The Use of Catalysts in the Production of Fuel for Agricultural Machinery

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Abstract. Fischer–Tropsch synthesis is the main process for obtaining synthetic hydrocarbons from a mixture of CO and H_2, called synthesis gas. The process is carried out using catalysts based on cobalt or iron, supported on carriers of various nature. The composition of the resulting product depends on the process conditions and the catalyst used [1]. The authors obtained a cobalt-magnesium-zirconium catalyst of the following composition: Co—100; MgO—6,5; ZrO2—9,8; carrier—200. Diatomite from the Malchevskoye deposit of the Rostov region was chosen as a carrier. The mechanical strength, chemical composition, degree of reduction of catalysts, as well as their activity and selectivity with respect to the target fraction have been investigated. 225–335 °C. Catalytic tests were carried out in a laboratory unit under conditions close to industrial technological parameters. Based on the study, the data obtained on the activity and selectivity of the catalyst in the process of obtaining synthetic hydrocarbon fuel by the Fischer–Tropsch method allow us to speak about its operating parameters and evaluate them as satisfactory in comparison with similar catalytic systems.

Keywords: Fischer–Tropsch synthesis · Diatomite · Called synthesis gas · Cobalt-Magnesium-Zirconium catalyst · Diesel fuel · Catalyst · Estimation of greenhouse gas emissions

1 Introduction

Industrial demand for hydrocarbon fuels is increasing every year and, according to BP Global energy forecasts, by 2040, electricity and hydrocarbon fuels will account for about two-thirds of the energy used in industry. At the same time, the cost of fuel is increasing, as well as the natural reserves of oil and gas are rapidly decreasing. Consequently, technologies are needed to synthesize fuel from alternative sources of oil. Reference [2] Solid fossil fuels, household waste and other hydrocarbon-containing raw materials are processed in various ways into synthesis gas (a mixture of CO and H2), from which components of motor fuel and raw materials for petrochemical processes are obtained using the Fischer–Tropsch technology.

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Currently, experts from all over the world note an increase in emissions into the atmosphere of exhaust gases containing oxides of nitrogen, carbon, sulfur, as well as benzopyrene and other substances, therefore, countries have regulations that strictly determine the quality of fuels in terms of permissible emissions of harmful substances during fuel combustion in engine. The fuel obtained by the Fischer–Tropsch method practically does not contain compounds of sulfur, nitrogen and aromatic substances, therefore, the emissions of fuel combustion products into the atmosphere are significantly reduced. In addition, researchers note a decrease in emissions of hydrocarbons, polyaromatic hydrocarbons and particulate matter during the combustion of fuel fractions of the Fischer–Tropsch synthesis in comparison with diesel fuel obtained directly from oil [3–7].

The Fischer–Tropsch synthesis is a promising technological process that makes it possible to obtain high-quality fuel fractions for internal combustion engines of agricultural machinery [8]. The main advantages of the process [9, 10] are:

- economic efficiency of the technology as a result of the development of catalysts with high selectivity for fuel fractions;
- use of synthesis gas, which can be obtained from any hydrocarbon feedstock, including household waste;
- low costs of transportation of liquid products compared to gaseous;
- high cetane number of the resulting diesel fuel, which is due to the low content of aromatic hydrocarbons;
- process flexibility provided by the ability to use various hydrocarbon feedstocks and at the same time obtain a wide range of products for various industrial sectors;
- the possibility of compounding the resulting fuel fractions with various mixtures of hydrocarbons, including using fractions of organic origin (seed oil).

The composition and yield of synthesis products depend on the ratio $CO:H_2$ in synthesis gas, technological parameters of the process, as well as the catalyst used [11].

Basically, works devoted to the study of catalysts for the synthesis of motor fuels were carried out in order to determine the effect of the nature of the catalyst carrier, the type and amount of additives to the active component on the activity and selectivity of catalysts, depending on the process conditions.

The activity of catalytic systems in the Fischer–Tropsch synthesis and their selectivity with respect to the formation of liquid hydrocarbons of fuel fractions substantially depends on the carrier used [12, 13].

The study of catalysts is of a comprehensive nature, ensuring the identification of their main consumer characteristics. These include, first, activity, mechanical strength and stability in work [14].

The choice of catalytic systems depends on the required composition of the synthesis products. At the same time, changes in catalyst preparation technologies, the use of synthetic carriers, and the delivery of diatomite from abroad require significant costs. The work is devoted to the study of the activity and physicochemical properties of cobalt catalysts, as well as the influence of the carrier and the conditions of the process of synthesis of hydrocarbons from synthesis gas on the composition and yield of products.

