



## STUDY OF THE KINETICS OF THE REACTION OF HIGH MOLECULAR HYDROCARBONS WITH SYNTHESIS GAS

**Rakhmatov Khudoyor**

Candidate of Chemical Sciences, Professor, Karshi Engineering and Economic Institute, Karshi, Kashkadarya region, Uzbekistan.

E.mail: [zavod.lab@mail.ru](mailto:zavod.lab@mail.ru).

**Togayev Abror**

Senior Lecturer, Karshi Engineering and Economic Institute, Karshi, Uzbekistan

doi: [10.48047/ecb/2023.12.si4.1307](https://doi.org/10.48047/ecb/2023.12.si4.1307)

**Annotation.** In this work, the kinetics of the reaction of obtaining high-molecular hydrocarbons from synthesis gas was studied. In the first series of experiments, the initially activated catalyst 15%Co-15%Fe-5%Ni-1%ZrO<sub>2</sub>-1%CaO/y-Al<sub>2</sub>O<sub>3</sub> was developed in synthesis gas with the composition CO/H<sub>2</sub>=1/2 at a pressure of 0.1 MPa, space velocity 100 h<sup>-1</sup>. The temperature was raised from 150 to 190°C in increments of 10°C. The duration of daily operation at each temperature was 5 hours. At a temperature of 190°C, the volumetric rate of synthesis gas transfer increased from 400 to 500 h<sup>-1</sup>. The calculated values of E for various gas transfer volumetric rates and the calculated average values of k for each temperature are given. The root-mean-square error in the calculation of the activation energy is 3.19%. At a temperature of 180°C, the average value of the rate constant is 4.52 h<sup>-1</sup> with a standard deviation of 8.56%. The activation energy of the reaction at 190 and 200°C can be calculated from two values of the rate constant. It is 89.31 kJ/mol.  
**Keywords:** synthesis gas, rate constant, reaction rate, temperature, activation energy.

### INTRODUCTION.

The purpose of the work is to study the kinetics of the reaction of obtaining high-molecular hydrocarbons from synthesis gas.

The production of lower olefins is growing on a large scale and continuously [1]. Thermal pyrolysis and catalytic cracking remain the main production methods for ethylene and propylene. The growth rates of ethylene and propylene consumption significantly exceed the scale of their production, which forces us to look for other, cheaper and more convenient hydrocarbon raw materials. Such a raw material is natural gas, the extraction and large-scale use of which is predicted for a long time. The most popular and studied method for obtaining chemical products from natural gas is their production by preliminary conversion of natural gas into synthesis gas (CO/H<sub>2</sub>).

At present, of great interest is the option of obtaining C<sub>2</sub>-C<sub>3</sub> olefins from synthesis gas using dimethyl ether (DME), which makes it possible to obtain lower olefins with high yield and high selectivity [2, 3]. DME can be considered as one of the main possible tools for converting non-petroleum feedstocks into valuable chemical products such as olefins [4]. A new catalyst for the synthesis of lower olefins from DME is a high-silicon zeolite of the ZSM-5 type. The properties of zeolite catalysts are directly affected by modification with metal compounds [5-9], which can lead to changes in their structure and acidic properties [10-12]. Many works have appeared in the literature, in which the influence of the nature of the modifying element on the properties of zeolite catalysts has been extensively studied [13-17], but the concept of understanding the role of nature has not yet been developed. A number of works have been carried out on the synthesis of lower olefins from DME [18-28].

