

The process of modification of gas condensate gasolines with monohydric alcohols with subsequent cavitation treatment of these mixtures has been investigated. The expediency of using alcohol additives in fuels and the relevance of introducing into gasoline production such chemical technologies that use cavitation processing of raw materials and selective energy supply to the reaction zone have been substantiated. The expediency of the production of high-octane gasolines on the basis of a combination of the processes of mechanical mixing of hydrocarbon gasolines with alcohols and the processes of cavitation treatment of alcohol-gasoline mixtures is also substantiated. The description of the laboratory setup and the experimental methodology is given. The influence of the intensity of cavitation treatment on the increase in the octane number is studied and it is proved that there is some optimal intensity at which a constant value of the octane number of the mixture is achieved.

With an increase in the content of bioethanol in the mixture, the number of cavitation cycles (intensity) required to achieve the steady-state value of the octane number decreases from 8 cycles of gas condensate without bioethanol to 4 cycles with a bioethanol content of 3% and more. To achieve the octane number of the mixture corresponding to gasoline A-92 and A-95, it is necessary to add 2% and 5% bioethanol, respectively. It is shown that the use of cavitation can increase the octane number up to 2.6 points in comparison with simple mechanical mixing of alcohol and gasoline. A comparison is made of the efficiency of using bioethanol and isobutanol for modifying gas condensate gasoline in a cavitation field. The effect of cavitation on the octane number was studied with a change in the concentration of alcohol in the mixture.

A new way of modifying low-octane motor gasolines with bio-ethanol and other mixtures of alcohols of biochemical origin, which contain water impurities, is shown

Keywords: gas condensate gasoline, cavitation, monohydric alcohols, octane number, alcohols of biochemical origin

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MODIFICATION OF GAS CONDENSATE GASOLINE BY SINGLE ATOMIC ALCOHOLS WITH THE USE OF CAVITATION

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1. Introduction

One of the ways to reduce environmental pollution is to reduce the toxicity of emissions from motor gasoline. To achieve this goal, alternative technologies for the production of motor fuels are used, which also reduce the cost of gasoline production. In the future, it is possible to reduce the cost of gasoline production in chemical-technological processes by changing the method of supplying energy to the reaction zone.

The main method of supplying energy to the reaction zone is heating the feedstock and (or) catalyst to the required temperature and increasing the pressure. But the selectivity of this method of energy supply is extremely low. Therefore, energy consumption takes the second place in terms of volume in calculating the cost of motor fuels. The first place remains for the cost of raw materials.

But not always traditional technologies of homogeneous and heterogeneous catalysis can be effectively used for the production of high-octane gasolines. The use of traditional

catalysis is complicated by the presence of mechanical impurities in the feed, the content of catalytic poisons in the feed, low concentrations of reagents, and many more factors. Processes that use physical methods of affecting raw materials and catalyst can become promising alternative technological processes. The key advantage of physical methods of energy supply over thermal methods is the ability to selectively supply energy to reaction centers. In the future, this will help to reduce the total energy consumption for the production of products in industrial technological processes. Bioethanol is a common ethyl alcohol produced from plant materials. Bioethanol can be used as a standalone motor fuel, or as a high-octane gasoline additive. The use of bioethanol can be economically viable. This alcohol has a high octane number – 107–108 units according to the research method. The presence of an oxygen atom in the molecule reduces the formation of soot during the combustion of bioethanol and bioethanol-gasoline mixtures in car engines. This lengthens engine life and reduces exhaust emissions.

Bioethanol is a renewable resource. The use of bioethanol as a fuel does not lead to an increase in the amount of greenhouse gases. Upon receipt and subsequent combustion of bioethanol, the same amount of CO₂ is emitted as was removed from the atmosphere by plants, which were then processed into bioethanol.

The use of bioethanol reduces exhaust toxicity by 21 %. Oxygen present in ethanol allows more complete combustion of fuel hydrocarbons. Adding 10 % ethanol to gasoline reduces particulate matter emissions by 50 % and carbon monoxide emissions by 30 %. Bioethanol is biodegradable and does not irreversibly pollute the environment.

Some studies show that bioethanol has a negative energy balance. The production of bioethanol uses more energy than can be obtained from the combustion of bioethanol in engines. But the energy balance can be very different when bioethanol is produced from different plants. In addition, the production of high-octane hydrocarbon gasolines by traditional thermocatalytic methods also requires more energy than is released when these gasolines are burned. That is, bioethanol is a real competitor to hydrocarbons in the manufacture of high-octane motor gasolines.

Bioethanol also has its drawbacks. The heat of combustion of bioethanol is lower than in hydrocarbon gasolines – 25 MJ/kg in bioethanol versus 42 MJ/kg in gasoline.

Also, the presence of oxygen in the molecule makes bioethanol less energy intensive – 1 liter of ethanol contains 37 % less energy than 1 liter of hydrocarbon gasoline. This leads to a higher specific consumption of alcoholic fuels compared to hydrocarbon fuels. Bioethanol has a low vapor pressure and a high evaporation temperature. This makes it difficult to start the engine at low temperatures. Fuel containing bioethanol with water impurities will be highly corrosive. In some operating modes of the engine, incomplete combustion of bioethanol may occur. This will lead to the formation of toxic aldehydes in the exhaust gases. Due to the presence of these disadvantages, bioethanol, as a rule, is not used in pure form, but in the form of a mixture with hydrocarbon fuel. At the same time, the performance properties of gasoline are improved, and hydrocarbon resources are saved.

Isobutanol. This alcohol can become a real competitor to methanol and bioethanol as a high-octane gasoline additive due to its relatively low cost. Also, isobutanol, together with isopropanol and isoamyl alcohol, form the basis of fusel oils, which are a waste in the production of bioethanol and can be effectively used to increase the octane number of motor gasolines. Such use will improve the environmental characteristics of gasoline production processes and reduce the amount of waste in the production of bioethanol.

Thus, the development of new chemical technologies for the production of motor fuels with improved technical, economic and environmental characteristics is an urgent task for science and industry.

2. Literature review and problem statement

There are various methods of physical impact on raw materials and catalyst: acoustic methods, electromagnetic, mechanical and hydromechanical methods.

