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CONVERSION OF SYNTHESIS GAS IN AEROSOL OF FE-CU-K-CATALYST PARTICLES AT PRESSURES OF 0.1–1.0 MPA

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Chemical conversion of synthesis gas to hydrocarbons and other products under the condition of the method known as "aerosol nanocatalysis" has been studied.

A laboratory installation was developed and experimental studies were carried out in the range of process-dependent parameters: pressure from 0.1 to 1.0 MPa, temperature from 483 to 533 K, catalyst concentration from 5 to 25 g/m^3 of reactor volume, and mechanochemical activation intensity from 4, 0 to 11.2 Hz. It was found that an increase in pressure from 0.1 to 1.0 MPa gradually increased the conversion degree from 44.1 % to 56.5. An increase in pressure of the FTS process in conditions of aerosol catalysis from 0.1 to 1.0 MPa contributed to a stable yield growth from 14 to 17 %. Selectivity reached its maximum value of 93.1 % at a pressure of 0.3 MPa. Dependence of selectivity on the catalyst MCA intensity was characterized by the constant growth of selectivity of carbon monoxide conversion to hydrocarbons with an increase in MCA frequency from 4 to 8.5 Hz while maximum selectivity reached 91 %. With a further increase in MCA frequency to 11.2 Hz, a decrease (to 83.5 %) in the value of selectivity of carbon monoxide conversion to hydrocarbon products in the FTS process was observed. Therefore, it was recommended to consider the value of the MCA frequency from 6 to 10 Hz as an acceptable range. Maximum yield (73 wt %) of hydrocarbon fraction with a chain length from 5 to 6 carbon atoms was observed for a pressure of 0.3 Pa. The minimum yield was 35 wt % for a pressure of 1.2 MPa. At other pressure values (0.1–0.2 and 0.4–1.1 MPa) of experimental studies, the yield of this fraction varied within 38–52 wt %. A block diagram of experimental-industrial FTS installation based on principles of aerosol nanocatalysis was offered

Keywords: synthesis gas, aerosol nanocatalysis, mechanochemical activation, synthetic hydrocarbons, production of motor fuels

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1. Introduction

Conversion of synthesis gas (SG) into synthetic hydrocarbon and oxygen-containing compounds (Fischer-Tropsch synthesis, FTS) is the main stage in many technologies of obtaining liquid motor fuels of high quality and environmental friendliness. The obtained synthetic substances can also be used as raw materials for organic synthesis processes. The urgency of the development of industrial FTS based technologies is determined by the need to develop technologies for producing liquid motor fuels from coal, the most common carbon-containing raw material. The use of FTS for working out the technologies of qualified processing of plastics contained in solid waste may also be relevant. The introduction of FTS technologies will make it possible to increase the share of renewable sources of raw materials of biological origin in the energy balance. Relevance of FTS technologies also lies in the need for qualified processing of unconventional carbon-containing resources including associated gases from oil production, waste gases from refineries, oil shale, acid tar, and more.

FTS technologies can help reduce carbon dioxide emissions into the atmosphere. Chemical conversion of carbon dioxide from flue gases of power units into carbon monoxide occurs during contact with solid carbon by the Boudoir reaction. Next, the obtained carbon monoxide is mixed with hydrogen which can be obtained by electrolysis of water using renewable energy sources. This technology will enable obtaining of synthesis gas with minimal involvement of fossil raw materials. These are promising ecology-oriented technologies. Theoretically, emissions from vehicles can also be used as raw materials under the condition of their qualified collection.

Synthesis gas contains almost no sulfur compounds, so motor fuels produced according to the FTS technologies will have improved environmental performance meeting the most stringent standards. The ability to influence the composition of hydrocarbons used in FTS processes will enable obtaining gasoline and diesel fuels with a minimum content of benzene and other aromatic compounds regulated by quality standards.

The development and commercialization of FTS technologies are slowed down by the complexity of catalytic conversion technologies and stringent requirements for the quality of heterogeneous catalysts. Maintaining high activity and selectivity of catalysts for a sufficient period is the current topical task of FTS. The FTS reactions are highly exothermic and maintaining a constant temperature throughout the entire reaction space is a complex and resource-intensive process. The FTS process should be carried out at elevated pressure to intensify heat and mass transfer and increase specific catalyst productivity. Iron-based catalysts are most suitable for the production of motor fuels using STF technologies because they make it possible to obtain hydrocarbons that correspond to synthetic oil by their composition.

The aerosol nanocatalysis (AnC) method can be a real alternative to conventional technologies of heterogeneous catalysis for realizing the FTS reactions. The AnC method is based on creating and maintaining a constant high aerosol activity of 8–100 nm size particles of the catalytically active component. Activity is maintained through continuous mechanochemical activation (MCA) of the catalytically active component by means of a dispersing material at a prescribed intensity. Three methods of dispersing and activating catalysts in AnC have been studied: in a fluidized bed, in vibrofluidized beds of the dispersing material, and in rotating reactors. These methods ensure chemical conversion with reactor productivity exceeding conventional heterogeneous catalysis at aerosol concentrations of the activated catalytically active component 0.1–10 g per cubic meter of the reactor. Such ultra-low concentrations of the required catalyst can significantly reduce its cost which in its turn reduces the production cost. Continuous MCA significantly intensifies the processes of heat and mass transfer and this makes it possible to reduce the temperature gradient in the reaction space and ensure uniformity of raw material concentrations. This significantly improves the catalysis selectivity. The AnC method was used to develop technologies of catalytic oxidation of more than 70 various industrial wastes, processes of thermocatalytic hydrocarbon conversion, processes of steam conversion of raw materials of various types and FTS at atmospheric pressure. All studied processes showed high efficiency due to the application of the AnC method. Therefore, the development of the FTS technology at high pressure using the AnC method is an urgent scientific and practical problem.

2. Literature review and problem statement

The search for rational designs of reactors for high-exothermic conversion, development of process flowsheets, and operating practices with positive economic effects are relevant areas of studying the FTS processes. Atypical raw materials (XTL, anything-to-liquid) are increasingly used in the industrial production of synthetic hydrocarbons.

A review of FTS technologies is given in [1] where special attention is paid to the tendencies of technological development in 2005–2014. General information on the technology of synthetic fuel including the process chemistry, typical solutions on design features of main devices, problems of raw materials, information on catalysts are given. It was shown that modern industrial technologies based on FTS (XTL) significantly differ from those used in the 1st generation of this process in the 1930s and 1940s. The most acute problems of the current, third generation of technologies include high specific capital investment and too wide a range of by-products. New, 4th generation technologies are in the process of transition from experimental to industrial technologies. The goal of the 4th XTL generation developers consisted in the creation of a technology that opens up new possibilities for industrial application through simplicity, compactness, and a radical reduction in specific investment and operating costs.

