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Energy accumulation system based on gas hydrates

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Abstract

Accumulation of primary energy of natural gas is a perspective option to store natural gas as artificially created hydrate, where this matter can be stored and, if necessary, can be released to cover energy peaks. Gas can be stored this way at partially higher temperatures and low pressures compared to other storage technologies. The technique of rapidly and continuously producing hydrates of gas could compete with the existing means for storing and transporting these energy reserves in more than an economically effi-cient aspect, but again these new technologies need development. Transporting and storage of natural gas is economically and technologically demand-ing, which is always reflected in the resulting price. Natural gas hydrates al-low transport and storage at low pressures and relatively favorable tempera-tures. Presented article deals with design of new energy accumulation system based on gas hydrates. In article is presented the main design and also a nu-merical model, where the parameters of created hydrate are qualified.

Keywords: gas hydrate, energy storage, numerical simulation

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1. Gas hydrate as energy storage

The natural gas energy storage in hydrate structures is advantageous in terms of storage safety, because the hydrate structure enables to store the gas at higher temperatures and lower pressures in comparison to other storage technologies such as liquefaction or compression. The gas hydrate is a huge source of energy that is included in the considerations as gas supply source for the next decades. It is estimated that 99% of the global gas hydrate supply occurs in marine sediments, in seabed sediments, at depths from 300 m to 4000 m. Hydrates can also occur on land, but exclusively in permafrost areas, in frozen areas, with temperatures below 0° C throughout the year. To store energy in a suitable form, transport the hydrate and release the energy, constitutes a current challenge in processes where the need for energy storage is exploited. At the present time, there is a strong pressure on the efficiency of these processes, efficiency of energy use, to increase efficiency and security in this energy storage technology. But the practical use of methane hydrates can be not only in way of storing energy, but also to ensure coverage of gas peak demands in processes, by this gas released from hydrates. [1, 2]

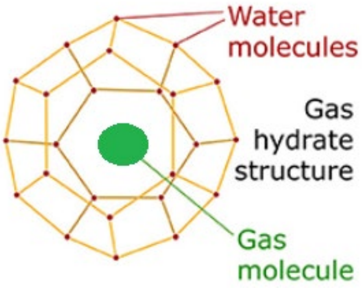

Figure 1. Gas hydrate model [frontiersin.org]

Hydrate is in general a compound containing water and gas molecules bound in water structure. Naturally occurring hydrates are considered to be a huge energy

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source, especially in countries with no access to conventional energy in raw materials or through conventional energy routes. The natural gas hydrate forms a solid form, which constitutes about 85% of the water and the rest is the gas bound in the clathrate. Clathrates are non-stoichiometric compounds without strict chemical composition. The amount of methane molecules captured is depending on the crystalline lattice shape and the pressure at which the hydrate was formed. Gas hydrate can be a major source of energy that has to be included in the balance of natural gas supplies for decades to come. It is estimated that 99% of the global gas hydrate stock is present in marine sediments with specific temperature and pressure conditions, in seabed sediments, at depths ranging from 300 m to 4000 m. Storage of natural gas energy by targeted hydrate formation under controlled conditions can also provide long-term energy storage option in a suitable form as safe storage with low pressure vessels.

The following phenomena have a negative effect on the hydrates formation of in pipelines:

- mixing the substance in the pipeline,
- system geometry and flow mode;
- ideal for hydrates are places where the velocity of the substance is high.