The article [1] shows the effect of hydrodynamic cavitation on the viscosity of heavy oil in the presence of metal nanoparticles and a hydrogen donor, which can be a gasoline

fraction. It is shown that the addition of 0.01 liters of gasoline per 1 liter of heavy oil during a 10-minute cavitation cracking process (at 80 °C and at atmospheric pressure) reduces the viscosity of heavy oil by about 20 %. However, the issues related to the influence of cavitation on the formation of catalytic activities of the metal remained unresolved, although it is about the formation of active catalyst nanoparticles. In [2], tetrahydronaphthalene was used as a hydrogen donor. Cavitation treatment also made it possible to redistribute hydrogen and reduce the viscosity of heavy oil, but the change in the octane number of the gasoline fraction of oil and its composition have not been determined.

Study of the influence of ultrasonic cavitation processing of raw materials on the physicochemical properties and the content of asphaltenes in oil residues is shown in [3]. It is shown that intense cavitation action leads to a decrease in the total amount of asphaltenes and to a decrease in viscosity characteristics, since the initiation of cracking reactions of high molecular weight hydrocarbon molecules was achieved by cavitation. But in this article the mechanism of the effect of cavitation on the chemical composition of products was not determined, it does not make it possible to optimize the cavitation mode with a given composition of products.

The influence of hydrodynamic cavitation on the composition of cracking products even when cavitation is a side parameter is shown in [4]. The ability to change the fractional composition of products and characteristics of gasoline when exposed to cavitation in the pump before the fractionation column of the catalytic cracking unit has been proven. Although the effect of cavitation on the octane number has not been experimentally confirmed.

In studies of the influence of cavitation on the cracking of hydrocarbon molecules with the number of carbon atoms in the article [5], ultrasonic cavitation in the diesel fraction was used and leads to the formation of soot nanoparticles. But the mechanism for the formation of soot is not associated with the intensification of reactions; this, in parallel, affects the octane number of gasolines.

The work [6] substantiated the amount of energy required to break chemical bonds in oil under the influence of cavitation. The possibility of carrying out the processes of raw material cracking solely by the influence of cavitation has been proved. But the issues related to the influence of this process on the production technology of individual components and commercial brands of gasoline remained unresolved.

Hydrodynamic cavitation is an attractive option as a technology for intensifying the processes of heavy oil refining [7], and these processes are promising for the modernization of oil refineries, but proposals for the design of technological processes have not been provided.

The mechanism by which cavitation technologies intensify the demulsification of water in emulsions, a decrease in the viscosity of crude oil, oxidative desulfurization and demetallization of oil and individual fractions is provided in [8]. It is shown that cavitation is a promising technology for complex impact on oil fractions. However, it is shown how water impurities affect the chemical transformations of hydrocarbons under the action of cavitation.

The study of various technological modes of processing oil fractions with the implementation of the hydrocracking process of hydrocarbons is shown in [9], but the change in the gasoline fraction, the main product of

these processes, is not shown in this work. The influence of cavitation on fuel combustion processes was studied in [10], however, the processes of fuel fabrication and their combustion under the influence of cavitation treatment are not related.

The studies given in [11] showed the influence of the bioethanol content and the parameters of the cavitation field on the quality indicators of motor gasolines. It has been proven that the impact of bioethanol and cavitation treatment of bioethanol-gasoline mixture will make it possible to produce automotive fuel for different climatic zones, or winter (summer) versions of gasoline, but no practical recommendations for the technological process have been provided.

In [12], the effect of cavitation on the octane number for gas condensate gasoline with the addition of isopropanol in an amount of 0–12 % by volume and on the intensification of cracking reactions of petroleum products was studied.

In [13], studies of the composition of alcohol-gasoline mixtures after cavitation treatment showed an increase in the content of ethers. A mechanism of chemical transformations was proposed that explains the increase in the octane number (ON) of alcohol-gasoline mixtures under the influence of cavitation.

In work [14] it is shown that the use of isopropyl alcohol (IPA) and cavitation treatment of alcohol-gasoline mixtures will make it possible to produce trademarks of gasoline with lower raw material costs in comparison with traditional technological processes. But the question remained unresolved related to the existence of the optimal intensity at which a constant value of the octane number of the mixture is achieved.

Thus, the possibility and prospects of introducing cavitation treatment technologies into fuel modification processes is beyond doubt. Analysis of possible pathways for chemical transformations of alkanes and alcohols in a cavitation field allows to conclude that the products of cavitation processing are high-octane components of motor fuels. In this case, the reactions of the formation of ethers from alcohols will make it possible to obtain chemical substances that are stabilizers of emulsions. This makes it possible to obtain an alcohol-gasoline fuel that is resistant to delamination even in the presence of water in the mixture. This opens up a new way of modifying low-octane automobile gasolines with bioethanol and other mixtures of alcohols of biochemical origin, which contain water impurities.

The study of the process of modifying gas condensate gasoline with bioethanol and isobutanol (which is one of the main components of fusel oils in the production of bioethanol) using the mechanochemical activation of alcohol-gasoline mixtures, expressed through their cavitation treatment, is an urgent scientific and practical task. The solution to this problem will create an energy and resource efficient technology for the production of motor gasoline with the involvement of biological raw materials in the technological process, reduces the “carbon footprint” from the use of such fuels and improves their environmental performance.

3. The aim and objectives of research

The aim of research is to develop a process for modifying gas condensate gasoline with bioethanol and isobutanol under conditions of mechanochemical activation, achieved through cavitation treatment of alcohol-gasoline mixtures with a given intensity.

To achieve this aim, it is necessary to solve the following objectives:

- to study the influence of the intensity of cavitation treatment on the increase in the octane number and to prove the existence of an optimal intensity at which a constant value of the octane number of the mixture is achieved;
- to investigate the effect of the concentration of bioethanol in gas-condensate gasoline on the octane number under conditions of cavitation treatment;
- to reveal the influence of the intensity of cavitation on the increase in the octane number for a mixture of gas condensate gasoline with isobutanol in various concentrations;
- to determine the effect of the concentration of isobutanol on the octane number of the modified gasoline under conditions of cavitation treatment.

4. Materials and methods of research

The main task of the laboratory unit for studying the effect of cavitation treatment on the octane number of alcohol-gasoline mixtures is as close as possible to the conditions of future industrial technology. Therefore, the laboratory unit reproduces all the necessary technological stages of mixing alcohol with hydrocarbon gasoline fractions, cavitation treatment, recycling of raw materials, separation of alcohol-gasoline mixture from gaseous products, analysis of the liquid and gas phases.

