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Modification of Low-Octane Gasoline for Improvement of Its Environmental and Operating Characteristics

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ABSTRACT: In recent years, with an increasing number of ground vehicles with internal combustion engines, the need for fuel, including motor gasoline, has increased significantly. It is known that during the operation of vehicles, a large number of exhaust gases are emitted into the atmosphere, containing such substances as carbon oxides, nitrogen oxides and benzapyrenes. The main source of education benzapyrene are aromatic hydrocarbons, primarily benzene. In this regard, the content of aromatic hydrocarbons in motor gasoline is subject to strict environmental requirements Euro-5. As the object of research was taken gasoline AI-80. All studies were conducted in accordance with State standards and generally accepted practical guidelines for the analysis of petroleum products.

KEY WORDS: gasoline, aromatic hydrocarbons, azeotropic distillation, extraction, rectification, adsorption

I. INTRODUCTION

Motor gasoline is one of the most multi-tonnage refined products. The ubiquitous and socially significant gasoline has undergone great changes in the component, hydrocarbon and chemical composition over the past period in accordance with the constantly growing requirements for the quality and environmental safety of vehicles [1].

One of the conditions for preserving the ecological safety of the state is “ensuring a favorable state of the environment as a necessary condition for improving the quality of life and public health” [2].

Road transport is one of the most unfavorable environmental factors in protecting public health and the environment. In fact, in our time, he has become a rival of man for living space. An urgent task in solving environmental and transport problems is the preservation and development of an air basin protection system. Improvement of the country's ecological system, compliance with international standards for the qualitative characteristics of fuels and emission standards of toxic substances are those steps that can positively affect the ecology of airspace [3].

The EU Euro-1 environmental standard has become the first step towards improving the environmental situation [4]. Since 1995, it has been replaced by the Euro-2 Environmental Standard [5]. In the Euro-3 standard, permissible emission indicators were reduced by 30 - 40%, and in the Euro-4 standard by 65 - 70% [6].

In 2000, the EU introduced toughened gasoline specifications related to the Euro-3 environmental program for motor vehicles, and since 2005, Euro-4 [7]. Since 2009, the EU Directive on the introduction of even more stringent Euro-5 requirements has been adopted (Table 1) [8].

In this regard, there is a need to develop processes for refining AI-80 gasoline - partial dearomatization and denormalization in order to meet gasoline with Euro 5 Euro specifications [9].

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Table 1
Modern requirements for the quality of gasoline

Indicators	Requirements			
	Euro 2 1995 y	Euro 3 2000 y	Euro 4 2005 y	Euro 5 2009 y
Benzene content, not more than,%	5.0	1.0	1.0	1.0
Sulfur content,%	0.05	0.015	0.005	0.001
The content of aromatic hydrocarbons,%	–	42	35	35
The content of olefinic hydrocarbons,%	–	18	14	14
Oxygen content,%	–	2.3	2.7	2.7
Fractional composition,%:				
distilled up to 100 ° C, not less	–	46	46	46
distilled up to 150 ° C, not less	–	75	75	75
Saturated vapor pressure, kPa, no more	–	summer 70 winter 90	summer 70 winter 90	summer 70 winter 90

The Euro-5 environmental standard has been in force in Europe since 2009. For this class, a new type of fuel has already been produced that minimizes environmental pollution [10].

Environmental requirements for fuels are as follows:

- strict restriction of benzene content in motor gasolines;
- limiting the content of aromatic hydrocarbons in gasoline and diesel fuel, polycyclic in diesel fuels;
- limiting the content of olefinic hydrocarbons in gasoline;
- restriction of sulfur content in gasolines and diesel fuels up to thousandths of a percent;
- gradual limitation of the emission of products of incomplete combustion: carbon monoxide, hydrocarbons, particulate matter and nitrogen oxides [11].

Starting July 1, 2016, all vehicles imported into Europe must comply with the Euro-5 environmental class, i.e. concentrations of harmful substances in the exhaust gases should not exceed the levels established for this ecological class (table. 2) [12].

