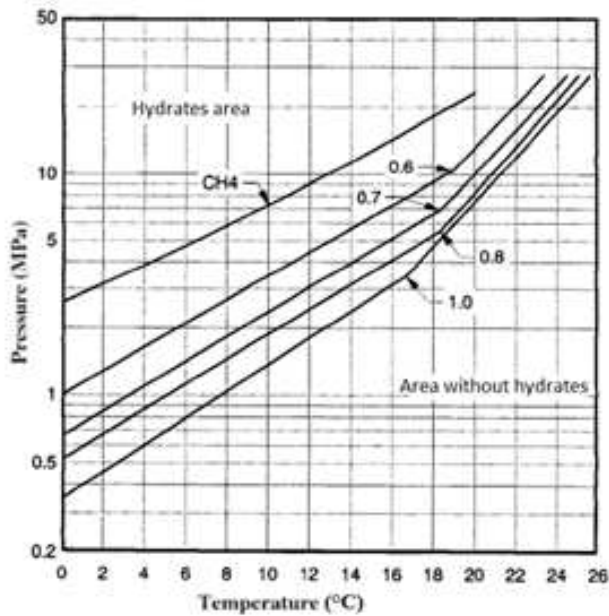


Figure 4 Occurrence of natural gas hydrates, gas gravity method

Another method is the K-factor method. The K-factor (distribution coefficient) is determined as the distribution of components between hydrate and gas:

$$K_i = \frac{y_i}{S_i} \quad (1)$$

Where y_i and S_i are molar fractions of component i in steam and in hydrate respectively. Water is not included in the calculation. Graph versions are available in SI units, for each of the components commonly found in natural gas such as methane, ethane, propane, isobutane, n-butane, hydrogen sulphide and carbon dioxide. This method is not suitable for high pressures ~ 10 MPa. For pure methane, it does not provide results at pressures above 20 MPa. It is rational to use a K- factor of up to 7 MPa and a temperature of 0 - 20 °C. This method is less accurate for mixtures. The accuracy of this method is in the range of 10-15% [8].

Another method for predicting hydrates is named after Baellia and Witchert. The basis for this method is the gravity of the gas, but the graph (Figure 5) is much more complicated than the gas gravity method of Katz-a. The main difference is the presence of hydrogen sulphide (up to 50 mol%) and propane (up to 10%). The effect of propane comes in the form of temperature correction, which is a function of hydrogen sulphide pressure and concentration. Said method is intended for use with sour gas and is thus significantly different from the above-mentioned methods [7].

The graph was designed to predict at what temperature a hydrate is formed that contains oxygen gas of known composition at a given pressure. For application of the diagram, the content of hydrogen sulphide in the sour gas may range from 1 to 50%. While the hydrogen sulphide to

carbon dioxide ratio is between 10: 1 and 1: 3. Under these conditions, according to the graph, hydrate formation can be assumed ± 1.11 ° C for 75% of cases. Baillie and Witchert claim that for a given pressure their table estimates the hydrate temperature to 1.7 °C for 90% of their tests [7].

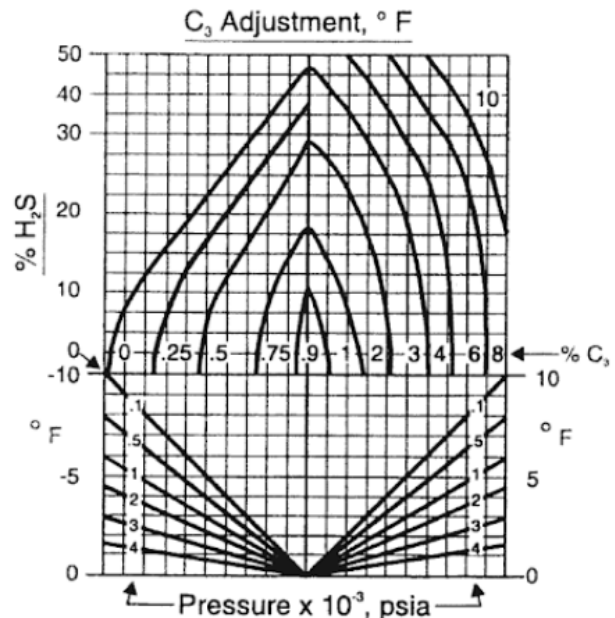


Figure 5 Baillie-Witchert chart for estimating hydrate formation conditions in SI units

3.2 Computer calculation method

They use complex algorithms based on phase equilibrium of chemical potentials. Phase Equilibrium, van der Waals and Platteeuw, Parrish and Prausnitz, Ng and Robinson, and there are several commercial hydrate software such as EQUI-PHASE Hydrate or CSMHYD [7].