Experimental studies were carried out on an original laboratory unit, schematically shown in Fig. 1.

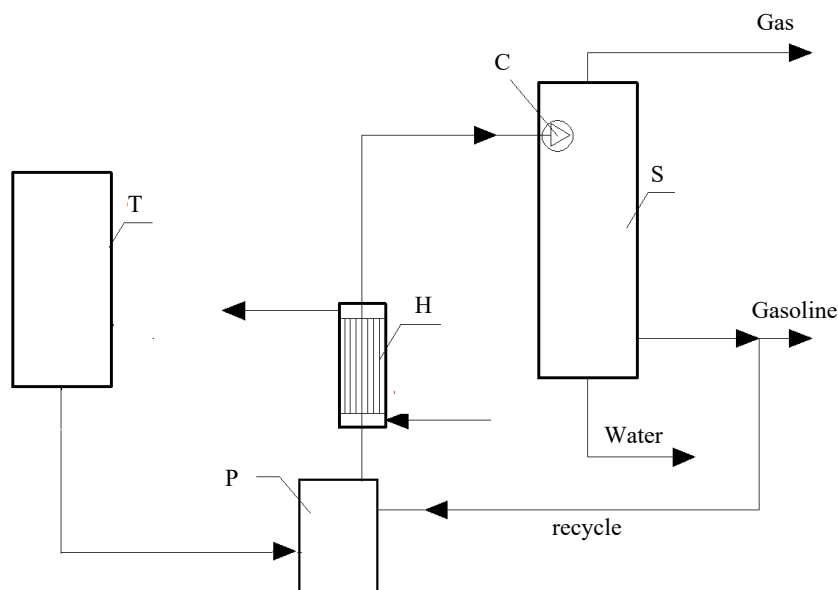


Fig. 1. Diagram of a laboratory unit for studying the effect of cavitation treatment on the octane number and composition of gasolines modified with alcohols: T – tank with raw materials; P – high pressure pump; H – heat exchanger; C – cavitation nozzle; S – separator

Dynamic cavitation is realized on a nozzle that has the shape of a subsonic Laval nozzle. The pressure at the inlet of the nozzle is 9.0 MPa. This pressure is sufficient to carry out the necessary chemical transformations with minimal energy consumption. A change in the number of cycles of cavitation processing of raw materials leads to a change in the intensity of mechanochemical activation of an alcohol-gasoline mixture and affects the composition of the products and the octane number. By varying the intensity of mechanochemical activation through cavitation, it is possible to achieve the required octane number for alcohol-gasoline mixtures. And also to obtain trademarks of A-95 and A-98 gasolines with the lowest possible alcohol consumption, in the future industrial technology will reduce the cost of production by reducing the cost of raw materials.

The experiments were carried out in this way. Gasoline is mixed with alcohol in the required proportion and enters the container, from which the raw material is dosed by the regulator using a high-pressure pump to the nozzle-reactor. The high-pressure pump creates a pressure at the nozzle inlet at the level of 9.0 MPa. The pressure at the inlet of the nozzle is controlled by a pressure gauge, and the change in the flow rate, pierces through the nozzle, is achieved through a change in the diameter of the nozzle. At the outlet of the nozzle, cavitation cavities are formed, which are mini-reactors. Chemical transformations take place in them. Cavitation cavities are also formed when droplets of raw material, escaping from the nozzle at a speed of more than 140 m/s, collide with the walls of the reactor and with a cone-shaped baffle located in the separator directly in front of the nozzle.

The separator collects raw materials and degassing them from air and possible gaseous products. The gas phase at the top of the separator is analyzed chromatographically for hydrocarbon content. The liquid phase, which is the target product, is sent for analysis of octane number and chemical composition. The intensity of cavitation treatment is regulated both by replacing the nozzle (by changing the pressure) and by varying the number of cavitation treatment cycles. For this, the possibility of raw material recycling is provided.

Analysis of the process of modification of motor gasolines in a cavitation field made it possible to conclude that the output parameters of the process (fractional composition and volatility) are regulated by changing the mixture flow rate, bioethanol content and pressure at the inlet of the nozzle.

Fractional composition of raw materials and products was determined according to ISO 3405-88. The octane number according to the research method was determined using a portable SHATOX SX-150 Octane Meter (manufactured by the Institute of Petroleum Chemistry, Tomsk, RF, release date 12.10.2009) with a measurement error of no more than 0.2 points. The stability of raw materials and products was determined in accordance with GOST 7685: 2015 "Gasoline. Method for determination of oxidation stability (induction period method)". Vapor pressure was determined ac-

ording to 6 ASTM 323-08 Standard test method for vapor pressure of petroleum products (Reid method). The content of individual hydrocarbons, alcohols, ethers in the samples was determined chromatographically on a Kristall-2000 chromatograph (Russia).

5. Results of studies of the influence of cavitation treatment on the octane number of gasoline

5.1. Influence of the intensity of cavitation treatment on the increase in the octane number of the mixture

Below let's consider the cavitation treatment of a mixture of gas condensate gasoline with bioethanol of various concentrations. A constant cavitation effect is achieved by several passes of the mixture through a cavitation nozzle with a pressure of 9.0 MPa. The experimental data with the change in the octane number of the mixture with the research method (RON) and the octane number by the motor method (MON) are given in Table 1.

