MECHANOCHEMICAL SYNTHESIS OF HYDROCARBONS WITH COMPLICATED STRUCTURE FROM LIGHT COMPONENTS OF NATURAL GAS CONVERTED INTO HYDRATE

Elena Shitz*, Liudmila Kalacheva, Aytalina Fedorova, Vladilina Koryakina, Edward Bondarev
Laboratory of Technogenic Gas Hydrates, Institute of Oil and Gas Problems
Syberian Branch of Russian Academy of Sciences
Yakutsk, Sakha Republic
RUSSIA

ABSTRACT
Experimental studies of the patterns of chemical conversions of lower alkanes during mechanical activation of natural gas hydrates were conducted. It is confirmed that in the gas phase alkanes concentration decreases, significant amounts of hydrogen and C5-hydrocarbons are generated which not involved in the formation of hydrates. The liquid phase contains new hydrocarbons: C6-C7 cyclic and normal alkanes, C10 arenes. Investigations of the solid phase showed the absence of carbon and iron carbide. Consequently, lower alkanes, and what is more important - methane, without undergoing degradation to carbon and hydrogen, are involved in chemical transformations by mechanical influence on gas hydrates.

Keywords: gas hydrates, mechanical activation (MA), mechanochemical synthesis.

NOMENCLATURE
H - Hyperfine magnetic field strength [kOe]

INTRODUCTION
Low molecular weight hydrocarbons are widely available and cheap raw materials to produce motor fuels and chemical products. The major sources of lower paraffins are natural and associated petroleum gas. Natural gas, despite its vast resources as a raw material, is used in only a few processes that associated with the problem of involvement of methane in the chemical transformations [1, 2]. One way to initiate the chemical reactions of gaseous hydrocarbons is considered the mechanical activation (MA), when reaction system is subjected to intensive mechanical stress [3, 4]. Mechanical effect on the substance can cause its different chemical reactions initiated by the formation of active radicals on the surface, a significant increase of local temperatures in the shock processing of solid bodies with each other and on the reactor walls [5, 6].

Studies conducted in recent years on the effects of mechanical treatment of natural gas, light oil fractions and individual hydrocarbons in the power density devices such as ball mills, have shown that mechanical activation of hydrocarbons leads mainly to their destruction to a low molecular weight homologues, carbon and hydrogen [7, 8]. Studies on the mechanical activation system of "natural gas-water" were also carried out which showed that similar processes occur that the processing of natural gas [3]. Therefore, in terms of studying the laws of chemical transformations of alkanes, it was interesting to conduct research on mechanical activation of natural gas hydrates – clathrates – which crystal lattice is composed of hydrogen-bonded water molecules and gas
molecules trapped into cavities of the crystal lattice.

**EXPERIMENTAL**

**Natural gas hydrate synthesis**

Hydrate samples (pic.1) were obtained in the high-pressure cell for 20 days at a temperature of 278K and a pressure of 2.0 MPa from distilled water and natural gas of Irelyakh gas-oil field (Republic of Sakha (Yakutia), Russia).

Gas emitted during the decomposition of the synthesized hydrates was collected to determine its composition.

**Mechanochemical activation**

Mechanochemical activation of natural gas hydrates was carried out for 60 seconds and 300 seconds in an AGO-2C planetary ball mill. The steel balls were used (ShKh-15) as grinding media with 8 mm in diameter, vials are made of steel (40 × 13 grade). During operation the vials were cooled by running water. Acceleration factor of grinding media was 65 g. Hydrate mass was 40 g; the mass ratio of hydrate to balls was 1:4. Loading of hydrates samples into the vials was carried out at room temperature.

**Products analysis**

Mechanoactivation of natural gas hydrates leads to formation of three phases - gas, liquid and solid. Liquid products were analyzed by chromato-mass-spectrometry on the system equipped with Agilent 6890 gas chromatograph with Agilent 5973N high-efficiency mass-selective detector (Agilent Tech., Inc.). We used a quartz capillary column with dimensions of 30 m × 0.25 mm impregnated with HP-5MS; carrier gas – helium – flow rate of 1 ml / min; determination of hydrogen and helium was carried out using a stainless steel column of 3 m × 3 mm, filler - zeolite CaA, carrier gas – argon – flow rate of 30 ml / min, detector temperature of 190°C, temperature rate of 10°C/min. Solid products of mechanical activation hydrates were studied by YAGRS-4M Mössbauer spectroscopy working in constant acceleration mode with a source of 57Co γ-radiation in Cr matrix. Measurements were performed at room temperature. Restoration of the distribution functions of hyperfine magnetic fields P(H) of the spectra was performed using a generalized regular algorithm for solving ill-posed problems [9].

Auger spectra were obtained on JAMP-10S spectrometer at an accelerating voltage of 10 kV and current of 7.10 A, electron probe diameter of 300 nm. Vacuum in the chamber of the spectrometer is 7.10 Pa. Etching of the samples was carried out by Ar ions with an energy of 3 kV, the etching rate of ~ 0.3 nm / min. Analysis of the spectra was carried out in accordance with [10].

**RESULTS**

Analysis of the gas, resulting in the decomposition of the synthesized hydrates, showed that there is redistribution of natural gas components during hydrate formation (Table 1).

