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*Дослідження кінетики процесу Фішера-Тропша є досить важливим завданням, так як даний процес дуже чутливий до температурного режиму, та характеристик каталізатору. Також даний процес супроводжується багатьма побічними реакціями, які негативно впливають на швидкість та селективність реакції. Синтез Фішера-Тропша є альтернативним джерелом отримання якісного палива не з нафти, а з вугілля або біомаси. Тому дослідження кінетики реакції Фішера-Тропша спрямовані на підвищення селективності і активності каталізаторів, визначення констант швидкості хімічних реакцій є актуальними.*

*Вибір каталізатору є одним з основних факторів, що впливають на якість і вихід продукту по синтезу Фішера-Тропша. Для дослідів виготовлено два зразки кобальтових каталізаторів. Перший зразок каталізатору Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> містить наночистинки кобальту одного розміру. Другий зразок каталізатору (Co)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> отриманий методом просочення носія розчином нітрату кобальту. Каталізатор отриманий методом просочення (Co)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> виявив на порядок вищу активність в порівнянні з монодисперсним. Однак монодисперсний каталізатор показав високу селективність за нижчими вуглеводнями.*

*Для розрахунку кінетики процесу Фішера-Тропша та для знаходження констант швидкості реакцій, було створено програмний модуль, який розроблявся в середовищі MS Visual Studio 2017 на мові C# з використанням технологій .NET Framework v4.6. За допомогою розробленого програмного модуля було розраховано константи швидкості реакції процесу Фішера-Тропша. Проаналізувавши отримані дані, видно, що відносна похибка лежить в межах 2...3 %, що свідчить про адекватність запропонованої моделі розв'язку зворотної задачі хімічної кінетики. Тому можна засвідчити, що дану модель розрахунку констант швидкості можна використовувати для дослідження процесу Фішера-Тропша*

*Ключові слова: реакція Фішера-Тропша, кобальтовий каталізатор, зворотна задача кінетики, константа швидкості*

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# MATHEMATICAL MODEL OF OBTAINING A HYDROCARBON FUEL BASED ON THE FISCHER-TROPSCH PATHWAY IN A STATIONARY LAYER OF THE COBALT-BASED CATALYST

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## 1. Introduction

At present, the processes for obtaining a synthetic liquid fuel from gases that contain a mixture of carbon monoxide and hydrogen include the Fischer-Tropsch process (FT-synthesis) [14]. The FT-synthesis is an alternative source for obtaining high-quality fuel from coal or biomass, rather than petroleum.

Given a decrease in the oil stocks in the world, mankind has begun to look for alternative sources in order to obtain fuel whose production volumes grow every year. Conversion

of synthesis-gas to liquid hydrocarbons using the Fischer-Tropsch process (FT-synthesis) [1–4] is an alternative technique for obtaining the motor fuel.

The Fischer-Tropsch synthesis is an important technology, aimed at converting coal, natural gas, or biomass, into valuable products, such as motor fuels or raw materials for petrochemicals [1, 3]. The process is named after Franz Fischer and Hans Tropsch [3, 4], who showed the possibility of this reaction in 1923, by converting a mixture of carbon monoxide and hydrogen into hydrocarbons using an iron catalyst.

Even though almost hundred years have passed since the discovery, a given method of production of synthetic hydrocarbons has been attracting the attention of researchers and engineers due to the possibility of obtaining motor fuels and valuable petrochemical products.

Studying the kinetics of the Fischer-Tropsch process is a very important task, as a given process is very sensitive to a temperature mode, as well as characteristics of the catalyst. In addition, this process is accompanied by many side reactions that negatively affect the rate and selectivity of the reaction. Therefore, studies into FT-synthesis, aimed at enhancing the selectivity and activity of catalysts, determining the rate constants of chemical reactions, are relevant.

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## 2. Literature review and problem statement

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The Fischer-Tropsch synthesis is a chemical process in which carbon monoxide CO and hydrogen H<sub>2</sub> are converted into different liquid hydrocarbons in the presence of a catalyst. The most commonly used catalysts contain iron and cobalt [5, 6]. The FT-synthesis is a heterogeneous-catalytic process that proceeds with a release of huge amount of heat. The reactions proceed, depending on the catalyst used in the process, at atmospheric or high pressure in the temperature range of 160...375 °C [3, 6, 7]. The FT-synthesis is an important industrial process for converting the synthetic gas (H<sub>2</sub>/CO) derived from carbon sources, such as coal, peat, biomass, and natural gas, into the oxygen-saturated hydrocarbons [1, 2].

The product of the FT-synthesis is a complex multi-component mixture of linear and branched hydrocarbons and oxygen-containing compounds. The fuel, which is produced by the synthesis, is of high quality and it contains no sulfur. Significant progress has been made over the past two decades in the development of more active and selective catalysts of cobalt, iron, and many other effective technologies, modernizing the reactor and the process.

The choice of the catalyst is one of the main factors that affect the quality and output of the product obtained using the FT-synthesis. The issue of the selection of the optimal catalyst for conducting the process is fundamental in the study of the Fischer-Tropsch process.

It is shown that the best catalysts for the FT-synthesis are those catalysts that are based on ferrum and cobalt [6, 8–12, 15]. Paper [10] compares these catalysts. Cobalt catalysts are used at lower temperatures than the catalysts based on iron. Using other metals as catalysts, such as nickel, leads to the formation of toxic compounds. Cobalt catalysts slow down side reactions in the FT-synthesis, while using the catalysts based on ferrum leads to that there is always a reaction that forms water vapor. The activity of the catalysts is affected by the chemical nature of the substance (a carrier), upon which the catalyst is applied, surface and porous structure of the carrier.

In paper [13], authors conducted a kinetic study into and modeling of the Fischer-Tropsch process on a ferrum-catalyst. They investigated the mechanisms of formation of products from CH<sub>4</sub> to C<sub>n</sub>H<sub>2n+2</sub>. However, as noted, the Fischer-Tropsch process on the ferrum-containing catalysts proceeds at higher temperatures, by 50...150 degrees. In addition, in parallel to the main reaction, there is an intensive side reaction that converts water vapor. That leads to inhibiting the primary reaction of the FT-synthesis.

Cobalt is one of the most active metals for the FT synthesis. However, the activity of the cobalt catalyst is influenced

by many factors related to both the preparation of the catalyst and the process parameters.

Papers [7, 14, 16, 18] described mathematical models for the kinetic studies into the FT-synthesis without solving a problem on finding the kinetic constants.

The implementation of the FT-synthesis process is carried out in chemical reactors with a motionless or condensed layer of a catalyst [1, 8, 14]. However, the papers cited lack the mathematical models applicable for calculating or controlling these reactors.

Special attention should be paid to paper [14], which employs a microreactor for the FT-synthesis.

The papers reviewed [8–15] lack solutions to the problems on calculating the kinetic constants for the Fischer-Tropsch synthesis. Finding the rate constants for chemical reactions or solving the inverse problem of chemical kinetics is a non-trivial task [19, 20]. And since the Fischer-Tropsch process is a complex process, which lacks a model to search for the reaction rate constants, it was decided to find and suggest a solution to searching for the reaction rate constants of a given process.