Table 1

Change (RON) and (MON) from the number of cavitation treatment cycles for gas condensate with the addition of bioethanol

ON, scores	Number of cavitation treatment cycles										
	0	1	2	3	4	5	6	7	8	9	10
Gas condensate without bioethanol additive											
RON	78.6	78.3	78.7	79.0	79.1	79.2	79.2	79.3	79.3	79.5	79.6
MON	76.0	75.8	76.2	76.3	76.4	76.5	76.5	76.6	76.5	76.7	76.7
Gas condensate with an addition of 0.5 % vol. bioethanol											
RON	87.2	87.9	87.9	88.1	89.1	88.6	88.9	89.3	89.3	89.8	89.4
MON	80.6	81.0	81.0	81.2	81.6	81.4	81.5	81.7	81.7	81.9	81.7
Gas condensate with an addition of 1 % vol. bioethanol											
RON	81.1	82.5	83.1	83.6	84.6	84.8	85.5	85.8	86.0	85.5	86.2
MON	77.6	78.4	78.7	78.5	79.6	79.6	79.9	80.0	80.1	79.9	80.2
Gas condensate with an addition of 1.5 % vol. bioethanol											
RON	91.5	91.9	92.1	92.1	92.1	92.2	92.4	92.4	92.4	92.3	92.3
MON	82.8	83.0	83.2	83.1	83.1	83.2	83.4	83.5	83.4	83.3	83.4
Gas condensate with an addition of 2 % vol. bioethanol											
RON	90.8	91.1	91.3	91.3	91.7	91.6	91.4	91.4	91.8	91.6	91.7
MON	82.4	82.5	82.7	82.6	82.8	82.8	82.8	82.7	82.9	82.8	82.9
Gas condensate with an addition of 3 % vol. bioethanol											
RON	93.9	94.4	94.1	94.4	94.4	94.5	94.5	94.6	94.6	94.7	94.6
MON	84.1	84.4	84.1	84.4	84.4	84.5	84.5	84.6	84.6	84.7	84.6
Gas condensate with an addition of 4 % vol. bioethanol											
RON	94.9	95.0	95.1	95.1	95.1	95.3	95.7	95.4	95.4	95.5	95.7
MON	84.9	85.0	85.1	85.1	85.1	85.3	85.7	85.4	85.4	85.5	85.7
Gas condensate with an addition of 5 % vol. bioethanol											
RON	96.3	96.5	96.6	96.9	97.0	97.0	97.0	97.0	96.9	96.8	97.2
MON	86.3	86.7	87.0	87.2	87.2	87.2	87.2	87.2	87.2	87.2	87.2

5.2. Influence of the bioethanol content in the gas condensate of the mixture on the increase in the octane number

Below is considered the change in the octane number during cavitation treatment of a mixture of gas condensate gasoline with bioethanol of various concentrations according to the research method (RON) and the motor method (MON). The experimental data with an increase in the octane number due to the cavitation action is given in Table 2.

Table 2

The change in the octane number according to the research method (RON) and according to the motor method (MON) before and after cavitation treatment, depending on the bioethanol content in the gas condensate

No.	Bioethanol content in gas condensate, % vol.	RON		MON		Octane number increase, points	
		Be-fore	After	Be-fore	After	RON	MON
1	0	78.6	79.6	76.0	76.7	1.0	0.7
2	0.5	87.2	89.4	80.6	81.7	2.2	1.1
3	1.0	81.1	86.2	77.6	80.2	5.1	2.6
4	1.5	91.5	92.3	82.8	83.4	0.8	0.6
5	2.0	90.8	91.7	82.4	82.9	0.9	0.5
6	3.0	93.9	94.6	84.1	84.6	0.7	0.5
7	4.0	94.9	95.7	84.9	85.7	0.6	0.8
8	5.0	96.3	97.2	86.3	87.2	0.9	0.9

In the absence of bioethanol additives, the RON of gas condensate increased by almost 1 point according to the research method, and 0.7 points according to the motor method during cavitation treatment. That is, the hydrocarbon mixture undergoes cavitation treatment and chemical transformations occur, which lead to an increase in high-octane components in the gas condensate.

5.3. Influence of the intensity of mechanochemical activation, expressed by the change in the number of cavitation treatment cycles on the octane number of gas condensate gasoline with bioethanol additives

The most effective was a mixture of 99 % gas condensate and 1 % bioethanol. Already simple mechanical mixing of condensate and bioethanol increased RON by 2.5 points and MON increased by 1.7 points. The total increase in RON during cavitation treatment was 5.1 points, and MON – 2.6 points. In this case, there is no delamination of the mixture.

A further increase in the amount of bioethanol in the mixture reduces the effect of cavitation treatment, although the initial RON and MON are much higher. For example, for a mixture of 97 % condensate and 3 % bioethanol, RON increased by almost 15.3 points compared to pure gas condensate, and the increase in MON was 8.1 points. During the cavitation treatment, the increase in RON and MON was 0.7 and 0.5 points, respectively. That is, there is a certain optimal concentration of bioethanol in a mixture with gas condensate, at which cavitation treatment gives the greatest increase in octane number. It has been experimentally established that such is the concentration of 1.0 % by volume of bioethanol in gasoline. Mixtures with a concentration of 2 %, 3 %, 4 %, 5 % bioethanol show approximately the same octane increase due to cavitation treatment. Starting from a

concentration of 2 %, a small amount (about 0.1–0.2 % by volume of the mixture) of the heavy phase – water with impurities of alcohols and ethers – is peeled off in the mixture.

Fig. 2 shows the nature of the change in the octane number according to the research method from the number of cavitation treatment cycles. It can be noted that 3–5 cavitation treatment cycles were sufficient to achieve the steady-state value of RON. Although for a mixture with an admixture of 1.0 % bioethanol a little more intensity of cavitation treatment was required – a constant octane number was achieved after 7 cycles.

The nature of the change in the octane number of gas condensate gasoline, modified bioethanol in various concentrations, from the number of cavitation treatment cycles can be described by equations (1)–(6), are given in Table 3. This makes it possible to optimize the consumption of bioethanol for modification from the selected mode of mechanochemical activation of gasoline through cavitation for the production of commercial brands of gasoline A-92, A-95, etc.

Table 3

Modeling the effect of the intensity of mechanochemical activation of N_{MCA} (through cavitation) on the octane number at various concentrations of bioethanol in gas condensate gasoline

No.	Bioethanol content, % vol.	Equation of the influence of MCA on RON
1	–	$RON = -0.0055 \cdot (N_{MCA})^2 + 0.1666 \cdot N_{MCA} + 78.431$
2	1	$RON = -0.0547 \cdot (N_{MCA})^2 + 1.0148 \cdot N_{MCA} + 81.266$
3	2	$RON = -0.0111 \cdot (N_{MCA})^2 + 0.1825 \cdot N_{MCA} + 90.902$
4	3	$RON = -0.0066 \cdot (N_{MCA})^2 + 0.1273 \cdot N_{MCA} + 94.023$
5	4	$RON = -0.002 \cdot (N_{MCA})^2 + 0.0934 \cdot N_{MCA} + 94.893$
6	5	$RON = -0.012 \cdot (N_{MCA})^2 + 0.1854 \cdot N_{MCA} + 96.342$