Table 2
Technical standards of environmental standards Euro 1-5

Eco standard	Carbon monoxi-de (II) CO	Hydrocar-bon	Volatile organic substances	NitricOxide(NO_X)	HC+NO_X	Suspended particles(PM)
Euro 1	2.72 (3.16)	-	-	-	0.97 (1.13)	-
Euro 2	2.2	-	-	-	0.5	-
Euro 3	2.3	0.20	-	0.15	-	-
Euro 4	1.0	0.10	-	0.08	-	-
Euro 5	1.000	0.100	0.68	0.060	-	0.005

In connection with the foregoing, the following goal has been set in this work - the study of AI-80 motor gasoline to improve its environmental and operational characteristics.

II. RELATED WORK

Jones EM, Smith LA, Emelyanov V.E., Akhmetov A.F., were engaged in scientific research on the development of technologies to improve the physicochemical, environmental and operational properties of motor gasoline, to reduce the content of aromatic hydrocarbons, in particular benzene, in its composition. Byakov A.G., PetrovI.Ya., Abdulminiev K.G., Kazakov M.O., Kapizova N.B., Soloviev A.S., Gerasimov D.N., Kaldygozov A.E., PoletaevaO .U., As well as domestic scientists SaydakhmedovSh.M., Khamidov B.N., Yunusov MP, Narmetova G.R. and etc.

III. METHODS

A complex of classical and modern research methods was used in the work, which allows one to determine the physical, physicochemical characteristics, functional composition, study the processes occurring in the original

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automobile gasoline and gasoline subjected to various refinement processes, in particular, dearomatization, and also establish chemical compositions, structure, chemical nature and their stability. It should be noted that the AI-80 industry gasoline does not meet the European standard quality requirements.

As the object of study was taken AI-80 gasoline. All studies were conducted in accordance with State standards and generally accepted practical guidelines for the analysis of petroleum products [13].

The study of AI-80 gasoline was carried out using a set of physical and chemical methods [13]:

1. Method for determining the acidity of fuel by titration with KOH;
2. Determination of water content by the method of Dean and Stark;
3. Determination of solids by weight method;
4. Test method on a copper plate;
5. Method for the determination of water soluble acids and alkalis;
6. Method for determining the density (pycnometer);
7. Determination of the refractive index (IRF-22);
8. Determination of molecular weight by cryoscopic method.
9. The molecular weight and group hydrocarbon composition of gasoline were determined by the adsorption - cryoscopic method [14].

The hydroisomerization of the benzene-containing gasoline fraction AI-80 was carried out in a special high pressure autoclave.

The connection scheme of the equipment during hydrogenation processes in a laboratory autoclave is shown in Fig. 1.

The autoclave is a thick-walled steel vessel designed for high pressure. The dimensions of the autoclave with a capacity of 1 liter are designed for an operating temperature of 450 - 500 °C and a pressure of 300 *atm*. The supply of hydrogen in the autoclave is carried out either directly from the bomb, or using a compressor. Heating is done either by gas or by electricity.

The height of the casing (to the lower flange) is 340 mm, the inner diameter is 100 mm, the wall thickness is 10 mm, the diameter of the flange and cover is 270 mm, and the thickness is 46 mm.

The autoclave body is made of steel; the flange is screwed onto the housing by thread. The lid of the autoclave is attached to the flange with twelve bolts, it is equipped with a thermocouple pocket, a pressure gauge and a pressure-reducing valve, which serves to release hydrogenation products from the autoclave. The tightness of the lid to the flange is ensured by a red copper shutter.

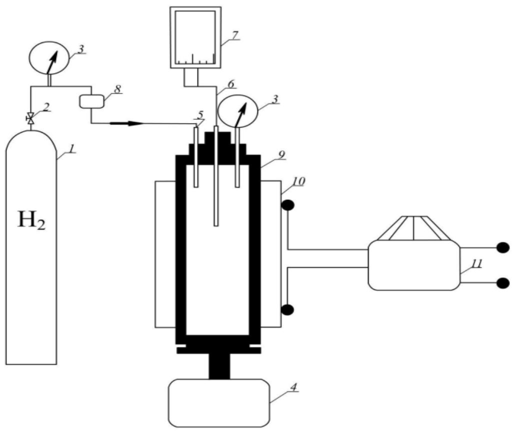

Figure 1. Experimental equipmentscheme

1 - cylinder with hydrogen; 2 - needle valve; 3 - pressure gauge; 4 - rotary motor; 5 - tube for supplying raw materials and gas; 6 - thermocouple; 7 - millivoltmeter; 8 - gearbox; 9 - an autoclave; 10 - electric oven; 11 – transformer