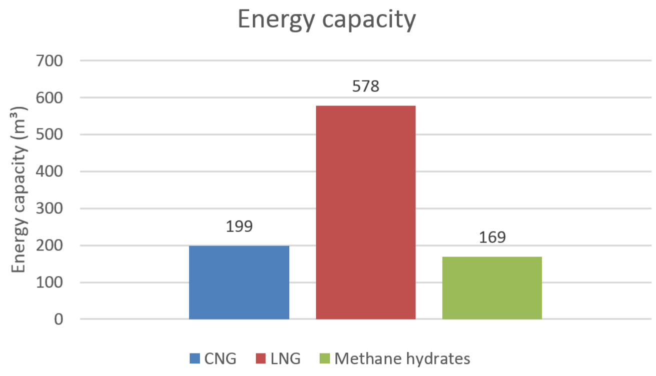

Figure 2. Energy capacity for different storage technologies

The energy capacity of gas hydrate, as shown in Figure n.2, is far lower than the one of LNG. This means, that to store same amount of energy, there is a need to have more volume of gas hydrate. As mentioned before, other parameters have also a significant role. It is the pressure and temperature of formation and storage parameters. To store CNG high pressure tank is needed and the safety measures are very strict. To store LNG, pressure tank is also needed, but the safety measures are not so severe. Methane hydrates allow storage of energy at mild temperatures and pressures near atmospheric. Important is also the overall energy input, as shown in Table n.1, where it is obvious that gas hydrates have the lowest energy input compared to other storage technologies.

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 to reduce the amount of emissions discharged into the environment. Subsequent passage through the valve, for example, attenuates this velocity and usually results in a significant drop in temperature at the site, a suitable place - places where is a higher tendency to phase change from liquid to solid. These are, for example, narrowing caused by dirt deposits, weld imperfections or knees, valves, etc.

However, the hydrate-forming technology is also applicable to other gases, it seems advantageous to store greenhouse gases in stable hydrate structures and thereby reduce the amount of emissions into the environment. Currently, experimental hydrate plants are in operation, particularly in Japan and in the USA.

2. Energy accumulation site

The three basic conditions for hydrate formation include the right combination of temperature and pressure, where hydrate formation is promoted at low temperatures and high pressures. The gases forming hydrates with the water molecules are in particular methane, carbon dioxide. Other hydrate-promoting effects are, for example, turbulence, where hydrate formation is promoted at high flow sites. This can occur at gas throttling points. The increase in gas velocity is caused by flow through the reduced space on the valve. Here is the usual temperature drop due to the Joule-Thomson effect. Gas mixing plays an equally important role where gas hydrates can be formed as a result of gas mixing in the pipeline or during storage. The equipment for storing natural gas energy and greenhouse gas emissions by hydrate formation is specific to the wide range of conditions for hydrate formation. The devices enable the realization of the whole cycle of gas hydrate production. The technology provides hydrate in a form in container suitable for transport and long term storage without additional cooling. The initial step is to create a pressure difference between the suction line of the pump, the hydrate separator and the hydrate reactor, where circulation of the water mixture through the mixture collector into the hydrate separator with the filter element occurs. From there water flows through the hydrate separator filter element to the pump. The desired pressure in the reactor is in the range from 6 to 25 MPa, the injection of natural gas into the water in the reactor takes place for example via the injection nozzle.

Our department developed new method for gas hydrate creation. The schema is shown in next picture. The device was designed according to known parameters of methane hydrate formation process. The experimental device consists of 2 main parts – methane part and water part.

The methane part consists of a gas source, compressor and injection nozzle. The water part consists of pressure reservoir, where the water is stored, pump and cooler. These lines are connected in injection nozzle, where the hydrate in reactor and in hydrate separator is created. Pressure of water and gas can be adjusted, and also the nozzle opening pressure can be set independently. This allows to study the behavior of hydrate forming process and impact of pressure at forming conditions.

