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# THE KINETICS OF THE METHANE DIMERIZATION REACTION

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## ABSTRACT

The article studies the influence of parameters on the reaction rate of catalytic dimerization of methane, kinetic relations in the flow differential quartz reactor (P=0,1 MPa, Vcat =0.5÷2 ml, CH4:O2=2:4, contact time 0.1÷0.09 sec) in the temperature range of 750-580 ℃. The influence of temperature on methane conversion and product selectivity, the influence of oxygen and hydrogen impurities on methane conversion and acetylene selectivity, and the dependence of ethane selectivity on temperature were discussed. At different concentrations of methane with a volume ratio of CH4:O2=3:1 in the mixture, the influence of temperature parameters on selectivity for acetylene was studied, a reaction mechanism was proposed and a kinetic model was developed for obtaining ethane, ethylene, acetylene and acetic anhydride from methane.

## KEYWORDS

Methane, ethane, ethylene, acetylene, catalyst, kinetic equation, mechanism, contact time, dimerization.

## INTRODUCTION

Currently, the demand for petrochemical products is increasing worldwide. Vinyl chloride, polyethene, ethylene oxide, vinyl acetate, lavsan, etc. are in high demand. The main raw material for all the above-mentioned substances is ethylene. Currently, ethylene is mainly produced by the thermal decomposition of gasoline. The dynamic growth of demand for motor fuels is pushing to find another innovative way to obtain the main organic synthesis product. One such innovative method is the catalytic dimerization of methane to ethylene [1-6].

At the same time, ethylene extraction from methane has not been established. The main reason for this is that the equipment for the process is not equipped and the optimal mode is not selected. It is necessary to study the kinetic laws of the reaction transition to determine the appropriate mode and equip the devices.

Several works have been published [7-11] on the catalytic oxidative transformation of methane, and various absorbed catalysts have been proposed for the production of ethylene and ethane from methane. The peculiarity of the methane oxidation condensation reaction is that in all known catalysts the reaction takes place at a high temperature and the process is strongly exothermic. In addition, the $CH_4 + O_2$ mixture has strong explosive properties. At the same time, the activity and selectivity of catalysts are low.

In addition, the kinetics of the methane dimerization reaction in the catalysts of all studied literature $Bi_2O_3 \cdot 9\%$ $K_2CO_3/Al_2O_3$; 34% $PbO/Al_2O_3$; 4% $Na_2MoO_4*10\%Mn-O/SiO_2$ has not been fully studied without taking into account the

processes involving catalysts. In the reactions with the mentioned catalysts, formal rank equations were used for the kinetic expression of the process. In all works, ethylene was obtained as the target product [12-19].

**Prospects for the practical application of the catalytic dimerization of methane.** The yield of $C_2$ hydrocarbons strongly depends on the content of $CH_4$ + oxygen in the reaction mixture. To obtain $C_2$-hydrocarbons in high yield, it is necessary to use a non-diluted reaction mixture. It is better to have a volume ratio of $CH_4/O_2$=4-5.

The practical implementation of the catalytic dimerization reaction of methane has the following difficulties:

1) As a result of the reaction, ethane, ethylene, and a small amount of propane and propylene, which are more reactive than methane, are formed. The resulting products are completely oxidized to $CO_2$ in the presence of a catalyst.

2) The reaction products react more easily with oxygen than with methane in the gas phase. Therefore, it is necessary to portion out oxygen or quickly remove the reaction products from the reaction zone.

3) A large amount of heat is released during the catalytic dimerization of methane, which requires efficient use [21-27].

## MATERIALS AND METHODS

The reactor is a quartz tube with a length of 650 mm and an internal diameter of 8 mm. The size of the catalyst is 0.25-0.5 mm. To reduce the volume, quartz crystals were placed on the bottom and on top of the catalyst. The catalytic activity of the catalyst in a flow differential quartz reactor

(P=0.1 MPa, Vkat=0.5 ml÷2 ml, $CH_4:O_2=2÷4$, contact time 0.1-0.09 sec) in the temperature range of 750-850 ℃ studied [23, 21-26].

The temperature was changed in the range from 700 to 850 ℃. Under the given conditions, the conversion of methane varies from 1 to 35%, and the conversion of oxygen varies from 4 to 98%. The selectivity for reaction products varies from 30 to 70%.