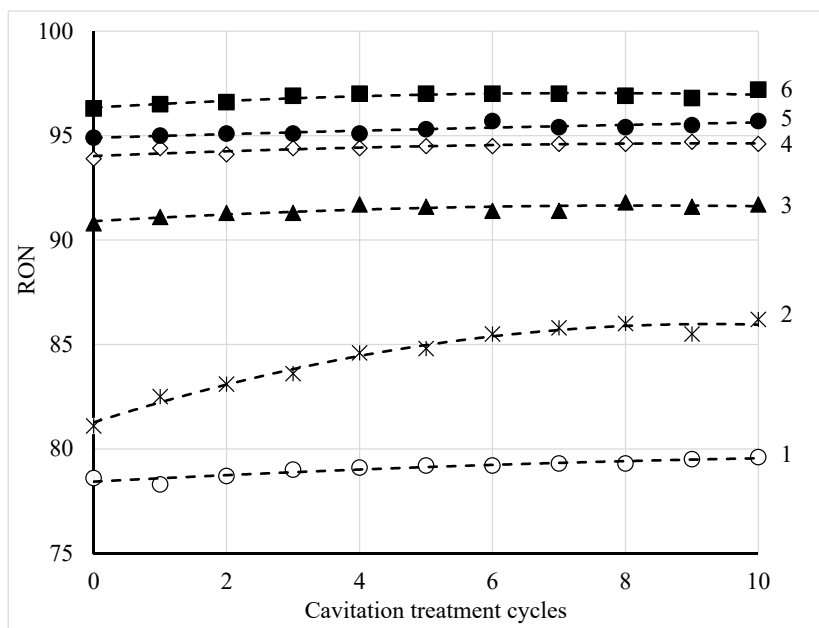


Fig. 2. Influence of the number of cavitation treatment cycles on the octane number of gas-condensate gasoline modified with bioethanol: 1 – no bioethanol; 2 – 1 % bioethanol; 3 – 2 % bioethanol; 4 – 3 % bioethanol; 5 – 4 % bioethanol; 6 – 5 % bioethanol

An increase in the number of cavitation treatment cycles to 30 did not give an effect higher than that achieved for 5–7 cycles. Although, it is possible that by increasing the pressure in front of the nozzle above 9.0 MPa, it will be possible to achieve high octane increase rates.

5.4. Influence of the intensity of cavitation on the increase in the octane number for a mixture of gas condensate gasoline with isobutanol

Isobutanol can become a real competitor to methanol and bioethanol as a high-octane additive due to its relatively low cost. The use of biobutanol, which is one of the main components of fusel oils, will further reduce the production

cost of A-95 and A-98 gasoline. Biobutanol has a lower specific oxygen content in the molecule, therefore, biobutanol-based fuels will have a higher specific energy content than fuels with an admixture of bioethanol and isopropanol. The experimental data are given in Table 4.

It should be noted that the use of isobutanol requires a greater number of cavitation treatment cycles to achieve a stable increase in ON than bioethanol and isopropanol [12]. For the industry, this will mean high energy consumption for the production of similar grades of fuel. But the promise of isobutanol lies in the fact that higher energy costs for cavitation treatment will be compensated by a lower cost of raw materials.

Table 4

Octane number change by research (RON) and motor (MON) methods versus the number of cavitation treatment cycles for gas condensate with the addition of isobutanol

ON	Number of cavitation treatment cycles													
	0	1	2	3	4	5	6	7	8	9	10	15	20	25
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Gas condensate without isobutanol addition														
T	25.3	24	24	24.5	24.7	25.1	25.3	26	25.9	26.4	27	27.4	27.9	28.6
RON	93.4	94	94	94.1	94.3	94.4	94.3	95	94.7	94.7	94.8	94.9	95	95
MON	83.8	84	84	84.1	84.3	84.4	84.4	85	84.7	84.7	84.8	84.9	85	85
AKI	88.8	89	89	89.1	89.3	89.4	89.6	90	89.8	89.8	90	90.3	90.7	90.7
Gas condensate with an addition of 0.5 % vol. isobutanol														
T	26.5	26	27	27.2	28.1	28.8	29.3	30	30.5	30.8	30.8	30.8	30.6	30.2
RON	94.7	95	95	94.8	94.9	94.9	95.1	95	95.7	95.8	95.8	95.9	95.9	95.9
MON	84.7	85	85	84.8	84.9	84.9	85.1	85	85.7	85.7	85.8	85.9	85.9	85.9
AKI	89.7	90	90	89.8	89.9	90	90.1	90	90.7	90.8	90.8	90.9	90.9	90.9
Gas condensate with an addition of 1 % vol. isobutanol														
T	25.8	26	26	26.8	27.4	28.4	29.4	30	30.2	30.8	30.9	31.1	31.6	31.7
RON	94.8	95	95	94.9	95	95.1	95.6	96	95.8	95.9	95.9	96.2	96.2	96.2
MON	84.8	85	85	84.9	85	85.1	85.1	86	85.7	85.8	85.9	85.9	86.1	86.2
AKI	89.8	90	90	89.9	90	90.1	90.6	91	90.8	90.9	90.9	91.1	91.2	91.2
Gas condensate with an addition of 3 % vol. isobutanol														
T	29.5	29	30	30.1	30.4	31	31.6	32	32.5	32.8	33.5	33.5	33.5	33.6
RON	96.4	96	96	96.5	96.9	96.9	97.3	97	97.4	97.5	97.6	97.6	97.7	97.7
MON	86.5	87	87	86.8	87.1	87.2	87.3	87	87.4	87.5	87.6	87.6	87.7	87.7
AKI	91.6	92	92	91.8	92	92.2	92.3	92	92.4	92.5	92.6	92.6	92.7	92.7
Gas condensate with an addition of 5 % vol. isobutanol														
T	31.5	30	30	30.5	30.9	31.6	32.4	33	33.3	33.6	34	34.1	34.4	34.1
RON	97.8	98	98	97.8	97.9	98	98.3	98	98.7	99	99.1	99.1	99.2	99.2
MON	87.8	88	88	87.8	87.9	88	88.4	89	88.9	89.1	89.1	89.2	89.2	89.2
AKI	92.8	93	93	92.8	92.9	93	93.4	94	93.8	94	94.1	94.1	94.2	94.2
Gas condensate with an addition of 10 % vol. isobutanol														
T	25.6	26	26	26.3	26.7	27.8	28.4	29	29.6	30	30	28.1	28.7	29.8
RON	101.3	101.3	101.3	101.5	101.7	101.8	102	102.2	102.4	102.4	102.6	102.6	102.6	102.6
MON	91	91	91	91.4	91.5	91.7	91.8	92	92	92.1	92.2	92.2	92.2	92.2
AKI	96.2	96	97	96.7	96.8	97	97.1	97	97.3	97.3	97.4	97.4	97.4	97.4
Gas condensate with an addition of 15 % vol. isobutanol														
T	28.9	29	28	28.6	28.9	30.1	30.1	30	30.6	30.5	30.6	30.8	31	31
RON	105.6	105.6	105.7	105.8	105.9	106	106.1	106.2	106.3	106.4	106.5	106.6	106.5	106.5
MON	95.5	96	96	95.8	95.9	96.1	96.1	96	96.3	96.5	96.5	96.6	96.6	96.6
AKI	100.5	100.6	100.7	100.8	100.9	101	101.1	101.2	101.3	101.4	101.4	101.4	101.4	101.4

