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Calculation of the Eroei Coefficient for Natural Gas Hydrates in Laboratory Conditions

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Abstract. In the 1960s, scientists discovered that methane hydrate existed in the gas field in Siberia. Gas hydrates are known to be stable under conditions of high pressure and low temperature that have been recognized in polar regions and in the uppermost part of deep-water sediments below the sea floor. The article deals with the determination of the EROEI coefficient to generate the natural gas hydrate in the device under specific temperature and pressure conditions. Energy returned on energy invested expresses ratio of the amount of usable energy delivered from a particular energy resource to the amount of exergy used to obtain that energy resource. Gas hydrates have been also discussed before decades like potential source mainly for regions with restricted access to conventional hydrocarbons also tactic interest in establishing alternative gas reserves.

INTRODUCTION

The large amount of hydrate methane that is isolated in shallow terrestrial and marine sediments make this methane an attractive target for those concerned about future energy requirements and resources. The fact is that natural gas hydrate is metastable and affected by changes in pressure and temperature. Any released methane makes an attractive opportunity that could affect global climate include oceanic, atmospheric chemistry. Natural gas-hydrate occurrence have a potential effects on future human welfare, if will be used as a potential energy resource useful and explain the increasing worldwide interest about it [1].

Hydrates created crystalline solid compounds formed from water and small molecules - they are a subset of compounds known as clathrates or inclusion compounds. A compound of clathrate is one where a molecule of one substance is enclosed in a structure built up from molecules of another substance. Here, water builds up the structure and the other molecule resides within. The size of the other molecule must be such that it can fit within the water structures [2]. The article introduces natural gas hydrates and calculation of coefficient eroei for creation of natural gas hydrates in laboratory condition in experimental facility also provides a background for understanding its occurrence and describes the hydrate gas compositions.

NATURAL GAS AND NATURAL GAS HYDRATES

Natural gas is a naturally occurring hydrocarbon gas mixture from physical point of view consisting primarily of methane. Methane is it the principal combustible component of natural gas. In natural gas are commonly include different amounts of other higher alkanes and small percentage of nitrogen, hydrogen sulfide, helium whether carbon dioxide, see tab. 1. Depending on its quality, natural gas contains 75 to 99 per cent methane. At a normal atmospheric pressure at the Earth’s surface and room temperature methane exists like a gas [3].

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TABLE 1. Typical Natural Gas Composition

Components	Chemical composition	Range (mole %)
Methane	CH_4	70-90
Ethane	C_2H_6	0-20
Propane	C_3H_8	0-20
Butane	C_4H_{10}	0-20
Carbon dioxide	CO_2	0-8
Oxygen	O_2	0-0.2
Nitrogen	N2	0-5
Hydrogen sulphide	H2S	0-5
Rare gases	A, He, Ne, Xe	trace

Gas hydrates are also called gas clathrates ice - as crystalline solids compounds that occur when water forms a cage-like structure around smaller guest molecules. Gas hydrates can be one of the important energy sources for natural gas hydrocarbon industry in future. Flammable sample of methane hydrate is shown at Fig. 1. For formation hydrates are necessary presence of water and methane and suitable combination of pressure and temperature. Hydrate formation is possible in any place where water exists with such molecules-in natural or artificial environments and at temperatures above and below 0 °C when the pressure is elevated. A typical negative phenomenon of hydrates is the blockage of natural gas in gas pipelines. It often arise at gas-shutoff sites, valves, so on. One of the way how to protect before creation of hydrate in pipelines is regulation of pipeline water content or large amount quantities of methanol injection into pipelines. In the permafrost and deep oceans an exist large natural reserves of hydrocarbons. According to conservative estimates is evaluation of these reserves is highly uncertain but also indicate that there is perhaps twice as much energy in hydrated form as in all other hydrocarbon sources combined [3].

