Microwave Plasma-Chemical Reactor for the Natural Gas Conversion into Nanocarbon Material and Hydrogen


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Abstract – The experimental results of investigation of the natural gas conversion (\(\text{CH}_4 \approx 95\%\)) to the nanocarbonic material (NCM) and hydrogen in the microwave discharge plasma of atmospheric pressure in the microwave plasmachecmical reactor are presented. The reactor peculiarity providing its continuous operation is the available auxiliary discharge system in the reactor for initiation and maintenance of the primary microwave discharge. The dependence of the conversion level on the energy input, consumption and composition of the plasma-forming gas has been investigated. The increase (up to 70%) in the gas conversion level is shown in comparison with the process of the high-temperature pyrolysis. The experimental results on the energy efficiency of the plasmachemical process, composition and characteristics of the obtained NCM are given.

1. Introduction

One of the directions of a deep processing of the hydrocarbon raw material is the natural gas conversion (\(\text{CH}_4 = 95-97\%\)) to carbon and hydrogen. Among many existing nowadays methods of this process realization, a special attention is drawn to application of the microwave discharge plasma. As is noted in paper [1] this type of discharge enables to realize a number of endothermic plasmachemical processes with high energy efficiency. In particular, the process of thermal decomposition of methane to carbon and hydrogen under the influence of the microwave repetitively-pulsed pseudocorona discharge of atmospheric pressure on the preliminary heated methane is examined in [2]. It is noted that the microwave discharge plasma generation of chemically active particles contributing to the methane decomposition provides the reaction acceleration under the discharge effect.

A new method of the natural gas conversion to hydrogen and carbon based on the joint effect of the catalyst and microwave field on the natural gas is considered in the present paper [3]. A description of the plasmachemical system in which the given conversion method is realized is given. The results of experimental investigations of the natural gas conversion to the nanocarbonic material (NCM) and hydrogen in the microwave discharge plasma of atmospheric pressure in the microwave plasmachecmical reactor are presented.

2. Experimental setup

The experimental setup for the natural gas conversion to carbon and hydrogen is realized in accordance with the structural chart (Fig. 1).

![Fig. 1. Structural chart of the setup](image)
crowave power supply effecting the catalyst was organized on top of reactor by means of the built on waveguide-to-coaxial adapter (WCA). The same WCA was used to introduce the microwave energy to the discharge chamber from the second magnetron with the output controlled power to 3 kW \((f_p = 2450\,\text{MHz})\) in the continuous generation mode. Both magnetrons of the setup at that are connected to the load through the circulators with the purpose of decoupling of each one with its load and measuring the reflected power level (it is not shown in figure). The agglomerator and a system of filters with cyclone trap of the carbon nanoparticles are provided for collection of the plasmachemical reaction products.

The endothermal reaction \((75\,\text{kJ/mol})\) of the methane decomposition to hydrogen and carbon \(\text{CH}_4 = \text{C}_0 + 2\text{H}_2\) was realized in the described setup in the following way.

On the first stage, the metal catalyst (Fe, Ni, TiNi) is heated in the reactor using the microwave energy in the nitrogen current to the temperatures of the order \(520\div560\,\text{°C}\) at the expense of the dissipative losses on the catalyst. Then, the cold natural gas was supplied to reactor with consumption of 0.05\div1.0\,\text{m}^3/\text{hour}, nitrogen supply was switched off, a system of the additional discharge formation like the glow one was switched on for the microwave discharge initiation, based on a principle of a separate gas supply (nitrogen and methane) to the microwave torch zone [4], and the microwave discharge ignited in the discharge chamber. At that the catalyst temperature decreased to the values of \(450\div480\,\text{°C}\) depending on the natural gas consumption. The temperature decrease in reactor and hydrogen occurrence in the residual gases testified the reaction beginning. Simultaneously the visual observation of the process through the discharge chamber window was realized on the discharge glow and the carbon flow presence.

The worked reaction products due to insufficient exhaustion in the system were transported to the carbon collectors through a number of filters.