5. 5. Influence of isobutanol concentration on the octane number of modified gasoline under cavitation treatment

The change in the octane number during the cavitation treatment of a mixture of gas condensate gasoline with isobutanol of various concentrations according to the research method (RON) and the motor method (MON) is considered. The experimental data with an increase in the octane number due to the cavitation action is given in Table 5.

When carrying out this series of experiments, a significant increase in the temperature of the mixture of gas condensate gasoline with alcohol was noticed after 15–25 cycles of cavitation treatment. An increase in temperature led to an additional increase in the ON of the mixture, therefore, a significant increase in ON is observed immediately after the end of cavitation treatment and a gradual decrease in ON by 0.6–1.2 points as a result of cooling the mixture.

In Fig. 3 it can be seen that the achievement of the steady-state value of ON is achieved after 8–10 cycles of cavitation treatment. Among the alcohols studied, isobutanol showed the need to supply the greatest amount of energy through cavitation treatment to achieve a stable effect of increasing the octane number. If to compare bioethanol, isopropanol and isobutanol, it can be seen that the lower the molecular weight of the alcohol, the less energy must be supplied to achieve a stable effect from cavitation. But in absolute terms, the greatest increase in the octane number was shown by bioethanol – the alcohol with the lowest molecular weight among the studied alcohols.

The nature of the change in the octane number of gas condensate gasoline modified with isobutanol in various concentrations, depending on the number of cavitation treatment cycles, can be described by equations (7)–(9) given in Table 6. Polynomial dependences allow not only to foresee the consumption of isobutanol required for the modification of gas condensate gasoline, according to the selected mechanochemical activation mode, but also provide for an increase in the octane number when the number of MCA cycles is above 25. Perhaps this is due to the initiation of a new wave of chemical transformations – this requires additional research.

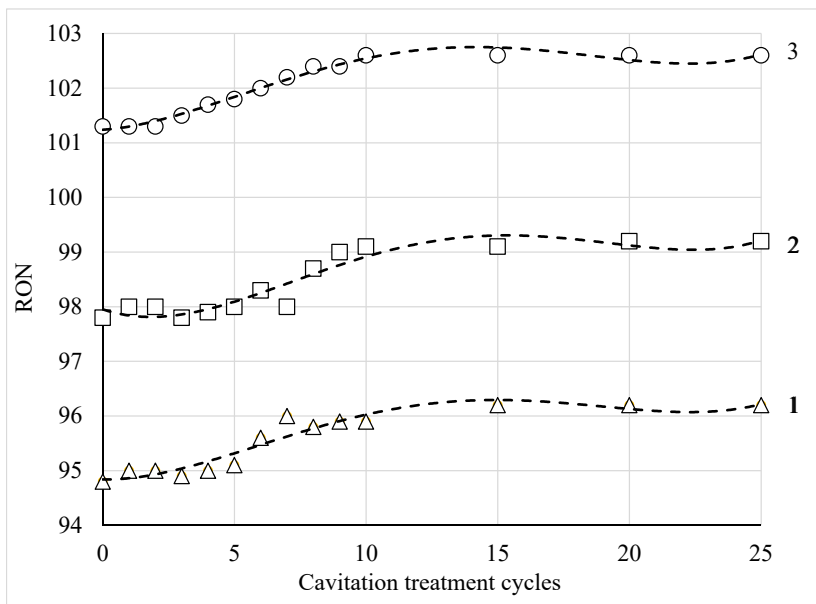


Fig. 3. Influence of the number of cavitation treatment cycles on the octane number of gas condensate gasoline modified with isobutanol: 1 – 1 % isobutanol, 2 – 5 % isobutanol, 3 – 10 % isobutanol

Table 6

Modeling the effect of the intensity of mechanochemical activation of NMXA (through cavitation) on the octane number at various concentrations of isobutanol in gas condensate gasoline

No.	Isobutanol concentration, % vol.	Equation of the influence of MCA on RON
7	1	$RON = 5 \cdot 10^{-5} \cdot (N_{MCA})^4 - 0.0022 \cdot (N_{MCA})^3 + 0.0303 \cdot (N_{MCA})^2 - 0.0052 \cdot N_{MCA} + 94.838$
8	5	$RON = 7 \cdot 10^{-5} \cdot (N_{MCA})^4 - 0.0035 \cdot (N_{MCA})^3 + 0.0541 \cdot (N_{MCA})^2 - 0.1644 \cdot N_{MCA} + 97.953$
9	10	$RON = 5 \cdot 10^{-5} \cdot (N_{MCA})^4 - 0.0022 \cdot (N_{MCA})^3 + 0.0269 \cdot (N_{MCA})^2 + 0.0349 \cdot N_{MCA} + 101.24$

Among the alcohols studied, isobutanol showed the need to supply the greatest amount of energy through cavitation treatment to achieve a stable effect of increasing the octane number. If to compare bioethanol, isopropanol and isobutanol, it can be seen that the lower the molecular weight of the alcohol, the less energy must be supplied to achieve a stable effect from cavitation. But in absolute terms, the greatest increase in the octane number was shown by bioethanol – the alcohol with the lowest molecular weight among the studied alcohols. When adding isobutanol, it is necessary to supply the greatest amount of energy through cavitation treatment in order to achieve a stable effect of an increase in octane number.

