Investigation of the Natural Gas Components Redistribution in the “Gas-Hydrate” System

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Abstract. The paper studies the degree of C2-C4 components redistribution in hydrates during their formation in water and mineralized solutions of hydrocarbonate and chloride types. It was found that in brines of the chloride type, in comparison with hydrocarbonate waters, there is a noticeable concentration of propane and isobutane. Such selective enrichment of hydrate gas with methane homologues leads to increasing in their fat coefficient and calorific value. Compared with the original natural gas, the fat coefficient of gases in hydrates obtained in hydrocarbonate waters increase by 3.0-3.2 times, the combustion heat of gases - by 17.2-18.0%. In brines of the chloride type, the fat coefficient of gases in hydrates in comparison with that one of the natural gas increase by 4.4-4.9 times, and the combustion heat - by 26.2-30.5%. Experimental studies have shown the possibility of using surface and ground waters in the industrial production of hydrates. The use of natural waters in the technological process of hydrates obtaining in special installations makes it possible to exclude the stage of water treatment, which can significantly reduce the cost of the hydrates production. And the selective fractionation of C2-C4 hydrocarbons leads to an increase in the energy value of the "hydrate" fuel.

1. Introduction

For the first time, a change in the composition of natural gas during the formation of hydrates was discovered by Hammerschmidt [1]. He suggested that an increase in the proportion of propane and isobutane in the hydrate can be caused by their adsorption by hydrate crystals. Wilcox, Carson, and Katz, while studying the equilibrium conditions of the hydrates formation of three natural gases of different composition, also found a change in the hydrate composition with pressure increasing [2]. Therefore, mixed hydrates were considered as solid solutions in equilibrium with the gas (liquid) phase containing the same components [3-6]. When mixed hydrates melt, their composition changes [7]; therefore, using the process of the hydrate formation, gas or liquid mixtures can be separated. Later, Barrer and Stuart formulated the theoretical foundations for the separation of gas mixtures by studying the hydrate formation of binary mixtures [8]. Selective concentration of individual components of a gas mixture in hydrates is used to separate gas mixtures in order to concentrate the most valuable component or purify them from unwanted impurities [9-10]. The processes of the water desalination using the hydrate formation process have been considered since the second half of the 20th century. However, the effectiveness of this technology is associated with the problem of the brine complete separation from the hydrate and low rate of the hydrate formation [11, 12]. In recent years, investigations of hydrate-gas phase equilibrium in multicomponent gas mixtures [13-21] have been carried out.
The authors of the present work are interested in concentrating of methane homologues during the hydrate formation from the point of view of obtaining a "hydrate fuel" with a higher calorific value compared to the original natural gas. In Russia, the combustion heat of 1 kg (mass) or 1 liter (volume) of fuel is taken as a unit of equivalent fuel (standard fuel), which for solid and liquid fuels is 29.3 MJ/kg, and for gaseous fuels - 29.3 MJ/m³ [22]. The International Energy Agency (IEA) has adopted a unit of the oil equivalent, usually denoted TOE (ton of oil equivalent). One ton of oil equivalent 1 TOE represents the energy obtained from the combustion of one ton of oil, equal to 41.868 GJ. This unit is considered the equivalent of approximately 7.4 barrels of oil, either 1.4 tons of coal or 1,270 cubic meters of natural gas. The calorific value of a gas depends on its chemical composition, which is characterized by the fat coefficient (the ratio of the sum of methane homologues to the methane content). According to the fat coefficient (Vysotsky's classification), dry (0.3-8%), semi-fat (8-20%), fatty (20-30%) and high-fat gases (> 30%) are distinguished [23]. In [24, 25], an increase in the content of C2-C4 hydrocarbons in hydrates was shown during their formation from natural gas in water and saline solutions, which leads to an increase in the calorific value of the gas. The aim of the work is to study the redistribution of natural gas components in the process of the hydrate formation in different liquid phases and to assess the calorific value of the obtained hydrates.

2. Experimental

In the process of the hydrate formation, water, sodium bicarbonate solutions with concentrations of 2.5 (1) and 19.6 (2) g / l were used as liquid media; sodium chloride with concentrations of 51.48 (3) and 168.48 (4) g / l, which corresponds to the salinity of surface and ground waters. The composition of natural gas from the Otradninskoye gas condensate field, the hydrates of which were obtained and studied, is the following (mol %): CH₄ - 85.4; C₂H₆ - 4.24; C₃H₈ - 1.24; i-C₄H₁₀ - 0.13; n-C₅H₁₀ - 0.37; n-C₆H₁₂ - 0.09; i-C₆H₁₂ - 0.11; n-C₆H₁₄ - 0.07; non-hydrocarbon components - 8.31. The gas fat coefficient is 7.0%. Methods for the formation and decomposition of natural gas hydrates are described in detail in [24, 26]. The component compositions of the original natural gas and gases obtained by the decomposition of hydrates were analyzed by gas-adsorption chromatography according to GOST 31371.7-2008 [27]. The combustion heats of gases are calculated respectively to their component composition in accordance with GOST 31369-2008 [28].