### Methods.

Catalytic experiments on the synthesis of high-molecular hydrocarbons were carried out on a flow-type laboratory setup with a built-in reactor. A fixed bed of 5 catalysts is placed in the reactor in the

form of a steel pipe with an inner diameter of 20 mm. The activity of hydrocarbon synthesis catalysts was evaluated by the following parameters: CO conversion, selectivity, and productivity for hydrocarbons. The calculation error did not exceed 2.5%. CO conversion was calculated using the following formula:

$$X_{CO} = \frac{V_{vix} \cdot c(CO)_{vix} - V_{vin} \cdot c(CO)_{vin}}{V_{vix} \cdot c(CO)_{vix}} \cdot 100\%$$

Where  $V_{in}$ ,  $V_{out}$  - gas flow rate at the inlet to the reactor and at the outlet of the reactor,  $dm^3/h$ ;  $c(CO)_{input}$ ,  $c(CO)_{output}$  - CO concentration at the inlet and outlet of the reactor, units.

Selectivity for methane was calculated using the following formula:

$$S_{CH_4} = \frac{V(CO)_{CH_4}}{V(CO)_{np}} \cdot 100\%$$

Where  $V(CO)_{CH_4}$  is the volume of CO used to produce methane,  $dm^3$ ;  $V(CO)_{np}$  - CO volume in terms of methane,  $dm^3$ .

Selectivity for C<sub>5+</sub> hydrocarbons was calculated using the formula:

$$S_{C_{5+}} = \frac{V(CO)_{C_{5+}}}{V(CO)_{np}} \cdot 100\%$$

Where  $V(CO)_{C_{5+}}$  is the volume of CO consumed for the formation of C<sub>5+</sub> hydrocarbons,  $dm^3$ .

The yield of C<sub>5+</sub> hydrocarbons was calculated using the following formula:

$$G_{C_{5+}} = \frac{m_{C_{5+}}}{V_{cat} \cdot t}$$

Where

$m_{C_{5+}}$  - mass of C<sub>5+</sub> hydrocarbons, kg;

$V_{cat}$  is the catalyst volume,  $m^3$ ;

$t$  - time, hour.

Gas adsorption chromatography and two columns with the active phase Haysep R and NaX molecular sieves on a Kristall 5000 chromatograph (Khromatek, Russia) analyzed the composition of the gaseous synthesis products with a thermal conductivity detector. The analysis mode is temperature-programmed with a heating rate of 8°C/min. The composition of C<sub>5+</sub> hydrocarbons was determined by capillary gas-liquid chromatography-mass spectrometry on a gas chromatograph (Agilent, USA) with an MSD 5975C mass selective detector.

### Results.

To design Fischer-Tropsch reactors using mathematical modeling, it is necessary to have information about the reaction kinetics. Moreover, it should be expressed not in the form of a graph or table, but in the form of a kinetic equation. It is desirable that the structure of this equation reflects the chemistry of the process as much as possible, otherwise the inevitable operations of data interpolation and especially extrapolation will become less reliable.

The following equation is widely used in the literature to describe the kinetics of the Fischer-Tropsch process:

$$W_{CO} = k'_{CO} P_{H_2}$$

We sought to obtain the dependence of the catalyst activity on the conditions - pressure, temperature, space velocity and check their compliance with the equation.

Based on the law of mass action, the expression for the reaction rate can be written as:

$$W_{CO} = -k_{CO} C_{H_2}^a C_{CO}^b$$

The rate constants and activation energies were calculated using a computer program.

Several series of experiments were carried out, in each of which, for the purpose of testing, one of the synthesis parameters was changed - temperature, space velocity, total and partial pressures of the synthesis gas components.

The apparent activation energy is calculated on the basis of experimental data using the Arrhenus equation:

$$\ln(k) = \ln(A) - \frac{E}{RT}$$

Calculations of the rate constants and activation energies were carried out using a computer program.

Several series of experiments were carried out, in each of which one of the synthesis parameters was varied - temperature, space velocity, total and partial pressures of the synthesis gas components - to check the fulfillment of the equation.