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## 3. The aim and objectives of the study

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The aim of this work is to calculate rate constants for a system of the Fischer-Tropsch reactions in the presence of heterogeneous catalysts based on the obtained experimental data. That would make it possible to pass over to modeling and calculation of industrial reactors with both a stationary layer of catalyst and reactors of more sophisticated designs. For the already existing reactors, the constructed mathematical models could enable the optimal control.

To accomplish the aim, the following tasks have been set:

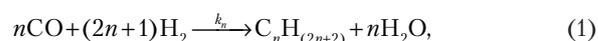
- to analyze theoretically a mathematical model of the kinetics of the Fischer-Tropsch reaction;
- to study experimentally the Fischer-Tropsch process;
- to construct a mathematical model for the kinetics of the heterogeneous catalytic Fischer-Tropsch process and a build a calculation scheme of the reaction rate constants;
- to process the obtained experimental data using the developed software and to calculate reaction rate constants for the Fischer-Tropsch process.

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## 4. Theoretical analysis of the mathematical model for the kinetics of the Fischer-Tropsch reaction

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The Fischer-Tropsch process on cobalt catalysts in the general case is described by the following summarizing equation:



where  $k_n$  is the rate constant of the  $n$ -th reaction,  $n=1, 2, 3, \dots, 7$  is the number of the examined reactions.

The experimental setup has a reactor of small size, with a very small amount of the catalyst, sprayed on the carrier; the result implies that the reactor produces little hydrocarbon products. Consequently, we can accept following assumptions for our calculations:

- constant temperature was maintained in the reactor, it should be noted that the reactor operates under isothermal mode, that is

$$T = \text{const};$$

$$dT/d\tau = 0;$$

– pressure in the reactor was 1 atm, it was maintained at a given level, one can note that pressure did not change over time as well, that is

$$P = \text{const};$$

$$dP/d\tau = 0;$$

– the concentrations of CO and H<sub>2</sub> are in great excess and remain nearly unchanged over time, that is,

$$C_{CO} = \text{const};$$

$$dC_{CO}/d\tau = 0;$$

$$C_{H_2} = \text{const};$$

$$dC_{H_2}/d\tau = 0.$$

The rate of hydrocarbon formation in the system is expressed by the following formula:

$$W_{C_n H_{(2n+2)}} = \frac{dC_{C_n H_{(2n+2)}}}{d\tau} = k_n C_{CO}^n C_{H_2}^{(2n+1)}. \quad (2)$$

For convenience, we denote the concentrations of the reaction products based on the number of hydrocarbons in the chain: C<sub>1</sub> – C<sub>CH<sub>4</sub></sub>; C<sub>2</sub> – C<sub>C<sub>2</sub>H<sub>6</sub></sub>; ...; C<sub>n</sub> – C<sub>C<sub>n</sub>H<sub>(2n+2)</sub></sub>. Then the reaction rate can be expressed by the following formula:

$$W_n = \frac{dC_n}{d\tau} = k_n C_{CO}^n C_{H_2}^{(2n+1)}. \quad (3)$$

Substitute the derivative from the product concentration over time with the finite differences:

$$\frac{dC_n}{d\tau} = \frac{\Delta C_n}{\Delta \tau} = \frac{C_{n_i} - C_{n_{i-1}}}{\tau_i - \tau_{i-1}}, \quad (4)$$

where C<sub>n<sub>i</sub></sub>, C<sub>n<sub>i-1</sub></sub> are the values of concentration of hydrocarbon components n at respective time τ<sub>i</sub>, τ<sub>i-1</sub>.

Thus, we derive a formula to calculate the concentration of components based on the time of reaction:

$$C_{n_i} = C_{n_{i-1}} + k_n * C_{CO}^n * C_{H_2}^{(2n+1)} * (\tau_i - \tau_{i-1}). \quad (5)$$

Taking into consideration that the concentrations of CO and H<sub>2</sub> are taken in great excess, and remain almost unchanged over time, we can calculate the rate constant for each reaction from the following formula:

$$\ln(W_n) = \ln(k_n) + n * \ln(C_{CO}) + (2n + 1) * \ln(C_{H_2}). \quad (6)$$

Hence:

$$k_n = e^{\ln(W_n) - n * \ln(C_{CO}) - (2n+1) * \ln(C_{H_2})} \quad (7)$$

or

$$k_n = \frac{e^{\ln(W_n)}}{e^{n * \ln(C_{CO})} * e^{(2n+1) * \ln(C_{H_2})}}. \quad (8)$$

To calculate the quantity of reaction products, we shall write down the balance for the amount of substances, which enter the reactor, and which exit the reactor:

– entering the reactor:

$$N^0 = N^0_{CO} + N^0_{H_2}; \quad (9)$$

– exiting the reactor:

$$N = N_{CO} + N_{H_2} + N_{H_2O} + \sum N_{C_n}. \quad (10)$$

Based on the system of equations for reaction (1), we shall record the amount of CO, H<sub>2</sub> and H<sub>2</sub>O substances, following the reaction:

$$N_{CO} = N^0_{CO} - \sum_{n=1}^7 n N_{C_n}, \quad (11)$$

$$N_{H_2} = N^0_{H_2} - \sum_{n=1}^7 (2n + 1) N_{C_n}, \quad (12)$$

$$N_{H_2O} = \sum_{n=1}^7 n N_{C_n}. \quad (13)$$

Substituting equations (11) to (13) into equation (10), we obtain:

$$N = N^0_{CO} + N^0_{H_2} - \sum_{n=1}^7 2n N_{C_n}. \quad (14)$$

Next, by substituting (9) and (11) into (14), we obtain:

$$N = N^0 + 2n N_{CO} - 2n N^0_{CO}. \quad (15)$$

The volume of CO, H<sub>2</sub> and C<sub>1</sub> after reaction is derived from the experimentally found LHM chromatogram, by finding the area of peaks that correspond to the given substances. Knowing the amounts of these substances, one can find the volumetric concentrations from formulae:

$$g_{CO} = \frac{V_{CO}}{V_p} = \frac{N_{CO}}{N}, \quad (16)$$

$$g_{H_2} = \frac{V_{H_2}}{V_p} = \frac{N_{H_2}}{N}, \quad (17)$$

$$g_{C_1} = \frac{V_{C_1}}{V_p} = \frac{N_{C_1}}{N}, \quad (18)$$

where V<sub>p</sub> is the volume of loop for the sample at the LHM chromatograph; V<sub>CO</sub>, V<sub>H<sub>2</sub></sub>, V<sub>C<sub>1</sub></sub> are the volumes of CO, H<sub>2</sub> and CH<sub>4</sub>, respectively.