FIGURE 1. Flammable of methane hydrate

Result of the hydrogen bond is that water can form hydrates. The fact that the water molecules to align in regular orientations causes hydrogen bond. The presence of certain compounds causes the aligned molecules to stabilize, and a solid mixture precipitates. The water molecules are referred to as the host molecules, and the other compounds, which stabilize the crystal, are called the guest molecules [4].

Requires for hydrate formation are following: right combination of pressure and temperature. Low temperature and high pressure is suitable for hydrate formation. The exact temperature and pressure depends on the composition of the gas; however, hydrates form at temperatures greater than 0 °C the freezing point of water. For example for methane hydrate forming conditions at temperature 30 °C pressure is 859 bar which is probably a limit to that encountered in normal petroleum operations. Second one is a hydrate former. Hydrate formers include methane, ethane, and carbon dioxide. Also sufficient amount of water that mean not too little, not too much. Hydrates are classified by the arrangement of the water molecules in the crystal, and hence the crystal structure. Structures are type

I and type II, type H as you can see at Fig.2. Hydrates are solid containers similar to ice, whose crystal structure is composed of polyhedron cavities consisting of water molecules connected by hydrogen bonds. For example, $5^{12}6^{2}$ means 14 cavities with 12 pentagons and 2 hexagons. The following cavity types have so far been recognized: 5^{12}, $5^{12}6^{2}$, $5^{12}6^{4}$, $5^{12}6^{8}$, and $4^{3}5^{6}6^{3}$. At Fig. 2 type I consist of 46 water molecules and is a combination of 6 polyhedrons ($5^{12}6^{2}$) containing 14 facets with 2 polyhedrons (5^{12}) containing 12 facets, type II in Fig. 2 is composed of 136 water molecules and is a combination of 16 polyhedrons (5^{12}) containing 12 facets with 8 polyhedrons ($5^{12}6^{4}$) containing 16 facets, and type H is formed by 34 water molecules see Fig. 2 is a combination of 3 polyhedrons (5^{12}) containing 12 facets with 2 polyhedrons ($4^{3}5^{6}6^{3}$) containing 16 facets and 1 polyhedron ($5^{12}6^{8}$) containing 20 facets [4,5].

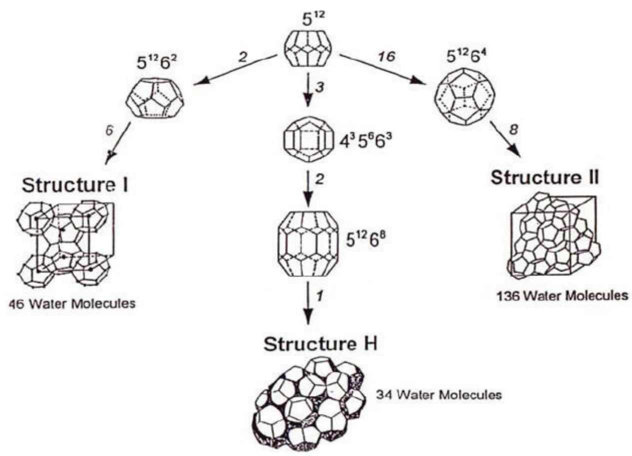

FIGURE 2. Different gas hydrate structures

EXPERIMENTAL DEVICE

Accumulation energy into natural gas hydrates it seems as suitable way how to use energy and then release it where it is needed. We proposed an experimental device, for natural gas hydrate production where we are trying to find out theoretical energy consumption by coefficient EROEI. Experimental equipment is currently under development. One cubic meter of hydrate can contain about 150-170 cubic meter of methane under standard condition. Experimental device is designed for pressure under 250 bar. Temperature in device will be set within the range 0-20 °C. Experimental device is shown at Fig. 3.

Description of individual parts: 1 nozzle, 2 high pressure vessel, 3 flange on the container, 4 sapphire sight glass, 5 high pressure vessel, 6 plunger pump, 7 methane cylinder, 8 container refrigeration, 9 container discharge, 10 pressure accumulator, 11 circulation thermostat with pump, 12 pressure gauge pointer, 13 electronic manometer, 14 hose for natural gas, 15 hose, 16 seamless tube, 17 seamless tube, 18 gas detector, 19 check valve, 20 safety valve 250bar, 21 drain valve, 22 reduction valve (from 250bar to atmospheric pressure).