The use of diatomites of the Malchevskoye field as carriers of catalysts for the synthesis of diesel fuel by the Fischer–Tropsch method has been investigated. Studies of the chemical composition of diatomites are presented in Table 1.

Table 1. Chemical composition of diatomites

Diatomite	Oxide content, %							
	SiO_2	Al_2O_3 + TiO_2	Fe_2O_3 + FeO	K_2O	Na_2O	CaO	MgO	SO_3
Kisatibsky	85.0–96.8	0.9–6.2	0.36–3.2	0.5	0.6	0.19	0.06	–
Malchevsky	66.0–72.0	12.0–16.0	3.6–7.2	–	–	0.9–3.0	0.3–1.3	0.01–0.8

In its natural form, in addition to minerals, diatomites contain a large amount of ballast inclusions, which are firmly bonded with the minerals that make up the structure of diatomite, therefore, it is necessary to separate pollutants from the natural material.

2 Methodology

2.1 Preparation of the Catalyst

For thyye research, the catalyst was prepared with the composition: Co—100; MgO—6,5; ZrO_2—9,8; carrier—200.

In a special container, the coprecipitation of metals and the carrier was carried out at a temperature 95 °C. The resulting mass was filtered, the precipitate was washed with hot distilled water to pH 7.5–8 in washing waters, and the catalyst was molded by extrusion into particles with a diameter of 3–4 mm. The resulting catalyst was dried at a temperature 120–130 °C, crushed and sieved. The catalyst grains with a size of 1.0–5.0 mm were reduced in the reactor until 60% of cobalt was transformed into a metallic state at a volumetric velocity of hydrogen 3000 h–1 and temperature 400 °C. After the completion of the reduction, the catalyst was cooled in a weak flow of carbon dioxide.

2.2 Determination of the Catalysts' Chemical Composition

The chemical composition of the obtained catalysts was determined by the method of trilonometric titration: cobalt—in acetone and ammonium thiocyanate, zirconium—in xylene orange, and magnesium—in the environment of eriochrome black.

2.3 Determination of the Catalysts' Mechanical Strength

Strength tests were carried out in the following way: a weighed portion of the catalyst (100 g) and a metal ball with a diameter of 8 mm were placed in a drum rotating at a speed of 1200 rpm. For 15, abrasion was carried out, then particles less than 2 mm in size were sifted out and the sample was weighed.

$$Y = \frac{m_0 - m}{m_0} \tag{1}$$

where

Y abrasion, %;
m_0 sample weight before abrasion, g;
m sample weight after abrasion, g.

2.4 Determination of the Degree of Catalyst Reduction

The degree of cobalt reduction in the catalyst was determined by trilonometric titration in acetone with ammonium thiocyanate taking into account the dilution of solutions.

2.5 Study of Catalytic Properties

The rate of reaction in the presence of a catalyst can serve as a measure of catalytic activity. When assessing the activity of contact masses under production conditions, the reaction rate is usually calculated with respect to a unit volume of catalyst per unit time [12, 15].

There are many methods for determining the kinetic characteristics of catalysts, which can be divided into two main groups:

- static, carried out in closed systems;
- dynamic—in open systems.

2.6 Static Method

The reaction is carried out in a closed volume until thermodynamic equilibrium is established or until one of the starting reagents is completely converted. The concentration of the reagents changes from the initial to the equilibrium one, and accordingly the reaction rate changes according to the law of effective masses.

Static methods can only be used to study stationary catalysts in relation to reaction mixtures.

2.7 Dynamic (Flow) Methods

The most common are flow-through methods for measuring catalytic activity. In flow-through installations, a stream of reagents is passed at a certain rate through the reaction volume containing the catalyst, and the process parameters are measured, compositional analyzes are performed at the inlet and outlet of the reactor and, if possible, at various points in this volume. Flow-through methods make it possible to carry out kinetic studies under steady-state conditions, i.e. at constant initial concentrations, temperatures, pressure, degree of mixing and other parameters in each individual experiment. During the transition from one experiment to another, certain process parameters are changed by a predetermined value.

The flow method is integral and continuous. It allows you to carry out the process for as long as you like at given concentrations, temperatures, pressures, linear and volumetric velocities of the gas flow at the inlet to the reactor. Naturally, the concentrations of reactants and other parameters change along the height of the reactor as a result of chemical transformation. The hardware design of such installations is simpler, and the sensitivity is lower than that of static ones.

The main advantage of the flow-through method is the ability to determine the catalytic activity at a steady state of the catalyst. Significant disadvantage—the impossibility of direct measurement of the reaction rate and the difficulty of realizing the ideal displacement regime in real conditions.