Philosophy of XTL technologies, analysis of modern production, and consumption of potential sources of raw materials (natural gas, oil, coal, bituminous sands, biomass) for the processes of production of synthetic hydrocarbons were considered thoroughly in [2]. The study presents current data on available sources of these raw materials in the world as well as promising catalysts and promoters of FTS. The study [3] substantiates the feasibility of using coal as a source of synthesis gas. In-depth thermochemical processing of coal to obtain ready-made energy products, substitutes for natural gas, is especially relevant in the context of its ever-increasing prices around the world. A relationship between qualification indicators of coal has been established which makes it possible to predict the chemical activity of coal [4]. Conditions for collecting gases in degassing coal-seams by the average indicator of vitrinite reflection, the yield of volatile substances in the dry ashless state, and thickness of a plastic layer were determined in [5]. Elemental and technical analysis of coal was carried out. It has shown that there is a wide range of changes in the coal-seam moisture and oxygen content in organic matter at the carbon content of up to 75 % indicating slight changes in coal at the early stages of metamorphism [6]. Studies [4–6] expand possibilities of obtaining SG from methane-containing gas from coal of different degrees of metamorphism but there is no information about the calorific value of synthetic natural gas.

Results of experimental studies of the catalytic process of methane oxidation with a wide range of parameter variations such as excess oxidant and temperature are presented in [7]. Based on these results, a mathematical model of the process is proposed which makes it possible, inter alia, to predict the yield of carbon monoxide [8]. Studies [7, 8] can form a basis for technologies of coal gasification through FTS and its subsequent oxidation in catalytic heat generators as an alternative to natural gas to replace it in public utilities. Experience of commercialization of coal gasification technologies in an indirect way is also considered in [3] including the technologies of conventional and plasma gasification. The advantages and disadvantages of these technologies are systematized and a hypothesis is put forward regarding the prospects of plasma coal gasification technology in comparison with conventional analogs based on the Fischer-Tropsch process.

The study [9] considers the dynamics of the development of mini-technologies for processing natural gas into synthetic liquid hydrocarbon products. Such processes can be applied to relatively small hydrocarbon sources. However, the paper does not reveal technological aspects and does not explain how the high activity and selectivity of FTS catalysts can be maintained. Unresolved mechanistic details of monomer formation in FTS and oxygen rejection ways are considered in [10] by combining kinetic and theoretical analyses of elementary steps on representative Fe and CO surfaces saturated with chemisorbed CO. Direct CO dissociation pathways make a small contribution to Fe monomer formation and may be favorable at high temperatures on alkali-stimulated catalysts. The merging of experiment and theory has led to clarification of constant mechanistic issues that have not previously been resolved by separate experimental and theoretical studies.

The current state of the art in the synthesis of soluble Ru, Co, and Fe nanoparticles stabilized by organic molecules is described in [11]. The use of nanocatalysts based on soluble metals in the Fischer-Tropsch reaction using water, ionic liquids and organic solvents with high boiling points is considered. The study shows that it is possible to achieve higher activity and selectivity of catalysis than when using conventional catalysts on the carrier. However, the study does not solve the problem of separating catalysts from the product which is the most relevant and resource-intensive in this type of catalysis.

Technological aspects of the influence of pressure on activity and selectivity of FTS catalysts are considered in [12]. Operating practices that provide high selectivity have been found and the positive effect of pressure increase on specific productivity of the reactor and catalyst have been shown. It is also indicated that the carrier of the heterogeneous catalyst has a negative effect on activity which makes it desirable to implement heterogeneous catalytic conversion on a pure catalytically active component. However, no recommendations were provided on a possible technological design of such a process.

Paper [13] shows the results of FTS studies in a reactor with a stationary layer of Co-containing catalyst (20 % $Co/0.5$ % $Re/\gamma\text{-}Al_2O_3$). It is noted that the process takes place at temperatures of 210 and 230 °C, the ratio of $H_2/CO=2.55–1.12$, and conversion of CO in the range of 15–75 %. Selectivity for C_{5+} is 79–87 %. However, the authors did not sufficiently consider the issue of maintaining constant activity and selectivity of catalysis.

Synthesis of new types of Fe-C-containing nanoparticles (Fe, Fe_5C_2, Fe_3C, and Fe_7C_3) which were tested for activity as catalysts for Fischer-Tropsch synthesis was noted in [14]. The influence of the structure of the created catalysts on their activity was studied on the example of Fischer-Tropsch synthesis. It was found that the structure of Fe_5C_2 nanoparticles has shown activity the highest of the studied catalysts: about $2.3\cdot10^4$ $mol_{CO}/g_{Fe}\cdot s$. However, the process took place in a quartz reactor at 270 °C and pressure of 30 bar. Such a reactor is quite difficult to adapt to the conditions of the industrial production process.

Studies of the creation of an iron-containing catalyst in which iron ions are promoted on the surface of activated carbon (Fe/AC) are described in [15]. The study results show that 0.9 wt % of potassium promoted in the Fe/AC catalyst reduces the production of n-paraffins and olefins with a double bond within the chain, increasing the amount of branched kinds of paraffin and α-olefins. C_{5+} hydrocarbons and $C_2–C_5$ alcohols can be selectively obtained on this catalyst, however, the issues of maintaining activity and selectivity of the catalyst have not been considered.

Study [16] presents a critical review of the production of low molecular weight olefins by the Fischer-Tropsch method. The authors analyze the impact of metals, promoters, and carriers on the process. They note that the process run on the iron-containing catalyst takes place at temperatures of 260–350 °C, the pressure of 1–20 bar, the ratio $H_2/CO=1–3$ and selectivity for $C_2–C_4$ varies from 15 to 55 %. The paper does not consider the possibility of obtaining higher molecular weight olefins that could become components of automotive fuels.

Thus, studies [1–16] reveal a variety of FTS technologies, catalysts, technological operating practices, and types of raw materials. The processes combining within one production technology the conversion of synthesis gas into synthetic hydrocarbons with the formation of catalyst nanoparticles directly in the reaction space during the process (in situ) and maintaining constant high activity and selectivity of such catalysts have not been found in the available literature.

Peculiarities of the process of coal gasification in conditions of aerosol nanocatalysis are studied in [17]. The study [18] reveals the influence of mechanochemical activation on the rate of release of synthesis gas from coal and the gas composition. Studies [17, 18] have shown a possibility of obtaining synthesis gas of a given composition and the use of this gas as a raw material for FTS. Previous studies of FTS [19] using the MCA catalyst have shown the feasibility of studies on the effect of pressure on the activity and selectivity of Fe-Cu-K catalyst under AnC conditions at a pressure of 0.1–1.2 MPa.

3. The aim and objectives of the study

The study objective implied creating a synthetic hydrocarbon technology based on controlled mechanochemical activation of the catalyst with a given intensity. This will make it possible to develop a technology for the industrial production of synthetic motor fuels from coal at lower catalyst costs and improved product yields.