The plasmachemical conversion of methane realized in the setup happens in our opinion in the following way. On the heated catalyst there occurs the preliminary excitation of the methane molecules and the beginning of reaction of the unsaturated hydrocarbons formation (ethylene, acetylene) which are transported by a gas flow to the discharge chamber where the plasmachemical reaction takes place. The plasma torch removes the reaction products to the post-reactor space.

### 3. Experimental results

In the course of realization of the developed technology of methane conversion on the basis of the joint effect of the catalyst and microwave discharge plasma it was shown that under given conditions the conversion level increases (to 70\%), so does the hydrogen and nanocarbonic material yield [5]. It involves: carbonic multilayer, monolayer, bulbous nanotubes with the specific surface of \(30\div100\,\text{m}^2/\text{g}\); amorphous carbon with the specific surface of \(200\div400\,\text{m}^2/\text{g}\). The size of the amorphous carbon particles was from 10 to 50 nm. The lateral dimension of the nanotubes changed within 5–27 nm. The types of the formed nanotubes and their sizes are given in Table.

After ascertainment of the role and degree of the microwave discharge plasma influence on the efficiency of the methane conversion process as a result of investigations conducted on the hot and cold catalyst [5], a number of experiments on the estimation of the conversion level, energy efficiency, energy cost of the process depending on the plasma-forming gas consumption and value of the microwave power introduced to the discharge chamber (specific energy input) was executed.

The output power of the microwave generator varied within \(0.9\div2.5\,\text{kW}\) in the experiments. The gas consumption was within 0.05\div1\,\text{m}^3/\text{h}. With these indices of powers and consumptions the energy input from 5 to 40\,\text{eV/mol}\) was realized.

The experiments were conducted at the pressure of the order \(7\cdot10^2\,\text{mm}\,\text{Hg}\). The methane conversion level was determined by a chromatographic method.

Figure 2 shows the experimental dependences of the natural gas conversion level versus value of energy input to the discharge chamber. The parameter here is the consumption. The analysis of dependences shows that the conversion level increases (to 70\%) at the consumption reduction and growth of power input to the discharge.

From this it is seen that at consumption of about \(0.4\,\text{m}^3/\text{h}\), the specific energy input is about 5\,\text{eV/mol} for different levels of power introduced to the discharge. This value is of one order with the theoretically minimal “energy cost” of methane conversion, corresponding to 1\,\text{eV/mol}, which confirms the perspective of the developed technology and the setup for methane conversion using microwave discharge.

Dependences of specific energy input on the basis of one molecule versus gas consumption are given in Fig. 3.

<table>
<thead>
<tr>
<th>Catalyst composition</th>
<th>MWCNT, %</th>
<th>SWCNT, %</th>
<th>Onions, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>19.4</td>
<td>14.9</td>
<td>35.6</td>
</tr>
<tr>
<td>Fe</td>
<td>28.2</td>
<td>12.4</td>
<td>33.0</td>
</tr>
<tr>
<td>Mo</td>
<td>47.0</td>
<td>26.3</td>
<td>20.1</td>
</tr>
</tbody>
</table>
The reduction of the energy efficiency of the process at high specific energy inputs (at low costs) presumably can be explained by the consumption of part of the discharge energy for excitation of the methane conversion products. Possibly, at low consumptions (to 0.4 m$^3$/h) the microwave power levels used in the experiments and introduced to the discharge are excessive. This issue requires additional investigations.

Figure 4 shows the dependences of the volume concentration of the plasmachemical reaction products (methane, hydrogen, acetylene) at variable consumptions. As follows from these results, at consumptions from 0.6 m$^3$/h and higher which are of practical interest, the hydrogen yield is $\geq 40$ vol.%. At that there was fixed the presence of 5 vol.% C$_2$H$_2$ in the reaction products.

### 4. Conclusion

The experimental results obtained in this paper confirmed the practical expediency of the application of the microwave discharge of atmospheric pressure in combination with the catalyst for the methane conversion to hydrogen and carbon.

Considerable concentration of hydrogen in the residual gases makes this conversion method promising for obtaining of both nanocarbon material and hydrogen in industrial scales.

A sufficiently efficient microwave plasmachemical reactor of continuous operation for the natural gas conversion to nanocarbonic material and hydrogen was created.

### References