<table>
<thead>
<tr>
<th>Component</th>
<th>In feed gas</th>
<th>Duration of gas hydrate synthesis, days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In hydrate</td>
<td>After MA of hydrate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>86,1</td>
<td>85,9</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>3,45</td>
<td>5,49</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0,069</td>
<td>0,41</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>0,18</td>
<td>0,36</td>
</tr>
<tr>
<td>i-C₄H₁₀</td>
<td>0,074</td>
<td>0</td>
</tr>
<tr>
<td>n-C₅H₁₂</td>
<td>0,082</td>
<td>0</td>
</tr>
<tr>
<td>O₂</td>
<td>0,25</td>
<td>0,21</td>
</tr>
<tr>
<td>CO₂</td>
<td>0,01</td>
<td>0,074</td>
</tr>
<tr>
<td>N₂</td>
<td>8,37</td>
<td>3,4</td>
</tr>
<tr>
<td>H₂</td>
<td>0,16</td>
<td>0</td>
</tr>
<tr>
<td>He</td>
<td>0,055</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1. Compositions of feed gas (used for hydrate synthesis), gas in hydrate phase and gas
formed after MA of hydrates synthesized for 5 and 20 days. The clathrate phase enriches by C2-C4 hydrocarbons with lengthening the time of hydrate synthesis. Increasing of ethane concentration in the hydrate phase is characteristic.

After mechanical activation of hydrates with different composition, there is a noticeable decrease in methane concentration, as well as reducing ethane and propane concentrations (Table 1, Figure 3).

If i-butane completely decomposed at hydrate mechanoactivation, the concentration of n-butane after mechanical activation of the hydrate, which was synthesized for 20 days, increased (Figure 4).

Also in the gas phase after the MA of the hydrate, synthesized 20 days, i- and n-pentane were produced which are not involved in the formation of hydrates (Figure 5). After mechanical activation of hydrates with different composition the presence of hydrogen was revealed in the gas phase. The longer time of hydrate synthesis, the higher of hydrogen concentration in the gas phase (Table 1).

Figure 3. Concentrations of (a) methane, (b) ethane and (c) propane in natural gas, hydrate phase and gas obtained after MA

Figure 4. Concentrations of (a) i- and (b) n-butane in natural gas, hydrate phase and gas obtained after MA

Figure 5. Concentrations of (a) i- and (b) n-pentane in natural gas, hydrate phase and gas obtained after MA
are involved in chemical transformations by mechanical influence on gas hydrates. The main direction of mechanochemical transformations of gas hydrates is a lengthening of the carbon skeleton of hydrate.

![Graph](image1.png)

**Figure 5.** Concentrations of (a) i- and (b) n-pentane in natural gas, hydrate phase and gas obtained after MA

Reducing the concentration of alkanes and a significant formation of hydrogen could be explained by destruction of hydrocarbons, however, Mössbauer studies showed the absence of carbon and iron carbide in the solid phase (Table 2).

<table>
<thead>
<tr>
<th>Spectrum component</th>
<th>H, kOe</th>
<th>Phase</th>
<th>Iron atoms concentration in phase, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sextet</td>
<td>323</td>
<td>α-Fe+ solid solution</td>
<td>64</td>
</tr>
<tr>
<td>Singlet</td>
<td>19</td>
<td>Fe-Cr</td>
<td>13</td>
</tr>
<tr>
<td>Doublet</td>
<td>0-70</td>
<td>Fe-O or FeOOH</td>
<td>14</td>
</tr>
<tr>
<td>Sextet</td>
<td>450-550</td>
<td>Fe$_3$O$_4$</td>
<td>9</td>
</tr>
</tbody>
</table>

**Table 2.** Mössbauer spectra characteristics

Consequently, methane and other alkanes without undergoing degradation to carbon and hydrogen

![Graph](image2.png)

**Picture 6.** Mass spectrum of liquid organic phase obtained after MA of hydrate synthesized for 5 days

The process of lengthening of the hydrocarbon chain is confirmed by increasing the concentration of n-butane and the formation of pentanes in the gas phase, as well as the discovery of a new hydrocarbons not involved to hydrate formation: mechanoactivation of hydrates synthesized for 5 days leads to the formation of C7-cyclic and n-alkanes (Figure 6), while hydrates synthesized longer time give C10-cyclohexane and the C10-arenes (Figure 7).

![Graph](image3.png)

**Picture 7.** Mass spectrum of liquid organic phase obtained after MA of hydrate synthesized for 20 days
CONCLUSION

Natural gas in hydrate state under intensive mechanical stress undergoes chemical reactions that contribute to processes of carbon skeleton elongation of hydrocarbons. Formation of hydrocarbons with longer carbon chain during the mechanical activation of natural gas hydrates is a new, unusual result, since the evidence to date indicates the occurrence of the opposite process - the destruction of the molecules of gaseous hydrocarbons including mixture of natural gas and liquid water. Therefore, the elucidation of regularities of the process of carbon chain lengthening is a complicated task because a heterogeneous system containing a gas, liquid and solid phases are exposed to mechanical stress; moreover, different mechanisms of chemical transformations can be superimposed on each other. Perhaps this issue will be possible at least partly answered if further research on MA of individual gas hydrates - natural gas components, such as methane and ethane - will be conducted.

REFERENCES

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