



Science

PRIMARY ENERGY ACCUMULATION THROUGH ADVANCED GAS HYDRATES SYSTEM

Peter Durcansky ^{*1}, David Hecko ¹, Milan Malcho ¹

¹ University of Žilina, Faculty of Mechanical Engineering, Department of Power Engineering,
Univerzitna 1, 010 26 Žilina, Slovakia



Abstract

Accumulation of primary energy of natural gas is a perspective industrial area mainly for countries dependent on the import of energy and raw materials. Transporting and storage of natural gas is economically and technologically demanding, which is always reflected in the resulting price. Natural gas hydrates allow transport and storage at low pressures and relatively favorable temperatures. Another no less important area is the storage of energy in biogas plants where gas formation is time-dependent. Biogas hydrates would allow short-term storage at room temperature and atmospheric pressure. This article deals with the design of a functional prototype for the production of hydrates and numerical simulation.

Keywords: Primary; Energy; Accumulation; Hydrates System.

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1. Introduction

Gas Hydrate as Energy Storage

The storage of natural gas in hydrates is particularly advantageous in terms of storage capacity, but also in terms of gas storage safety, which is possible at higher temperatures and lower pressures compared to other storage technologies such as liquefaction or compression. The gas hydrate can be a great source of energy that begins to be included in the considerations of gas supply for the next decades. It is estimated that 99% of the global gas hydrate supply occurs in marine sediments under the corresponding temperature and pressure conditions, in seabed sediments, at depths from 300 m to 4000 m. [1, 2]

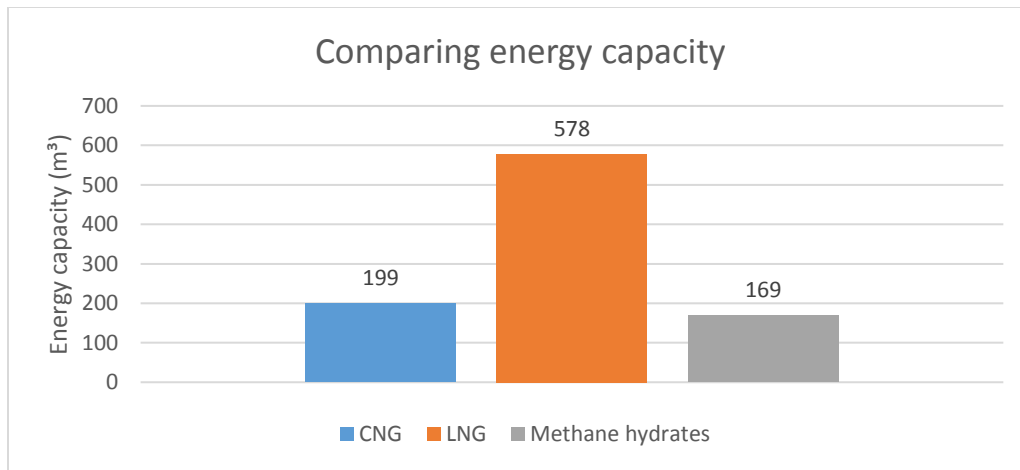


Figure 1: Comparing energy capacity

The gas hydrate can be a great source of energy that begins to be included in the considerations of gas supply for the next decades. It is estimated that 99% of the global gas hydrate supply occurs in marine sediments under the corresponding temperature and pressure conditions, in seabed sediments, at depths from 300 m to 4000 m. The storage of natural gas energy by targeted hydrate formation under controlled conditions can provide long-term energy storage options in a convenient form for safe storage. However, the technology of hydrate formation is also applicable to other gases, the storage of greenhouse gases into stable hydrate structures appears to be advantageous, thereby reducing the amount of emissions discharged into the environment.

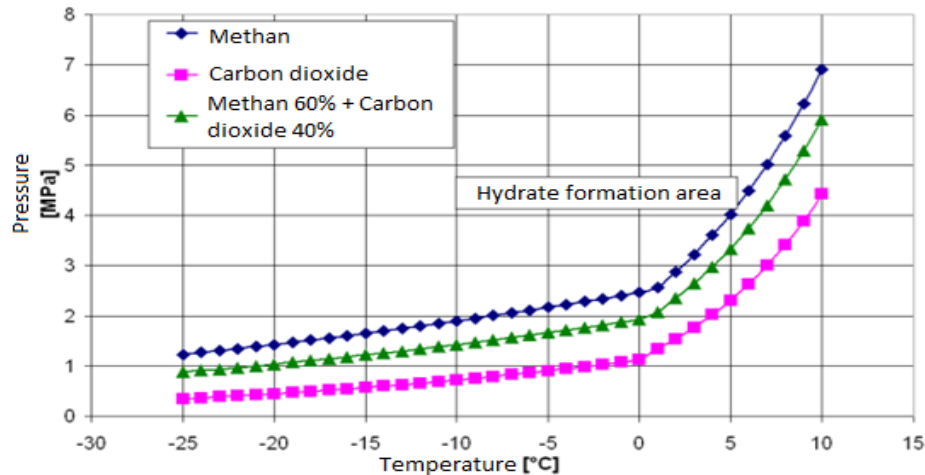
Table 1: Schematic positions on the experimental equipment.