We find from formulae (16) to (18):

$$N_{CO} = g_{CO} * N, \quad (19)$$

$$N_{H_2} = g_{H_2} * N, \quad (20)$$

$$N_{C_1} = g_{C_1} * N. \quad (21)$$

Substituting equation (19) into equation (15), we obtain:

$$N = N^0 + 2n * g_{CO} * N - 2n * N^0_{CO},$$

or, after transforms:

$$N = \frac{N^0 - 2n * N_{CO}^0}{1 - 2n * g_{CO}} \quad (22)$$

Thus, by finding the total amount of a substance after the reaction, one can calculate the amount of formed methane from formula (21).

## 5. Experimental study of the Fischer-Tropsch process

The purpose of the experimental research was to study the Fischer-Tropsch process and to obtain data for the further research into the kinetics of the process and calculation of rate constants for the process (solving an inverse problem of chemical kinetics).

We studied the reaction at the installation using a reactor of the flow-through type with a fixed layer of the catalyst (Fig. 1). This is a metallic reactor with a volume of 2 ml. Hydrogen was additionally purified from the traces of oxygen on the industrial catalyst Ni/Cr at  $T=300$  °C, and of water – on zeolite NaA.

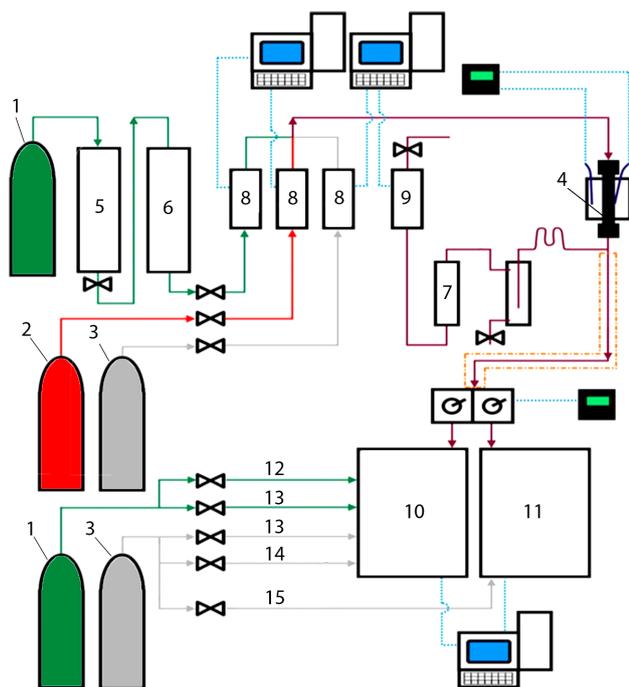


Fig. 1. Experimental installation. Feed cylinders: 1 – H<sub>2</sub>, 2 – CO, 3 – Ar; 4 – reactor; filters: 5 – Ni/Cr, 6 – CaA, 7 – SiO<sub>2</sub>; 8 – flow regulators El-Flow; 9 – pressure regulator El-Press; 10 – Selmi, 11 – LHM; feed flows: 12 – Selmi detector, 13 – Selmi carrier; 14 – Selmi blower; 15 – LHM carrier

The supply of gases was controlled by mass controllers: for CO, H<sub>2</sub> and Ar – model F-211CV-AAD-22-V (Bronkhorst High-Tech B. V.). Pressure in the installation was controlled and maintained using the digital pressure sensor P-502-C-100A-AAD (Bronkhorst High-Tech B. V.).

To analyze reaction products, the reaction mixture after the reactor was throttled using a heated valve to the atmospheric pressure; next, through two consistently connected six-way valve-dispensers, the gas samples were taken for chromatographic analysis.

Analysis of a gas mixture at the inlet to the laboratory reactor was run at LHM chromatograph. Analysis of the organic products of the vapor-gas phase reaction was performed at the chromatograph SelmiKhrom-1.

The purpose of the first experiment was to study the influence of the method for preparing the cobalt catalysts of carbon monoxide hydrogenation in the process of FS-synthesis for activity and selectivity of catalysts at elevated pressures. We used the industrial sample of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as carriers.

Two samples of cobalt catalysts were fabricated for the experiments. The first sample of the catalyst Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> contains cobalt nanoparticles of the same size. The second sample of the catalyst (Co)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was obtained by applying the method of impregnating the carrier with the solution of cobalt nitrate.

Monodispersed cobalt nanoparticles (a diameter of particles of 6.5 nm) were obtained by decomposing cobalt (II) oleate in dibenzyl ether. Photographs of the catalyst and the size distribution of Co particles are shown in Fig. 2, 3.

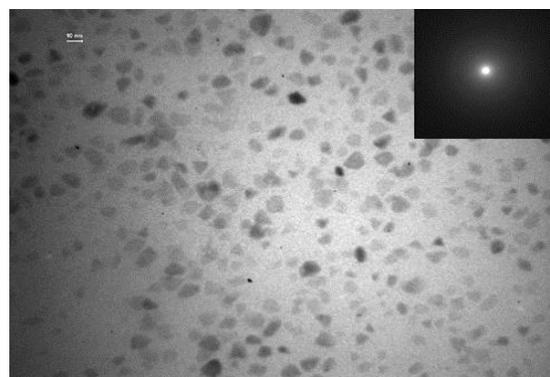


Fig. 2. Photographs of cobalt particles from a microscope

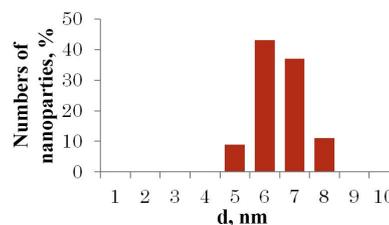


Fig. 3. Size distribution of Co particles depending on size

All catalysts contained cobalt in the amount of 3 % by weight.

### Preparation of catalyst.

1. *The synthesis of cobalt nanoparticles.* We first synthesize cobalt (II) oleate. To this end, the three-headed reactor with a capacity of 1 l, installed in a water bath, is connected to the cylinder with argon and is equipped with a stirrer with a top drive and an air refrigerator. Water bath is used for heating. We first dissolve in 100 ml of the deionized water 8.7 g of cobalt (II) nitrate; 4.8 g (5.45 ml) of 25 % ammonia solution are separately dissolved in 100 ml of the deionized water. The resulting solutions are placed into the reactor with the agitation switched on; a suspension of cobalt (II) hydroxide is obtained. The resulting suspension of cobalt (II) hydroxide is added with 2 g (2.23 ml) of oleic acid and 200 ml of octadecene. Next, we open the flow of argon and heat the water bath to the boiling point of water. Under such conditions, the reaction mixture is aged for 30 min. Thus,

the cobalt oleate forms, which passes into the organic phase of octadecene.

Upon completion of the reaction, the contents of the flask are transferred to a separating funnel; we select the organic phase, washing it with distilled water.

**2. Obtaining Co nanoparticles.** The installation for obtaining the nanoparticles of cobalt oleate consists of the reactor with a capacity of 500 ml, a flask heater, a cylinder for argon, two consistently connected air coolers and a stirrer with a top drive.

The resulting solution of cobalt oleate is taken to the reactor with a capacity of 500 ml. The reactor is mounted onto the heater; a cylinder with argon is connected; two consistently connected air coolers and a stirrer with a top drive are added. We heat the flask to 100 °C and age at such a temperature for 60 min in order to evaporate residues of the water phase. Next, we intensify the heating and bring octadecene to a boiling point (270 °C). The reaction mixture is aged for 5 hours under such a temperature.