Comparison of the results of studies on the octane number increase for alcohol-gasoline mixtures modified with bioethanol with the data of studies of mixtures modified with isopropanol given in [12].

Graphical dependences of changes in ON according to the research method for gasoline with different amounts of added bioethanol and isopropanol are shown in Fig. 4. When using bioethanol, the effect of cavitation

The change in the octane number according to the research method (RON) and according to the motor method (MON) before and after cavitation treatment, depending on the content of isobutanol in the gas condensate

No.	Isobutanol content in the gas condensate, % vol.	RON		MON		Octane number increase, points	
		Before	After	Before	After	RON	MON
1	0	93.4	94.97	83.8	84.97	1.57	1.17
2	0.5	94.7	95.90	84.7	85.90	1.2	1.2
3	1.0	94.8	96.20	84.8	86.07	1.40	1.27
4	3.0	96.4	97.67	86.5	87.67	1.27	1.17
5	5.0	97.8	99.17	87.8	89.20	1.37	1.40
6	10.0	101.3	102.60	91	92.20	1.3	1.2
7	15.0	105.6	106.53	95.5	96.60	0.93	1.1

Table 5

is much more pronounced at low alcohol concentrations – up to 1 % vol. This may be due to both the intensification of chemical transformations and the homogenization of the emulsion formed when water from bioethanol gets into gasoline.

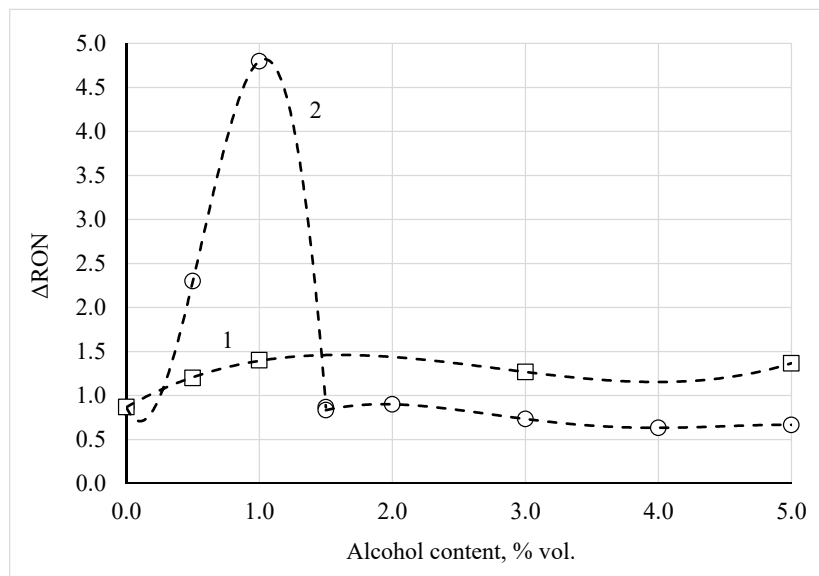


Fig. 4. Change of octane number according to the research method during cavitation treatment of gas condensate gasoline at different concentrations of alcohols: 1 – isobutanol; 2 – bioethanol

Octane increase of gas condensate gasoline, modified bioethanol in different concentrations compared to the data for isobutanol addition in the same concentration range. Mathematical dependencies are described by equations (10)–(12) and are given in Table 7. If for the addition of bioethanol there is a clear optimum in concentration, at which a significantly greater increase in octane number is achieved under the action of mechanochemical activation through cavitation, then for isobutanol the optimum is almost unnoticeable – in the entire studied range of concentrations, the effect of mechanochemical activation makes it possible to achieve an additional increase in the octane number by 1.4–1.5 points, which is slightly more than for bioethanol, excluding concentrations up to 1 % vol.

Table 7

Modeling the influence of the alcohol concentration C_a on the additional increase in the octane number under the action of MCA through cavitation in gas condensate gasoline

No.	Alcohol concentration range	Equation of influence of C_a on ΔRON
10	0–2 % vol. bioethanol	$\Delta\text{RON} = -10 \cdot (C_a)^3 + 17.133 \cdot (C_a)^2 - 3.2 \cdot C_a + 0.8667$
11	2–5 % vol. bioethanol	$\Delta\text{RON} = -0.0235 \cdot (C_a)^4 + 0.34 \cdot (C_a)^3 - 1.7346 \cdot (C_a)^2 + 3.5733 \cdot C_a - 1.6524$
12	0–5 % vol. isobutanol	$\Delta\text{RON} = 0.045 \cdot (C_a)^3 - 0.3771 \cdot (C_a)^2 + 0.8594 \cdot C_a + 0.867$

It should be noted that the phenomenon of the resonant effect of the intensity of mechanical activation, which includes cavitation, was also observed for other technologies using mechanical methods for selectively supplying energy to reaction centers. For example, in the method known as

“aerosol nanocatalysis” [9], the catalyst is activated due to a change in the vibration frequency of the vibroreactor. The conducted studies of various processes of hydrocarbon processing by this method showed the presence of anomalous maximum dependences of the effective rate constant of cracking reactions at certain vibration frequencies, as well as a change in the yield of individual products.

For cavitation treatment, the resonance phenomenon can be explained through the creation of an optimal concentration of activated particles. In this case, the rate of consumption of activated particles by target reactions exceeds the rate of consumption by side reactions. With a further increase in concentration, off-target reactions are accelerated, for example, reactions for the production of n-alkanes and densification reactions.

Fig. 4 illustrates the possibility of establishing optimal alcohol concentrations at which the technology of cavitation processing of raw materials gives the maximum effect. The original ON of the gasoline fraction can be changed by compounding it with high-octane fractions. Further addition of IPA or other alcohols will allow organizing the process of obtaining gasolines A-95, A-98 with minimal energy and raw material inputs.

