Transformation of n-alkanes of gasoline into components of motor fuels in cavitation field

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Summary. To ensure compliance with modern standards for motor fuels, particularly gasoline, a significant amount of additives are added to their composition. This problem can be solved by converting n-alkanes of the source gasoline, which, in fact, spoil its quality indicators, into the motor fuel components, which will improve its quality, for example, in methanol, toluene, isoalkanes and others. The cavitation technology for conversion of hydrocarbons into methanol has been used for this purpose. The reactor and the process flow diagram have been developed. The optimal parameters of the process have been determined, which allowed increasing the octane number of the source gasoline by 10-12 units.

Key words: motor fuel components, n-alkanes, cavitation, hydrogen peroxide, reactor, process diagram, chromatographic analysis, octane number, methanol, toluene, isoalkanes

INTRODUCTION

Competitive struggle for world markets encourages car manufacturers to continuously improve their car production technologies, as well as quality indicators and environmental performance of engines. This, in its turn, poses new and more complex tasks for manufacturers of motor fuels as for production of a range of motor fuels that meet modern requirements. Modern gasoline and diesel fuel are either derived from petroleum feedstock in traditional oil refineries or synthesized from synthesis gas. However, in both cases, a large range of additives, usually having a synthetic origin, is used for production of commercial gasoline and diesel fuel. The main purpose of these additives is to bring the quality indicators of motor fuels to the required values: octane/cetane number, temperature and combustion rate, environmental performance of exhaust gases, etc. [1, 2]

In fact, modern motor fuel, including gasoline, is a mixture of hydrocarbons belonging to different classes of compounds. It is known that increase in the proportion of n-alkanes in gasoline leads to damage of its qualitative characteristics, for example, the octane number. So, it is precisely their conversion into motor fuels components, for example in methanol, toluene and others, in a simple, inexpensive and efficient way that interests us. In our opinion, the proposed in [3] cavitation technology for hydrocarbons processing can cope with this problem.

The purpose of the work is to develop and study the cavitation technology for conversion of n-alkanes into the motor fuel components through initiating action of hydroxyl radicals.

MAIN BODY

It is known that starting with C_5 (pentane) alkanes are liquids. A typical representative of liquid alkanes is gasoline (C_5-C_{10}). To improve the quality of motor fuels, including gasoline, n-alkanes should be converted into isomers (isoalkanes) or oxygenates, for example in methanol. The authors [4, 5] show that it is possible to solve this problem by using interaction of n-alkanes with a hydroxyl radical. The most efficient way is to conduct the process in the liquid phase for direct conversion of n-alkanes (C_5-C_{10}) into methanol. This will prevent evaporation and further condensation of gasoline, which will ultimately lead to significant energy savings. The process of dynamic cavitation of the aqueous solution of hydrogen peroxide is proposed as a generator of hydroxyl radicals in this case. [6-11]

The mechanism of the activation process of n-alkanes is the same as for the process of direct conversion of propane and butane gas into methanol. [8] However, given the fact that C_5H_{12} has three isomers and $C_{10}N_{22}$ seventy-five, the probability of formation of other oxygen-containing products alongside with methanol appears. In addition, due to interaction of hydrocarbon "fragments", there will also be observed the isomerization process.

To implement the cavitation technology, there have been developed a cavitation reactor [9,10] and an installation [12-15], shown in Fig. 1 and 2 respectively.

