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The Effect of Oxygen Components on the Deposit Forming Properties of Auto Gasoline Components

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ABSTRACT: Tar generation of gasoline mixtures with different properties containing different amounts of tar was studied. It has been proved that tar formation of gasoline mixtures has variable properties. The inclusion of oxygenates in the composition of gasolines of various properties reduces their formation of tar. A significant positive synergistic effect was shown by low molecular weight alcohols and amines, as well as complex esters such as MTBE.

KEYWORDS: automobile gasoline, antioxidant additives, additive, reformate, catalyst, induction period.

I. INTRODUCTION

Modern commercial gasoline is a multi-component mixture consisting of hydrocarbons, organic and inorganic substances [1-2] . Today, oxygen-preserving additives with high detonation stability and improved environmental properties are included in automobile gasoline, and their amount is increasing year by year. If previously the amount of these compounds in gasoline did not exceed 3-5%, today their amount can exceed 50%. Among these compounds, mainly alcohol, ether and amines are widely used [3-4]. For example, the composition of E-85 car gasoline consists of 85% ethyl alcohol and the rest of the gasoline fraction.

However, the influence of these compounds and amines on the precipitation formation process of gasoline with different compositions, consisting of various components (gasoline fractions of secondary processes such as straight-burned gasoline fraction, isomerization, reforming, catalytic cracking) has not been fully studied [5-7].

II. SIGNIFICANCE OF THE SYSTEM

Tar generation of gasoline mixtures with different properties containing different amounts of tar was studied. It has been proved that tar formation of gasoline mixtures has variable properties. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

III. METHODOLOGY

The purpose of the study is to study the effect of anti-detonation devices on the process of precipitation formation of automobile gasolines and their fractions.

The object of research is the gasoline fractions produced in local oil refineries: reformate from the catalytic reforming process, straight gasoline fraction, catalyst from the catalytic cracking process.

In this research work, the precipitation formation of the compositions of gasoline fractions with alcohols, ethers and amines of different molecular weights was evaluated. In the study, the precipitation formation process was determined according to GOST 32404-2013 for determining the amount of tars in gasoline and its components. The research device is shown in the figure below.

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Picture. The device for determining the amount of tars FS-10

At the same time, the hydrocarbon content of gasoline fractions was determined by the adsorption-cryoscopic method [8]. The density of the research objects was determined by the pycnometric method according to GOST 3900-85.

IV. EXPERIMENTAL RESULTS

At the beginning of the study, we determined the physico-chemical properties of gasoline components produced at local oil refineries. These indicators serve as a basis for evaluating their physico-chemical changes after adding various additives to them. The physical and chemical properties of gasoline fractions used in the study are presented in Table 1.

Table 1
Physical and chemical properties of used gasoline components

Gasoline type	Amount of resins, mg/100cm ^{3}	Density, g/cm ^{3}	Amount of hydrocarbons, % mass.	
			Aromatic hydrocarbons	Unsaturated carbohydrates
AI-80 gasoline	1141.20	0.772	48.78	3.21
Reformat (R)	1457.00	0.7912	78.12	8.22
Straight Driven Gasoline (THB)	12,20	0.7915	2.12	0.98
Catalyst (K)	1235.10	0.7885	31.14	6.31

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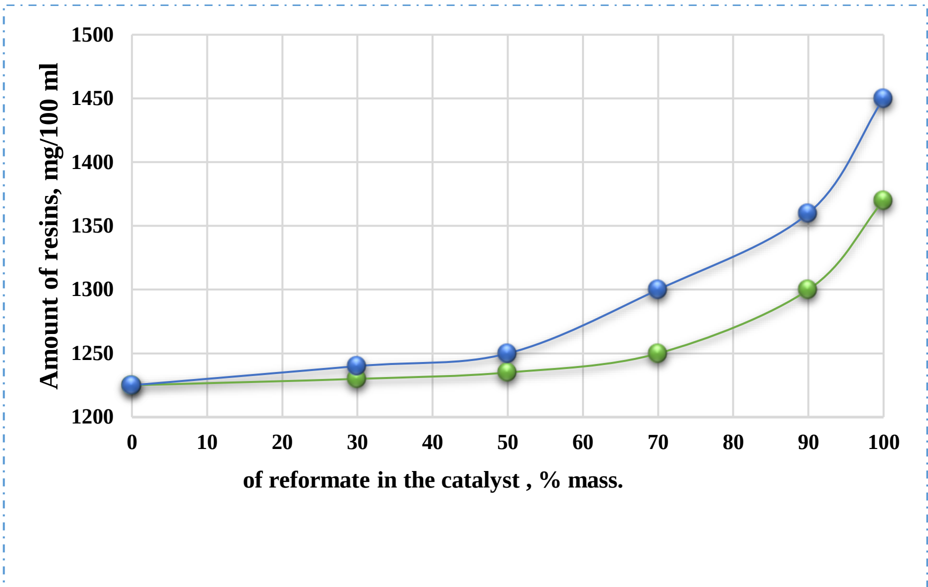