In the first series of experiments, the initially activated catalyst 15%Co-15%Fe-5%Ni-1%ZrO<sub>2</sub>-1%CaO/γ-Al<sub>2</sub>O<sub>3</sub> was developed in synthesis gas with the composition CO/H<sub>2</sub>=1/2 at a pressure of 0.1 MPa, space velocity 100 h<sup>-1</sup>. The temperature was raised from 150 to 190°C in increments of 10°C. The duration of daily operation at each temperature was 5 hours. At a temperature of 190°C, the volumetric rate of synthesis gas transfer increased from 400 to 500 h<sup>-1</sup>. The catalyst loading volume was varied so that the linear velocity was the same in all experiments (see the previous section). The obtained CO conversion values and the calculated rate constants are summarized in Table 1 using the equation according to the equation  $W_{CO} = k'_{CO} P_{H_2}$ . Obviously, GHSV scores of 100 and 200 h<sup>-1</sup> should not be considered in the final table, since they have reached full development of CO. As can be seen from the calculations, the rate constants change unsatisfactorily - the error is at least 12% in the temperature range of 190-210°C. Obviously, GHSV scores of 100 and 200 h<sup>-1</sup> should not be considered in the final table, since they have reached the full development of CO. As can be seen from the calculations, the rate constants change unsatisfactorily - the error is at least 12% in the temperature range of 190-210°C.

**Table 1. Rate constants according to the equation (R=0.1 MPa, T=190°C)**

| Volumetric speed hour-1 | K <sub>CO</sub> , % | k, hour <sup>-1</sup> |
|-------------------------|---------------------|-----------------------|
| 100                     | 78                  | 48.8                  |
| 200                     | 4                   | 59.6                  |
| 400                     | 30                  | 59.8                  |

**Table 2. Rate constants according to the equation (R=0.1 MPa, T=200°C)**

| Volumetric speed hour-1 | K <sub>CO</sub> , % | k, hour <sup>-1</sup> |
|-------------------------|---------------------|-----------------------|
| 100                     | 89.9                | 67.9                  |
| 200                     | 68.8                | 84.3                  |
| 400                     | 31.7                | 66.2                  |

**Table 3 Rate constants according to the equation (R=0.1 MPa, T=210°C)**

| Volumetric speed hour-1 | K <sub>CO</sub> , % | k, hour <sup>-1</sup> |
|-------------------------|---------------------|-----------------------|
| 100                     | 99                  | 109.78                |
| 200                     | 84                  | 109.38                |
| 400                     | 49                  | 102.45                |

**Table 4 Rate constants according to the equation (R=0.1 MPa, T=230°C)**

| Volumetric speed hour-1 | K <sub>CO</sub> , % | k, hour <sup>-1</sup> |
|-------------------------|---------------------|-----------------------|
| 100                     | 100                 | 109.8                 |
| 200                     | 100                 | 219.6                 |
| 400                     | 67                  | 163.4                 |

$W_{CO} = k'_{CO}P_{H_2}$  together with the rate constants calculated according to the equation, at a synthesis pressure of 2.0 MPa and a volumetric feedstock transfer rate in the range of 180-240 ° C, the temperature dependence of CO conversion is presented in Table 4. According to the Arrhenius equation, the apparent activation energy of the reaction was 74.28 kJ / mol, which is comparable to the value obtained in the previous experiment. In the linear equation, the correlation coefficient is 0.9841, which indicates a good approximation (Fig. 1).

**Table 5 Reaction rate constants and activation energy**

| Volumetric speed hour-1 | K <sub>CO</sub> , % |      |       |        | k, hour <sup>-1</sup> |
|-------------------------|---------------------|------|-------|--------|-----------------------|
|                         | 190                 | 200  | 210   | 230    |                       |
|                         |                     |      |       |        | kJ/mol                |
| 100                     | 48.8                | 67.9 | 109.9 | -      | 74.58                 |
| 200                     | 59.2                | 84.3 | 109.5 | -      | 56.33                 |
| 400                     | 59.3                | 66.4 | 102.5 | 164.24 | 55.81                 |