The investigated raw materials (1 l) were loaded into an autoclave. After pouring the product, the autoclave was closed with a lid, the nuts were tightened with a wrench (the nuts should be tightened gradually and be sure to properly, and not in a row to avoid skewing the lid). Then, a coil was screwed to the nipple of the pressure reducing valve, it was checked whether the pressure reducing valve was closed, and the autoclave was installed in a special stand with slots for the burners.

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The temperature of the autoclave was kept constant with an accuracy of ± 1 ° C using a temperature controller. The temperature of the reaction zone was controlled using a chromium - aluminum thermocouple placed in the catalyst bed. The pressure of the autoclave was determined by a pressure gauge, which is mounted on the autoclave. Each experiment lasted 2 hours.

Before each experiment, the used catalyst was activated by a stream of hydrogen for 4 hours.

IV. RESULTS

Table 3 shows the physical and chemical characteristics of the object of study.

Table 3

Physical and chemical characteristics of the object of study

№	Indicators	gasoline AI-80
1.	Colour	Lightyellow, clear, transparent
2.	Knockresistance:	
	Octane number by research method	80
	Octane number by motor method	76
3.	Density at 20 °C, g/cm3	0,770
4.	Refractiveindex, n_D^{20}	1,4631
5.	Copper plate test	withstands
6.	Water content	absence
7.	Solids content	absence
8.	Fractional composition: distillation start temperature, °C	36
	distillation limits, ° C: 10%	50
	50%	104
	90%	150
	The end of the boil, ° C	180
	The residue in the flask,%	1,5
	Loss%	3,0
9.	Mass fraction of sulfur, in%	0,02
10.	The content of water soluble acids and alkalis	absence
11.	Acidity, mg KOH on 100 cm^3 of gasoline	3,0
12	The content of actual resins, mg/100 cm^3	1140
13.	Hydrocarbon composition, % mass .: aromatic hydrocarbons	48,24
	n-paraffin hydrocarbons	15,3
	iso-paraffin + naphthenic hydrocarbons	36,46

As can be seen from the data presented, gasoline has a light yellow color, it is transparent, O.Ch. according to the research method 80, motor - 76, with a density of 0.772 g / cm3 and a refractive index of 1.4632, it withstands the test on a copper plate, there is no water and no mechanical impurities. According to the fractional composition, 50% is distilled at 104 ° C, 90% is distilled at 150 ° C, the end of boiling is 180 ° C.

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It should be noted that in connection with changes in the ratio of the composition of crude oil: gas condensate, from which automobile gasoline AI-80 (A-80) is obtained at the Bukhara oil refinery, the content of aromatic hydrocarbons and benzene also changed. A sample of gasoline in 2014, which was produced from oil and gas condensate raw materials, where the ratio of oil to gas condensate was 7: 3, and the content of benzene (5%) and aromatic hydrocarbons (not normalized) corresponded to the European standard. This sample practically corresponded to Eurostandard-3 - when determining the group content of aromatic hydrocarbons by the adsorption-cryoscopic method, it amounted to 44.7% of the mass.

But subsequently, when the composition of the oil and gas condensate feed was changed in the direction of increasing gas condensate to 65-70% due to a reduction in oil reserves, the total aromatic hydrocarbon content reached 48.78% and, in particular, benzene, increased to 8.46 (in% mass.).

In this regard, there was a need to develop processes for dearomatization and refinement of AI-80 gasoline in order to comply with European specifications Euro-4 and Euro-5.

In order to reduce the content of benzene and aromatic hydrocarbons in the composition of the object of study, we distilled low boiling fractions from which AI-80 gasoline by fractional distillation, in which a high content of benzene is observed.

Although the boiling point of benzene is 80 ° C, the distillation was carried out to 120 ° C. the elasticity of its vapor was taken into account.