After five hours from the start of octadecene boiling, the heating is switched off to allow the reaction mixture to cool. Then the contents of the flask, where cobalt nanoparticles have already formed, are taken to the centrifuge tubes (2 ml per a tube), adding the excessive ethanol as an extractant. The mixture is agitated and centrifuged until the nanoparticles are deposited. Next, the supernatant is decanted while the solid residue in each tube is dispersed into hexane (2 ml of hexane per each tube). The hexane is again added with an excess of alcohol, we agitate and centrifuge it. The top layer of the solvent is decanted; this operation is repeated three times. After that, the solid residue is dispersed into hexane, it is taken to the measuring beaker, then we add hexane to the volume of 100 ml.

**3. Obtaining 3 % Co on aluminum oxide.** First, we prepare 10 g of the carrier with a fraction size of 1–2 mm by shredding the granules and sifting at the sieves.

To prepare 10 g of the catalyst containing Co in the amount of 3 % by weight, granules in the amount of 9.7 g are put into a weighing bottle; we add, in parts, the prepared suspension of nanoparticles, or a solution of salt depending on the moisture capacity of the carrier. The catalyst is shaken periodically and kept in a closed weighing bottle for 24 hours. Next, the catalyst is dried for 16 hours at 40 °C. These operations are repeated until the content of Co on the carrier reaches 0.3 g. The resulting catalyst is placed in a porcelain cup, put in a muffle, and baked for 6 hours at 320 °C.

#### Conditions for conducting the experiment.

The batch of catalysts was 0.5 g. Prior to the experiment, the catalysts were reduced in two stages.

Reduction conditions for the first stage: temperature – 280 °C; time<sub>2</sub> – 60 min.; gas flow rate – 30 cm<sup>3</sup>/min; gas mixture – H<sub>2</sub> (5 % by volume) + Ar (95 % by volume); pressure – atmospheric.

Reduction conditions for the second stage, which took place directly after the first: temperature – 320 °C; time – 90 min.; gas flow rate – 30 cm<sup>3</sup>/min; gas mixture – H<sub>2</sub> (5 % by volume) + Ar (95 % by volume).

Conditions for conducting the experiment: the temperature varied (190 °C, 215 °C, 240 °C); time – 60 min.;

gas flow rate – 30 cm<sup>3</sup>/min; gas mixture – H<sub>2</sub>/CO=2.5; pressure – 30 bars.

The result of our study is the obtained dependence of the catalyst activity (per a gram of the product formed per a gram of the catalyst per second) on temperature of the course of the reaction (Fig. 4) [21].

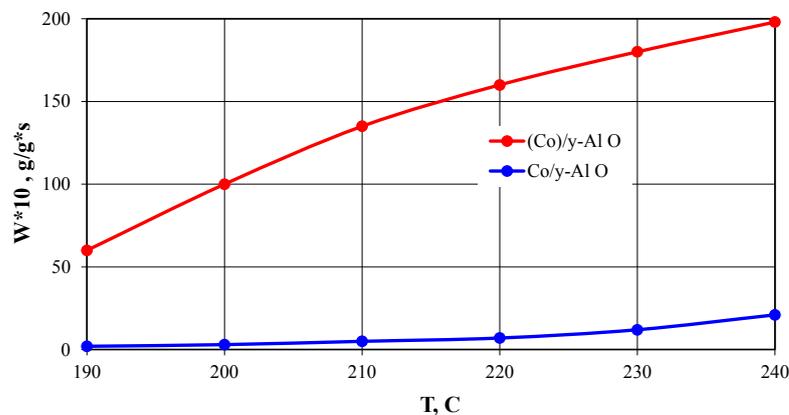


Fig. 4. The catalyst activity dependence on temperature

Fig. 4 shows that the catalyst that was obtained using the method of impregnating (Co)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> demonstrated the activity higher by an order of magnitude compared with the monodispersed one. However, the monodispersed catalyst showed higher selectivity for the lower hydrocarbons.

Compared with the monodispersed catalyst, the catalyst that was obtained using the method of impregnation, demonstrates in the CO hydrogenation reaction the formation of a broad spectrum of hydrocarbons – from C<sub>1</sub> to C<sub>8</sub>. At the same time, the main product of the CO hydrogenation on the monodispersed catalysts was methane.

The purpose of the second experiment was to study the influence of the surface modification of catalyst based on cobalt with the ions of metals, specifically magnesium.

The carrier used was the industrial sample of silica gel KSKG (Coarse Silica gel, Large porosity, Granulated,  $x$ SiO<sub>2</sub>· $n$ H<sub>2</sub>O). The catalyst was obtained using a standard method of impregnating the carrier with a water solution of cobalt nitrate in which the active phase are the particles of polydispersed cobalt.

#### Preparation of the catalyst.

Spherical KSKG (balls the size of 3–5 mm) with a weight of 590 g is baked in the air at 250 °C for 3 hours. Next, the cooled silica gel is impregnated to a full moisture capacity with a water solution of magnesium nitrate (110 g of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O+385 g of distilled H<sub>2</sub>O). Impregnation was performed at a room temperature with intensive agitation. Next, it was air dried at 150 °C for 8 hours.

The drying was followed by the calcination in the air at 350 °C (10 hours). The cooled baked catalyst was impregnated to a full moisture capacity with a water solution of cobalt nitrate (930 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O + 380 g of distilled H<sub>2</sub>O) at a room temperature with intensive agitation over 4 hours. The impregnated contact mass was dried in the air at 150 °C, intensely agitating for 8 hours. It was followed by the calcination in the air at 350 °C for 10 hours and cooling in a flow of inert gas (nitrogen, argon) to 260 °C. The catalyst was then reduced with a mixture of argon + hydrogen with a hydrogen content of 3...5 %.

On baking, the catalyst was cooled in a flow of inert gas (nitrogen, argon) to 260 °C. It was then reduced with the

gas mixture Ar+H<sub>2</sub> containing hydrogen in the amount of 3–5 % by volume, increasing the temperature to 350 °C over 14 hours at a volumetric speed of 3–4 thousand h<sup>-1</sup> (about 3,500 l/hour for the reducing mixture).

Next, the reduced catalyst was cooled to room temperature, blown with nitrogen, until the oxygen content at the inlet and outlet was the same (approximately 14 hours).

*Conditions for conducting the experiment.*

We investigate the reaction at the same installation using a reactor of the flow-through type with a fixed layer of the catalyst (Fig. 1).

The batch of catalysts was 0.3 g. Prior to the experiment, the catalyst was also reduced. Conditions for the catalyst reduction: temperature – 350 °C; time – 10 h; gas flow rate – 30 ml/min; composition of the gas mixture: Ar+H<sub>2</sub> with a hydrogen content of 33 % by volume; pressure – 1 bar.