To achieve this objective, it was necessary to solve the following tasks:

– study the effect of temperature and pressure on the degree of conversion of synthesis gas, product yield, and selectivity of catalysis;

– determine the effect of MCA intensity and catalyst concentration on product yield;

– identify the effect of pressure on the composition of hydrocarbon products;

– obtain a mathematical description of experimentally identified dependences for the FTS process in conditions of aerosol nanocatalysis;

– develop a basic process flowsheet of an experimental and industrial installation that combines the stage of steam conversion of coal by aerosol nanocatalysis and the stage of obtaining synthetic hydrocarbons by Fischer-Tropsch synthesis.

4. The study materials and methods

All main general scientific study methods were used in performing this study. Methods of the empirical study included:

– experiment setting on an original laboratory installation;

– direct static measurements of variable parameters (temperature, pressure, airflow, MCA frequency, catalyst concentration, synthesis gas composition) and obtained experimental data (product composition);

– quantitative and qualitative description of the obtained results.

Mathematical formalization methods, axiomatic method, and hypothetical-deductive method were used to build a hypothesis on the FTS process running in conditions of aerosol nanocatalysis based on obtained experimental data. General logical methods were used in processing experimental data: comparison, abstraction, analysis and synthesis, generalization, analogy, modeling, induction, and deduction.

The operator diagram of the laboratory installation for the production of synthetic hydrocarbons by Fischer-Tropsch synthesis under pressure with the ability to influence the catalyst activity by mechanical factors is shown in Fig. 1.

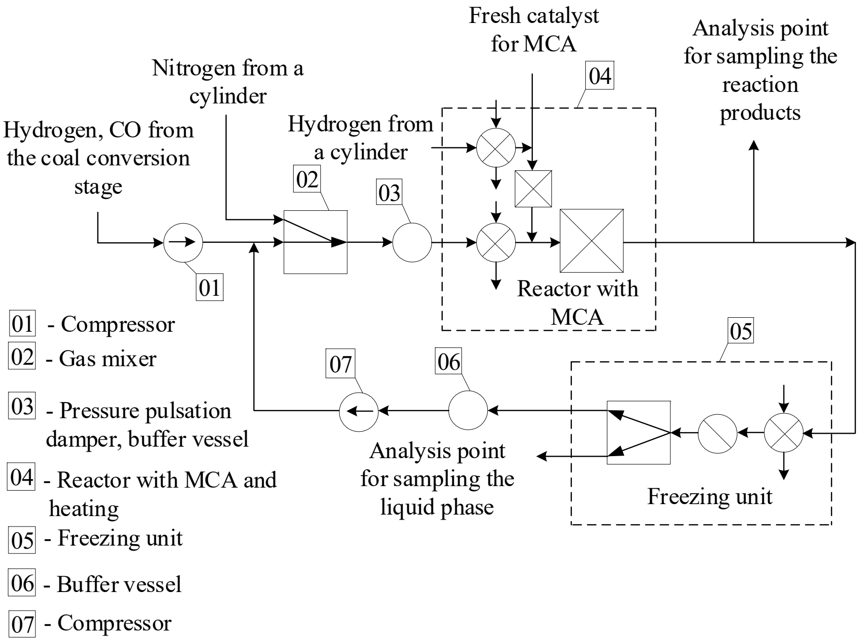

Fig. 1. Operating diagram of a laboratory installation for the production of synthetic hydrocarbons by Fischer-Tropsch synthesis under pressure with the ability to influence the catalyst activity by mechanical factors and additional gas recycling

The principle of operation of the laboratory setup: synthesis gas enters the buffer vessel connected to compressor 1 through a pipeline. Maximum gas pressure at the compressor outlet is 3.0 MPa. Before the start of synthesis and supply of synthesis gas, the whole set is inertized with nitrogen from the cylinder. Compressed gas from compressor 1 enters the 10-liter gas mixer 2. Next, the gas enters buffer vessel 3 via the pipeline. This vessel serves as a damper of pressure pulsation. A needle valve installed on the pipeline periodically adjusts pressure in the synthesis zone in cases of overpressure in the gas mixer 2. Pressure in compressor 1 and gas mixer 2 is controlled by manometers P_1, P_2. Synthesis gas is supplied to reactor 4 with MCA and heating from the buffer vessel 3 via the pipeline.

The reactor is a 50 cm^3 welded vessel with a sealing surface of "male-female" type and a built-in thermal pocket. The reactor is mounted in an electric heater and connected to a vibrating device. Vibration frequency and heating temperature are adjusted automatically in set limits by means of the control unit. Current temperature and vibration frequency values are displayed on the control unit in real time. To compensate for the effect of voltage ripple in the power net, an uninterruptible power supply was additionally installed on the control unit. The vibration amplitude was 10 mm and constant. The heating temperature was controlled by a thermocouple installed in the reaction zone in the reactor thermal pocket and connected to the control unit. The reactor performed reciprocating motions in the vertical plane. The frequency and amplitude of the reactor oscillations were adjusted in the range of 4–12 Hz. The catalytic system in the reactor consisted of a dispersing material (DM), namely, glass beads with an average diameter of 1–1.2 mm and a catalyst powder with an average initial particle size of 50–200 μm. A metal filter made of sintered and compressed metal fibers was installed in the middle of the reactor to prevent the loss of DM and catalyst particles. Formation of a vibrating fluidized bed of DM particles, synthesis of catalyst nanoparticles, and mechanochemical activation of their surface in situ take place during the reactor running with a certain frequency and amplitude.

The catalytic material in the reactor is pre-reduced with hydrogen supplied from a cylinder for 5 hours at 450 °C. The reactor is cooled to the synthesis temperature after the reduction stage. A mixture of reaction products and unreacted gas passes the metal filter and enters the pipeline connected to the freezing unit 5. This pipeline also provides pressure control and an analysis point for sampling the reaction products followed by pressure reduction by the needle valve. The freezing unit is a freezer with a freezing temperature down to −15 °C into which pipelines connected to a glass heat exchanger (a U-shaped tube) enter and exit through foamed plastic seals. Unreacted reaction products and unreacted gas after freezing at the pipeline enter the buffer vessel 6. This vessel is also equipped with an analysis point. Analysis of the reaction products was performed chromatographically. Pre-calibrated LKhM-8, Crystal-5000 M gas chromatographs to determine liquid and gaseous hydrocarbons, and Tsvet-500 to determine the composition of nonreacted synthesis gas coming from the reactor were available.

The catalytic system was weighed before and after the experiment to determine the possible weight gain in the case of deposition of free carbon and other reaction products.

The catalyst system was oxidized by oxygen at 500–550 °C after each experiment to remove unwanted reaction products from its surface (if any). The catalyst system was then weighed and could be used again in experiments.

The method of preparation of the catalyst system was as follows. 1.0–1.1 mm diameter glass beads in a volume of 25 cm^3 were loaded into a glass flask together with the catalyst powder weighed on analytical balances with an accuracy of 0.001 g. The flask was closed with a stopper and shaken at room temperature for 10–15 min. The catalyst system was then discharged from the flask and sieved to separate the unabsorbed catalyst. The removed catalyst was weighed on analytical balances. If the catalyst weight was less than its initial value, a new batch of catalyst was taken, added to the glass beads and the flask was shaken again. The process was repeated until the mass of the catalyst removed after shaking was equal to the amount loaded into the flask before the last dusting.