	Energy capacity (m^3)	Specific energy ($MJkg^{-1}$)	Energy density (MJm^{-3})	Energy input ($kJkg^{-1}$)
CNG	198,81	48,95	6913,74	2429,58
LNG	577,77	48,95	20092,67	907,89
Methane hydrates	168,9	6,53	5879,5	416,35

2. Computational Methods

Computational methods of hydrate formation are generally divided into methods based on phase equilibrium of chemical potentials and methods based on three-phase equilibrium liquid water - hydrate - water vapor. The simplest methods include gas density determination. The advantage of this method is its simplicity, including only the graph. FIG. 2 is a plot of pressure versus temperature. The third parameter is the gas density. This can be easily calculated on the basis of the gas composition. The disadvantage of this method is its inaccuracy over experimental results. (Carroll, 1958)

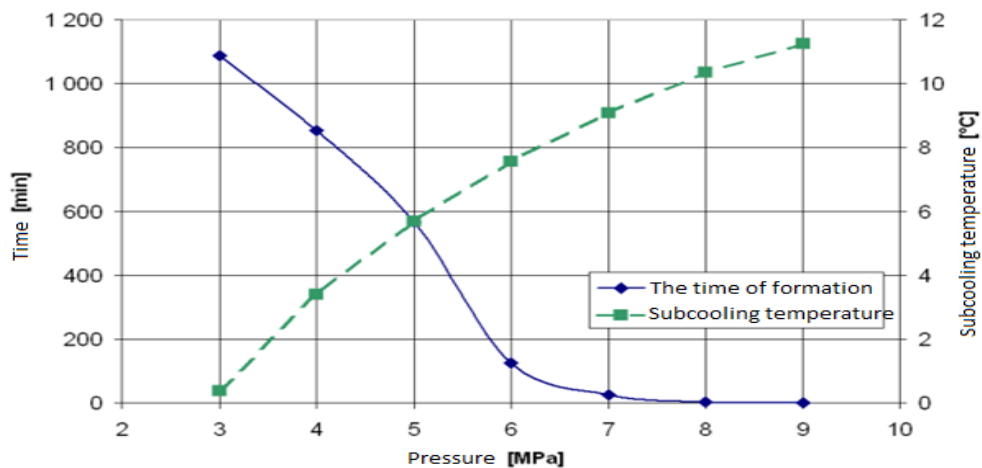
Another method is to establish a balance based on phase diagrams for water, hydrocarbon and CO₂. These diagrams differ considerably from normal hydrocarbon phase diagrams mainly due to the linkage of hydrogen and hydrocarbon bonds.



Graph 2: Diagram of methane hydrate, CO₂ and their blend.

Graph. 2 shows the phase diagram of the individual gases. This method provides acceptable results for pure gases. However, it differs considerably from the fair values for mixtures. From these equilibrium it is clear that the presence of CO₂ in the hydrocarbon gas shifts the balance of hydrate formation to higher temperatures and lower pressures. (Sloan, 2008)

A very important characteristic is also the time required for hydrate formation. The rate of hydrate formation is strongly influenced by temperature and pressure. While the time required to form hydrates at close to equilibrium conditions can be considerably long and can be as high as 24 hours, significant decreases in temperature formation or pressure build-up occur. An important criterion for determining the speed of creation is the so-called. the subcooling temperature (T_{subc}), which is defined as the difference between the actual temperature and the equilibrium temperature of hydrate formation at a given pressure. Knowing the equilibrium temperature, the rate of hydrate formation can then be calculated using empirical equations, depending on the temperature of the undercooling. (Kim, 2009)



Graph 3: Dependence of hydrate on pressure at 1°C (Kim, 2009).