Figure 1. Amount of tars in gasoline samples with different gasoline fractions and oxygenates added to them

In order to evaluate the effect of oxygenates and amines on the formation of deposits of gasoline and its components of different composition, alcohols, amines and ethers of different molecular weight were included in 10% mass. entered in the amount:

- alcohols: ethyl alcohol (ES), isopropyl alcohol (IPS), ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG);
- ethers: methyl tert-butyl ether (MTBE);
- amines: monoethanolamine (MEA).

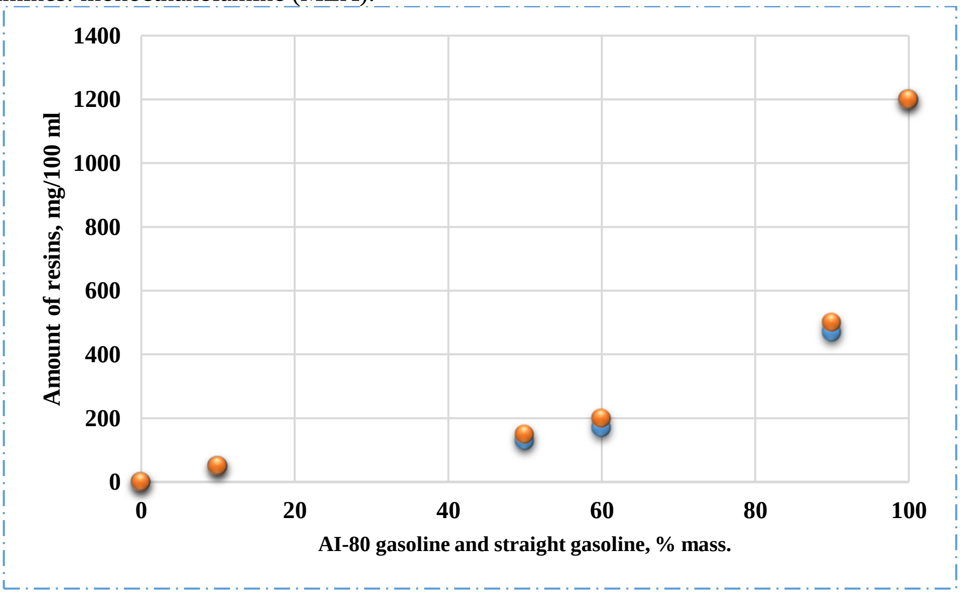

Figure 2. Amount of tars in gasoline compositions with different characteristics

The results of the study show that the tar formation of gasoline compositions with different mixtures has a variable character (Fig. 1). Due to the synergistic effect, it is possible to observe a decrease in the amount of tars in mixed gasolines. In this case, multi-tar gasolines showed a lower index in terms of the amount of tars compared to the additive size (Fig. 2). When the amount of tars in gasoline is sufficient, the excess tars stop further tar formation.

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When alcohol, ether and amines are added in the amount of 10%, it can be seen that the amount of tars drops significantly in gasoline compositions (Fig. 1). A synergistic effect is observed [9-10].

In order to evaluate the effect of oxygenates on the amount of tars in samples with different mixtures, the concentration dependence of the composition of reformat + straight gasoline compositions containing 10% oxygenates and amine was determined. The R+THB gasoline blend was chosen due to the large difference in additive magnitude. In the assessment of tar formation in the presence of oxygenates, the highest deviation index for tars from the mixture composition indicators was used (Fig. 1).