Conditions for conducting the experiment: the temperature varied within 250...300 °C; time – 30 min.; gas flow rate – 40 ml/min; composition of the gas mixture – H<sub>2</sub>:CO=3:1; pressure – 1 bar.

The result of the experiment is the charts acquired from the chromatographs LHM and Selmi, based on which we calculated the amount of hydrocarbon products of the reaction. An example of chromatograms, at a reaction temperature of 300 °C, is shown in Fig. 5, 6.

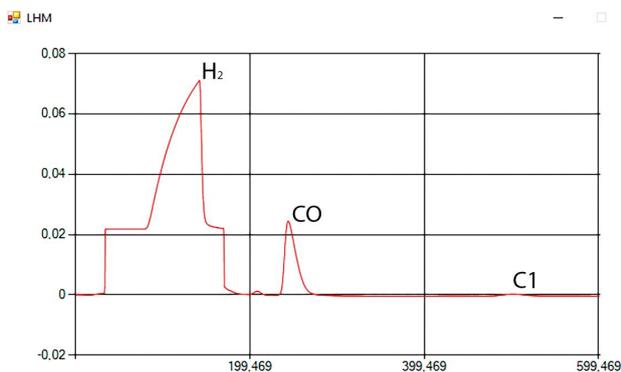


Fig. 5. LHM chromatogram

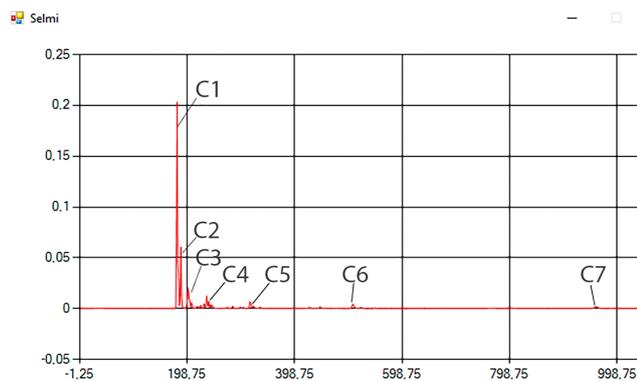


Fig. 6. Selmi chromatogram

Fig. 5 and Fig. 6 show that the result of the reaction is the formed series of hydrocarbon products whose molecules have in their chain from 1 to 7 carbon atoms.

Based on the Selmi chromatograph, the ratios between the obtained hydrocarbon products are directly proportional to the ratio of the areas of peaks that correspond to the given substances (Fig. 6). That is, we shall write for the kinetic system:

$$\frac{S_2}{S_1} = \frac{m_{C_2}}{m_{C_1}}; \frac{S_3}{S_1} = \frac{m_{C_3}}{m_{C_1}}; \dots$$

By finding the mass of C<sub>1</sub> from formula (23), one can find masses of other hydrocarbon reaction products using formula (24):

$$m_{C_1} = N_{C_1} * M_{C_1}, \tag{23}$$

$$m_{C_n} = m_{C_1} * \frac{S_n}{S_1}. \tag{24}$$

Knowing the masses of hydrocarbons, one can find their amount and concentration:

$$N_{C_n} = \frac{m_{C_n}}{M_{C_n}}, \tag{25}$$

$$C_{C_n} = \frac{N_{C_n}}{V_p}. \tag{26}$$

We shall give an example of calculating the amount of reaction products, using the acquired experimental data (Fig. 4, 6) from formulae (16) to (26).

The calculation is conducted under the following conditions of the experiment:

- CO flow rate – 10 ml/min;
- H<sub>2</sub> flow rate – 30 ml/min;
- temperature in the reactor – 300 °C.

Using the LHM chromatogram, we find the amount of CO and CH<sub>4</sub> at the outlet from the experimental reactor. To this end, it is necessary to find the areas of the corresponding peaks from the chart, shown in Fig. 5, and multiply them by a ratio coefficient that shows the connection between a volume of the respective substance and the area of the corresponding peak:

$$V_{CO} = 1.6 \cdot 0.3846 = 0.61538 \text{ ml};$$

$$V_{C_1} = 0.75 \cdot 0.01646 = 0.01235 \text{ ml}.$$

Knowing the volume of CO and CH<sub>4</sub>, we shall find their molar concentrations from formulae (16) and (18):

$$g_{CO} = 0.61538 / 4.5 = 0.13675;$$

$$g_{C_1} = 0.01235 / 4.5 = 0.00274.$$

Next, knowing the amount of substance at the inlet to the reactor, from formula (22), we shall determine the total amount of a substance at the outlet to the reactor:

$$N = (2.009 \cdot 10^{-4} - 2.5 \cdot 0.2 \cdot 10^{-5}) / (1 - 2 \cdot 0.13675) = 1.382 \cdot 10^{-4}.$$

Next, knowing the total amount of a substance at the outlet from the reactor and the molar concentration of CH<sub>4</sub>, we find from formulae (21) and (23) the amount and mass of the formed methane:

$$N_{C_1} = 2.74 \cdot 10^{-4} \cdot 1.382 \cdot 10^{-4} = 3.79 \cdot 10^{-7},$$

$$m_{C_1} = 3.79 \cdot 10^{-7} \cdot 16 = 6.071 \cdot 10^{-6}.$$

The concentration of component C1 derived from formula (26) is equal to:

$$C_{C1} = (3.79 \cdot 10^{-7}) / 0.0045 = 8.432 \cdot 10^{-5}$$

Based on the Selmi chromatogram (Fig. 6), knowing the mass of methane at the outlet from the reactor, and by defining the areas of peaks for the hydrocarbon substances, we shall determine the mass, quantity, and concentration of each component (formulae (24), (25), (26)). The following calculation is only for component C<sub>2</sub>H<sub>6</sub> (C2):

$$m_{C2} = 6.071 \cdot 10^{-6} \cdot (0.11209 / 0.46626) = 1.459 \cdot 10^{-6}$$

$$N_{C2} = (1.459 \cdot 10^{-6}) / 30 = 4.865 \cdot 10^{-8}$$

$$C_{C2} = (4.865 \cdot 10^{-8}) / 0.0045 = 1.081 \cdot 10^{-5}$$

Calculations for all components of the reaction mixture are included in the developed software module. Now, knowing the concentration of reaction products, one can proceed to the calculation of reaction rate constants.

### 6. Calculation of reaction rate constants based on the obtained experimental data

A model of the system of kinetic equations of the Fischer-Tropsch reaction for the derived experimental data and for the calculation of kinetic constants based on formulae (2), (5), (8) is summarized in Table 1.