Tables 1 and 2 show the component compositions of gases in hydrates obtained in water and solutions (1), (2), (3) and (4). The redistribution degree B is calculated as the ratio of the concentration of the i-th component of the gas in the hydrate to its concentration in natural gas: \[ B = \frac{C_i(\text{in hydrate})}{C_i(\text{in natural gas})} \]. The compositions of gases and the degree of their redistribution are given only for C1-C4 hydrocarbons, since pentanes and hexane do not participate in the hydrate formation. N-butane does not form individual hydrates, but is capable of being included in the composition of mixed hydrates. In fresh, brackish and salty waters of the bicarbonate type, during the hydrate formation, the concentration of C2-C4 hydrocarbons occurs; the redistribution degree of natural gas components is practically not affected by water salinity (Table 1). With an increase of the sodium bicarbonate concentration in the solution, the content of propane and i-butane, ethane and n-butane increases - it decreases at a constant value of the methane concentration.

In brines of the chloride type, in comparison with bicarbonate waters, there is a noticeable concentration of propane and isobutane (table 2). When the concentration of sodium chloride increases by 2 times, the content of hydrocarbons C3 and C4 increases by 1.47 and 1.54 times, respectively. From the data in Tables 1 and 2, it follows that the concentration of hydrocarbons in hydrates occurs in accordance with an increase in the dissociation pressure Pdiss of simple hydrates formed by individual components of natural gas [7, 17].
The concentration of methane homologues in hydrates naturally leads to an increase in the fat coefficient and the combustion heat of gases (figure 1). For practical purposes, when determining the quality indicators of fuel, as well as in thermal engineering calculations, the lowest combustion heat is usually used, which is the most important thermal and operational characteristic of the fuel. Therefore, in the present work, we further consider only the lowest combustion heat of gases contained in hydrates.

The fat coefficients of gases in hydrates obtained in fresh, brackish, and salt water of the carbonate type exceed the calorific value of a unit of equivalent fuel by 32.5 TOE of heat. The amount of energy in hydrates obtained in chloride waters is equal to 1 TOE by 26.2-30.5%.

Comparison of the inferior calorific value of gases in hydrates with a unit of equivalent fuel shows that natural gas and hydrates as a fuel have a higher calorific value. Gases in hydrates obtained in water and waters of bicarbonate type exceed the calorific value of a unit of equivalent fuel by 32.5-33.4%, and in chloride waters - by 42.7-47.5%. The inferior calorific value of the natural gas from the Otradinskoye gas condensate field is almost equivalent to 1 TOE. The hydrates obtained in water and waters of the bicarbonate type contain 1.18-1.19 TOE of heat. The amount of energy in hydrates obtained in chloride waters is equal to 1.27-1.31 TOE.

Experimental studies have shown the possibility of using surface and ground waters in the industrial production of hydrates. Obtaining of hydrates in different mineralized solutions leads to an increase in the fat coefficient and calorific value of the original natural gas. The use of natural waters in the technological process of hydrates obtaining in special installations makes it possible to exclude the stage of water preparation, including desalination, clarification, sedimentation of solids, and softening.

### Table 1. Component content of gases in hydrates and the redistribution degree of C1-C4 hydrocarbons depending on the bicarbonate type water salinity.

| Component  |   |   |   | water |   |   |   | water | 1 | 2 |
|------------|---|---|---|-------|---|---|---|-------|---|---|
|            | Content, % mol. | B   |   |       |   |   |   |       |   |   |
| methane    | 79.05 | 79.03 | 79.44 | 0.93 | 0.93 | 0.93 |   |   |   |   |
| ethane     | 11.55 | 11.06 | 10.10 | 2.72 | 2.61 | 2.38 |   |   |   |   |
| propane    | 4.57  | 5.10  | 5.38  | 3.69 | 4.11 | 4.34 |   |   |   |   |
| i-butane   | 0.454 | 0.452 | 0.524 | 3.54 | 3.53 | 4.09 |   |   |   |   |
| n-butane   | 0.985 | 0.998 | 0.869 | 2.66 | 2.69 | 2.34 |   |   |   |   |

### Table 2. Component content of gases in hydrates and the redistribution degree of C1-C4 hydrocarbons depending on the chloride type water salinity.

| Component  |   |   |   |   | water |   |   |   |   |
|------------|---|---|---|---|-------|---|---|---|---|
|            | Content, % mol. | B   |   |   |       |   |   |   |   |
| methane    | 74.51 | 72.10 | 0.87 | 0.84 |   |   |   |   |   |
| ethane     | 12.82 | 10.14 | 3.02 | 2.39 |   |   |   |   |   |
| propane    | 8.33  | 12.22 | 6.72 | 9.85 |   |   |   |   |   |
| i-butane   | 0.855 | 1.322 | 6.68 | 10.32 |   |   |   |   |   |
| n-butane   | 0.926 | 0.872 | 2.50 | 2.35 |   |   |   |   |   |
Figure 1. Fat coefficients of natural gas, gases in hydrates and their inferior calorific value in comparison with unit of the equivalent fuel.

Concentration of the C2–C4 components in hydrates can partially replace the methods of separating these valuable components from natural gas, such as: compression, oil adsorption, low-temperature condensation and rectification. Gas enriched with methane homologues is a valuable raw material for the petrochemical industry, and a hydrate is a higher energy fuel compared to natural gas. However, in order to make a final decision on the use of natural waters in the hydrates production, it is necessary to investigate the kinetics of their decomposition in mineralized solutions, since this issue has not yet been fully studied.

3. References

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