The essence of the method lies in the fact that a flow of synthesis gas at a certain rate was passed through a fixed catalyst bed, while simultaneously fixing the process parameters and analyzing the composition of the initial gas and reaction products. The use of this method is based on simplified assumptions about the ideal displacement mode at a steady state of the catalyst and a quasistationary state of the system; deviations from such modes are caused by the presence of certain gradients—concentration, temperature, etc., arising in the system under consideration.

2.8 Determination of the Activity and Selectivity of Catalysts

The tests of the activity and selectivity of the catalysts were carried out in continuous operation, changing the temperature of the process, maintaining the contraction K = 50–60%. Preliminarily at atmospheric pressure and synthesis gas space velocity equal to 50–80 h^{-1} catalyst was developed in a flow of synthesis gas, then the temperature was raised to 100 °C, from 100 to 160 °C the rise in temperature was carried out at a speed 3–5 °C, from 160 °C every 8 h the temperature was raised by 2 °C to contraction equal 45%. The contract is determined by the formula:

$$K = \frac{C_{out} - C_{in}}{C_{in}} \cdot 100\% \tag{2}$$

where

K contraction;
C_{out} tail gas concentration of carbon dioxide;
C_{in} concentration of carbon dioxide at the inlet to the installation.

2.9 Determination of Synthesis Products' Composition

The component composition of the hydrocarbons obtained during the Fischer–Tropsch synthesis was determined by gas chromatography. The essence of the method lies in the separation of hydrocarbon mixtures introduced into a chromatograph equipped with a capillary column with methylsiloxane as a stationary phase.

2.9.1 Characterization of Substances—Ecological and Safety Aspects

Carbon monoxide—flammable gas, explosive, poisonous, colorless and odorless, lighter than air, non-irritating.

MPC—0,02 mg/l, explosion limit of carbon monoxide—12,5–75,0%.

Hydrogen—odorless, colorless, tasteless, non-toxic gas. Explosive, flammable, lighter than air. Explosive limits—4,1–75%.

Paraffinic hydrocarbons—mixture of gaseous, liquid and solid substances. The mixture is flammable, explosive. MPC = 300 mg/m^3. Fire and explosive properties of hydrocarbons (for gasoline):

flash point—(–20 °C);
autoignition temperature—234 °C;
ignition area—1,2–7,5%;

2.9.2 Estimation of Greenhouse Gas Emissions

It is planned to carry out calculations to estimate the annual emissions of combustion products of the resulting diesel fuel into the atmosphere. Reduction of greenhouse gas emissions [16, 17] from the combustion of the resulting synthetic fuel is calculated according to the formula presented in Directive 2009/28/EU of the European Parliament and of the Council of April 23, 2009:

$$\mathrm{E}(\mathrm{E_F} - \mathrm{E_B})\big/\mathrm{E_F} \tag{3}$$

where

E	total emissions from fuel use;
$\mathrm{E_B}$	total emissions from Fischer–Tropsch fuels;
$\mathrm{E_F}$	total emissions from equivalent fossil fuels.

Carbon dioxide emissions from fuel combustion in internal combustion engines are estimated by the expression:

$$\mathrm{E} = \mathrm{M} \cdot \mathrm{K_1} \cdot \mathrm{TH_3} \cdot \mathrm{K_2} \cdot 44/12 \tag{4}$$

where

E	total annual emission $\mathrm{CO_2}$;
M	actual fuel consumption per year;
$\mathrm{K_1}$	fuel carbon oxidation ratio (fraction of carbon burned);
$\mathrm{TH_3}$	net calorific value;
$\mathrm{K_2}$	carbon emission factor;
44/12	factor for conversion of carbon emissions C into carbon dioxide $\mathrm{CO_2}$.

For diesel fuel, net calorific value $\mathrm{TH_3} = 43{,}02$ TJ/thousand tons; fuel carbon oxidation ratio $\mathrm{K_1} = 0{,}995$; carbon emission factor $\mathrm{K_2} = 19{,}98$ tC/TJ. The conversion factor for CO2 emissions from fossil fuel combustion for diesel is 3,15 t $\mathrm{CO_2}$/t or 2,6–2,8 kg $\mathrm{CO_2}$/l depending on the temperature of the fuel and its brand.

3 Results

Diatomite is used in industry as the main carrier for precipitated catalysts for the Fischer–Tropsch synthesis. The results of the study of the chemical composition, strength and degree of reduction of the obtained catalysts are presented in Table 2.

Table 2. Chemical composition and physicochemical properties of catalysts (Co content 100 parts by weight)

Catalyst	Chemical composition, %			Abrasion, %	Cobalt recovery time, min	Recovery rates, %
	Co	MgO	ZrO_2			
1	22.1	1.3	2.3	8.1	20	60
2	22.3	1.3	2.1	8.0	25	59
3	22.5	1.2	2.1	7.9	20	58
4	24.2	1.5	2.5	7.2	20	58

The data obtained allow us to say that the studied catalysts contain approximately the same amount of active components, and the degree of reduction of cobalt to the metallic state, as well as the recovery time of the catalyst, practically do not depend on its composition.

