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Comparative Characteristics of Octane-Increasing Additives based on Local Raw Materials

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Annotation. BMS tests in real operating conditions of trucks at different times of the year and in different climatic zones have shown positive results: the operational reliability of vehicles does not deteriorate, the level of toxicity of exhaust gases (incomplete combustion products by 30-40%, nitrogen oxides by 8-10%) decreases , a medical examination of the drivers showed that no deterioration in health was found.

Keywords: acetaldehyde, crotonaldehyde, acetic acid, ammonia, ethanol, propyl alcohol, isobutyl alcohol.

Introduction

In Uzbekistan, the production of alcohols is well established - ethanol, aldehydes-formaldehyde, acetaldehyde, crotonaldehyde, acetic acid, ammonia, etc.

Among oxygen-containing compounds, alcohols and ethers are widely used as additives.

Currently, OJSC "Navoiazot" has a methanol production unit with a capacity of 35 thousand tons per year.

In this regard, we have developed new octane-increasing additives based on aliphatic alcohols - methanol, ethanol, propyl alcohol, isobutyl alcohol, esters and ethers - methyl acetate, ethyl acetate, a mixture of acetates, methyl tert-butyl ether, as well as amines - hexamethylenetetraamine, acetonitrile , metal acetates [1-4].

To increase the octane number of low-octane gasolines, oxygen-containing compounds - oxygenates - alcohols and ethers - are used instead of highly toxic tetraethyl lead (TPP). Esters are the most widely used additives. However, recently, due to the revealed cases of groundwater pollution, in some countries the use of MTBE in gasoline is limited.

Alcohol additives to gasolines are used to a lesser extent than ethers, but nowadays interest in them has increased.

In the USA, a high-octane fuel formulation has been developed and is used, containing 85-96% of gasoline, 4.0-15% of a mixture of alcohols (ethyl, isopropyl and isobutyl). Since 1981, Germany has been using I-15 gasoline containing 15% methanol. Benzomethanol mixtures are used in Italy, Japan, Poland, France, India and other countries of the world.

In the CIS countries, studies on the use of benzomethanol mixtures in vehicles were carried out at the Institute of the State Research Institute of Methanolproekt (now the Institute "Khimtekhnologiya" together with the Lugansk Engineering Institute).

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The leading institutes for oil refining (VNIIPT) and automotive industry (NAMI) were involved in the work. A formulation of a benzamethanol mixture (BMS) was developed, the pilot batches of which according to TU 60332-1-181 were produced by the Kembilev Chemical Plant:

The composition of the BMS-15,% wt.

Gasoline A-72 (unleaded)	-44,5-77,5
Methanol	-14,5-15,5
Isobutanol	-5,0-10,0
Water, no more	-0,1
Cloud point	not higher than minus 45^0C
Engine octane number	-80,0

BMS tests in real operating conditions of trucks at different times of the year and in different climatic zones have shown positive results: the operational reliability of vehicles does not deteriorate, the level of toxicity of exhaust gases (incomplete combustion products by 30-40%, nitrogen oxides by 8-10%) decreases, a medical examination of the drivers showed that no deterioration in health was found.

Isobutanol in BMS stabilizes a mixture of gasoline and methanol, prevents the separation of this mixture, especially in the presence of water at low temperatures.

Due to the fact that the production of isobutanol by oxo-synthesis from propylene and carbon monoxide requires high specific capital investments and energy and material costs, the cost of isobutanol is quite high (more than USD 800 per ton), which limits its use as an additive to gasoline. Preferred production of isobutanol by combined synthesis of methanol and aliphatic alcohols C_2-C_4 from synthesis gas.

In a number of countries of the world, the process of joint synthesis has been implemented on an industrial scale, and the synthesis products - methanol - aliphatic alcohols C2-C4 are used as a highly effective additive to gasoline. (Idemutsu Kosan, Japan), Lurgi (Germany), (French Petroleum Institute, etc.).