**Table 6 According to the equation, the reaction rate constants are R=2.0 MPa, T=190°C.**

| Volumetric speed hour-1 | K <sub>CO</sub> > % | k, hour <sup>-1</sup> |
|-------------------------|---------------------|-----------------------|
| 1000                    | 18                  | 4.42                  |
| 2000                    | 12                  | 5.29                  |
| 3000                    | 8                   | 4.85                  |

**Table 7 Reaction rate constants according to equation (1), R=2.0 MPa, T=210°C**

| Volume speed, c <sup>-1</sup> | K <sub>CO</sub> > % | k, hour <sup>-1</sup> |
|-------------------------------|---------------------|-----------------------|
| 1000                          | 35                  | 8.88                  |
| 2000                          | 26                  | 13.53                 |
| 3000                          | 19                  | 14.08                 |

**Table 8 CO conversions and rate constants at R=2.0 MPa, space velocity 2000 h<sup>-1</sup>**

| T, °C | K <sub>CO</sub> >, % | k, hour <sup>-1</sup> | T, °C | K <sub>CO</sub> , % | k, hour <sup>-1</sup> |
|-------|----------------------|-----------------------|-------|---------------------|-----------------------|
| 180   | 8                    | 3.3                   | 215   | 23                  | 11.93                 |
| 190   | 9                    | 3.4                   | 220   | 27                  | 13.84                 |
| 195   | 12                   | 5.9                   | 225   | 30                  | 15.01                 |
| 200   | 11                   | 5.9                   | 230   | 36                  | 18.78                 |
| 205   | 14                   | 6.5                   | 235   | 39                  | 20.93                 |
| 210   | 17                   | 8.4                   | 240   | 52                  | 28.88                 |