99.9% pure methane and pure oxygen were used for the reaction. The gases were mixed before entering the reactor. A laboratory device with a flow differential reactor was created to study the kinetic laws of the methane oxycondensation reaction.

The gas products of the reaction were chromatographically analyzed using a thermochemical detector with an additional thermostat "Gazochrom3101" was analyzed in a chromatograph under the following optimal conditions: column thermostat temperature -100 ℃, carrier gas (air) flow rate -35 ml/min, column length filled with activated carbon - 1 m, internal diameter - 3 mm. Quantitative analysis was performed using the absolute ranking method [20, 21-24].

**Results and discussion**

The effect of some parameters on the rate of catalytic dimerization of methane was studied. The obtained results are presented in Figure 1.
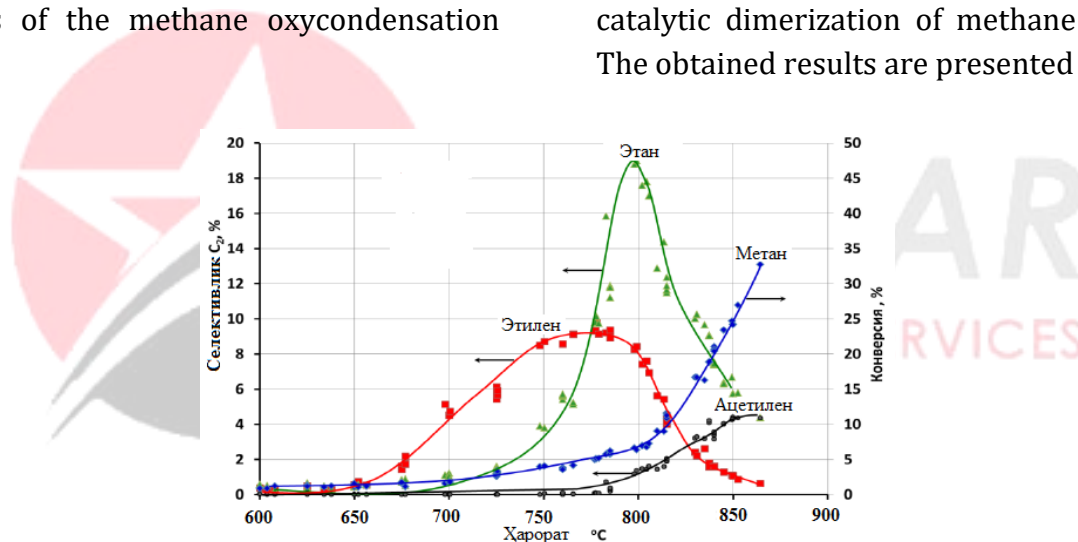


**Figure 1. Effect of temperature on methane conversion and product selectivity**

Figure 1 shows the temperature dependence of the conversion of methane (X) and the selectivity of the formation of reaction products. As can be seen from Figure 2, the conversion of methane starts at 600 ℃. The first product of the oxidative dimerization reaction of methane is ethane and a small amount of ethylene. When the temperature is further increased, the selectivity of the formation of ethane and ethylene increases, and the selectivity to ethane reaches a maximum of 800 ℃. At 800 ℃, the selectivity of ethane is about 2 times higher than the selectivity of ethylene. But 820-830 ℃ the selectivity of all products drops sharply. After the temperature exceeds 8000, peaks (rounds) characteristic of acetylene appears in the chromatograms. Temperature 850℃after exceeding, its selectivity increases sharply. Also, the selectivity of the formation of

ethane and ethylene is 900 ℃ reaching the second maximum at

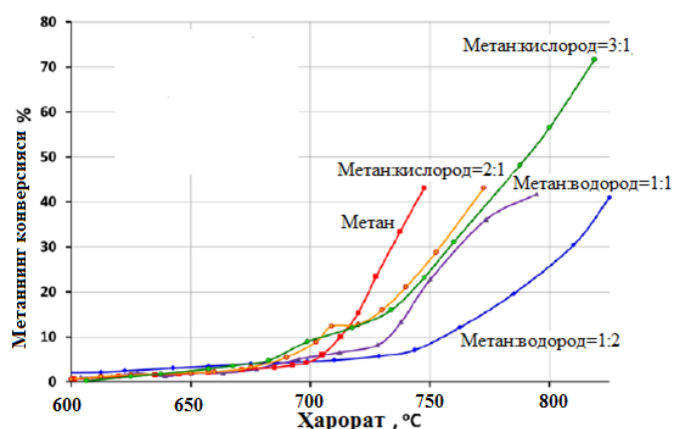Figure 2 below examines the effects of oxygen and hydrogen additions on methane conversion and acetylene selectivity.