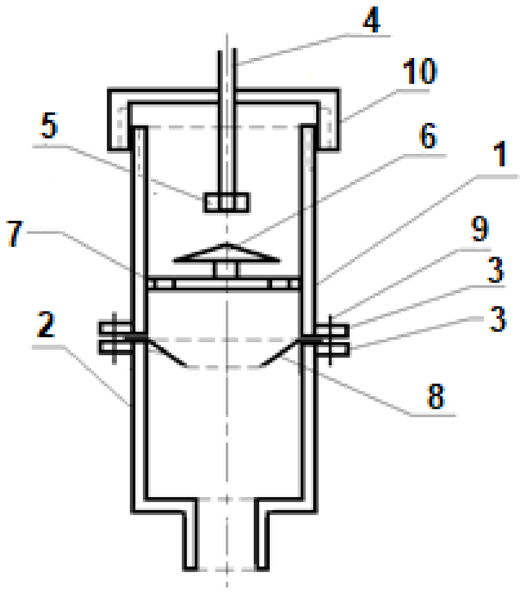

Fig. 1. Cavitation reactor for processing n-alkanes into the motor fuels components: 1, 2 – upper and bottom parts of the reactor; 3 – flange connection; 4 – inlet pipe of the high pressure line; 5 – nozzle; 6 – conical barrier; 7 – mesh lattice; 8 – diffuser; 9 – pin; 10 – cover

The reactor consists of two parts: upper 1 and bottom 2, connected by means of flange connection 3 with the help of pin 9. The top of the reactor has cover 10. In the cover, an inlet pipe of the high pressure line is mounted with the help of a threaded joint. Nozzle 5 is swirled on the inlet pipe of the high pressure line. The expanded fluid is directed to conical barrier 6. The purpose of the conical barrier is to create the second wave of cavitation. The flow is directed to reactor wall 1 from barrier 6. The reaction mixture formed in such a way goes through mesh lattice 7 and enters the middle part of the reactor over diffuser 8. The purpose of diffuser 8 is to create conditions for condensation of the liquid phase. The reaction products are withdrawn from the reactor through the nozzle, which is located at the bottom of reactor 2 and directed to the separator.

The threaded joint of the cover and the inlet pipe of the high pressure line will allow moving nozzle 5 in relation to conical barrier 6 to determine the cavitation distance optimal for the process.

The proposed design of the cavitation reactor allows forming three zones of cavitation. The first zone of cavitation is formed at the outlet of the hydrogen peroxide solution from the nozzle. The second wave of cavitation is formed on the conical barrier when the flow separates from it. The third wave of cavitation is formed when the flow of the hydrogen peroxide solution smashes into the reactor wall. Due to this effect, the aqueous solution of hydrogen peroxide is almost perfectly mixed even with gasoline.

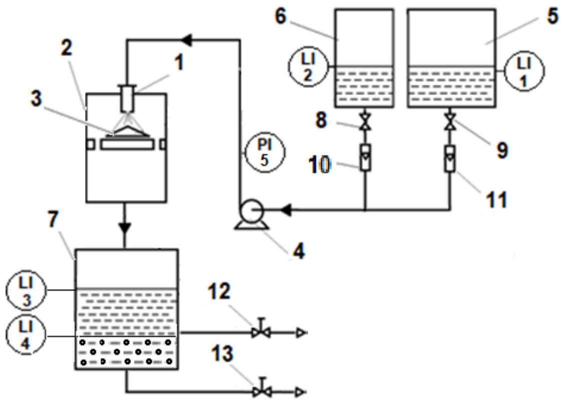

Fig. 2. Diagram of the laboratory cavitation installation for conversion of n-alkanes into the motor fuels components: 1 – nozzle, 2 – cavitation reactor, 3 – conical barrier, 4 – high pressure pump, 5, 6 – tanks with the hydrogen peroxide solution and feedstock, 7 – tank for reaction products, 8, 9, 12, 13 – regulating valve, 10, 11 – rotameter

The cavitation installation works in the following way. The hydrocarbon feedstock, for example gasoline, from tank 5 is fed to suction of high pressure pump 4 through regulating valve 9 and rotameter 11. The aqueous solution of hydrogen peroxide from tank 6 is also fed to suction of the pump through regulating valve 8 and rotameter 10. Given that the gasoline and the aqueous solution of hydrogen peroxide do not mix, the aqueous solution of hydrogen peroxide is fed into the centre of the flow through a special means. After pumping in high pressure pump 4, the mixture with pressure up to 30 MPa is fed into cavitation reactor 2, where nozzle 1 directs the flow to conical barrier 3. At the outlet of reactor 2, the reaction mixture is fed into product tank 7. After settling, the recycled gasoline and the aqueous solution of hydrogen peroxide are withdrawn for analysis through valves 12 and 13 respectively. [16-21]