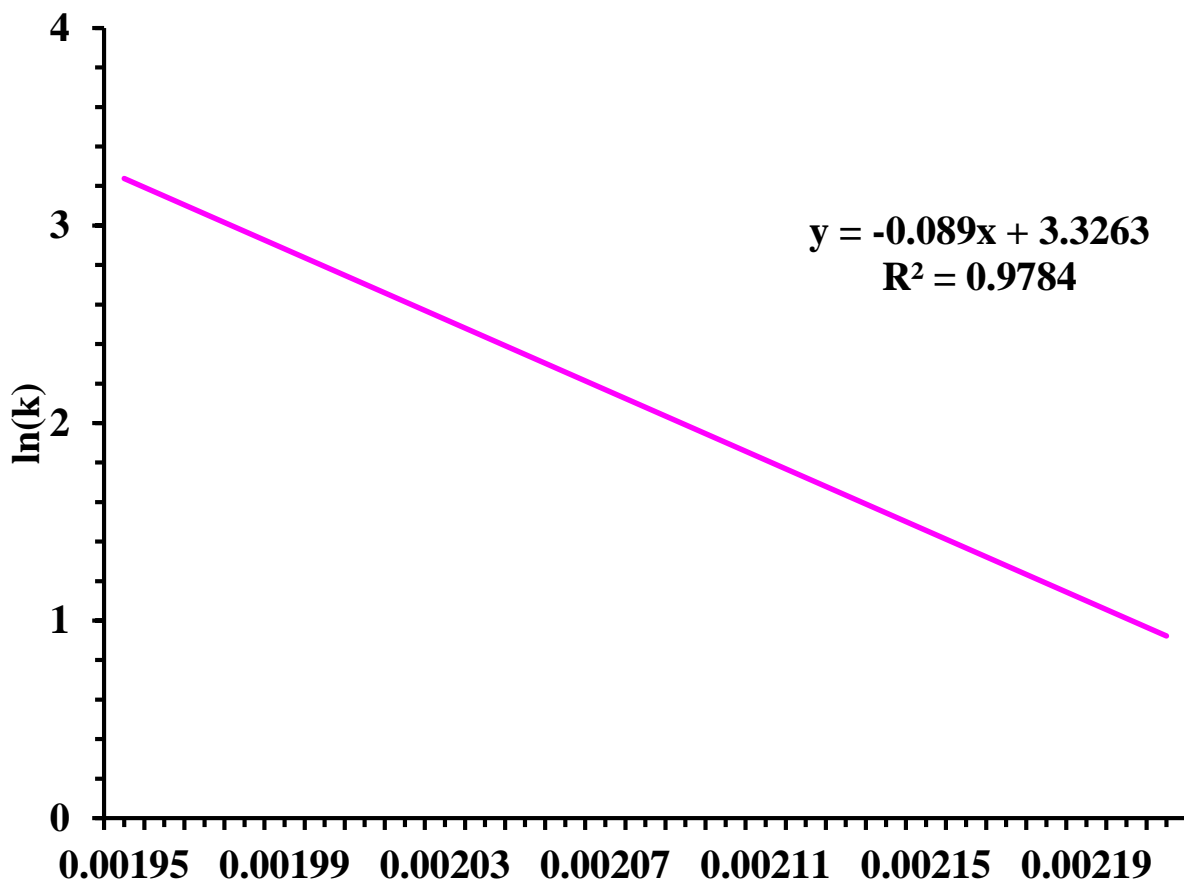


Figura - 1. Dependence of the rate constant on temperature. R=2.0 MPa, space velocity 200 h<sup>-1</sup>

**Conclusion.** The calculated values of the constants are given in tables 5 and 6. The spread of values is very large and the rate constant decreases with increasing pressure. Moreover, the values differ greatly from those obtained at the same temperature but at atmospheric pressure (Table 1).  $W_{CO} = k'_{CO}P_{H_2}$  This means that the accepted kinetic model is inadequate 6.

#### LITERATURE

1. Брагинский О.Б. Нефтехимический комплекс мира. М.: Academia, 2009. 800 с.
2. Hajjar Z., Khodadadi A., Mortazavi Y., Tayyebi S., Soltanali S. // Fuel. 2016. V. 179. P.79.
3. Kolesnichenko N.V., Kolesnikova E.E., Kitaev L.E., Biryukova E.N., Trukhmanova N.I., Khadzhiev S.N. //Petrol. Chemistry. 2012. V. 52. № 3. P. 155.
4. Khadzhiev S.N., Kolesnichenko N.V., Ezhova N.N. //Petrol. Chemistry. V. 48. № 5. P. 325.
5. Tamm S., Ingelsten H.H., Skoglundh M., Palmqvist A.E.C. //J. of Catalysis. 2010. V. 276. P. 402.
6. Миначев Х.М., Дергачев А.А. //Изв. АН СССР. Сер.Хим. 1993. № 6. С. 1018.
7. Seddon D. // Catal. Today. 1998. № 6. P. 351.
8. Choudhary V.R., Banerjee S., Devadas P. // J. Catal.2002. № 2. V. 205. P. 398.
9. Dmitriev R.V., Shevchenko D.P., Shpiro E.S, Dergachev A.A.,Tkachenko O.P., Minachev Kh.M. // Stud. Surf. Sci.Catal. 1991. V. 69. P. 381.
10. Freeman D., Wells R.P.K., Hutschings G.J. // J. Catal.2002. V. 205. № 2. P. 358.
11. Kolesnichenko N.V., Goryainova T.I., Biryukova E.N.,Yashina O.V., Khadzhiev S.N. // Petrol. Chemistry. 2011. V. 51. № 1. P. 55.
12. Mikhailov M.N., Kazansky V.B., Kustov L.M. // Catal.Lett. 2007. V. 116. P. 81.