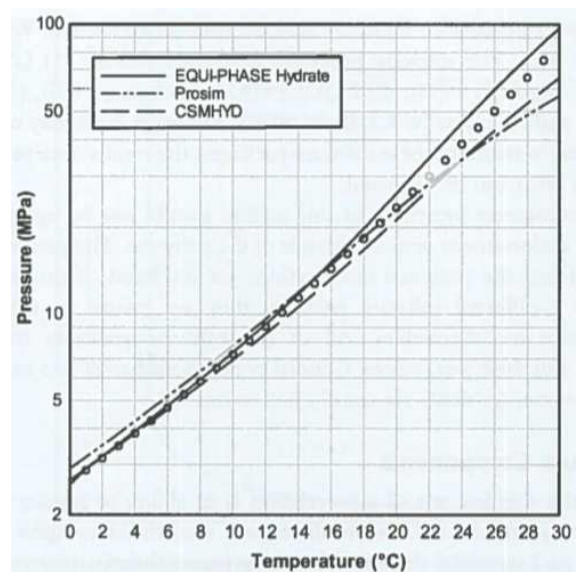


Figure 6 Hydrate Locus Loci of Methane

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Figure 6 shows the hydrate locus for pure methane. Throughout the range of pressure shows on this plot, all three software packages are of acceptable error. Only at extreme pressures do the errors exceed 2 °C.

First, consider pressures below 10 MPa, which is a reasonable pressure limit for the transportation and processing of natural gas. However, it is not sufficient for the production of gas [9].

4 Design for experimental device

The design of the experimental device was based on these temperature and pressure requirements (Figure 7). Temperature 0 °C to 20 °C and pressure 25 MPa.

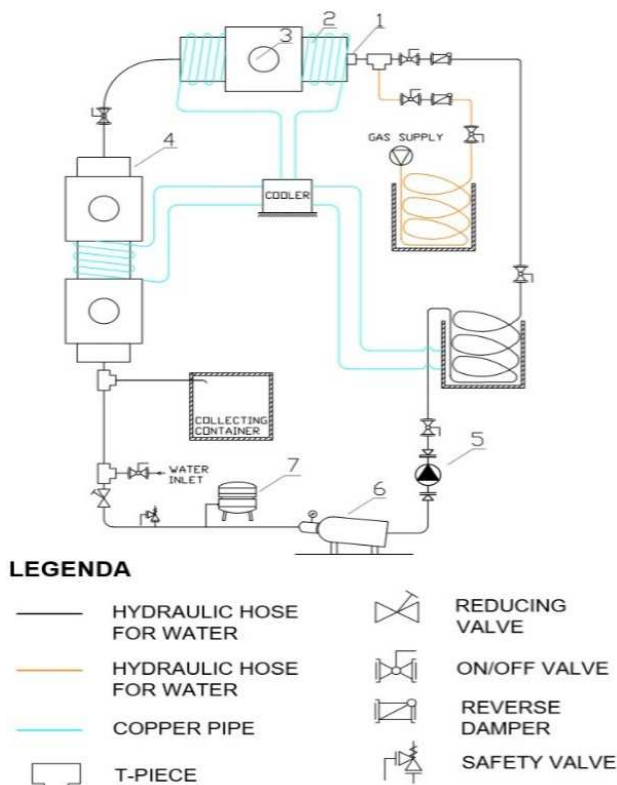


Figure 7 Schematic of experimental device

Table 2 Schematic positions on the experimental device

Part of device	Model/type
1	Nozzle Spray angle 51° and 155°
2	Vessel VN1 φ175/146,9 mm,
3	Sapphire visor Normal φ 50 mm
4	Vessel VN2 Φ175/146,9 mm
5	Plunger pump P = 4,7 kW, Q = 5,1 l.min-1,
6	Accumulator Volume 20l, working pressure 207 bar
7	Expansion tank Reflex-refix DT 80, working pressure 16 bar,

The experimental device forms a closed circuit of the elements listed in Table 2, which are interconnected by hydraulic hoses. Before commissioning the system, it is necessary to fill the system with water through the water supply. The circulation of water in a closed circuit will provide a plunger pump that will suck and compress the water to the desired pressure of 25 MPa. The water after cooling will be cooled by the cooling device and then under the required pressure of 25 MPa it will flow through the hydraulic hose, through the non-return valve towards the nozzle. The device consists of two high-pressure circuits. In the first circuit, as mentioned, the working medium is water. The second circuit is a natural gas compressor, which compresses the gas to a desired pressure of 25 MPa.

The compressed gas is then cooled to the desired temperature and will pass through the hose through the non-return valve towards the nozzle where it is mixed with the pressurized water. The resulting mixture flows into the nozzle where it is atomized into small particles. Subsequently, various forms of hydrate will be formed. The water and natural gas mixture will initially flow from the vessel through the pipe to the high pressure vessel after filling. After filling the high pressure vessels with the gas and water mixture to the visible area, the shut-off valve is closed. From that moment on, the seeds of the hydrate will be formed and the time after the formation of the hydrate will be measured. Through the sapphire visors placed on the outer casing of the container, it will be observed how the natural gas hydrates occur.

5 Conclusion

The article presents a schematic of experimental equipment that is primarily intended for the continuous generation of natural gas hydrates. The design and principle of the device function are based on the knowledge of typical mechanisms of methane hydrate formation. Methane hydrates are formed in places where methane and water are found at temperatures and pressures that are favourable to hydrate formation. These conditions are most commonly found in marine sediments and arctic permafrost. Further research could proceed, for example, by rapidly and continuously producing methane hydrates in an economically efficient manner. Methane hydrates have the potential and therefore this issue would deserve increased attention and the necessary development of technology in this area.

Acknowledgments

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