The Fischer-Tropsch reaction pathway and the calculation of constants

Reaction pathway	Reaction rate	Calculation of reaction rate constant
CO+3H <sub>2</sub> →CH <sub>4</sub> +H <sub>2</sub> O	$W_1 = \frac{dC_{CH_4}}{d\tau} = k_1 C_{CO} C_{H_2}^3$	$k_1 = \frac{\exp(\ln(W_1))}{\exp(\ln(C_{CO})) * \exp(3 \ln(C_{H_2}))}$
2CO+5H <sub>2</sub> →C <sub>2</sub> H <sub>6</sub> +2H <sub>2</sub> O	$W_2 = \frac{dC_{C_2H_6}}{d\tau} = k_2 C_{CO}^2 C_{H_2}^5$	$k_2 = \frac{\exp(\ln(W_2))}{\exp(2 \ln(C_{CO})) * \exp(5 \ln(C_{H_2}))}$
3CO+7H <sub>2</sub> →C <sub>3</sub> H <sub>8</sub> +3H <sub>2</sub> O	$W_3 = \frac{dC_{C_3H_8}}{d\tau} = k_3 C_{CO}^3 C_{H_2}^7$	$k_3 = \frac{\exp(\ln(W_3))}{\exp(3 \ln(C_{CO})) * \exp(7 \ln(C_{H_2}))}$
4CO+9H <sub>2</sub> →C <sub>4</sub> H <sub>10</sub> +4H <sub>2</sub> O	$W_4 = \frac{dC_{C_4H_{10}}}{d\tau} = k_4 C_{CO}^4 C_{H_2}^9$	$k_4 = \frac{\exp(\ln(W_4))}{\exp(4 \ln(C_{CO})) * \exp(9 \ln(C_{H_2}))}$
5CO+9H <sub>2</sub> →C <sub>5</sub> H <sub>12</sub> +5H <sub>2</sub> O	$W_5 = \frac{dC_{C_5H_{12}}}{d\tau} = k_5 C_{CO}^5 C_{H_2}^{11}$	$k_5 = \frac{\exp(\ln(W_5))}{\exp(5 \ln(C_{CO})) * \exp(11 \ln(C_{H_2}))}$
6CO+13H <sub>2</sub> →C <sub>6</sub> H <sub>14</sub> +6H <sub>2</sub> O	$W_6 = \frac{dC_{C_6H_{14}}}{d\tau} = k_6 C_{CO}^6 C_{H_2}^{13}$	$k_6 = \frac{\exp(\ln(W_6))}{\exp(6 \ln(C_{CO})) * \exp(13 \ln(C_{H_2}))}$
7CO+15H <sub>2</sub> →C <sub>7</sub> H <sub>16</sub> +7H <sub>2</sub> O	$W_7 = \frac{dC_{C_7H_{16}}}{d\tau} = k_7 C_{CO}^7 C_{H_2}^{15}$	$k_7 = \frac{\exp(\ln(W_7))}{\exp(7 \ln(C_{CO})) * \exp(15 \ln(C_{H_2}))}$

Knowing the reaction rate constants, one can show the dependence of products concentration on the time of the reaction progress:

$$C_{CH_4} = C_{CH_4_{i-1}} + k_1 \cdot C_{CO}^1 \cdot C_{H_2}^3 \cdot (\tau_i - \tau_{i-1}),$$

$$C_{C_2H_6} = C_{C_2H_6_{i-1}} + k_2 \cdot C_{CO}^2 \cdot C_{H_2}^5 \cdot (\tau_i - \tau_{i-1}),$$

$$C_{C_3H_8} = C_{C_3H_8_{i-1}} + k_3 \cdot C_{CO}^3 \cdot C_{H_2}^7 \cdot (\tau_i - \tau_{i-1}),$$

$$C_{C_4H_{10}} = C_{C_4H_{10_{i-1}}} + k_4 \cdot C_{CO}^4 \cdot C_{H_2}^9 \cdot (\tau_i - \tau_{i-1}),$$

$$C_{C_5H_{12}} = C_{C_5H_{12_{i-1}}} + k_5 \cdot C_{CO}^5 \cdot C_{H_2}^{11} \cdot (\tau_i - \tau_{i-1}),$$

$$C_{C_6H_{14}} = C_{C_6H_{14_{i-1}}} + k_6 \cdot C_{CO}^6 \cdot C_{H_2}^{13} \cdot (\tau_i - \tau_{i-1}),$$

$$C_{C_7H_{16}} = C_{C_7H_{16_{i-1}}} + k_7 \cdot C_{CO}^7 \cdot C_{H_2}^{15} \cdot (\tau_i - \tau_{i-1}).$$

In order to calculate the kinetics of the Fischer Tropsch process and to find the reaction rate constants, we created a software module, which was developed in the programming environment MS Visual Studio 2017 in the programming language C# using the .NET Framework v4.6 technologies [21].

A given software module includes the following components:

- files of forms: *Form1.cs*, *Form2.cs*, *FormGraph.cs*, *FormHelp.cs*;

- project files: *Program.cs*, *Controller.cs*, *Model.cs*, *DB.cs*.

The scheme of interaction between the files and forms is shown in Fig. 7.

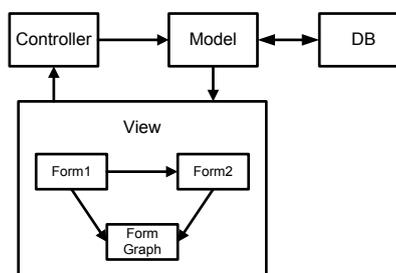


Fig. 7. Scheme of interaction between files and forms of the software module

Table 1

The main elements of the computational module:

- *Form1.cs* – the main form that contains two databases of experimental data acquired from the chromatographs LHM and Selmi, buttons for graphical representation of the recorded chromatograms, fields for entering the flow rates of incoming gases to the system, and a button to launch calculations;

- *Form2.cs* – a form to represent the results of calculations; it contains a table with the results of calculations, a chart that shows the distribution of the formed products, and buttons to graphically represent the solution to a direct problem of chemical kinetics;

- *FormGraph.cs* – a form to graphically display the results of calculations;

- *FormHelp.cs* – a form to display a Help program;

- *Program.cs* – a file class (a file, simply put), which initiates the program;

- *Controller.cs* – a file class, which is designed to link the forms and the file “Model.cs” (or the forms and the class *Model*);

- *Model.cs* – a file class, which keeps records of all the methods, designed for calculations in the program;

- *DB.cs* – a file class, which is designed to read data from TXT files. In addition, it contains certain data for calculations: a volume of the reactor, a loop volume of the chromatograph, the time of substance yield at the chromatograph LHM, and molar masses of the formed hydrocarbons.

A software module is designed to solve a direct and inverse problems of chemical kinetics for the Fischer Tropsch process using different catalysts. The application requires the following data:

- data from the chromatograph LHM;
- data from the chromatograph Selmi;
- flow rates of CO and H<sub>2</sub> at the inlet to the reactor in the dimensionality of ml/min.

Graphical user interface, which opens when downloading the software, is shown in Fig. 8.

Launching the software opens a form that shows the data acquired from the chromatographs LHM and Selmi, tools to change the file with the data acquired from the chromatographs and to display the chromatograms in the graphical form. In addition, this form contains a field for entering the flow rates of CO and H<sub>2</sub> at the inlet to the reactor in the dimensionality of ml/min, and a button that enables the calculation operation.

After pressing the button “Start calculation”, a software module would calculate the amount of the derived hydrocarbon products, concentration, and would determine the reaction rate constants. Next, the program launches the form “Form2” to display the results of calculations (Fig. 9).