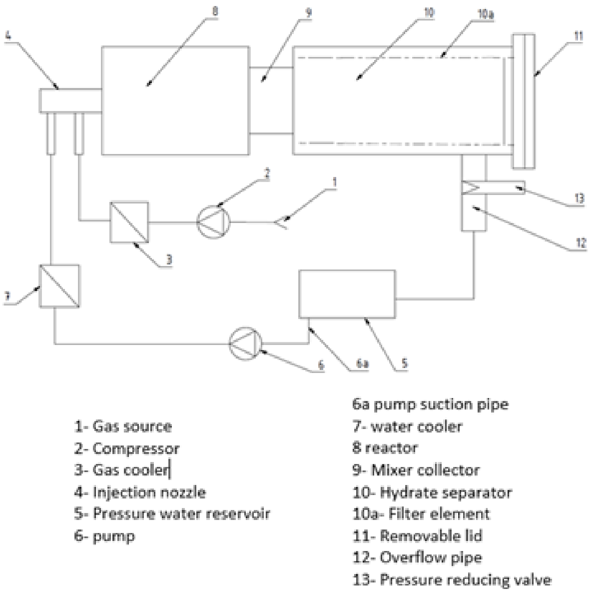

Figure 3. Proposed gas hydrate creation site

The gas is compressed from the gas source, additionally cooled in the cooler and fed to the injection nozzle. Hydrate particles are formed as a result of the high pressure. These are then entrained by the stream of the resulting mixture into the mixture collector and subsequently stream into the hydrate separator with the filter element on which they are trapped under pressure to form clusters of molecules and gradually fill the space of the separator. But there is still the need to cool down the mixture, so a variation of previous experimental equipment was developed. The hydrate particles that pass through the filter cartridge of the hydrate separator in the previous cycle are re-saturated with gas in the reactor, thereby increasing their dimensions and after passing through the mixture collector are retained on the filter cartridge. After filling the hydrate separator, the produced hydrate can be removed through a removable lid.

This hydrate formation process can be described in three phases:

1. - gas molecules are transmitted by diffusion into the liquid and the total Gibbs energy increases due to absorption of the gas enthalpy, the concentration of gas molecules in the liquid layer around the bubble is maximum;

2. the gas molecules are introduced into the stirred liquid, which ensures temperature and concentration of the gas molecules uniform, even if it is lower compared to the surface layer; 3. - diffusion of water gas molecules on the crystal surface and their incorporation into the gas hydrate structure.

To fill the system demineralized water was chosen, as inhibition structure, then starts adding the gas that we want to enclose in the hydrates. Both gas and water are cooled in separate heat exchangers to maintain the required temperatures in the system.

The water and gas are mixed in the duct just prior to supply to the first, main pressure vessel. At the inlet, water is sprayed using a nozzle. By spraying the liquid into small particles, we want to facilitate the process of closing the gas into the water grid.

We expect the formation of gas hydrates in the main pressure vessel. The resulting mixture of hydrates, unconverted water and gas then flows into a second pressure vessel. A fine mesh is placed in it to catch the hydrates. We expect that some of the hydrates can also be trapped in the following, smaller pressure vessel. A water pump is connected downstream of this vessel to circulate the medium. The gas hydrates themselves will be taken from the second pressure vessel by means of blind flanges.

The system also consists of an additional cooling circuit, which connects the two main pressure vessels and provides cooling if necessary. The system is secured by a pair of safety valves, which are located behind both main pressure vessels and in case of unexpected pressure increase the mixture is led to a separate pressure vessel.

3. Computational method

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 the simplicity. Figure 4 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 is the inaccuracy over experimental results for this method. (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. This method provides acceptable results for pure gases. However, it differs considerably from the fair values for mixtures. From this equilibrium it is clear that the presence of CO_2 in the hydrocarbon gas shifts the balance of hydrate formation to higher temperatures and lower pressures. (Sloan, 2008)

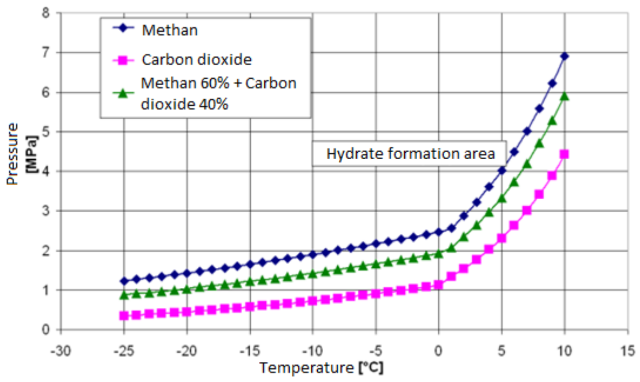

Figure 4. Diagram of methane hydrate, CO_2 and their blend.

