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Conditions Characterizing Hydrate Formation

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Abstract: For countries with limited access to conventional hydrocarbon gases, methane hydrates appear to be a potential source of energy. Given the demands of the European Union to reduce the energy intensity of technological processes, it shows as a prospective accumulation of natural gas and biomethane in the form of hydrate structures and, if necessary, release them. Storing gas in such a form creates an energy-efficient interest in developing and innovating technology in this area. However, the question arises: "How artificially accumulate methane energy into synthetically generated hydrates and practically implement it when needed?" Finding her answer is a current challenge in processes and technologies where energy needs to be stored.

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1 Introduction

We are currently at a very early stage in the development of methane hydrates. The transition from scientific theory to practical extraction is under way. Developments for viable energy-efficient recovery are currently feasible, but the potential of this new hydrocarbon source is undeniable. The main reason is the storage capacity of hydrates compared to other natural gas treatments (CNG, LNG). Therefore, they are being considered as a potential source of energy for the coming decades [1,2].

For countries that do not abound in traditional gas reserves or rich shale forms, these hydrates are seen as a lifeline - as an example, Japan is leading them in their research.

2 Conditions for hydrate formation

Hydrates are generally solid crystalline substances formed by the combination of water and hydrocarbon gas molecules. These include methane, ethane, carbon dioxide and hydrogen sulphide. The article will focus on clathrate bonds of water and the most used energy carrier in the gas industry, namely natural gas [3].

Hydrates of natural gas and other similar compounds are classified by arranging the water molecules in the crystal and thus the crystal structure of the lattice. Due to hydrogen bonds, water molecules are often organized into three-dimensional spherical structures called cages. The second molecule is located inside the cage and stabilizes the entire structure.

The following table defines the necessary pressure and temperature at which hydrate methane structures will be formed [4].

The chemical composition of the aqueous phase and the hydrate is expressed as a molar percentage of methane and for the vapor is expressed as a molar percentage of water.

It can be seen in the graph that for the ethane, propane and isobutane contained in the hydrate mixture it was a function of temperature or pressure (i.e. they are constant). The reason for this is that the hydrate structure is occupied by large cavities and the large

cavities have a high occupancy rate. The values given in the tables are essentially 100% saturation values.

Table 1 Methane hydrate formation conditions

Temperature (°C)	Pressure (MPa)	Substance quantity (mol%)		
		CH_4	H_2O	CH_4
		Water	Steam	Hydrate
0,0	**2,60**	**0,10**	**0,027**	**14,1**
2,5	**3,31**	**0,12**	**0,026**	**14,2**
5	**4,26**	**0,14**	**0,026**	**14,3**
7,5	**5,53**	**0,16**	**0,025**	**14,4**
10	**7,25**	**0,18**	**0,024**	**14,4**
12,5	**9,59**	**0,21**	**0,024**	**14,5**
15	**12,79**	**0,24**	**0,025**	**14,5**
17,5	**17,22**	**0,27**	**0,025**	**14,5**
20	**23,4**	**0,30**	**0,027**	**0,025**

The means for the aqueous phase, steam and, if any, non-aqueous liquid were calculated using the available software. The chemical composition of the hydrate is estimated from the combination of the experiment data, computer software and crystalline hydrate structure.

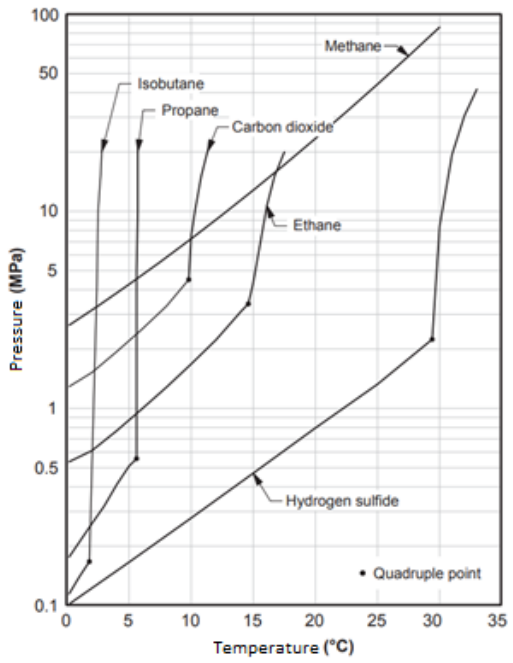

Figure 1 Conditions characterizing the formation of hydrate structures for several constituents present in natural gas [4]

For example, methane appears to be the most soluble of these hydrocarbons. The above values show significantly higher concentrations in the aqueous phase. However, solubility is a function of temperature and pressure. Methane is soluble at higher pressures compared to other hydrocarbons [4].