EXPERIMENTAL PART

We, together with the staff of TADI and FNPZ, improved the composition of the BMS. Since there is no butanol production in the Republic, methyl acetate and ethyl acetate in the amount of 5-10% and urotropin, the production of which has been established at Navoiazot, was proposed instead.

The studies carried out in the laboratory of the FNPZ showed that the introduction of pure methanol into the composition of A-76 gasoline in an amount of up to 20% leads to an increase in its octane number up to 3.0 units.

We have modified methanol with the addition of methyl acetate, acetone and urotropine in the following composition: wt%, methanol -70%, methyl acetate -10; acetone -13; acetonitrile -5.0, urotropine -2.0 and added to gasoline A-72 in the amount of 8%.

Physicochemical and antiknock properties of A-72 containing 8% OPD-12 (octane-enhancing additive) are shown in Table 2.6.

Compositions based on methanol, methyl acetate, acetone, acetonitrile, urotropine were prepared and their antiknock resistance was studied (Table 1).

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Table 1

Composition of octane-increasing additives

№ compositions	Состав, % об				
	Methanol	Methylacetate	Acetone	Acetonitrile	Urotropin
OPD -12	70	10	13	5	2
OPD -13	65	15	12	7	1
OPD -14	60	20	15	5	-
OPD -15	55	25	20	-	-
OPD -16	50	20	15	13	2
OPD -17	45	25	15	10	-
OPD -18	80	10	10	5	-

The anti-knock resistance of the developed compositions was tested on the UIT-85 unit (Table 2)

Table 2

Anti-knock resistance of compositions

№	Composition	Quantity, %	Octanenumber, OCHM		Octaneincrease
			withoutadditive	withaddition	
1	OPD -12	5,0	50	58	8,0
2	OPD -12	8,0	69	76	7,0
3	OPD -13	5,0	69	72,0	3,0
4	OPD -13	10,0	69	76,0	7,0
5	OPD -14	5,0	50	59,0	9,0
6	OPD -14	10,0	72	77,0	5,0
7	OPD -15	5,0	72	75,0	3,0
8	OPD -15	10,0	69	75,0	6,0
9	OPD -16	5,0	50	57,0	7,0
10	OPD -16	10,0	69	77,0	8,0
11	OPD -17	5,0	50	60,0	10,0
12	OPD -17	5,0	69	73,0	4,0
13	OPD -17	10,0	72	81,0	9,0

Table 3

Physicochemical and anti-knock properties of A-72 gasoline containing 8% OPD-12

№	Thenameofindicators	GOST 2084-72 requirements for gasoline A-72	Gasoline A-72 with 8% OPD -12
1	Detonation resistance of the octane number according to the motor method. ResearchOctaneNumber	76.0 notstandard.	83,0
2	Leadcontent 20 g / l	0,17	Ots.

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3	Fractional composition PC not lower 10% not more 50% not more 90% not more NK not higher Remaining% Losses,%	 35,0 55 100 160 185 1,5 4,0	 35,0 44 92,0 145 170 0,9 3,0
4	Acidity, mg KOH per 100 cm^3 of gasoline	3,0	2,8
5	Concentration of actual tar, mg per 100 cm^3 of gasoline	10,0	0,5
6	Inductionperiodmin.	900	890
7	Massfractionofsulfur, %	0,1	0,02
8	Copperstriptest	Endured.	Endured.
9	Water-soluble acids and alkalis	Ots.	Ots.
10	Saturated vapor pressure mm Hg	500-700	620
11	Mechanicalimpuritiesandwater	Ots.	Ots.
12	Density at 200 C kg / m^3	Endured.	0,722
13	Cloudpoint^{0}C	Endured.	minus 45^{0}C

The FRPZ laboratory investigated the effect of various additives, including methanol, on increasing the octane number of gasoline. At the same time, it was found that the addition of methanol in an amount of 20% to the base gasoline A-76 leads to an increase in its octane number up to 79.0 TCR. And the addition of 50 mg / l Hitech and 2% MMA to 75.6, i.e. 3.6 units.

In this regard, we have prepared various compositions based on methanol and tested their antiknock properties. Some of them are shown in Table 4.