Another method is the calculation of the distribution coefficient, also known as the K-factor method. Designed by Carson and Katz, it is based on the distribution of the individual gas components between the hydrate and the gas phase. The ratio is defined as:

$$K_i = \frac{y_i}{s_i}$$

where y_i and s_i are molar fractions in the gas phase and in the solid phase (in the hydrate), respectively.

Furthermore, the hydrate formation point must meet the following condition:

$$\sum_{i=1}^{n} \frac{y_i}{K_i} = 1$$

The value of the distribution coefficient is obtained using the 18-parameter equation, which includes temperature and pressure. They are important data that are necessary because they are characteristic of hydrates are their thermo-physical and thermodynamic properties together with their phase behavior. One of the critical data is the relationship between pressure and temperature as it defines the decomposition behavior of hydrates. The first of the two relations describing the dependence of pressure and temperature across three phases is the Kamath regression equation:

$$P = \exp\left(e_1 + \frac{e_2}{T}\right)$$

where the pressure P is given in KPa and the temperature T in Kelvin, and the coefficients are:

$$e_1 = \{\begin{matrix} 38{,}980 \\ 14{,}717 \end{matrix}, e_2 = \{\begin{matrix} -8533{,}80\ pre\ 0°C > T_c \geq 25°C \\ -1886{,}79\ pre - 25°C\ \geq T_c > 0°C \end{matrix}\ a\ T = T_c + 273{,}15$$

The second relationship is derived from several previous investigations and covers a temperature in wide range from 124 ° C to 48 ° C, which allows it to be used in experiments using N_2 to stabilize the hydrate.

Complications arise in the case of composite hydrates, i.e. hydrates that are composed of a mixture of multiple gases, since it cannot be assumed that the hydrate is a homogenous mixture of individual pure elements as hydrates, which behave separately and would give erroneous results. The solution is to use statistical thermodynamics, which can take into account a scale of hydrates thermophysical properties and its results have been successfully verified in comparison with laboratory experiments. However, statistical thermodynamics is far from being applicable to all the needs of numerical simulations, especially because of the high computing power requirements.

Also important is the relationship between ΔH^0 decomposition and temperature, since heat transfer plays an important role in controlling the decomposition process. It can be calculated as follows:

$$\Delta H^0 = C_1 + C_2 T$$

where ΔH^0 is given in cal / gmol and the temperature T in Kelvin,

$$C_i = \{\begin{matrix} 13{,}521 \\ 6{,}534 \end{matrix}, a\ C_2 = \{\begin{matrix} -4{,}02\ pre\ 0°C > T_c \geq 25°C \\ -11{,}95\ pre - 25°C \geq T_c > 0°C \end{matrix}$$

As we can see, ΔH^0 can be accessed as function of temperature. Some advanced studies have indicated that it is not temperature sensitive for a wide range of ΔH^0 temperatures.

Another important aspect is the kinetics of the hydration or decomposition equation. The following equation describes the reaction kinetics of methane hydrate:

$$Q_H = -K_0 \exp\left(\frac{\Delta E_a}{RT}\right) F_A A (f_{eq} - f_v)$$

where K_0 is the internal hydration constant [kg m^{-2} Pa^{-1} s^{-1}], ΔE_a represents the activation energy of hydration [J mol $^{-1}$], R is the universal gas constant [8.314 Jmol $^{-1}$K^{-1}], F_A is a factor the area of the surface involved in the reaction [m2], feq is the volatility in equilibrium at pressure T (Pa), and f_v is the gas phase volatility at specified temperature in (Pa). Kinetics only plays an important role in determining the decomposition processes in the short term (at intervals of a few minutes to several hours). In the long term, it is not considered in connection with gas production schemes.