3 Generation of synthetic natural gas hydrates

The following part of the thesis deals with the description of the existing equipment in order to create suitable conditions for the accumulation of gas into hydrate structures. The design of the device was based on foreign studies, theoretical. The apparatus was designed based on these temperature and pressure conditions, a temperature of 0°C to 20°C and a pressure of 25 MPa. Given that temperatures below 0°C would lead to freezing of excess water to hydrates, it is recommended to form hydrates at temperatures just above zero [5]. The determination of the optimum temperature will depend on the results of experimental measurements.

The hydrate formation process was based on the patented system of two high pressure vessels. In the first vessel, the methane is hydrated and then pumped into the second vessel, where the capture and dehydration process takes place, i.e. removal of excess water from the mixture. Removal of excess water from the mixture is important to reduce the total volume of the resulting hydrate.

The production of methane hydrates is conditioned by the formation of contacts between the liquid and the gas. Therefore, the method of injecting water droplets into the gas continuous phase was chosen. In an aqueous continuous system, due to the high heat capacity of the water, the heat generated during hydrate formation can be effectively dissipated in the aqueous component, but a large amount remains unchanged. The injection of water into the gas at the stage of their interaction causes the formation of hydrates. This phenomenon occurs in two phases: nucleation and embryo growth. During nucleation, methane gas is dispersed in the aqueous component. Dissolved methane in water forms the seeds of hydrates and crystallizes. In the growth phase, the embryos formed are sized or aggregated. The shape and size of the nozzle plays an important role in this process, since the shape of the droplets or their surface depends on it [6].

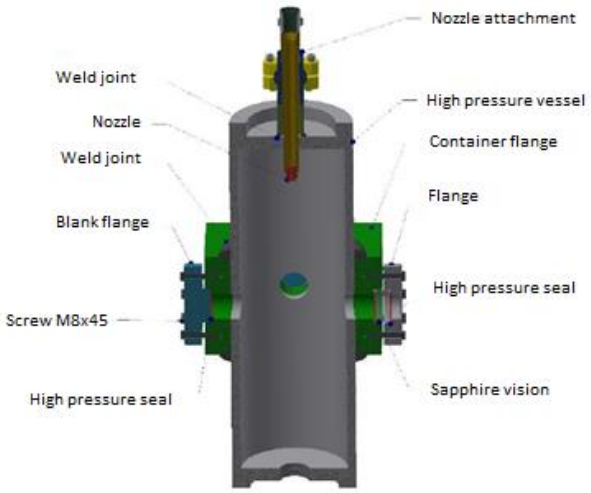

Figure 2 Location of the injection nozzle

The water and gas will be mixed in the pipeline just prior to supply to the first 5.7 litre main pressure vessel. The water / gas mixing ratio is 1/150 to 1/170. At the inlet to the container, the water will be sprayed by means of a nozzle. Spraying the liquid into small particles will facilitate the process of enclosing the gas into the water grid. In the design we consider two alternatives - nozzles with a spray angle of 55° and 150°. We assume that in practice a solution with a larger spray angle will prove to be more effective as it can cover a wider area with small particles of water [7].

4 Measuring and recording technology

The measurement of the required temperature and pressure parameters will be provided by means of sensors with electronic output for measuring temperature (NiCrNi thermocouples and Pt100 sensors) and pressure. The output is connected to the ALMEMO 5690-2 AHLBORN control panel and is connected to a computer. Data is written according to a specified time cycle in Excel. The NiCrNi thermocouple consists of two different metals welded at one end, where a thermoelectric voltage is generated as a function of temperature. The Pt100 resistor works on the principle of changing the electrical resistance depending on the temperature change of the sensor.

The experimental device has been innovated over time and has undergone many design changes to the final form shown in the *Figure 2*.