Table 1

Experimental studies of the effect of temperature and pressure on the process

No.	T, K	P, MPa	Parameters of AnC		Degree of CO conversion, %	Yield of all carbon-containing products, g/m^3 SG	Yield of hydrocarbons, g/m^3 SG	Selectivity of CO conversion to hydrocarbons, %
			MCA, Hz	C_{cat}, kg/m^3 of the reactor				
1	483	0.3	8.5	10	23.48	8.01	3.93	74.77
2	493	0.3	8.5	10	36.28	23.55	20.16	86.41
3	503	0.3	8.5	10	55.02	15.6	13.5	93.1
4	513	0.3	8.5	10	56.6	18.26	13.72	88.33
5	523	0.3	8.5	10	52.5	19.9	15.01	86.24
6	533	0.3	8.5	10	48.2	22.55	17.11	83.6
7	503	0.1	8.5	10	44.1	12.05	8.18	90.25
8	503	0.2	8.5	10	48.2	15.84	13.09	91.74
9	503	0.3	8.5	10	55.02	15.6	13.5	93.1
10	503	0.4	8.5	10	55.3	15.66	12.71	91.15
11	503	0.5	8.5	10	56.0	16.8	13.58	89.92
12	503	0.6	8.5	10	56.2	17.05	13.76	89.53
13	503	0.7	8.5	10	56.3	18.83	15.36	89.09
14	503	0.8	8.5	10	56.5	17.0	13.24	87.94
15	503	0.9	8.5	10	56.5	17.19	13.35	87.54
16	503	1.0	8.5	10	56.2	17.79	13.86	87.82

5. The results obtained in the studies of process-dependent parameter effect on the process in conditions of aerosol nanocatalysis

5. 1. Influence of temperature and pressure on the degree of synthesis gas conversion, product yield, and catalysis selectivity

The results obtained in the studies of synthesis gas conversion to hydrocarbons in conditions of aerosol nanocatalysis are given in Table 1. The data presented in Table 1 were obtained without taking into account the raw material recycling. The use of recycling makes it possible to achieve almost 100 % conversion degree in the entire studied range of variable parameters. The process was carried out at the following constant parameters:

– volume velocity of SG: 200 hr^{-1};
– catalyst: iron;
– vibroreactor;
– dispersing material: 1 mm diameter metal balls;
– the amount of DM in the reactor: 50 vol %.

With an increase in temperature in the range of 483–533 K (lines 1–6 of Table 1), the degree of conversion increased to 513 K followed by a gradual decrease. The presence of a maximum in the studied temperature range indicates that there are optimal conditions where the catalyst activity will be maximum.

It can be noted that the pressure growth from 0.1 to 1.0 MPa (lines 7–16 of Table 1) gradually increases from 44.1 % to 56.5 % and then remains unchanged in the studied interval. The FTS process runs with a decrease in the volume of products and an increase in pressure should lead to an increase in the equilibrium degree of conversion. A small change in the degree of conversion in the range of 0.3–1.0 MPa can be explained by initially high catalyst activity when a high degree of conversion is achieved at rather low pressure.

5. 2. Influence of mechanochemical activation intensity and catalyst concentration on the selectivity of chemical conversions

The study results are given in Table 2.

The influence of the MCA intensity specific for aerosol nanocatalysis (lines 1–7 of Table 2) is conventional for this technology. There is some optimum MCA frequency (8.5 Hz in this case) when the degree of conversion of raw materials and, accordingly, the total rate of all reactions and specific productivity of the reactor are maximum in the studied range.

Table 2

Experimental studies of the effect of mechanochemical activation intensity and catalyst concentration on the process

No	T, K	P, MPa	Parameters of AnC		Degree of CO conversion, %	Yield of all carbon-containing products, g/m^3 SG	Yield of hydrocarbons, t/m^3 SG	Selectivity of CO conversion to hydrocarbons, %
			MCA, Hz	C_{cat}, kg/m^3 of reactor				
1	503	0.3	4	10	22.3	8.13	3.92	72.66
2	503	0.3	5	10	28.4	8.63	4.76	80.16
3	503	0.3	6	10	35.6	9.0	5.23	85.28
4	503	0.3	7.2	10	44.9	12.05	8.18	87.49
5	503	0.3	8.5	10	55.02	15.6	13.5	93.1
6	503	0.3	9.5	10	42.6	8.24	4.99	88.95
7	503	0.3	11.2	10	33.1	9.6	5.83	83.38
8	503	0.2	8.5	5	43.2	9.12	6.07	89.66
9	503	0.2	8.5	10	55.02	46.47	43.96	93.054
10	503	0.2	8.5	15	38.7	11.3	8.03	87.7
11	503	0.2	8.5	20	36.4	11.71	8.33	86.46
12	503	0.2	8.5	25	32.3	14.18	10.6	84.12

The effect of catalyst concentration (lines 8–12 of Table 2) shows that the degree of conversion decreases from 55.02 to 48.2 % with an increase in the concentration of aerosol of catalyst particles from 10 to 25 g/m^3 of the reactor. This corresponds to the theory of chemical conversion in aerosol nanocatalysis when an increase in particle concentration leads to an increase in the number of activated catalyst nanoparticles formed *in situ*. This leads to an increase in the rate of coagulation of nanoparticles to micro sizes. As the concentration of the starting catalyst increases above the optimum value, the concentration of activated catalyst particles decreases. Accordingly, the degree of conversion of raw materials decreases.

5. 3. The effect of pressure on length of the hydrocarbon chain in products under conditions of aerosol nanocatalysis

It is known that hydrocarbons with different lengths of the hydrocarbon chain have different properties. The longer the chain the heavier the hydrocarbon. Hydrocarbons containing from 1 to 4 carbon atoms in their chain are characterized by boiling point under 273 K (<0 °C). They are gases under normal conditions. Hydrocarbons having 5 to 18 carbon atoms in their chain are liquids in normal conditions. The rest of the hydrocarbons with a chain consisting of 19 or more carbon atoms are in the solid state.

Experimental data from the study of the effect of pressure on the composition of the hydrocarbon fraction and length of the hydrocarbon chain in FTS products are given in Table 3. The process was carried out with the following constant parameters:

- volume velocity of SG: 200 hr^{-1};
- catalyst: iron;
- temperature: 503 K;
- CA: 8.5 Hz;
- C_{cat}: 10 kg/m^3 of reactor volume;
- dispersing material: 1 mm diameter metal balls;
- the amount of DM in the reactor: 50 vol %.