**Figure 2. Effect of oxygen and hydrogen additions on methane conversion and acetylene selectivity**

In oxidative dimerization, the conversion of methane in the desired composition of the reaction mixture is 600 ℃ starts from and increases with increasing temperature. When the concentration of oxygen in the initial reaction mixture is increased, the conversion of methane increases.
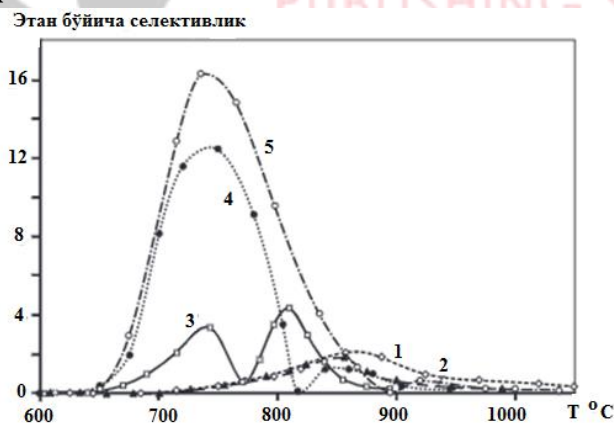


**Figure 3. Dependence of selectivity on ethane on temperature.**

The conversion of methane is almost unchanged when hydrogen is added to the initial reaction mixture. At this time, the formation of the first product of the reaction, ethane, does not depend on the reaction conditions. Ethane 680-700 when we carry out the reaction in the absence of oxygen (line 3). And in the presence of oxygen ($CH_4:O_2 = 3:1$ and $CH_4:O_2 = 2:1$; lines 4 and 5) 650 ℃ is formed in When obtained in $CH_4:H_2 = 1:1$ and

$CH_4:H_2$ = 1:2 ratios (lanes 2 and 1) 700 °C begins to form. Under these conditions, the selectivity to ethane is 750 °C will be the maximum.
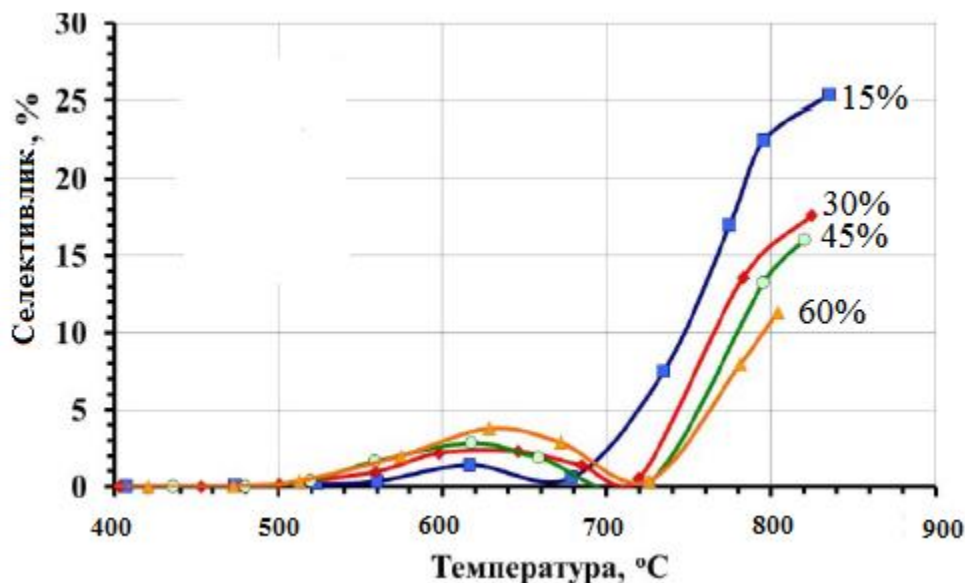


**Figure 4. Effect of temperature on acetylene selectivity for different concentrations of methane in $CH_4:O_2$=3:1 mixture**

As can be seen from the figure, when the effect of temperature on the selectivity for acetylene is studied for methane concentrations of 15%, 30, 45, and 60% in the $CH_4:O_2$=3:1 mixture, the selectivity to acetylene increases as the concentration of methane in the mixture decreases.