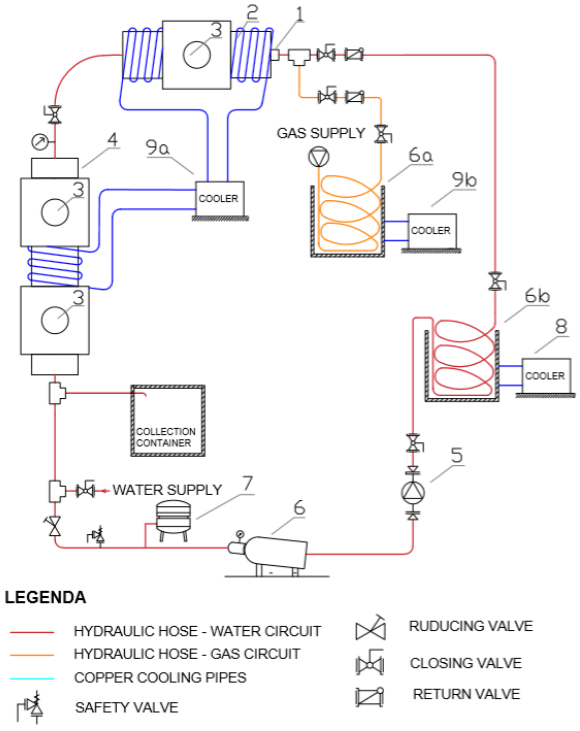

Figure 2 Wiring diagram of the experimental device

Table 2 Schematic positions on the experimental device

	Part of device	**Model/type**
1	Nozzle	Spray angle 51°/ 155°
2	Vessel VN1	φ175/146,9 mm,
3	Sapphhire visor	Normal φ 50 mm
4	Vessel VN2	Ø 175/146,9 mm
5	Plunger pump	P = 4,7 kW
6	Accumulator	Volume 20l,working pressure 207bar
6a	Cooling container	Plastic material
6b	Cooling container	Plastic material
7	Expansion tank	Working pressure 16 bar
8	Cooler	Q=60 $l.min^{-1}$, p_{max}= 6bar
9a/9b	Cooler	Q=11-16 $l.min^{-1}$, p_{max}= 0,45bar

The measurement methodology on the experimental device consisted of the following steps. First, the entire system is cooled to the desired temperature by actuating the cooling devices. The cooling process takes about 3 hours. Before the start of the measurement, the entire system is filled with water through the water inlet. When the system is filled with water, the gas branch opens. Compressed gas starts to push the water towards the pump suction while monitoring the level to drop to half the sapphire visor on the VN1 vessel. Further, the natural gas pressure will be increased to the desired value for measurement, e.g. to 120 bar. After reaching the desired pressure, the gas branch is closed. A high-pressure pump 5 is actuated to circulate the water and methane solution through the atomizing nozzle in the experimental apparatus. From this point on, a hydrate will be formed over time.

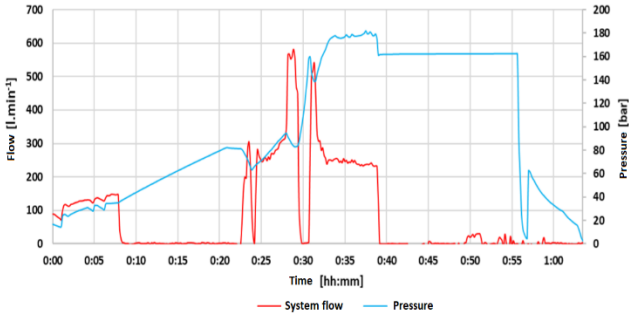

Figure 3 Flow and pressure measurement

The whole process is graphically depicted as a function of pressure over time. The measurement took about 1 hour and 4 minutes. At this time, the gradual filling of the natural gas system is included, followed by the displacement of water from the VN1 vessel to the visible part of the sapphire visor (the pressure in the graph rises; , within about 35 minutes). At 38 minutes, pump 6 was switched on, which maintained a nearly constant pressure for about 55 minutes. Then the pressure dropped sharply, which was probably due to water being absorbed into the hydrate structure and thus lack of water at the pump suction.

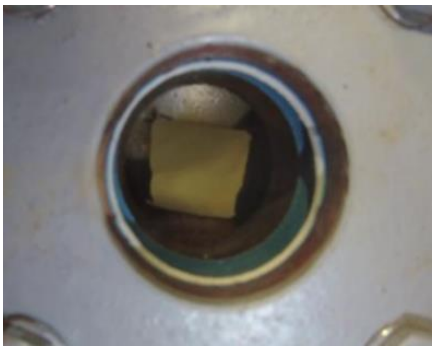

Figure 4 Recording of the hydrate formed

The *Figure 4* shoes the hydrate formed in the VN2 pressure vessel, at the bottom of the vessel.

In the measurement, natural gas consumption was 2,187 m^3, hydrate formation time of 2:00 minutes and an average pressure of 97 bar. Based on a subjective visual assessment and average pressure value, the hydrate structure appears to be perspective.

5 Conclusion

Hydrates of natural gas or methane have an interesting potential and therefore the future energy demand from hydrocarbon sources may be a requirement to improve synthetic hydrate formation processes. A prospective option is to accumulate standard natural gas in the form of artificially formed hydrates, with subsequent storage and, where necessary, covering energy peaks with future release. Gas can be stored in such a form at relatively high temperatures and low pressures compared to other hydrocarbon gas storage technologies.

Hydrates can become a current challenge for the future and, once verified, can find application in various sectors of technology or industry. A particular solution is appropriate to apply in the technology industry to cover energy-intensive peaks in cogeneration and trigeneration, e.g. with the option of using waste heat to heat and then release stored energy when necessary.

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