A very important characteristic is also the time required for hydrate formation. This 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 (Tsubc), which expresses 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)

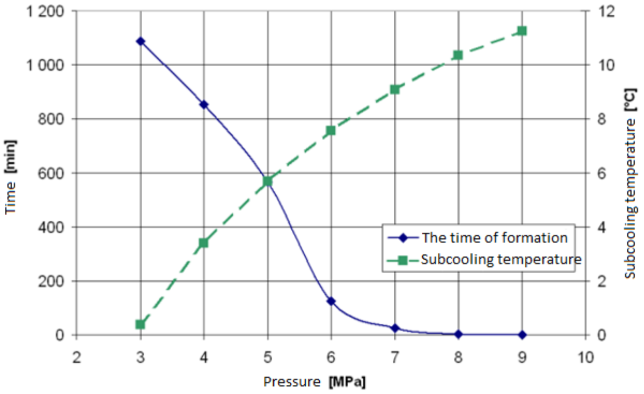

Figure 5. Dependence of hydrate formation time on pressure at 1°C (Kim, 2009).

3. Experimental method

The equipment was built as part of research activities. Main variable, pressure was projected with maximal value of 25 MPa, where the necessary state variables are expressed to create affordable parameters for the gas accumulation via hydrate structure. The equipment was proposed as based on several temperature and pressure variants, with temperatures in range between 0 ° C to 20 ° C with pressure varying up to approx. 20 MPa. Proposed experimental device is shown in following figure.

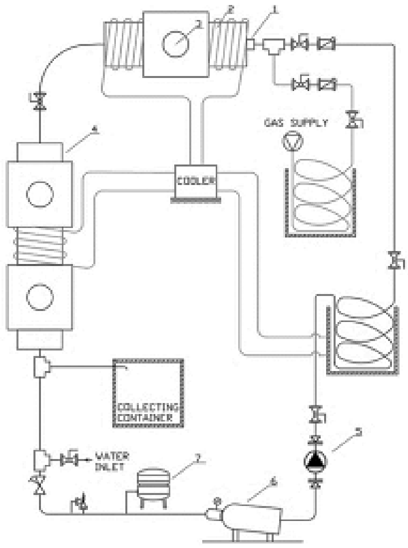

Figure 6. Schematic of experimental equipment

3. Results

The water with the gas will be mixed in the pipeline just prior to the inlet of the first 5,70 dm^3main 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. The next picture shows the temperature characteristics measured during the test.

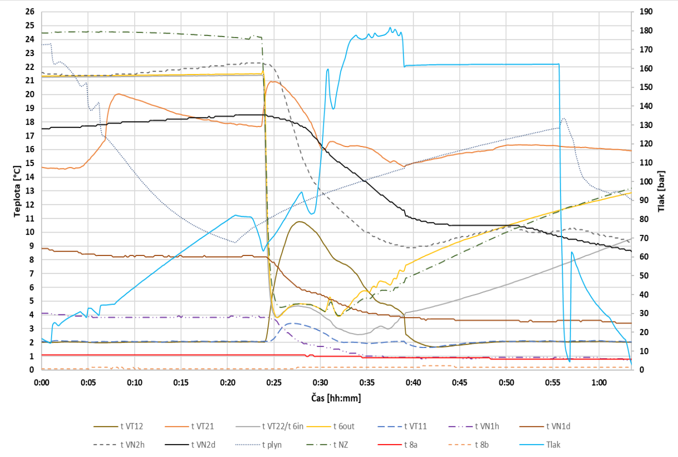

Figure 7. Measured temperature parameters

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°. While the time required to generate the necessary amount of hydrates could be reduced by significantly increasing production capacity (larger vessels, multiple production facilities operating simultaneously), the economic side requires a solution at the design level of the system itself. It would have to work much more efficiently, with more hydrate production and lower operating costs.

The potential use of hydrate formation in practice would also require connection to downstream processes such as storage and transport. For example, there is an additional automatic hydrate collection system.

The search for further, more economical solutions for the accumulation of hydrates should therefore be the subject of further research. In addition to artificial production, it is also necessary to further explore the possibilities of using natural deposits of methane hydrates, which according to available information represent a potentially beneficial source of green energy for the future.

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