Based on the results obtained
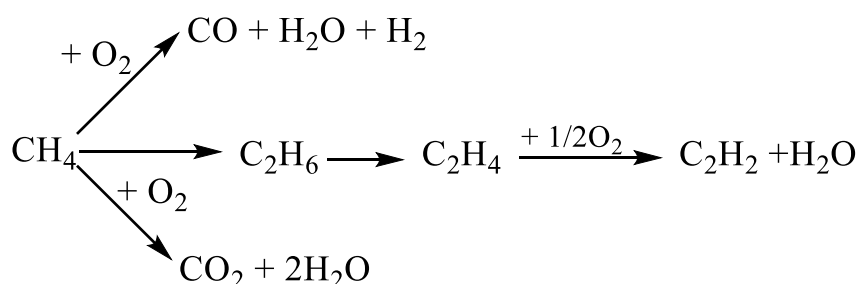


A reliable mechanism for the formation of ethane from methane can be expressed as follows:

we will consider the mechanisms and kinetic models of chain reactions.

$$2Z + O_2 \xrightarrow{k_1} 2ZO; \quad 2ZO + CH_4 \xrightarrow{k_2} ZOCH_3 + ZOH; \quad ZOCH_3$$

$$+ CH_4 \xrightarrow{k_3} C_2H_6 + ZOH$$

$$2ZOH \xrightarrow{k_4} H_2O + ZO + Z$$

$$0{,}5O_2 + 2CH_4 \rightarrow C_2H_6 + H_2O$$

Under the condition of stationarity, W1 = W2 = W3 = W4 and the total number of surface areas is constant ($\sum i = 1$), the equation for the rate of ethane formation according to the above mechanism is as follows:$\theta$
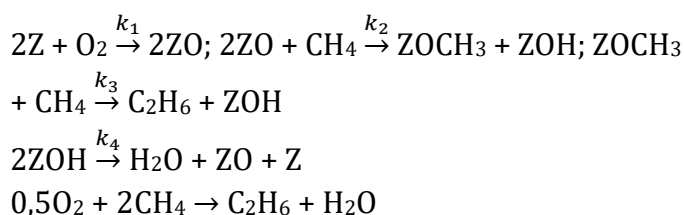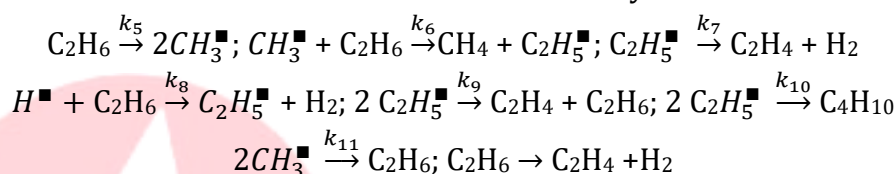
$$W_{C_2H_6} = \frac{k_3^2 P_{CH_4}}{4k_2} \left\{ -\left( \sqrt{\frac{k_2 P_{CH_4}}{k_1 P_{O_2}}} + \sqrt{\frac{k_2 P_{CH_4}}{k_4}} + 1 \right) + \sqrt{\left(\sqrt{\frac{k_2 P_{CH_4}}{k_1 P_{O_2}}} + \sqrt{\frac{k_2 P_{CH_4}}{k_4}} + 1\right)^2 + 4\frac{k_2}{k_3}} \right\}$$

The chain mechanism of the formation of ethylene from ethane:

$$C_2H_6 \xrightarrow{k_5} 2CH_3^{\bullet}; \quad CH_3^{\bullet} + C_2H_6 \xrightarrow{k_6} CH_4 + C_2H_5^{\bullet}; \quad C_2H_5^{\bullet} \xrightarrow{k_7} C_2H_4 + H_2$$

$$H^{\bullet} + C_2H_6 \xrightarrow{k_8} C_2H_5^{\bullet} + H_2; \quad 2\,C_2H_5^{\bullet} \xrightarrow{k_9} C_2H_4 + C_2H_6; \quad 2\,C_2H_5^{\bullet} \xrightarrow{k_{10}} C_4H_{10}$$

$$2CH_3^{\bullet} \xrightarrow{k_{11}} C_2H_6; \quad C_2H_6 \rightarrow C_2H_4 + H_2$$