Table 4

Composition of oxygen and nitrogen-containing compositions (% vol.)

№	Compositionsymbol	Methanol	Ethanol	Isobutanol	Methylacetate	Ethylacetate	Urotropin
1	OPD-19	70,0	10,0	8,0	8,0	2,0	2,0
2	OPD-20	72,0	8,0	10,0	6,0	4,0	-
3	OPD-21	74,0	6,0	10,0	8,0	20,0	-
4	OPD-22	70,0	-	20,0	8,0	-	2,0
5	OPD-23	65,0	-	27,0	6,0	-	2,0
6	OPD-24	75,0	-	17,0	6,0	2,0	-
7	OPD-25	75,0	-	13,0	10	5,0	-
8	OPD-26	60,0	5,0	-	20	15,0	-

The antiknock properties of the synthesized compositions showed that the most active are composition OPD-12. It is involved in base gasoline in the amount of 8% vol. Leads to an increase in octane number by 7 units.

The production of methanol and ethanol is well established in the Republic. In the production of ethanol by the biochemical method, a head fraction is formed, the so-called "ether-

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aldehyde fraction" (EAF), which contains up to 95% ethanol. On the basis of EAF, acetic acid, and methanol, we synthesized methyl and ethyl acetate by a known method. The obtained methyl and ethyl acetate were tested as antiknock additives. The test was carried out in the laboratory of the FNPZ. The test results are shown in Table 5.

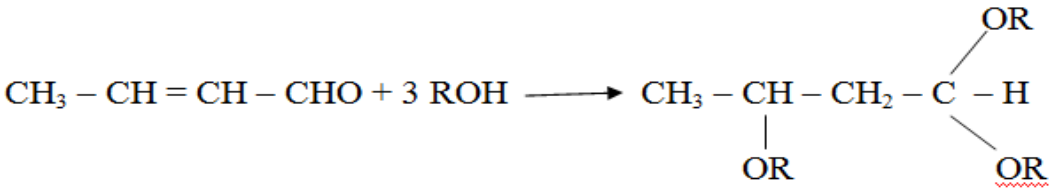
Table 5

Test results of methyl and ethyl acetate as octane-increasing additives (sample 1-methyl acetate:
sample 2 - ethylacetate)

№	Catalystbase: straightpetrol	Ochm	Additiveconcentration% vol.	Ochm	Octaneincrease
1	50:50	71,4	8% sample №1	72,0	0,6
2	50:5	71,4	10% sample № 1	72,8	1,4
3	50:50	71,4	10% sample№2	73,4	2,0
4	50:50	71,4	10% sample №2	75,6	4,2
5	40:60	71,8	8% sample №2	72,1	0,3
6	40:60	71,8	10% sample №2	72,0	0,2

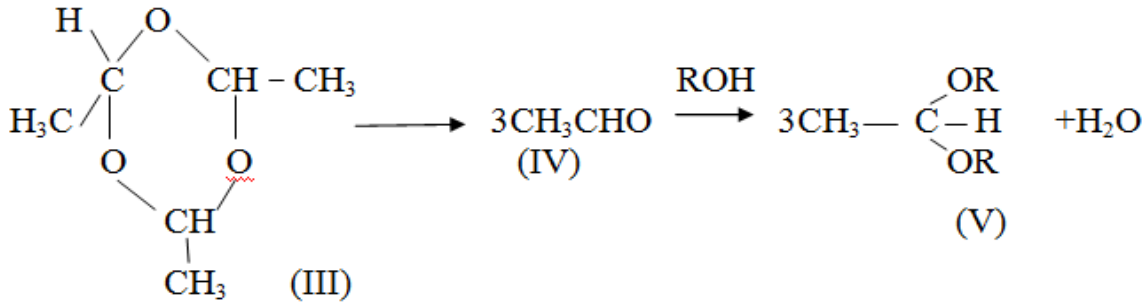
As can be seen from these tables, ethyl acetate is the most effective, when introduced into base gasoline in an amount of up to 10% of the mass, the octane number of gasoline increases to 4.2 units.