Table 3

The effect of pressure on composition of the hydrocarbon fraction for the process of synthesis gas conversion in the aerosol of catalyst particles

No.	P, MPa	Fraction share, wt % from all hydrocarbons that were obtained								
		CH_4	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_{9+}
1	0.1	3	1	1	1.2	18	20,8	25	12	18
2	0.2	2	1	2	1	21	17	30	10	16
3	0.3	1	0.3	0.5	0.4	58	15	20	5	9.4
4	0.4	1.5	0.5	0.8	1.2	38	14	20	12	12
5	0.5	1.5	0.5	1.2	1.8	28	16	18	15	18
6	0.6	1.8	0.8	1.5	2.0	24	16	20	16	17.9
7	0.7	1.2	0.6	0.5	0.5	22	23	30	12	11.2
8	0.8	1.8	1.2	0.8	0.9	15	26	29	10	15.3
9	0.9	2.0	1.6	1.2	1.4	16	25	22	12	18.8
10	1.0	2.0	1.2	0.8	1.2	15	28	20	12	19.8
11	1.1	1.8	1.0	0.6	0.8	12	28	24	17	12.8
12	1.2	2.8	1.6	1.0	1.2	10	25	27	12.8	18.6

The FTS hydrocarbon products can be divided by their fractions depending on their practical use. For example, a hydrocarbon fraction containing 1 to 4 carbon atoms in its chain may be considered a synthetic natural gas (SNG). A fraction with 5 to 6 carbon atoms evaporates easily. It is called naphtha and is used in the production of solvents. A fraction with 7 to 11 carbon atoms in its chain is used in the production of gasoline. Some literature sources call it a gasoline fraction, the hydrocarbon fraction C_{5+}, i.e., the one containing 5 to 11 carbon atoms in its chain. Other fractions with a length of their hydrocarbon chain of more than 12 carbon atoms are used in the production of kerosene, diesel fuel, fuel oil, lubricants, etc. They were not considered in this study.

Analysis of experimental data presented in Table 2 shows that the share of light fraction (SNG) with hydrocarbon chains consisting of 1 to 4 carbon atoms is small. Fraction C_{1-4} in the composition of FTS products does not exceed 6.6 wt %. Maximum concentration is observed at 1.2 MPa and minimum concentration (2.2 wt %) is observed at 0.3 MPa.

The maximum yield of the hydrocarbon fraction (73 wt %) with a chain length of 5 to 6 carbon atoms was observed at 0.3 MPa and the minimum yield of 35 wt % was at 1.2 MPa. At other pressure values (0.1–0.2 and 0.4–1.1 MPa) in experimental studies, the yield of this fraction varied within 38–52 wt %.

The yield of the hydrocarbon fraction with a chain length of more than 7 carbon atoms varied between 51.0 and 54.3 wt % at a pressure of 0.5–1.1 MPa. At a minimum pressure of 0.1–0.2 MPa yield is 55 and 56 wt %, respectively. The maximum yield of this fraction for the FTS process under conditions of aerosol nanocatalysis was 58.4 wt % at a pressure of 1.2 MPa and the minimum yield of 34.4 wt % was at a pressure of 0.3 MPa.

Thus, analysis of experimental data in Table 2 shows that the maximum yield of the gasoline fraction containing more than 5 carbon atoms in the hydrocarbon chain was at a pressure of 0.3 MPa while the share of $C_{5\ 6}$ hydrocarbons in the composition of this fraction is approximately 2.1 times more than that of C_{7+} hydrocarbons while the amount of C_{1-4} hydrocarbons was only 2.2 wt %. Also, it was shown that the ratio of hydrocarbons with different lengths of their hydrocarbon chains in the gasoline fraction can be adjusted by pressure change. For example, the ratio of C_{7+}/C_{5-6} was 1.67 for a pressure of 1.2 MPa.

5. 4. Mathematical description of dependences for the FTS process in conditions of aerosol nanocatalysis

This section presents mathematical data processing for experimental studies of the FTS process in conditions of aerosol nanocatalysis.

The dependence of the degree of conversion of carbon monoxide (the synthesis gas component) on the temperature of the FTS process is shown in Fig. 2. This dependence is extreme. With an increase in temperature from 483 to 513 K, the degree of conversion of carbon monoxide increased from 23 to 56.6 %. With a further increase in the process temperature to 533 K, the degree of carbon monoxide conversion has dropped to 48.2 %. Thus, the temperature of the FTS process is 513 K in conditions of aerosol nanocatalysis is characterized by a maximum value of the degree of carbon monoxide conversion.

Dependence of the degree of carbon monoxide conversion on the temperature of the FTS process can be mathematically represented as equation (1) with an error δ=±7 %:

$$X_{CO}=4\cdot 10^{-5}\cdot T^4-0.0872\cdot T^3+66.502\cdot T^2-22{,}512\cdot T+3\cdot 10^6. \quad (1)$$

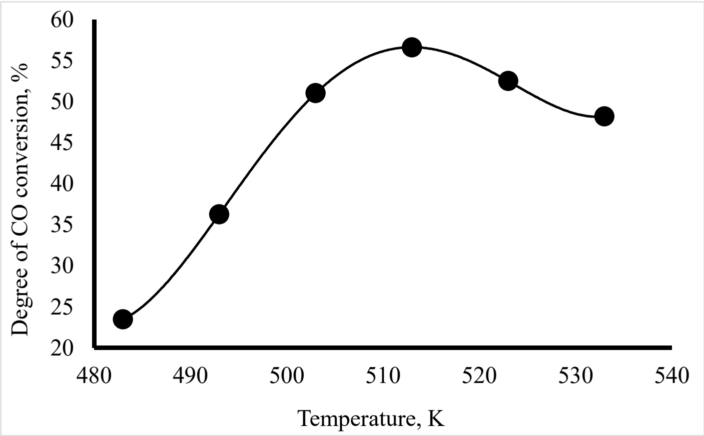

Fig. 2. Dependence of the degree of carbon monoxide conversion on the process temperature (P=0.3 MPa, MCA=8.5 Hz, C_{cat}=10 kg/m^3)

The dependence of yield of carbon-containing products of the FTS process in conditions of aerosol nanocatalysis on the pressure in the system is shown in Fig. 3.

An increase in the FTS process pressure from 0.1 to 1.0 MPa in conditions of aerosol catalysis contributes to a stable increase (from 14 to 17 %) in the yield of carbon-containing substances in the process products. This dependence can be mathematically represented as equation (2) with an error δ=±7 %:

$$X_C=18.196\cdot P^{0.1552}. \quad (2)$$

Fig. 4 shows the dependence of selectivity of carbon monoxide conversion to hydrocarbon products in the FTS process in conditions of aerosol nanocatalysis on the frequency of mechanochemical activation (MCA) of the catalytically active component by means of a dispersing material.

This dependence was characterized by a constant increase in selectivity of carbon monoxide conversion to hydrocarbons with an increase in MCA frequency from 4 to 8.5 Hz while maximum selectivity value (91 %) was reached. With a further increase in MCA frequency to 11.2 Hz, there was a decrease (to 83.5 %) in the value of selectivity of the carbon monoxide conversion to hydrocarbon products in the FTS process Therefore, MCA frequency from 6 to 10 Hz was recommended as acceptable.