Straight-run gasoline, light distillate and diesel fuel with the content of n-alkanes significant enough can be used as feedstock. To obtain a general picture of the processes occurring in the gasoline, experimental studies have been conducted with the purpose of determining the influence of hydrogen peroxide on the process. Narrowing devices were used as nozzles, the channel pattern in which was close to De-Laval nozzle. The diameter of the nozzles was 0.5, 0.7 and 1.0 mm. The motor fuel was fed from pressure vessel 5 with volume of 80 litres, and hydrogen peroxide from pressure vessel 6 with volume of 8 litres. In order to equalize pressure in pressure vessels 5 and 6, the covers of these two pressure vessels are connected by a pipeline. To ensure uniform feed of the hydrogen peroxide solution, it was fed into the flow of the motor fuel. Recycling products were collected in product tank 7 with volume of 100 litres. After settling and separation of hydrogen peroxide with the aqueous solution, the processing products were subjected to chromatographic analysis. [22-26]

The flow rate of the source gasoline varied in the range from 0 to 7 l/min. The aqueous solution of hydrogen peroxide with the predetermined concentration was fed with the flow rate of 0 to 0.7 l/min. The flow rate of the motor fuel and hydrogen peroxide was controlled using flow meters 10 and 11. The flow rate was controlled by means of regulating valves 8 and 9 installed in the feed line of the source gasoline and the hydrogen peroxide solution to suction of high pressure pump 4.

Experimental body

In order to study the influence of hydrogen peroxide concentration on the process of cavitation conversion of n-alkanes into the components of motor fuels, low octane gasoline with the total mass concentration of n-alkanes of 30.314% was chosen. The analysis of the mass composition of n-alkanes of the source gasoline is given in Table 1, and the analysis of the octane number of the source gasoline – in Table 2. The number of peaks on the chromatograph was 47. Identified – 42.

Table 1. Mass concentration of n-alkanes in the source gasoline,%

n-alkanes	**n-propane**	**n-butane**	**n-pentane**	**n-hexane**	**n-heptane**	**n-octane**	**n-nonane**	**n-decane**
Concentration,%	0.237	1.285	15.403	9.515	2.928	0.945	-	-

Table 2. Analysis of the octane number of the source gasoline

Group	Research method	Motor method
n-alkanes	16.096	15.651
Isoalkanes	27.958	24.940
Aromatics	11.362	9.684
Naphthenes	7.826	5.128
Olefins	3.555	3.709
Oxygenates	6.395	6.033
Unidentified	3.968	3.855
Total:	**77.159**	**68.991**

In the basic experiment, the source gasoline with the flow rate of 5.5 l/min was pumped through the cavitation installation. The flow rate of the hydrogen peroxide solution was 0 l/min. The pressure varied from 0 to 30 MPa. The diameter of the nozzle was 1 mm.

As an integral indicator of the gasoline quality, the octane number was selected, which was defined by the research and motor methods using the chromatograph "Crystal 2000" and the octane meter "Shatox SX 200". The results of the study of changes in the octane number of the gasoline depending on change in pressure before the nozzle are shown in Fig.