To study the individual composition of low-boiling gasoline fractions in order to determine the quantitative benzene content in each obtained fraction, gas-liquid chromatography was used. The results are shown in table. 4.

Table 4

Material balance of distillation of AI-80 gasoline by fractions and benzene content

No.	Fraction	Amount, ml	Amount of benzene%, vol.
1.	AI-80 gasoline	100	8,11
2.	start of boil -80^{o}C	28,5	17,4
3.	80 – 90^{o}C	9,7	15,5
4.	90 – 100^{o}C	11,2	11,35
5.	100 – 110^{o}C	2,4	7,8
6.	110 – 120^{o}C	7,5	4,7
7.	120 – 130^{o}C	8,4	0,04

As can be seen from the data presented, benzene almost does not remain after 120 ° C, and there is also a part of toluene in this gasoline fraction. Since our goal in gasoline is to reduce not only the amount of benzene (up to 1%), but also reduce the content of aromatic hydrocarbons (up to 35%), therefore, for the hydroisomerization process as a raw material, we used the NK fraction of gasoline - 120 ° C.

The results of the study of fractional distillation of AI-80 gasoline and some physico-chemical characteristics of gasoline fractions are presented in table. 5.

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Table 5

The hydrocarbon content in gasoline AI-80 and its fractions

№	Name of samples	Volume, ml	Refractive index	Density, g/cm^3	The hydrocarbon content,% of the mass.			The amount of benzene, %, vol.
					aromatic	*n-paraffin*	iso-paraffin + naphthenic	
1	AI-80 gasoline	100	1,4631	0,770	48,24	15,3	36,46	8,11
2	Fraction from start of boil - 120 °C	49,4	1,4455	0,740	42,12	12,2	45,68	13
3	Fraction above 120 °C	50,6	1,4850	0,790	55,32	6,89	37,79	0,03

According to the above data (Tables 4 and 5), it can be seen that during the rectification of gasoline, the amount of benzene decreased to the requirements of European standards. At the same time, the amount of gasoline decreased significantly.

To replenish the lost fraction and improve the hydrocarbon composition, the following tasks were set and solved:

- a change in the hydrocarbon composition of the isolated benzene-containing fraction with the conversion of benzene and toluene to naphthenic hydrocarbons and the addition of this fraction to gasoline as a high-octane and modifying component;
- the selection of catalysts and their optimal choice for the hydroisomerization process;
- determination of optimal conditions for the process of hydroisomerization.

Based on the foregoing, at the next stage of the studies, the benzene-containing fraction of AI-80 gasoline was hydroisomerized on a nickel-tungsten-containing catalyst, which is basic nickel and tungsten supported on chlorinated alumina. High acidity supports are used for many isomerization processes. To do this, during its preparation, various zeolites or a carrier are added, which are treated with halogens (Cl or F). We treated the support (γ-aluminum oxide) with HCl.

The AlNiW-Cl catalyst contains: 4.0% NiO, 5.0% WO_3, and 91% chlorinated Al_2O_3. The results of the hydroisomerization of the benzene-containing fraction of gasoline are given in table. 6.

As can be seen from the table, the content of aromatic hydrocarbons and n-paraffins in the catalysis significantly decreased at a pressure of 5 MPa and a temperature of 200-220 ° C.

Table 6

Group hydrocarbon composition of raw materials and products obtained using AlNiW-Cl catalyst

A. ***Hydrocarbons***	B. ***The composition of the raw materials,% of the mass.***	C. ***The composition of the products obtained at various temperatures,% of the mass.***					
		D. ***160***	E. ***180***	F. ***200***	G. ***220***	H. ***240***	I. ***260***
J. ***Pressure, 3 MPa***							
K. *Aromatic hydrocarbons*	L. *42,12*	M. *38,25*	N. *36,45*	O. *33,44*	P. *32,67*	Q. *35*	R. *36,24*