The equation for the reaction of ethylene formation according to the above mechanism:

$$W_{C_2H_4} = 3k_6 P_{C_2H_6} \left( 1 - \frac{0.33}{1+\frac{K_8}{k_9}} \right) + \frac{k_5 (\frac{k_7}{k_9})^{1/2}}{(1+\frac{k_8}{k_9})^{1/2}} P_{C_2H_6}^{1/2}$$
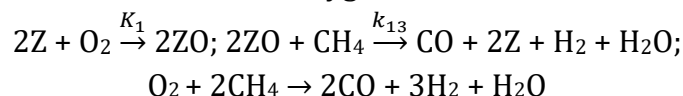
It was also found that the contact gases contained $CO_2$. $CO_2$ is mainly formed by the interaction of a weakly adsorbed oxygen molecule with methane:

$$O_2 + Z \xrightarrow{k_1^*} O_2Z; \quad CH_4 + Z \xrightarrow{k_2^*} CH_4Z; \quad ZCH_4 + 2ZO_2 \xrightarrow{k_{12}} 2CO_2 + 2H_2O + 3Z$$

The reaction rate of $CO_2$ formation:

$$W_{CO_2} = \frac{2k_{12}K_1^* P_{O_2} K_2^* \cdot P_{CH_4}}{(1 + K_1^* \cdot P_{O_2} + K_2^* \cdot P_{CH_4})^2}$$

Carbon dioxide is formed from the interaction between a methane molecule and dissociatively adsorbed oxygen:

$$2Z + O_2 \xrightarrow{K_1} 2ZO; \quad 2ZO + CH_4 \xrightarrow{k_{13}} CO + 2Z + H_2 + H_2O;$$

$$O_2 + 2CH_4 \rightarrow 2CO + 3H_2 + H_2O$$

The equation for the rate of formation of CO is:

$$W_{CO} = k_{13} P_{CH_4} \left( \frac{1}{1 + \sqrt{\frac{k_{13} P_{CH_4}}{K_1 P_{O_2}}}} \right)^2$$

The reaction rate constants were calculated according to the experimental results presented in Table 1.
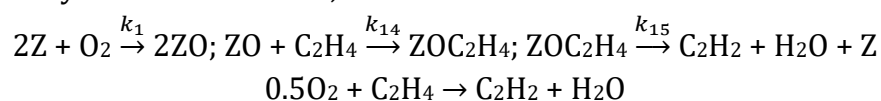
## Table 1. Experimental test results