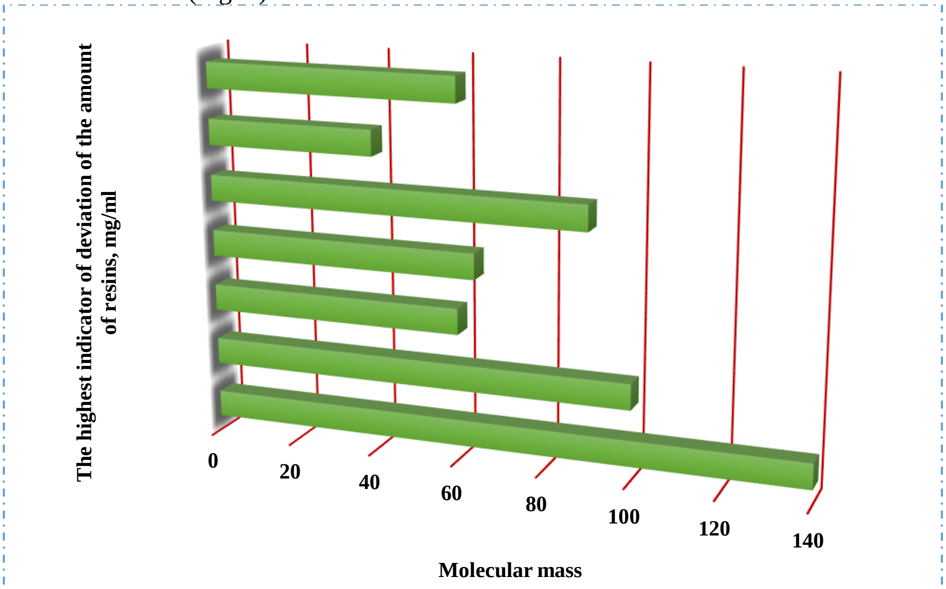

Figure 3. The deviation of the amount of tars in the R+THB gasoline sample with and without 10% oxygenate and amines, depending on their molecular mass

The results of the experiment showed that the degree of deviation from the additive size increases with a decrease in the molecular mass of alcohols, and the amount of resins decreases, respectively. It follows that low molecular weight alcohols and amines inhibit tar formation to a greater extent in various gasoline blends than high molecular weight alcohols. Both MTBE and MEA exhibit a positive synergistic effect in R+THB gasoline compositions and reduce tar formation (Figure 3).

In order to confirm the antioxidant efficiency of low molecular weight alcohols, the tar formation kinetics of gasoline compositions containing 5% ethyl alcohol was studied for 45 days (Fig. 4a). The results of the analysis showed that the addition of ethyl alcohol to the composition of car gasoline reduces the formation of tar. Although the rate of formation of tar was high in the reformate containing a large amount of aromatic and unsaturated hydrocarbons, the antioxidant effect of ethyl alcohol was better compared to the gasoline containing a relatively small amount of aromatic and unsaturated hydrocarbons and tar substances. This can be assessed by the rate of tar formation.

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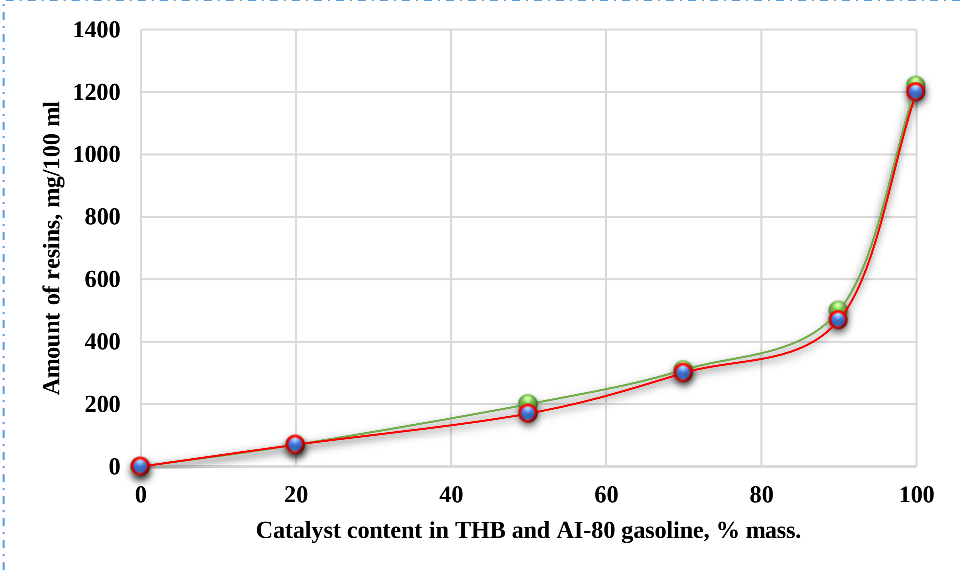