S. n-paraffin hydrocarbons	*T. 12,2*	*U. 11*	*V. 9,98*	*W. 8,14*	*X. 8,94*	*Y. 8,12*	*Z. 8,18*
AA. iso-paraffin and naphthenic hydrocarbons	*BB. 5,68*	*CC. 5 0,75*	*DD. 5 3,57*	*EE. 5 8,42*	*FF. 5 8,39*	*GG. 5 6,88*	*HH. 5 5,58*
*II. **Pressure, 4 MPa***							
JJ. Aromatic hydrocarbons	*KK. 2,12*	*LL.34,55*	*MM. 3 2,15*	*NN. 2 9*	*OO. 2 3,95*	*PP. 2 4,19*	*QQ. 2 6,12*
RR. n-paraffin hydrocarbons	*SS. 12,2*	*TT. 9,12*	*UU. 8 ,75*	*VV. 7 ,98*	*WW. 7 ,32*	*XX. 7 ,14*	*YY. 8,12*
ZZ. iso-paraffin and naphthenic hydrocarbons	*AAA. 5,68*	*BBB. 5 6,33*	*CCC. 5 9,1*	*DDD. 6 3,02*	*EEE. 6 8,73*	*FFF. 6 8,67*	*GGG. 6 5,76*
*HHH. **Pressure, 5 MPa***							
III. Aromatic hydrocarbons	*JJJ. 2,12*	*KKK. 2 8,45*	*LLL. 2 2*	*MMM. 1 6,1*	*NNN. 1 5,8*	*OOO. 2 0,4*	*PPP. 2 4,55*
QQQ. n-paraffin hydrocarbons	*RRR. 2,2*	*SSS. 7 ,41*	*TTT. 5 ,22*	*UUU. 1 ,4*	*VVV. 0 ,7*	*WWW. 0 ,5*	*XXX. 0 ,4*
YYY. iso-paraffin and naphthenic hydrocarbons	*ZZZ. 5,68*	*AAAA. 6 4,14*	*BBBB. 7 2,78*	*CCCC. 8 2,5*	*DDDD. 8 3,5*	*EEEE. 7 9,1*	*FFFF. 7 5,05*

Table 6 shows that with increasing pressure of the hydroisomerization process in the catalysis, the content of aromatic and n-paraffin hydrocarbons decreases, and the amount of iso-paraffin and naphthenic hydrocarbons increases.

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Based on this, it can be argued that the hydrogenation of aromatic hydrocarbons and the isomerization of n-paraffin hydrocarbons on the alumina-tungsten catalyst proceeds most actively at 5 MPa.

The yield of catalyzate to 200 °C decreases slightly, and with increasing process temperature the gas yield increases significantly. Based on this, we can say that with an increase in temperature above 200 ° C during hydroisomerization an increase in the hydrocracking reaction is observed. This can lead to significant loss of gasoline resource.

At the next stage, the obtained hydroisomerization product and heavy gasoline fractions were compounded with the ratio: modifier - 62.7%, heavy gasoline fraction 37.3% to obtain new modified gasoline samples. After that, the physical and chemical properties and group hydrocarbon composition of the obtained gasoline were determined. Physical and chemical characteristics of the resulting gasoline are given in table. 7.

Table 7
Physical and chemical characteristics of gasoline obtained using the AlNiW-Cl catalyst

№	Specification	Indicators
1	Colour	Light yellow, clear, transparent
2	Octane number by research method	95,8
3	Density at 20 °C, g/cm3	0,760
4	Refractive index, n_D^{20}	1,4370
5	Copper plate test	withstands
6	Water content	absence
7	Solids content	absence
8	Содержание фактических смол, мг/100 см3	absence
9	Hydrocarbon composition, % mass .: aromatic hydrocarbons	30,12
	n-paraffin hydrocarbons	3,44
	iso-paraffin + naphthenic hydrocarbons	66,44
10	The benzene content,% vol.	0,32

As can be seen, from the results of the analysis of the obtained modified gasoline, according to the content of benzene and aromatic hydrocarbons, it meets the standards of European standards.

On the basis of the conducted enlarged experiments on improving the environmental and operational characteristics and on bringing local AI-80 gasoline to Euro-4 and Euro-5 standards, a circuit diagram has been drawn up.

V. CONCLUSION

So, a method has been developed for modifying AI-80 motor gasoline in an enlarged pilot plant in the laboratory using the hydroisomerization method to bring the content of aromatic hydrocarbons to 35% of the mass. and benzene 1% vol., i.e. compliance of gasoline with Euro-4 and Euro-5 requirements.

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