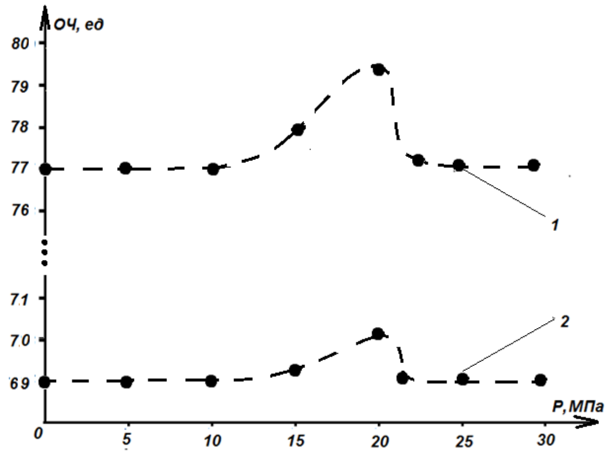

Fig. 3. Change in the octane number of the gasoline during cavitation treatment:
1 – research method; 2 – motor method

As it follows from the analysis of the dependencies shown in Fig. 3, at a pressure less than 10 MPa, no changes occur with the gasoline being studied. With increase in pressure from 10 MPa to 19 MPa, the octane number increases from 69 to 70.5 units by the motor method, and from 77 to 79.7 units by the research one. The results of the chromatographic analysis indicate that after cavitation treatment toluene appeared in the gasoline. The concentration of toluene was ~ 3%. At the same time, the mass concentration of n-hexane decreased from 9.52% to 5.92%. Besides, the amount of isoalkanes slightly increased from 31.22% to 32.61%. This happens due to the cavitation process in the gasoline, which takes place in the cavitation reactor. As a result of the cavitation influence, the *C-C* bonds in alkanes (mainly in n-hexane) are destroyed, and isoparaffins and toluene are formed further.

The maximum octave number reached was 19 MPa. With further increase in pressure, there is a reverse effect – the octane number begins to decrease. At a pressure of above 23 MPa, there were no changes in the composition of the gasoline any more. This is explained by the fact that with such parameters, all gasoline evaporates behind the nozzle and the cavitation effect does not occur. Consequently, the pressure of 19 MPa is optimal for cavitation treatment of the gasoline.

To define the influence of changes in the hydrogen peroxide concentration in the aqueous solution on the process of cavitation treatment of the gasoline, a series of experiments was performed in which the flow rate of the gasoline was 5 l/min, and the flow rate of the aqueous solution of hydrogen peroxide was 0.5 l/min. The hydrogen peroxide concentration in the aqueous solution varied in the range from 0 to 20%. The pressure was 19 MPa. The results of the research are shown in Fig. 4.

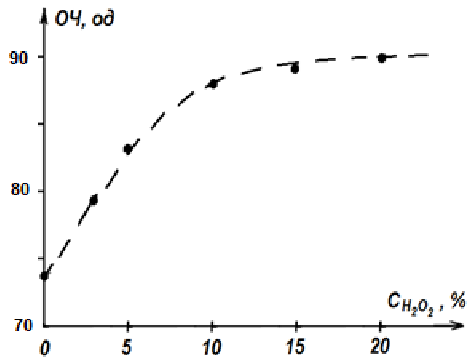

Fig. 4. Dependence of the octane number of the gasoline (research method) on the hydrogen peroxide concentration in the aqueous solution at a ratio gasoline - hydrogen peroxide solution 10:1

Basing on the analysis of the dependence shown in Fig. 4, one can conclude that addition of the aqueous hydrogen peroxide solution with a concentration of up to 10% to the gasoline leads to significant increase in the octane number of the cavitated gasoline. Thus it was possible to raise this figure up to 88.2 units. Further increase in the hydrogen peroxide concentration does not result in further significant increase in the octane number. So, at a concentration of hydrogen peroxide of 20%, the octane number was 89.9 units by the research method.

The analysis of the mass composition of gasoline n-alkanes after cavitation treatment with 10% aqueous solution of hydrogen peroxide at a pressure before the nozzle of 19 MPa (after settling) is given in Table 3.

Basing on the chromatographic analysis, it follows that the number of peaks on the chromatograph was 132, 110 of which were identified. As a result of cavitation treatment, the mass fraction of n-alkanes decreased from 30.314 to 18.601%. At the same time, the mass fraction of isoparaffins increased from 30.228% to 33.036%, and the mass fraction of aromatic hydrocarbons increased from 10.170% to 16.728%.