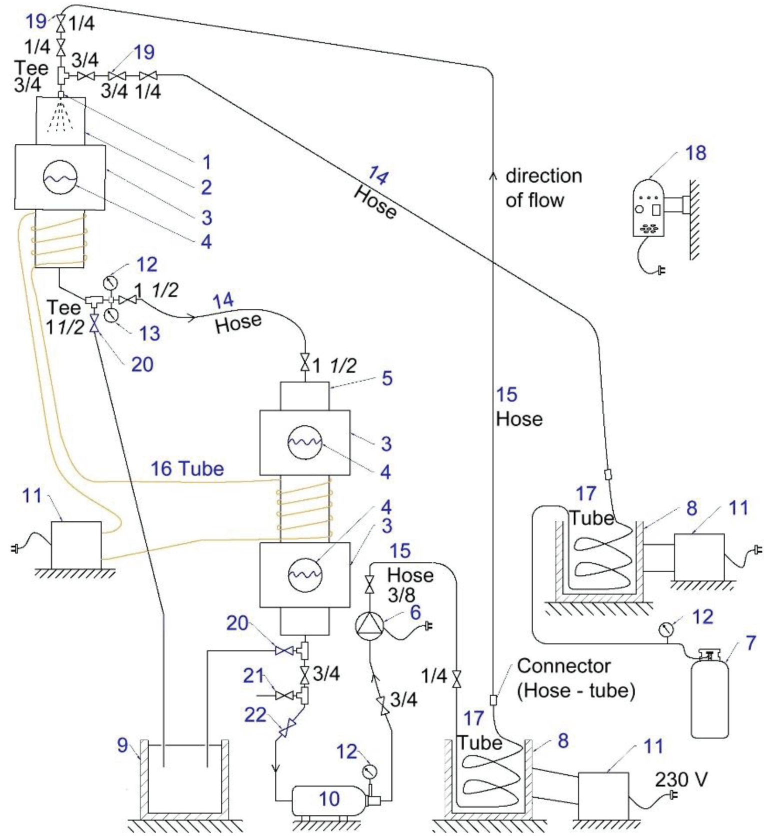

FIGURE 3. Experimental device

We assume that measuring will start at a pressure of 60 bar. Pump 6 will ensure pressure 60 bar of demineralized water and circulation passing through stainless steel tube 19. Circulation thermostats with pump 11 ensure cooling as gas part as water part of system. The compressed gas is mixed with the compressed water and together they enter the nozzle 1. The nozzle is designed to atomize the mixture of water and compressed gas into small particles, which will make possible a better binding to the natural gas-hydrate form of molecular bonds. Nucleation of hydrates will be observed through the sapphire sight glasses 4. After formation hydrates, it may takes several hours an entire device will be depressurized and hydrates remove through the flange or pressure accumulator 10 for further investigate under the microscope. In laboratory room is equipped with gas detector in terms of safety.

CALCULATION OF EROEI

Coefficient EROEI is simply the ratio of energy gathered to the amount of energy used to gather the energy (the energy invested). Sometimes is also listed as energy return on investment EROI. Energy consumption can be generally expressed by the eq. 1.

$$EROEI = \frac{\text{Energy used}}{\text{Energy invested}} \tag{1}$$

If the ratio is equal to or less than 1, source of energy becomes as energy sink and may not be already used as the primary power source. By Ruth (2015) EROI of natural gas has been decreasing since 1993 through 2006, from roughly 38:1 to 14:1 [6].