The window that appears in the upper left corner displays the calculated amounts of H<sub>2</sub>, CO and CH<sub>4</sub>, at the outlet from the reactor (relative to the loop of the LHM chromatograph, to which, in order to analyze, we take the sample of products formed as a result of the reaction. The total volume of the loop is 4.5 ml). In addition, the window displays molar concentrations of H<sub>2</sub>, CO and CH<sub>4</sub>, calculated per a mole of a substance, per a mole of the total amount of substances that exited the reactor.

In addition, the window displays calculation results on the amount, concentration, and constants of the formation rate of hydrocarbon products in the Fischer-Tropsch process.

The right part of the window that contains results of the calculations shows the distribution diagram of the amount of created hydrocarbon products, depending on the number of carbon atoms in molecules.

In addition, the window with the results of calculations has 2 buttons: “Concentration of reaction products dependent on time”, which opens a window shown in Fig. 10, and “Concentration of CO and H<sub>2</sub> depending on time”, which opens a window shown in Fig. 11.

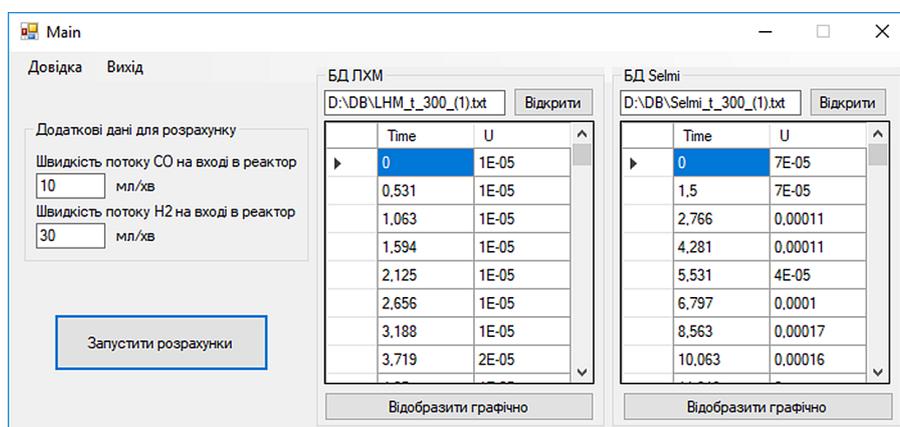


Fig. 8. Main software window

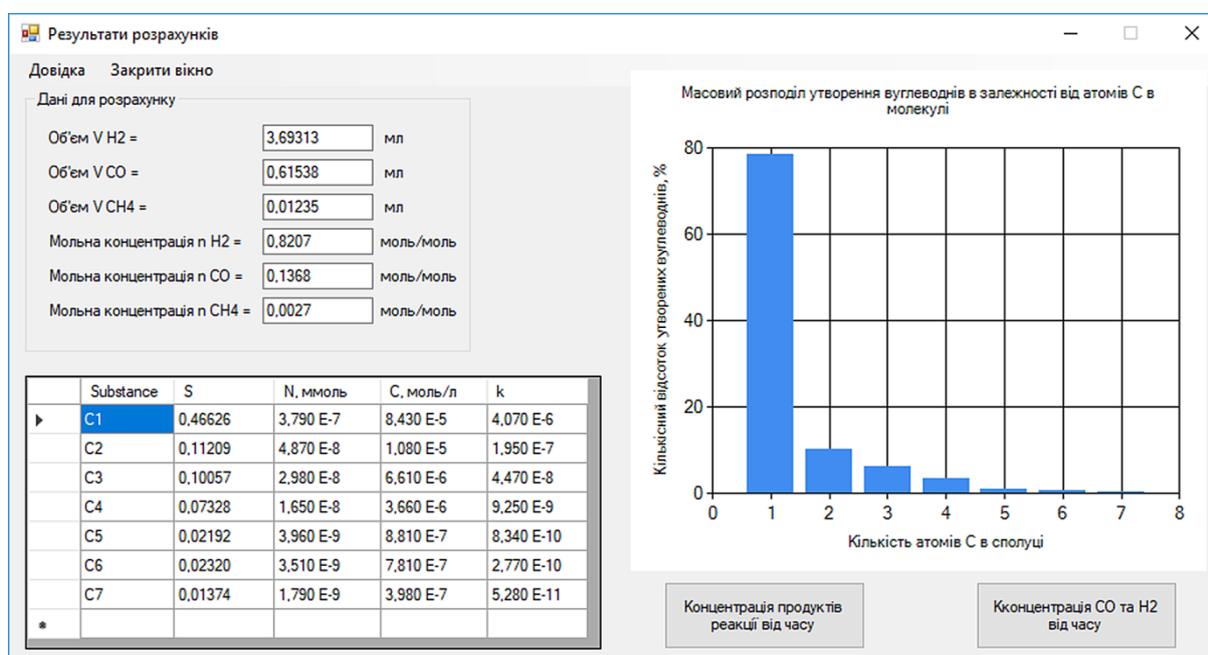


Fig. 9. Window that displays calculation results

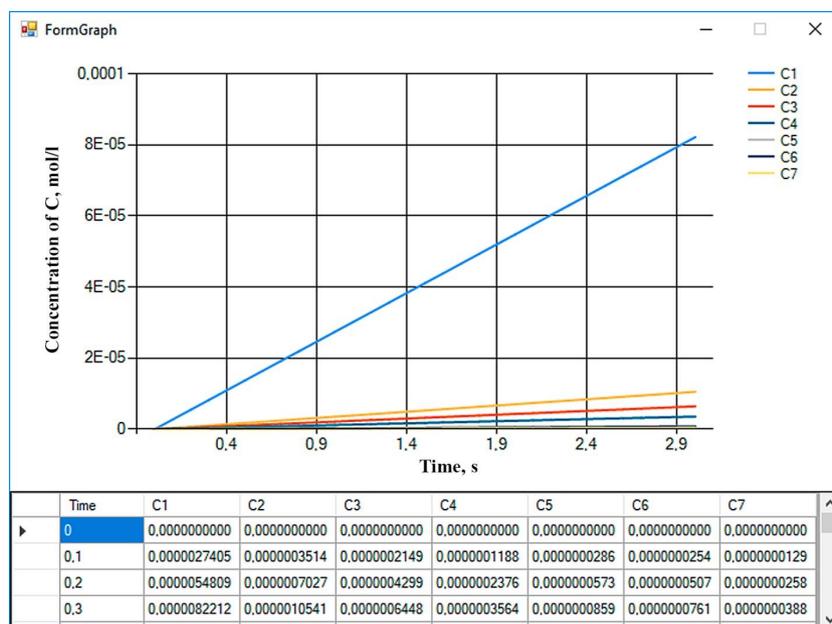


Fig. 10. Dependence of concentration of carbohydrate reaction products on time

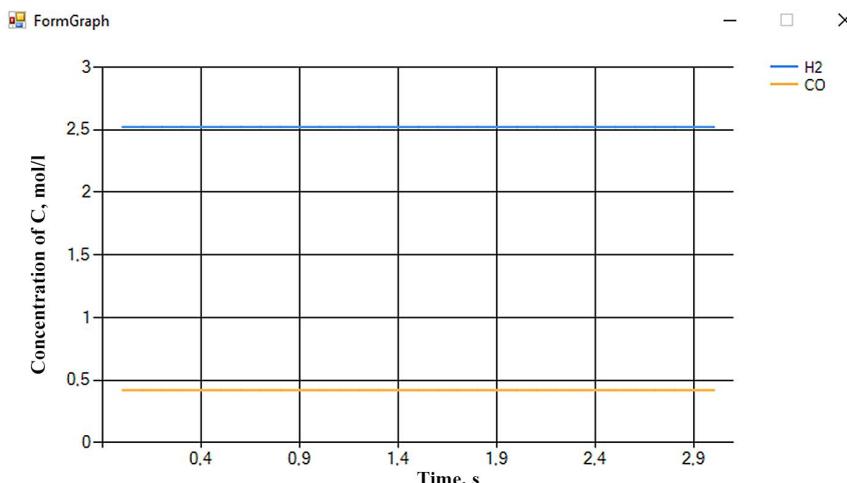


Fig. 11. Dependence of the CO and H<sub>2</sub> concentration on time

The result of the conducted experiments and calculation is the derived values for rate constants under different conditions of conducting the Fischer-Tropsch reaction. Estimation of the adequacy of the data obtained was performed by calculating the relative error  $\epsilon$ .

The first experiment: the flow rate of CO is 10 ml/min; the flow rate of H<sub>2</sub> is 30 ml/min; temperature in the reactor is 300 °C. The results of calculations are given in Table 2.

Table 2

Calculated data for the first experiment

<i>i</i>	$k_i$	$C_i$		Error $\epsilon$ , %
		Experiment	Calculation	
1	4.070E-6	8.43E-05	8.22E-05	2.51
2	1.950E-7	1.08E-05	1.05E-05	2.47
3	4.470E-8	6.61E-06	6.44E-06	2.55
4	9.250E-9	3.66E-06	3.56E-06	2.74
5	8.340E-10	8.81E-07	8.57E-07	2.68
6	2.770E-10	7.81E-07	7.60E-07	2.75
7	5.280E-11	3.98E-07	3.87E-07	2.84

The second experiment: the flow rate of CO is 20 ml/min; the flow rate of H<sub>2</sub> is 60 ml/min; temperature in the reactor is 300 °C. The results of calculations are given in Table 3.

Table 3

Calculated data for the second experiment

<i>i</i>	$k_i$	$C_i$		Error $\epsilon$ , %
		Experiment	Calculation	
1	9.02E-07	3.58E-05	3.49E-05	2.38
2	1.66E-08	3.21E-06	3.13E-06	2.52
3	2.18E-09	2.04E-06	1.99E-06	2.29
4	2.37E-10	1.08E-06	1.06E-06	2.15
5	9.61E-12	2.13E-07	2.08E-07	2.39
6	1.56E-12	1.68E-07	1.64E-07	2.50
7	1.61E-13	8.44E-08	8.22E-08	2.61

The third experiment: the flow rate of CO is 10 ml/min; the flow rate of H<sub>2</sub> is 20 ml/min; temperature in the reactor is 300 °C. The results of calculations are given in Table 4.

Table 4

Calculated data for the third experiment

<i>i</i>	$k_i$	$C_i$		Error $\epsilon$ , %
		Experiment	Calculation	
1	1.820 E-6	3.72E-05	3.63E-05	2.40
2	7.330 E-8	3.95E-06	3.85E-06	2.43
3	1.860 E-8	2.66E-06	2.59E-06	2.63
4	4.150 E-9	1.56E-06	1.52E-06	2.49
5	3.710 E-10	3.69E-07	3.60E-07	2.47