| Temperature, ⍰ | Component concentration, % mol | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $H_2$ | $CH_4$ | $O_2$ | $N_2$ | $CO_2$ | $C_2H_4$ | $C_2H_6$ | CO |
| Contact time-2 s | | | | | | | | |
| 700 | 1.9 | 24.8 | 0.8 | 56.8 | 2.4 | 8.7 | 1.3 | 0.4 |
| 730 | 0.8 | 25.6 | 1.1 | 57.3 | 3.6 | 8.0 | 1.2 | 0.3 |
| 735 | 1.8 | 24.6 | 1.8 | 57.4 | 2.8 | 8.0 | 1.2 | 0.3 |
| 750 | 4.6 | 26.2 | 1.7 | 53.3 | 3.4 | 8.5 | 0.7 | 1.3 |
| 750 | 3.8 | 22.4 | 1.5 | 58.6 | 3.9 | 8.0 | 0.8 | 1.1 |
| 800 | 8.4 | 24.0 | 0.3 | 49.8 | 3.5 | 8.0 | 0.2 | 3.8 |
| 850 | 14.8 | 23.7 | 0.2 | 42.0 | 2.2 | 6.9 | 0.0 | 8.1 |
| Contact time-1 s | | | | | | | | |
| 600 | 0.4 | 30.4 | 0.1 | 55.7 | 1.2 | 8.3 | 1.4 | 0.5 |
| 660 | 1.7 | 27.1 | 0.0 | 56.6 | 2.1 | 8.4 | 1.1 | 1.0 |
| 665 | 2.7 | 28.1 | 0.0 | 54.7 | 2.0 | 8.4 | 1.1 | 1.0 |
| 700 | 2.2 | 29.1 | 0.0 | 54.3 | 1.9 | 8.4 | 1.3 | 0.7 |
| 750 | 2.3 | 27.6 | 0.0 | 55.5 | 2.2 | 8.5 | 1.2 | 0.7 |
| 770 | 2.2 | 28.6 | 0.0 | 54.4 | 2.1 | 8.8 | 1.3 | 0.7 |
| 800 | 6.2 | 28.0 | 0.0 | 50.2 | 2.6 | 8.2 | 0.7 | 2.1 |
| Contact time-0.5 s | | | | | | | | |
| 615 | 2.8 | 26.1 | 1.0 | 56.1 | 1.3 | 5.8 | 0.8 | 2.0 |
| 650 | 3.9 | 27.2 | 0.0 | 54.1 | 1.7 | 6.0 | 0.6 | 2.6 |
| 700 | 3.2 | 27.6 | 0.0 | 54.6 | 1.4 | 5.9 | 0.6 | 2.3 |
| 750 | 2.8 | 27.2 | 0.0 | 55.6 | 1.5 | 6.0 | 0.6 | 2.3 |
| 800 | 5.1 | 28.9 | 0.0 | 51.3 | 1.9 | 5.9 | 0.6 | 2.4 |
| 800 | 3.7 | 24.9 | 0.0 | 56.1 | 1.5 | 5.8 | 0.5 | 3.3 |
| 850 | 4.3 | 24.6 | 0.0 | 55.7 | 1.6 | 5.8 | 0.4 | 2.5 |

In the catalytic dimerization of methane, acetylene is formed from the oxidative dehydrogenation of ethylene. At this time, the dissociatively adsorbed oxygen molecule interacts with the ethylene molecule to form the $ZOC_2H_4$ complex. This in turn splits into acetylene and water molecules:

$$2Z + O_2 \xrightarrow{k_1} 2ZO; \quad ZO + C_2H_4 \xrightarrow{k_{14}} ZOC_2H_4; \quad ZOC_2H_4 \xrightarrow{k_{15}} C_2H_2 + H_2O + Z$$

$$0.5O_2 + C_2H_4 \rightarrow C_2H_2 + H_2O$$

According to this mechanism, the rate of formation of acetylene:

$$W_{C_2H_2 = k_1 P_{O_2}} \left[ \frac{-1 + \sqrt{1 + 4\left(\frac{k_1 P_{O_2}}{k_{14} P_{C_2H_4}} + \frac{K_1 P_{O_2}}{k_{15}}\right)}}{2\left(\frac{k_1 P_{O_2}}{k_{14} P_{C_2H_4}} + \frac{k_1 P_{O_2}}{k_{15}}\right)} \right]^2$$

The above equations constitute the kinetic model of the process.

The parameters of the kinetic models were determined based on the experimental results using the following objective function:

$$F(x) = \sum_{1}^{N} \left[\frac{A_{\text{expe}} - A_{acc.}}{A_{\text{expe}}}\right]^2$$

where x is the kinetic parameter of the considered model; $A_{\text{expe}}$ $A_{acc.}$-experimental and calculated values of the yield of reaction products; Number of N-components.

The created kinetic model of the methane oxidation condensation reaction adequately represents the experimental values (the relative error of the experimental and calculated values does not exceed 10%).

## CONCLUSION

Thus, the factors affecting the rate of the catalytic oxidation dimerization reaction of methane, the kinetic laws of the reaction in a flowing differential quartz reactor (P = 0.1 MPa, $V_{cat}$ = 0.5 ml÷2 ml, $CH_4$:$O_2$ = 2÷4, contact time 0, 1-0.09 sec) was studied in the temperature range of 750-850 °C. Effect of temperature on methane conversion and selectivity of products, the effect of oxygen and hydrogen additives on methane conversion and selectivity on acetylene, and temperature dependence of selectivity on ethane, Based on the study of factors such as the effect of temperature on the selectivity for acetylene in the mixture $CH_4$:$O_2$=3:1, the mechanism of the reactions of the formation of ethane, ethylene, acetylene, and carbon dioxide from methane was proposed and a kinetic model was created.

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