13. Zhidomirov G.M., Shubin A.A., Kazansky V.B., VanSanten R.A. // Theoret. Chem. Account. 2005. V. 114.P. 90.
14. Borman S. // Chem. and Eng. News. 2005. V. 83. P. 15.
15. Stewart E. A., Johnson D.W., Shannon M.D. // Innovation in Zeolite Materials Science. 1988. V. 37. P. 57.
16. Vosmerikova L.N., Vagin A.I., Vosmerikov A.V. // Nefteper. iNeftehim. 2002. V. 2. P. 27.
17. Kubasov A.A., Kitaev L.E., Malyshev S.V., Novakovskaya Yu.V. // Vest. Mosk. Univer. Khim. 2010. V. 51.P. 339.
18. Aslanov, S.C., Buxorov, A.Q., Fayzullayev, N.I. Catalytic synthesis of C<sub>2</sub>-C<sub>4</sub>-alkenes from dimethyl ether// International Journal of Engineering Trends and Technology, 2021, 69(4), стр. 67–75
19. FN Temirov, J KhKhamroyev, NI Fayzullayev, G ShHaydarov and M KhJalilov. Hydrothermal synthesis of zeolite HSZ-30 based on kaolin //IOP Conference Series: Earth and Environmental Science. – IOP Publishing, 2021. – Т. 839. – №. 4. – С. 042099.
20. Khamroyev, J.K., Akmalaiuly, K., Fayzullayev, N. Mechanical activation of navbahorsk bentonite and its textural and adsorption characteristics//News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences, 2022, 1(451), стр. 167–174.
21. Xolmirzayeva H. N., Fayzullayev N. I. Obtaining Nanocarbon from Local Raw Materials and Studying Its Textural and Sorption Properties //International Journal of Engineering Trends and Technology, 2022 Volume 70 Issue 2, 163-171. ISSN: 2231 – 5381 /doi:10.14445/22315381/IJETT-V70I2P219
22. Buronov F., Fayzullayev N. Synthesis and application of high silicon zeolites from natural sources //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – Т. 2432. – №. 1. – С. 050004.
23. Bukhorov A. Q., Aslanov S. C., Fayzullaev N. I. Catalyst deactivation in synthesis of olefins below methanol //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – Т. 2432. – №. 1. – С. 050010.
24. Bukhorov A. Q., Aslanov S. C., Fayzullaev N. I. Conversion of dimethyl ether to lower olefines //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – Т. 2432. – №. 1. – С. 050011.
25. Bukhorov A. Q., Aslanov S. C., Fayzullaev N. I. Kinetic laws of dimethyl ether synthesis in synthesis gas //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – Т. 2432. – №. 1. – С. 050012.
26. Musulmonov N. X., Fayzullaev N. I. Textural characteristics of zinc acetate catalyst //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – Т. 2432. – №. 1. – С. 050015.
27. Bukhorov A. Q., Aslanov S. C., Fayzullaev N. I. Direct extraction of dimethyl ether from synthesis gas //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – Т.2432. – №. 1. – С. 050013.
28. Куйбокаров, О. Э., Бозоров, О. Н., Файзуллаев, Н. И., & Хайдаров, О. У. У. (2021). Синтез высокомолекулярных углеродов из синтетического газа при участии со-fe-ni-zro<sub>2</sub>/вкц (верхний крымский цеолит). *Universum: технические науки*, (12-4 (93)), 72-79.
29. Куйбокаров, О. Э., Бозоров, О. Н., Файзуллаев, Н. И., & Нуруллаев, А. Ф. У. (2022). Каталитический синтез высокомолекулярных углеводородов из синтез-газа в полифункциональном катализаторе. *Universum: технические науки*, (1-2 (94)), 93-103.
30. Куйбокаров, О., Бозоров, О., Файзуллаев, Н., Хайитов, Ж., & Худойбердиев, И. А. (2022, June). Кобальтовые катализаторы синтеза Фишера-Тропша, нанесенные на Al<sub>2</sub>O<sub>3</sub> различных полиморфных модификаций. In *E ConferenceZone* (pp. 349-351).

31.Қуйбоқаров, О. Э., Шобердиев, О. А., Рахматуллаев, К. С., &Муродуллаева, Ш. (2022). Полиоксидные катализаторы переработки метанав синтез газ. *Central Asian Research Journal for Interdisciplinary Studies (CARJIS)*, 2(5), 679-685.