6. Discussion of the results of studying the effect of cavitation intensity on the octane number of gasolines modified with monohydric alcohols

The studies have shown the effectiveness of cavitation to increase the RON of gas condensate gasoline with the addition of isobutanol and bioethanol. With an increase in the bioethanol content in the mixture, the number of cavitation cycles (intensity) required to achieve the steady-state value of ON decreases. According to Fig. 2, a decrease occurs from 8 cycles of gas condensate without bioethanol, to 4 cycles with a bioethanol content of 3 % and higher. To achieve the octane number of the mixture corresponding to gasoline A-92 and A-95, it is necessary to add 2 % and 5 % bioethanol, respectively. A certain limitation can be considered the fact that for a certain type of fuel it is necessary to select the ratio of bioethanol-gasoline and the intensity of cavitation.

The most effective for cavitation action was a mixture of 99 % gas condensate and 1 % bioethanol, when the total increase in RON was 5, points, and MON – 2.6 points. A further increase in the amount of bioethanol in the mixture reduces the effect of cavitation treatment, although the initial RON and MON are much higher. The higher the molecular weight of the alcohol, the more cavitation cycles it is necessary to carry out in order to achieve a stable increase in octane number.

The effect of the concentration of IPA on the ON of the modified gasoline under cavitation treatment conditions has a nonlinear character [12] with several maxima at certain concentrations – 1.0 % vol. and 3.5 % vol. and 6.5 % vol. IPA for the indicator (RON) and 3.5 vol. and 6.5 % vol. IRI for the indicator (MON). By varying the initial concentration

of IPA and ON of the gasoline fraction, it is possible to optimize the technological mode of production of A-95 and A-98 gasolines in terms of raw material costs and energy costs.

It is known that the RON increases with the addition of alcohol. The work [10] combines mixing IPA with gasoline and cavitation treatment. Unlike works [1, 3, 9], where chemical transformations of hydrocarbons and a decrease in the viscosity of heavy oil products were achieved, this work showed the possibility of increasing the ON of gasoline.

Among the alcohols studied, isobutanol showed the need to supply the greatest amount of energy through cavitation treatment to achieve a stable effect of increasing the octane number. If to compare bioethanol, isopropanol and isobutanol, it can be seen that the lower the molecular weight of the alcohol, the less energy must be supplied to achieve a stable effect from cavitation. But in absolute terms, the greatest increase in the octane number was shown by bioethanol – the alcohol with the lowest molecular weight among the studied alcohols.

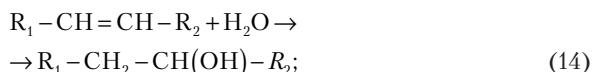
The disadvantage of using cavitation treatment is that intensive mechanochemical activation of raw materials leads to an increase in the content of olefins, which reduces the stability of gasoline. However, the benefits of increasing the RH prevail over this disadvantage. The limitation of this study is the ability of the laboratory installation to provide the pressure at the outlet of the nozzle at the level of 9.0 MPa. It is expected that for high pressures at the outlet from the nozzle in the modernized installation, the number of cavitation treatment cycles required to achieve the steady-state value of the octane number increase will be less.

The results of monitoring the change in the indicators of gas condensate gasoline modified with alcohols (a persistent additional increase in octane under the action of cavitation treatment compared to simple mechanical mixing, turbidity of gasoline six months after the experiment, an increase in the resistance of alcohol-bioethanol mixtures to delamination) suggest that under the action of mechanochemical activation, expressed through a change in the intensity of cavitation treatment, the following chemical transformations can occur in alcohol-gasoline mixtures, explain all observations:

– cracking with the formation of olefins and naphthenes



– hydration of olefins with the formation of alcohols



– formation of esters from olefins and alcohols



Cyclization, aromatization and densification reactions.

It is possible that isomerization reactions also occur under the action of a cavitation field. The sum of all chemical reactions gives an increase in the composition of the products of those chemicals with a higher octane number (alcohols, ethers, olefins, naphthenes), therefore, it can be expected that gasoline modified with alcohols treated

in this way will have higher ON values than with simple mechanical mixing.

Further research will be aimed at studying the effect of the intensity of cavitation treatment on the octane number of gas condensate gasolines modified with mixtures of alcohols. It is also planned to study the modification of gas condensate gasoline with fusel oils and other by-products of bioethanol production. In the future, this will make it possible to produce A-95 and A-98 gasolines on an industrial scale with the addition of the least possible amount of alcohol and through the use of bio-propanol and biobutanol, reducing the consumption of the alcohol part.

7. Conclusions

1. The influence of the intensity of cavitation treatment on the increase in the octane number was studied and it was proved that there is some optimal intensity at which a constant value of the octane number of the mixture is achieved. With an increase in the content of bioethanol in the mixture, the number of cavitation cycles, which is necessary to achieve the steady-state value of the octane number, decreases. The decrease occurs from 8 cycles of cavitation treatment of gas condensate without bioethanol, to 4 cycles with a bioethanol content of 3 % and more. To achieve the octane number of the mixture corresponding to gasoline A-92 and A-95, it is necessary to add 2 % and 5 % bioethanol, respectively.

2. The influence of the content of bioethanol in the mixture on the increase in the octane number was investigated. A further increase in the amount of bioethanol in the mixture reduces the effect of cavitation treatment, although the initial RON and MON are much higher. The higher the molecular weight of the alcohol, the more cavitation cycles it is necessary to carry out in order to achieve a stable increase in octane number.

3. The optimal ratio of gas condensate and bioethanol has been determined. The most effective for cavitation action was a mixture of 99 % gas condensate and 1 % bioethanol, when the total increase in RON was 5, points, and MON – 2.6 points.

4. It was revealed that the influence of the intensity of cavitation on the increase in ON for a mixture of gas condensate gasoline with isobutanol in various concentrations. The use of isobutanol requires a greater number of cavitation treatment cycles to achieve a stable increase in ON than bioethanol and isopropanol. For the industry, this will mean high energy consumption for the production of similar grades of fuel. But the promise of isobutanol lies in the fact that higher energy costs for cavitation treatment will be compensated by a lower cost of raw materials.

5. The influence of the concentration of isobutanol on the ON of the modified gasoline under the conditions of cavitation treatment has been determined. By varying the initial concentration of isobutanol and ON of the gasoline fraction, it is possible to optimize the technological mode of production of A-95 and A-98 gasolines in terms of raw material costs and energy costs.

All investigated alcohols have shown the possibility of modifying gas condensate gasoline in a cavitation field with an additional increase in ON by 1.2–2 points in comparison with simple mechanical mixing.

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