3. Gas Hydrate Production Site Proposal

The device is based on the knowledge of typical mechanisms of methane hydrate formation. Methane hydrate deposits are formed at sites where methane and water are located at temperatures and pressures that are favorable to hydrate formation. These conditions are most commonly found in marine sediments and arctic permafrost. The technique of rapidly and continuously generating gas hydrates in an economically efficient manner would necessarily merit increased attention and the necessary development and innovation of technology in this field. The following section of the article describes the experimental equipment with a projected pressure of 25 MPa, in which the necessary state variables are maintained to determine suitable parameters for the accumulation of gas into the hydrate structures. The experimental equipment was designed based on these temperature and pressure requirements, with temperature in range between 0 ° C to 20 ° C and pressure at approx. 25 MPa. A diagram of an experimental device for generating methane hydrates with individual elements is shown in the following figure.

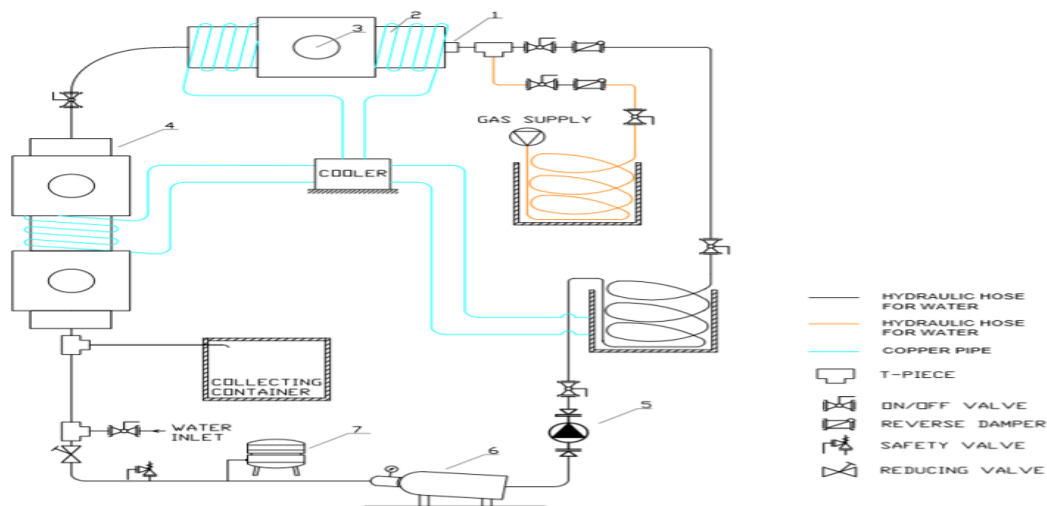


Figure 2: Schematic of experimental equipment

The experiment is carried out by first filling the entire system with water through the water inlet approximately halfway through the sapphire visor of the upper vessel. The plunger pump (5) will draw the water flowing out of the bottom vessel (4), which it will press to 25 MPa. The pipe for this circuit is wound into a spiral and placed in a plastic container. The vessel is connected to a cooling device which provides cooling of the water in the pipe after it has been pressed to a specified pressure. Symbols to the Figure 2 are in next table.

Table 1: Schematic positions on the experimental equipment.

Symbol	Part of the device	Model/type
1	Nozzle	Spray angle 51° and 155°
2	High pressure vessel VN 1	φ175/146,9 mm, m=42kg, 5,7 l
3	Sapphire visor	Normal φ 50 mm
4	High pressure vessel VN 2	Φ175/146,9 mm, m=73kg
5	Plunger pump	P = 4,7 kW, Q = 5,1 l.min-1, n = 1420 ot.min-1
6	Accumulator	Volume 20l, working pressure. 207 bar
7	Expansion tank	Reflex-refix DT 80, working pressure 16 bar,

Water at 25 MPa will flow through the hose, through the non-return valve towards the nozzle (1). On the other hand, the natural gas compressor (in our case a compressor is used, but a bottle of compressed methane can be used instead) will compress the natural gas a gas at a pressure of 25 MPa, which will flow through a conduit which is coiled into a spiral and placed in a vessel which is connected to a cooler. The cooler is intended to cool the gas after it has been pressed to the desired temperature. The compressed gas will pass through the hose, through the non-return valve and the T-piece, where it will mix with the pressurized water and co-enter the nozzle (1). In the nozzle, a compressed mixture of water and natural gas is atomized into small particles, whereby it will be possible to better bond the natural gas to the intermolecular structure of the water and subsequently to form various forms of hydrate. The water / natural gas mixture should initially flow from the vessel through the pipe to the high-pressure vessel after it is filled. After filling the high-pressure vessels with the gas / water mixture to the visible area, which can be seen through the sapphire visors, 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. It will be possible to observe the formation of natural gas hydrates through the said sapphire visors. The pressure is up to 25 MPa in the whole plant.