Figure 4a. Rate of formation of AI-80 gasoline and THB tar

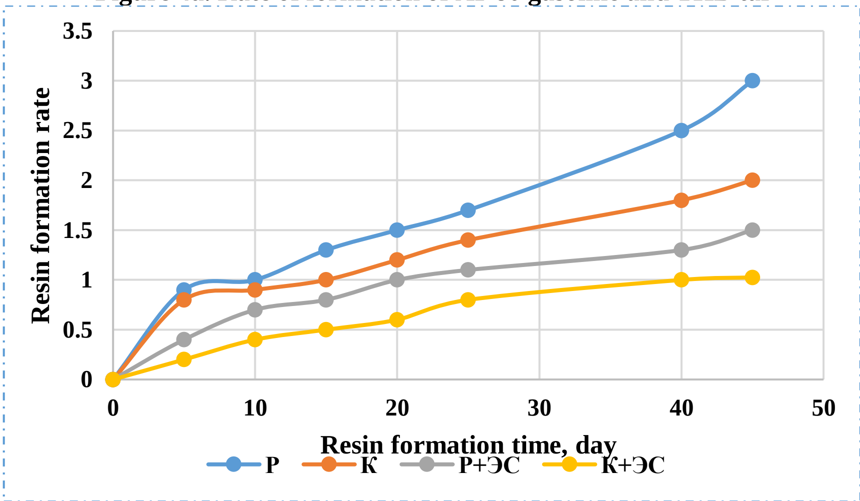

Figure 4b. Tar formation rate kinetics of gasoline compositions

We determined the rate of resin formation using the following formula:

$$v = \frac{F_1 - F_0}{t}$$

where: $v - t$ is the rate of tar formation per day of storage, *mg/100 cm* ^{3}; F_o is the concentration of tars at the beginning of the experiment, *mg/100 cm* ^{3}; F_1 – concentration of tars after t day of storage, *mg/100 cm* ^{3}.

Figure 4b shows that the rate of tar formation is high in gasoline containing high tar content, aromatic and unsaturated hydrocarbons. In this case, the rate of formation of tar within 10 days of gasoline containing and without ethyl alcohol is the same. Later, with increasing storage time, the rate of tar formation varies. In gasoline samples that do not contain ethyl alcohol, the rate of tar formation increases with increasing storage time, and after 45 days, its rate of tar formation increases up to 1.3-1.5 times.

In order to confirm the obtained results, we determined the induction time of gasoline compositions containing oxygenates. The results are presented in Table 2. The results showed that the induction time was longer in the presence of oxygenates.

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Table 2
Induction period

Gasoline type	Induction period, min.
Reformat	22
R+5% ES	24
Catalyst	27
K+5% ES	30
K+5% IPS	32

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V. CONCLUSION AND FUTURE WORK

Thus, based on the results of theoretical and practical research, the following can be concluded:

• The tar formation of various gasoline components and automobile gasolines is variable. Alternatively, the rate of tar formation when blending high-tar gasolines is lower relative to the additive size compared to blends of low-tar and high-tar gasolines.

• The addition of oxygenates of various properties to the composition of gasoline significantly reduces the amount of tars. Low molecular mass alcohols, amines and MTBE-type complex esters show a great positive synergistic effect.

• it is possible to clearly see the antioxidant effect of "stopping " ethyl alcohol in the formation of tar ..

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