6	1.460 E-10	3.84E-07	3.74E-07	2.55
7	2.720 E-11	1.89E-07	1.84E-07	2.59

The fourth experiment: the flow rate of CO is 10 ml/min; the flow rate of H<sub>2</sub> is 30 ml/min; temperature in the reactor is 250 °C. The results of calculations are given in Table 5.

Table 5

Calculated data for the fourth experiment

<i>i</i>	$k_i$	$C_i$		Error $\epsilon$ , %
		Experiment	Calculation	
1	8.290 E-9	3.08E-07	3.00E-07	2.60
2	2.850 E-10	4.72E-08	4.60E-08	2.54
3	4.410 E-11	3.27E-08	3.19E-08	2.45
4	1.460 E-11	4.84E-08	4.72E-08	2.48
5	6.360 E-13	9.42E-09	9.20E-09	2.34
6	1.260 E-13	8.37E-09	8.20E-09	2.03
7	3.000 E-14	8.87E-09	8.70E-09	1.92

The results of calculations show that the relative error of the calculations is within 2...3 %, indicating the adequacy of the proposed model for calculating the reaction rate constants.

## 7. Discussion of results of using a mathematical model for calculating the rate constants for a system of the Fischer-Tropsch reactions

Using the developed software module, we calculated reaction rate constants of the Fischer-Tropsch process (that is, we resolved the inverse problem of chemical kinetics for the Fischer-Tropsch process), which proceeded in the reactor

under an isothermal mode. In order to analyze and estimate the data obtained, we also solved a direct problem of chemical kinetics.

After analyzing the data acquired, we can see that the relative error is within 2...3 %, indicating the adequacy of the suggested model for solving the inverse problems of chemical kinetics. Therefore, we can attest that a given model for the calculation of rate constants could be used to study the Fischer-Tropsch process.

However, it should also be noted that the calculated values for rate constants will be different for a different quantity (mass or contact area) of the catalyst, which is why further research and description of the Fischer-Tropsch process should take this factor into consideration.

## 8. Conclusions

1. We have analyzed a mathematical model of the Fischer-Tropsch reaction kinetics. To find the rate constants of the Fischer-Tropsch chemical reactions, we constructed dependences for the calculation of constants and developed the algorithm for solving the inverse problem of kinetics. The numerical values for constants that we derived make it possible to pass over to modeling the reactor of the FT-synthesis. To calculate the rate constants, one should know the concentration of the mixture of reaction gases.

2. We studied experimentally, at the laboratory installation, the Fischer-Tropsch process on cobalt catalysts. We acquired the LHM and Selmi chromatograms for calculating the concentrations of a mixture of gases. It is shown that the catalyst, obtained by the method of impregnation, demonstrated a higher activity, larger by an order of magnitude than the monodispersed catalyst.

3. We have developed a software module in the programming environment MS Visual Studio 2017 in the programming language C# using the .NET Framework v4.6 technologies, for calculating the kinetics and for finding the reaction rate constants for the Fischer-Tropsch process.

4. We have calculated rate constants for the Fischer-Tropsch reactions based on data from four experiments at different flow rates of carbon monoxide and hydrogen and different temperature in the reactor. The relative error of calculations is within 2...3 %, indicating the adequacy of the proposed model.

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