The advantages of cobalt catalysts include the fact that they start to work at low pressure, and sometimes at atmospheric pressure.

Catalyst activity and selectivity tests were carried out under pressure 0,7–1,0 MPa on synthesis gas of composition, volume percent %: $H_2 = 58–61$; $CO = 26–31$; $CO_2 = 6–13$; $CH_4 = 1–3$; $N_2 = 2–3$. The volumetric flow rate of synthesis gas during activity tests was varied within 100 h^{-1}, syngas processing 52–58 volume percent % (Table 3).

Studies have shown that the developed catalysts have shown their activity in the process of obtaining hydrocarbons of the fraction C5 and higher. So, at a synthesis temperature equal to 173° C and volumetric velocity 94–98 h–1 there was received 146–150 g/nm3 of hydrocarbons composition C5 + , and with an increase in temperature to 176° C, degree of processing 97–99 h-1 the yield of the target fraction was 151–158 g/nm3.

One of the most important characteristics of catalysts, in addition to their activity, is their selectivity, which in this case was evaluated by the composition of the obtained hydrocarbons. Fractional composition data are presented in Table 4.

The products obtained were represented by a wide range of hydrocarbons with different boiling points. To determine the groups of hydrocarbons, we carried out fractionation of the obtained fractions. The yield of hydrocarbons in the temperature range 170–225° C was 15–25%, the yield of the target fraction 225–335° C was 32–41%, the fraction 335–450° C was 19–28%. The yield of ceresins with a boiling point above 450° C varied from 7 to 20%.

Table 3. Catalyst activity

Catalyst	Synthesis temperature, °C	Syngas volumetric velocity, h^{-1}	Syngas processing rate, %	Hydrocarbon yield C_{5+}, g/nm^3
1	173	94	52	146
	176	99	54	151
2	173	98	56	150
	176	97	55	156
3	173	95	54	145
	176	98	57	152
4	173	96	53	146
	176	99	50	158

Table 4. Fractional hydrocarbon composition of the resulting product

Catalyst component	Composition of hydrocarbons, % in the boiling range, °C					The dropping point of hydrocarbons with a boiling point above 450 °C
	To 170	170–225	225–335	335–450	Higher than 450	
1	6	15	32	28	19	102
2	6	16	31	27	20	102
3	4	17	37	26	16	102
4	6	25	41	19	7	102

The cost of the produced synthetic fuel [10] is determined by the formula:

$$\mathrm{LevelizedCost}_{\mathrm{FTDiesel}} = \frac{C_{\mathrm{ICP}} + C_{\mathrm{O\&M}} + C_{\mathrm{EI}} + C_{\mathrm{Feedstock}} + C_{\mathrm{U}} - C_{\mathrm{income}}}{\mathrm{AnnualFTDieselProduction} \times \mathrm{CapacityFactor}}. \tag{5}$$

where

C_{ICP}	the cost of installation, operation of the installation and its maintenance,
$C_{\mathrm{O\&M}}$	utility costs,
$C_{\mathrm{El.}}$	electricity cost,
$C_{\mathrm{Feedstock}}$	raw material,
C_{U}	by-products,
C_{income}	income from the sale of manufactured products.

4 Conclusion

In the course of research, the chemical and mineralogical composition of diatomite was established. The precipitation method was used to prepare samples of a cobalt-magnesium-zirconium mechanically strong catalyst for the synthesis of hydrocarbons from synthesis gas by the Fischer–Tropsch method. The relationship between the catalytic properties and the chemical and mineralogical composition of the carrier and its physicochemical properties has been established. Catalysts were tested under conditions close to industrial ones.

Based on the results obtained, it can be said that the use of diatomite as a carrier of a cobalt-magnesium-zirconium catalyst is very promising, since it allows one to reduce production costs and at the same time achieve an increase in the yield of the target fraction; therefore, the catalysts have good activity and selectivity.

The activity of the catalyst is due to the developed porous structure of the catalyst formed as a result of the deposition of active components and is determined by the structure of diatomite.

The studies carried out show the relevance of the development of new catalytic systems that can be used in various areas of the chemical and petrochemical industries, as well as the need to improve the technological processes themselves by changing the design of the devices used in technologies.

Instrumental methods of obtaining data are of great importance. The use of new devices for research and monitoring of ongoing reactions will allow reaching a new level of obtaining new catalysts and optimizing technological processes.

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