Ethyl acetate can be synthesized on the basis of local raw materials - ether aldehyde resin and acetic acid, which are available in our Republic. The synthesis of triethoxybutanes based on croton fraction and ether-aldehyde fraction has been studied. Thereactionproceedsaccordingtothescheme.



(I,II)

where R=-CH_3; (1,1,3-trimethoxybutane); R =-C_2H_5 (1,1,3-triethoxybutane). In this case, (I, II) paraldehyde and acetaldehyde also enter into the reaction.



The preparation reaction (I.II.V) was carried out according to a known method - condensation of the croton fraction with methanol and ethanol at a ratio of 1: 3 mol in the presence of catalysts.

Hydrochloric acid, ammonium chloride, calcium chloride and cation exchanger KU-2-8a

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BH^+ form were used as a catalyst; the target products were isolated by rectification. On the basis of methanol, trimethoxybutane (TMB), triethoxybutane (TEB), compositions were obtained that were tested as octane-increasing additives (Table 6).

Table 6

Composition and properties of octane-increasing compositions

№	Compositionofcompositions,% vol	The number of additives,% vol	Octonnumber (mm)		Octaneincrease
			Withoutadditives	with additives	
1	TMB -100	5,0	69,0	72,0	3,0
2	TMB -100	8,0	69,0	75,3	6,3
3	TEB -100	5,0	69,0	72,4	3,4
4	TEB -100	10,0	69,0	74,4	5,4
5	Methanol -75,0 acetaldehyde - 25,0	10,0	72,0	76,0	4,0
6	Methanol- 65,0 acetaldehyde- 20,0 TMB -15,0	10,0	72,0	78,4	6,4
7	Methanol -65,0 acetaldehyde- 20,0 TEB -15,0	10,0	69,0	75,0	6,0
8	Methanol -70,0 acetaldehyde - 20,0 TMB -9,0 urotropin-1,0 manganese acetate-30 mg / l	10,0	69,0	76,0	7,0

As can be seen from the data in the tables, compositions No. 6-8 are highly effective octane-enhancing additives. Their use improves the chemical and operational properties of gasoline and reduces the cloud point. If phase separation is observed when using pure methanol and methyl acetate, then it is not observed here. Urotropine and manganese acetate, in addition to being used as octane-increasing additives and stabilizers, also play the role of an antioxidant.

Conclusions.

1. Conducted systematic research on the development of new highly active environmentally friendly, energy and resource-saving octane-increasing additives to gasoline based on local raw materials.

2. For the first time, the use of 1,1,3-triethoxybutane, obtained from a secondary material - the production of acetaldehyde as an octane-increasing additive, has been shown. Establishment that the addition of 1,1,3-triethoxybutane to straight-run gasoline in the amount of 8.0% vol. will increase its octane number up to 12 units, in base gasoline in the amount of 10% by volume - up to 7 units.

3. For the first time, acetonitrile was used as an octane-increasing additive. Additives in an amount of 5% can increase its octane number to 10 units, and in base gasoline in an amount of up to 8% to increase its octane number to 9 OCHM units.

4. For the first time manganese, zinc, sodium, potassium and copper acetates were used as octane-increasing additives. It has been established that the addition of acetates to base gasoline from 80 to 100 mg / l makes it possible to increase its octane number to 10 units. It has been

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shown that the octane-increasing activity of acetates increases in the following order:

$$CH_3COONa<CH_3COOK<(CH_3COO)_2Zn<(CH_3COO)_2Cu<(CH_3COO)_2Mn$$

5. It was found that a composition consisting of methanol-70%, methyl acetate-10.0%, acetone-13%, acetonitrile-5.0%, urotropin-2.0%, manganese acetate 50 mg / l is the most effective for increasing octane number of gasolines. Adding it as 5-8% vol. allows you to increase the octane number of gasoline up to 7 units.

6. For the first time, ammonium nitrate was used as an octane-increasing additive. It is shown that the addition of ammonium nitrate to gasoline in the amount of 1.0-1.2 g / l makes it possible to increase its octane number to 7 units.

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