The dependence of selectivity of the carbon monoxide conversion to hydrocarbons on MCA frequency can be mathematically represented in the form of equation (3) with an error δ=±7 %:

$$S_{CO}=0.8738\cdot f^2+14.747\cdot f+27.873. \quad (3)$$

The value of catalyst concentration in the reaction space is one of the distinctive features characterizing the processes of chemical conversion in conditions of aerosol nanocatalysis. Figure 5 shows the dependence of selectivity of carbon monoxide conversion to hydrocarbon products in the FTS process in conditions of aerosol nanocatalysis on the concentration of the catalytically active component in the reaction system. Analysis of the presented data shows a slight increase (from 89.6 to 91.1 %) in the selectivity of the carbon monoxide conversion to hydrocarbons with an increase from 5 to 10 kg/m^3 in catalyst concentration in the reaction space.

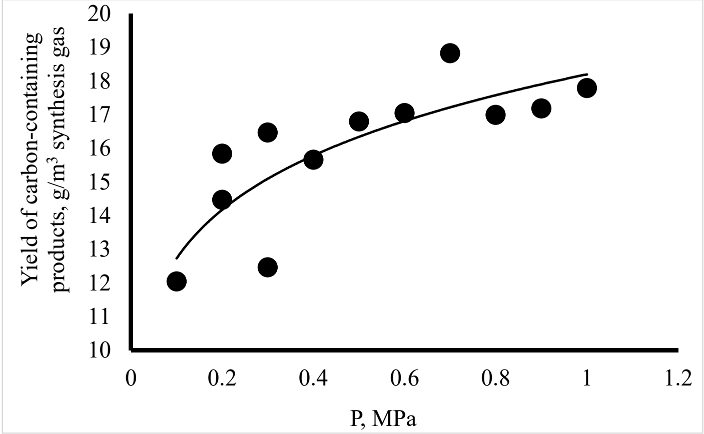

Fig. 3. Dependence of yield of carbon-containing products on the process pressure (T=503 K, MCA=8.5 Hz, C_{cat}=10 kg/m^3)

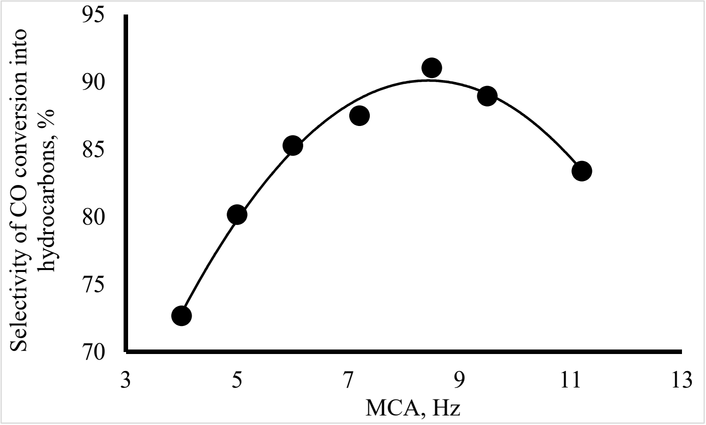

Fig. 4. Dependence of selectivity of the carbon monoxide conversion to hydrocarbon products on the frequency of mechanochemical activation (T=503 K, P=0.3 MPa, C_{cat}=10 kg/m^3)

The dependence of selectivity of carbon monoxide conversion to hydrocarbons on catalyst concentration in the reaction system can be mathematically represented as equation (4) with an error $\delta=\pm7$ %:

$$S_{\mathrm{CO}} = -0.0127 \cdot \mathrm{C}_{cat}^{2} + 0.086 \cdot \mathrm{C}_{cat} + 89.824. \qquad (4)$$

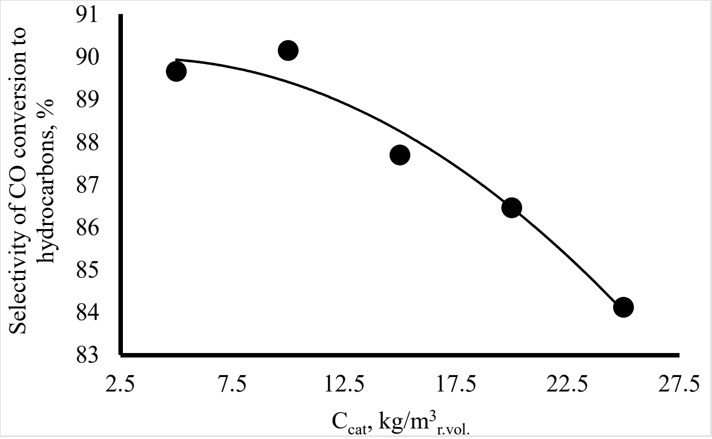

Fig. 5. Dependence of selectivity of carbon monoxide conversion to hydrocarbon products in conditions of aerosol nanocatalysis on the concentration of a catalytically active component in the reaction space (*T*=503 K, *P*=0.2 MPa, MCA=8.5 Hz)

With a further increase in catalyst concentration to 25 kg/m^3, a drop of selectivity of the carbon monoxide conversion to hydrocarbons to 84.1 % was observed. Thus, catalyst concentration of 5 to 10 kg/m^3 is acceptable for the FTS process in conditions of aerosol nanocatalysis.

5. 5. Schematic process flowsheet of an experimental-industrial installation for the production of synthetic hydrocarbons by aerosol nanocatalysis

The schematic process flowsheet of the experimental-industrial installation is presented in Fig. 6.

The synthesis gas (SG) obtained in the aerosol nanocatalysis reactor RB is sent to the CO stage for purification from impurities. The prepared SG sent to the stage of hydrocarbon synthesis (stream 5) enters the reactor R. MCA in the reactor can be carried out in several ways: catalytic system fluidization, vibrational fluidization, rotation of the reaction zone, etc.

There is a separation zone in the upper part of each reactor which prevents DM carryover from the reactor. There is a catalytic system in each reactor consisting of a dispersing material and a catalyst. The catalyst particle size is 10 to 200 μm before entering the MCA zone. Glass or metal balls of various diameters dusted with a catalyst to prevent the adhesion of free catalyst on their surface can be used as a dispersing material.

Additional heating of gas to the synthesis temperature occurs in the reactor due to the heat of exothermic synthesis reactions. Excess heat is removed with boiling water (stream 7) via built-in spiral heat exchangers (SHE). The catalyst is taken from the reactor to cyclones (C) and sent to the oxidation and reduction unit. Recovery units (RU) and oxidation units (OU) can be built in a reactor form with fluidized bed of the catalytic system. Initially, the catalyst enters the unit of oxidation (OU) of coke and hydrocarbon which may be deposited on the catalyst surface after its leaving the activation zone. Oxidation of reaction products to CO_2 and H_2O takes place there. Coke is burnt off with air (stream 4) at about 800 °C. Next, the flow containing the catalyst suspension and flue gases passes through the cyclone (C2) where flue gases are separated from it (flow 16). The separated catalyst is fed to the reduction unit (RU) where it is reduced in a stream of hydrogen (flow 18) at a temperature of 500 °C and hydrogen volume velocity of 200 h^{-1}. The catalyst recovered in this way comes out at the top together with the gas stream is separated from the reduction gases (flow 19) in the cyclone (C3). Fresh catalyst from the hopper (CH) (flow 17) is also fed to the recovery unit in an amount that compensates for its loss.