4. Simplified Numerical Simulation

Simulation of gas hydrate preparation processes in MatLab environment using block library Thermolib gives many various opportunities to create very useful models. There are countless possibilities of setting individual block components as well as the medium itself. The numerical model can be used for many applications. In our work we focused on exploring various options of involvement and use of this numerical method to describe proposed gas hydrate formation system.

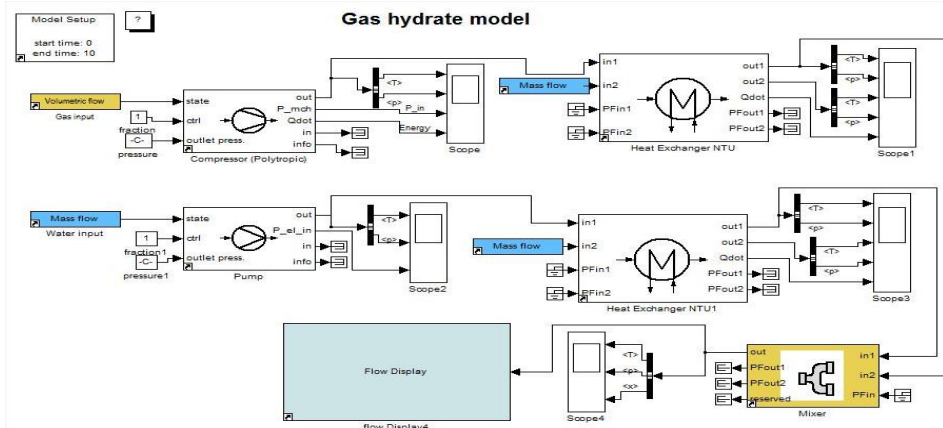


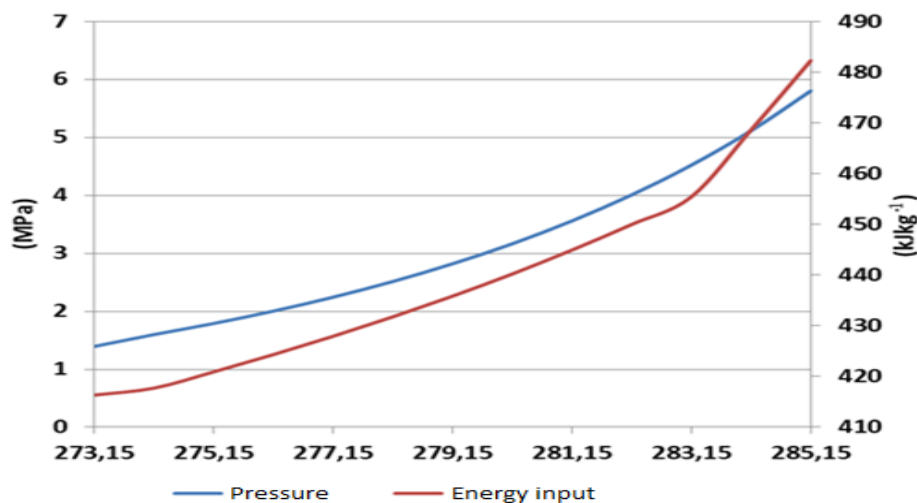
Figure 3: Simplified numerical model

5. Conclusion

The water with the gas will be mixed in the pipeline just prior to the inlet of the first $5,70 \text{ dm}^3$ main pressure vessel (TN1) where it will be in the 1/150 to 1/170 ratio. Water will be sprayed through the nozzle into that pressure vessel. By spraying the liquid onto small particles, we want to facilitate the process of closing 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 greater spray angle will prove as more effective because it can cover a wider area with small water particles.

At low, but still over-temperature and above 6 MPa, we assume the formation of crystalline water grids that form a cage around small gas particles. Gas in this process will significantly reduce its volume.

The resulting methane hydrates should then be directed to another 15 dm^3 (TN2) pressure vessel. Place a micron screen with a 25 μm mesh density in it to collect them through blind flanges on the container will be also a suitable solution.



Graph 4: Pressure needed to produce methane hydrates and energy input

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*Corresponding author.

E-mail address: peter.durcansky@fstroj.uniza.sk