Table 3. Mass composition of n-alkanes of gasoline after cavitation treatment with 10% aqueous solution of hydrogen peroxide, %

n-alkanes	**n-propane**	**n-butane**	**n-pentane**	**n-hexane**	**n-heptane**	**n-octane**	**n-nonane**	**n-decane**
Concentration,%	0.592	1.787	12.121	-	2.867	0.971	0.043	0.220

In addition, 4.5% toluene and 4.2% methanol were found in the test samples, which had not been found in the source gasoline.

Thus, basing on the above analysis, it can be concluded that n-alkanes decompose as a result of cavitation influence in presence of hydrogen peroxide, transform not only into isoparaffins and aromatic hydrocarbons, but also into oxygenates. In contrast to the process occurring without hydrogen peroxide, methanol appeared in the samples being analysed.

The analysis of the octane number of the gasoline subjected to cavitation influence with 10% aqueous hydrogen peroxide solution is given in Table 4.

Table 4. Analysis of the octane number of the gasoline after cavitation treatment with 10% aqueous hydrogen peroxide solution

Group	**Research method**	**Motor method**
n-alkanes	13.491	11.092
Isoalkanes	28.625	26.180
Aromatics	19.226	15.843
Naphthenes	5.321	4.189
Olefins	4.144	3.208
Oxygenates	4.098	3.868
Unidentified	13.306	9.721
Total:	**88.211**	**74.101**

The analysis of the above data suggests that as a result of cavitation treatment of the low octane gasoline with hydrogen peroxide in gasoline, methanol and toluene are formed from n-alkanes of the source gasoline. In addition, there is a process of partial isomerization of n-alkanes. This is confirmed by formation of new compounds in the final product (the number of peaks on the chromatogram of the source gasoline was 47, and the processed – 132). All this leads to increase in the octane number of the gasoline by 10-12 units. In addition, it should be noted that the content of benzene in the processed gasoline practically does not change and is 1% (mass). This complies with DSTU 7687:2015.

CONCLUSIONS

- Summing up the experimental study of conversion of n-alkanes into the motor fuels components in the cavitation field, it should be noted that as a result of the cavitation processing of the gasoline, isoalkanes and toluene are formed except of methanol, which ultimately results in increase in the octane number up to ~10-12 units. The process should be conducted at pressure of 19 MPa before the nozzle and the ratio of gasoline-hydrogen peroxide 10:1 at the hydrogen peroxide concentration of 10% in the aqueous solution.
- Consequently, direct conversion of n-alkanes of the C_5-C_{10} class into the motor fuel components such as methanol, toluene, isoalkanes and others can be considered as a way to improve the quality of motor fuels, particularly low octane gasoline.
- The advantage of this way of improving the quality of motor fuels is that the components that increase the octane number are not added to the source motor fuel, but are obtained during its processing from n-alkanes, that is precisely from the part of the fuel that spoils its quality.
- The process of cavitation treatment takes place in one installation. The process parameters are quite achievable under industrial conditions, and productivity of even the developed laboratory installation reaches 15 l/min.

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ПРЕОБРАЗОВАНИЕ *Н*- АЛКАНОВ БЕНЗИНА В КОМПОНЕНТЫ МОТОРНЫХ ТОПЛИВ В КАВИТАЦИОННОМ ПОЛЕ

А.Б. Целищев, М.Г. Лория, С.В. Бойченко, И.О. Шкильнюк, В.А. Носач

Аннотация. Разработан способ синтеза метанола из алканов с использованием динамической кавитации перекиси водорода, который характеризуется простотой и достаточной эффективностью. В основу способа поло-жено взаимодействие гидроксильного радикала с пропан-бутановым (C_3– C_4) газом с образованием пропил- и бутил-радикалов и последующим получением метанола и разработке на их основе новой технологии неполного окисления алканов в метанол в «мягких» условиях.

Ключевые слова: гидроксильный радикал, пропан-бутановый газ, метил-радикал, кавитация, метанол.