The mixture of synthesis products (flow 8) is sent for cooling and condensation in packed direct cooling scrubbers (PS) irrigated with water and is cooled there to a temperature of about 20–30 °C. The scrubber is filled with a packing filler divided into several sections in height and irrigated with circulating water (flow 10). The upper section of the packing material is irrigated with fresh water (flow 9) to provide better cooling and replenish the circulating water losses associated with evaporation, carryover, etc. The heavier part of the synthesis products must be condensed. Noncondensed products (gasoline vapors, C_5–C_7 hydrocarbons) are extracted from the gas through activated carbon absorption (adsorption process). Heavy hydrocarbon products fall from the bottom of the scrubber into the separator (S2) where stratification into aqueous and organic layers takes place. The aqueous layer is sent to the cooling tower (not shown in the diagram) for its cooling and reuse (flow 11). The organic layer (flow 12) containing heavy hydrocarbons is sent for further processing depending on the product requirements. Adsorption with activated carbon is carried out in several alternately working adsorbers. The unit usually consists of seven adsorbers (for example, the diagram shows four absorbers A2–A5). At any given time, two of them are working for adsorption and one for desorption, two for drying, and two for cooling.

Two concentric pipes connected to the bottom part of the absorber supply and take off steam and gas. The inner pipe passes through a layer of coal and ends above it at the top of the absorber and the outer one ends under the coal layer, directly at the bottom of the absorber.

Hydraulic valves installed in the pipes are provided for switching operations. The gas from the scrubber passes through the absorber (A2) where gasoline and C_5–C_7 hydrocarbon vapors are extracted from it. The gas is slightly heated due to the heat of adsorption. The purified gas passes through the refrigerator (T5) where it is cooled to the initial 20 °C and then the adsorbers standing on cooling (A5). The gas is heated there to an average of 40–50 °C and then passes into the heater (T7) to be heated up to 110 °C. The gas heated to this temperature passes through the absorber (A4) standing on drying and leaves the system. Water vapor (flow 13) is passed through the absorber (A3), from top to bottom at this time (gas flow direction in all other adsorbers is from bottom to top).

The vapor-gas desorption mixture is sent for condensation. The condensing system of the described adsorption unit consists of a heat exchanger (T6) where water and gasoline vapors are condensed and the separator (S3) from where the fraction C_5–C_7 (stream 14) and light hydrocarbons (stream 15) are removed.

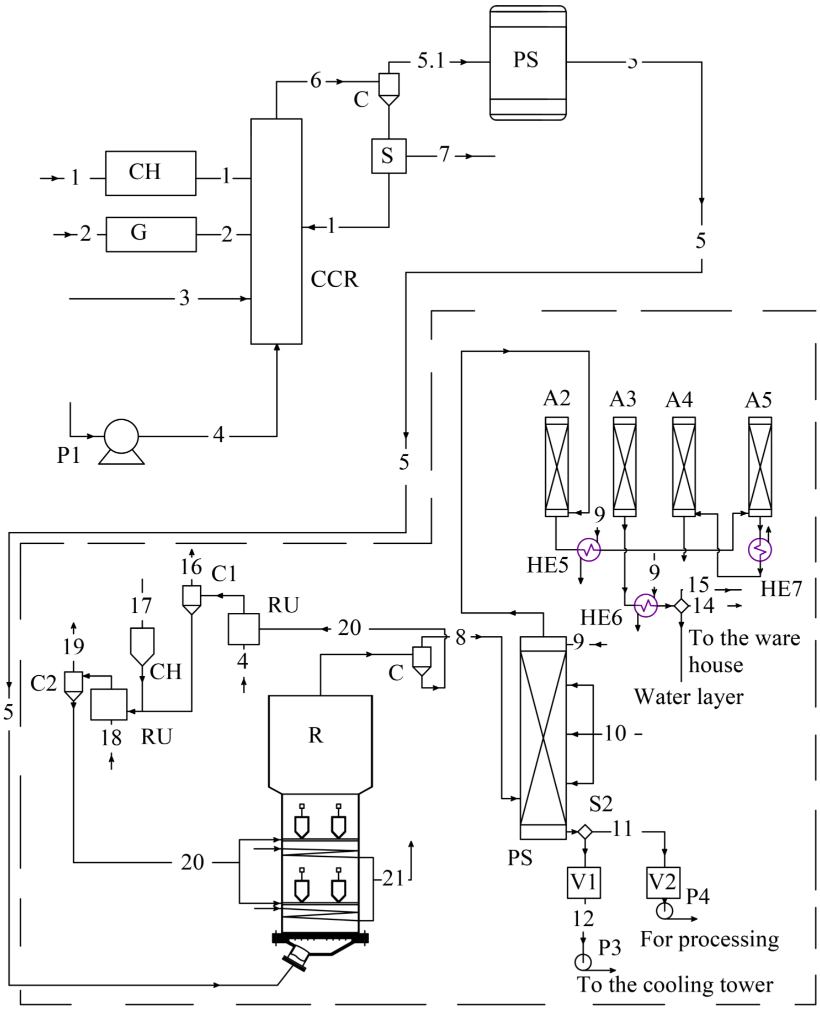

Fig. 6. Schematic process flowsheet of an experimental-industrial installation for the production of liquid hydrocarbons with activation of catalysts and raw materials on the principles of aerosol nanocatalysis. Devices: CCR – coal conversion reactor operating on the principles of aerosol nanocatalysis; C – cyclone; CH – catalyst hoppers; P – pump; S – separators; RU – recovery unit; PS – stage of purification and preparation of synthesis gas; A – adsorbers; V – vessels; R – reactor operating on the principles of aerosol nanocatalysis; PS – packed scrubber; Flows: 1 – catalyst; 2 – coal; 3 – steam; 4 – oxygen; 5 – synthesis gas; 5.1 – synthesis gas with impurities; 6 – a mixture of coal and synthesis gas; 7 – ash; 8 – synthesis products; 9 – water; 10 – return water; 11 – heavy hydrocarbons; 12 – water layer; 13 – steam; 14 – fraction C_{5+}; 15 – light hydrocarbons; 16 – flue gases; 17 – catalyst; 18 – hydrogen flow to recover the catalyst; 19 – hydrogen flow for drainage; 20 – catalyst; 21 – steam

6. Discussion of the results obtained in the study of the effect of cavitation intensity on the octane number of gasoline modified with monoatomic alcohols

The results obtained in the study of the effect of temperature on the course of synthesis gas conversion have shown that a temperature of 513 °C is optimal. However, a temperature of 493 °C is optimal for the yield of hydrocarbons (Table 1, row 2). The conversion process follows a more known course where the degree of conversion of the starting material grows with temperature rise. However, obtaining a required synthesis reaction product always takes place at a lower degree of conversion and by-products are formed in the reaction products. In this case, in addition to C_{5+} hydrocarbons C_1–C_4 and H_2 hydrocarbons can be obtained.