All calculation is proposed as framework with limited data. In this case energy inputs are relating to primary energy. The following equations are needed to estimate energy intensity of creation of methane hydrate. The following are mentioned nomenclature and method of calculation. Volume flow of methane was established at $\dot{Q}_M = 1.39 \times 10^{-3}\ m^3.s^{-1}$, volume flow water was established $\dot{Q}_W = 8.33 \times 10^{-6}\ m^3.s^{-1}$, operating water pressure $\Delta p_W = 6 \times 10^6$ Pa, pump efficiency $\eta_{Pl} = 0.6$, primary energy factor $f_e = 2.57$. Physical input power consumption of pump N_P [W] is calculated by using eq. (2) and substituting into eq. (3) is calculated primary energy of pump E_{PL} [W].

$$N_P = \frac{\Delta p_W . \dot{Q}_W}{\eta_{Pl}} \quad (2)$$

$$E_{PL} = N_P . f_e \quad (3)$$

It is also known inlet pressure $p_1 = 1 \times 10^5$ Pa, outlet pressure $p_2 = 6 \times 10^6$ Pa, polytropic exponent $n = 1.2$, compressor efficiency $\eta_C = 0.6$. Estimated compression power required to compress of methane to the cylinder according real compressor A_{TC} [W] is given by eq. (4) and substituting into the eq. (5) is obtain input power consumption of compressor P_C [W]. Primary energy of compression of methane E_{PCM} [W] is given by eq. (6).

$$A_{TC} = \frac{n}{n-1} . p_1 . \dot{V}_1 . \left[\left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right] \quad (4)$$

$$P_C = \frac{A_{TC}}{\eta_C} \quad (5)$$

$$E_{PCM} = P_C . f_e \quad (6)$$

Another well-known quantities are density of methane $\rho_M = 0.72$ kg.m^{-3}, demineralized water density $\rho_{DW} = 999.7$ kg.m^{-3} at 10 °C, specific heat capacity of methane $c_M = 1609$ J.m^{-3}.K^{-1}, specific heat capacity of water $c_{DW} = 4187$ J. kg^{-1}.K^{-1}, cooling factor $f_R = 3.5$, temperature difference $\Delta t = 30$ °C, it includes the ambient temperature 10 °C. Energy for cooling the methane $\dot{E}_M$ [W] is given by the eq. (7), input power consumption cooling of methane P_{ME} [W] is given by eq. (8). Energy for cooling the water $\dot{E}_W$ [W] is shown by eq. (9) and input power consumption of cooling water P_{DW} [W] is calculated by eq. (10).

$$\dot{E}_M = \rho_M . \dot{Q}_M . c_M . \Delta t \quad (7)$$

$$P_{ME} = \frac{\dot{Q}_M}{f_R} . f_e \quad (8)$$

$$\dot{E}_W = \rho_{DW} . \dot{Q}_W . c_{DW} . \Delta t \quad (9)$$

$$P_{DW} = \frac{\dot{Q}_W}{f_R} . f_e \quad (10)$$

Calorific value of natural gas is $Q_{CV} = 34 \times 10^6$ J.m^{-3}, primary usable energy E_{PU} [W] is given by eq. (11). Equations (3), (6), (8), (10), (11) were put into adjusted equation for calculating EROEI (12) under our case for methane hydrate formation.

$$E_{PU} = Q_{CV} . \dot{Q}_M \quad (11)$$

$$EROEI = \frac{E_{\mathrm{PU}}}{E_{\mathrm{PL}} + E_{PCM} + P_{ME} + P_{DW}} \quad (12)$$

CONCLUSION

After calculating all the values, in the above equations, value of the coefficient given by equation 12 is 10.4. The production of hydrate with this value of coefficient is generally good for example, by study [7] which says about fuel sources and regions oil and gas production for Canada EROEI value of 15 in year 2010 or [8] for crude oil where range of eroei depends also on the depth of the well and on whether the well is on- or offshore. In beginning of the years 21st century a range of 3-10 is often expressed. Calculation is framework, were used limited data and energy used is related to primary energy. In the next part of research we want to compare the theoretical coefficient of eroei and real energy consumption in the operation of experimental equipment.

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