The results have shown that with increasing pressure, the degree of CO conversion is stable at a level of 50 % and the highest selectivity of CO to hydrocarbon conversion occurs at 0.2–0.4 MPa at a level of 91 % (Table 1, lines 8–10). Pressure has shown a typical influence on the process of CO conversion. A typical pressure effect on hydrocarbon selectivity was also observed for aerosol nanocatalysis technology. Most processes using the technology of aerosol nanocatalysis take place at atmospheric pressure. This synthesis process has shown that the best pressure is slightly higher than atmospheric pressure.

The results have shown that oscillation frequency has a parabolic effect on the degree of CO conversion with a maximum at a level of 7.2–9.5 Hz. Also, the highest selectivity of hydrocarbons was obtained at a level of 80–90 % in the range of 7–9 Hz (Table 2, rows 4–6). This process control parameter is unique and important for aerosol nanocatalysis technology. It is used to determine the intensity of mixing the catalytic system in the reactor and affects the catalyst activity.

The results obtained on the effect of catalyst concentration on the synthesis gas flow have shown that the catalyst concentration of 10 kg/m^3 may be optimal for Fischer-Tropsch synthesis in conditions of catalyst aerosol. Maximum selectivity at a level of 90–92 % was obtained in the range of catalyst concentrations of 9–12 kg/m^3 (Fig. 5).

It was noted that the conversion degree has a polynomial mathematical dependence. It makes it possible to determine the value of the control parameter at which the degree of conversion reaches a stable or maximum value. The FTS process did not clearly indicate an optimal value of the parameter by the degree of conversion. Therefore, it was also to be checked by the hydrocarbon selectivity to enable the determination of optimal temperature and pressure parameters. Selectivity of hydrocarbon production has a parabolic mathematical dependence which shows a value of the control parameter when reaching maximum or minimum value. In this process, the maximum was obtained at a selectivity of 90 %, frequency of 8 Hz, and catalyst concentration of 10 kg/m^3 (Table 2, line 5).

The obtained results of the FTS process study have shown the possibility of its running in conditions of aerosol nanocatalysis technology. The following was found using the process control parameters: temperature, pressure, oscillation frequency, and catalyst concentration. All these parameters apply to AnC technology. This technology has proven itself better not only in oxidation processes but also in synthesis processes. The results were better than those for other technologies during the process running. However, the laboratory study in conditions of using the catalyst aerosol faced some difficulties in the process organization. They are also found in the process organization in the industry. Namely, it is the organization of catalyst supply to the reactor with vibrating and rotating fluidized beds of the catalytic system. This problem also exists when designing a reactor with vibrating and rotating fluidized beds of the catalytic system. Thus, designing the process flowsheet with such a reactor can last somewhat longer than its organization.

In general, the obtained results have made it possible to determine the following parameters of FTS process control: T=766 K, P=0.2–0.4 MPa, f=7–9 Hz, C_{cat}=10 kg/m^3.

The above optimal control parameters make it possible to obtain C_{5+} hydrocarbons by Fischer-Tropsch synthesis in conditions of the aerosol catalysis technology using iron as a catalyst for this process.

Disadvantages of this study include a relatively small capacity of the reactor (0.05 liters) which complicates interpretation of the obtained data for the scale of industrial plants. The study limitation is the maximum allowable pressure in the installation (3.0 MPa) which makes it impossible to conduct studies at higher pressure values.

The study may be expanded to searching optimal catalyst compositions which could give higher degrees of conversion, yields of individual hydrocarbons, and fractions from the synthesis gas of varied initial composition. It is also advisable to design a new laboratory unit that can operate at pressures above 3.0 MPa and redesign the reaction section of the unit with the organization of the catalyst recirculation system in a “reactor-trap-regenerator” loop.

7. Conclusions

1. Influence of temperature and pressure on the degree of synthesis gas conversion, product yield, and catalytic selectivity has been studied. With an increase in temperature in a range of 483–533 K, the maximum degree of conversion was 56.6 % at 513 K. Pressure growth from 0.1 to 1.0 MPa gradually raised the degree of conversion from 44.1 to 56.5 %. Raising the FTS process pressure in conditions of aerosol catalysis from 0.1 to 1.0 MPa contributed to a stable 14 to 17 % increase in the yield of carbon-containing substances in the process products. In this case, selectivity has taken a maximum value of 93.1 % at a pressure of 0.3 MPa.

2. Influence of MCA intensity and catalyst concentration on the selectivity of chemical conversion in conditions of aerosol nanocatalysis was established. Dependence of selectivity on the intensity of the catalyst MCA was characterized by a constant increase in selectivity of carbon monoxide conversion to hydrocarbons with a growth of the MCA frequency from 4 to 8.5 Hz while reaching a maximum selectivity of 91 %. With a further increase in MCA frequency to 11.2 Hz, a decrease to 83.5 % in the value of selectivity of the carbon monoxide conversion to hydrocarbon products of the FTS process was observed. With an increase in the concentration of catalyst particles in aerosol from 10 to 25 g/m^3 of the reactor, the degree of conversion decreased from 55.02 to 48.2 %. This corresponds to the theory of chemical conversion in aerosol nanocatalysis when an increase in the concentration of particles leads to an increase in the number of activated nanoparticles of the catalyst formed *in situ*.

3. The effect of pressure on the composition of hydrocarbon products was established. An increase in pressure from 0.1 to 1.0 MPa gradually increased the conversion degree from 44.1 % to 56.5. An increase in pressure of the FTS process in conditions of aerosol catalysis from 0.1 to 1.0 MPa contributed to a stable 14 to 17 % increase in yield of carbon-containing substances in the process products. Selectivity has taken a maximum value of 93.1 % at a pressure of 0.3 MPa.

4. Mathematical processing of the obtained experimental data has allowed us to establish the extreme nature of the effect of temperature on the degree of conversion of raw materials and has shown that there is an optimal temperature of 513 K at which the degree of conversion reaches a maximum of 56.6 %. Dependence of selectivity of carbon monoxide conversion to hydrocarbon products in the FTS process in conditions of aerosol nanocatalysis on MCA frequency was characterized by the growth of selectivity with an increase in MCA frequency from 4 to 8.5 Hz with reaching maximum selectivity of 91 %. With a further increase in the MCA frequency, a decrease in the value of selectivity to 83.5 % was observed.

5. A basic process flowsheet of experimental-industrial installation has been developed based on the study results and the known data on AnC. The installation has combined the stage of steam coal conversion by aerosol nanocatalysis and the stage of obtaining synthetic hydrocarbons by Fischer-Tropsch synthesis. It is possible to carry out FTS under pressure up to 3.0 MPa and influence the catalyst activity by mechanical factors.

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