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Resin Formation of Trademark Gasoline Components in the Presence of Oxygenates

[1]L.R. Baibekova, [2]A.V. Sharifullin, [2]A.A. Trofimov, [1]S.M. Petrov and [1]D.A. Feoktistov
[1]Kazan Federal University, Kremlevskaya Str. 18, 20008 Kazan, Russia
[2]Kazan National Research Technological University,
Karl Marx Str. 68, 420015 Kazan, Russian Federation

Abstract: Modern trademark gasolines are multicomponent mixtures composed of hydrocarbons and other organic and inorganic substances. Primarily involved the composition of motor gasolines includes oxygenates (alcohols and ethers) with a high detonation resistance and improved environmental properties. And, their share in the composition of gasolines increases more and more. Earlier, the share of oxygenates in the composition of gasoline did not exceed 3-5% of vol. but now the share of oxygenates may exceed 50% of vol. First of all, the thing is not about alcohols, ethers and amines. For example, the gasoline of E-85 grade contains at least about 85% of ethanol and the rest is presented by gasoline fractions. However, the effect of oxygenates and amines on the processes of gasoline gumming of different group composition formed from a variety of components (straight-run naphtha, gasoline fractions of "catalytic cracking, reforming, isomerization" secondary processes), containing different amounts of resin forming components is not clear. In this study, we evaluated the resin formation of gasoline fraction mixed compositions containing the alcohols, esters and amines of different molecular weight. These substances are often used as the additives to the commercial gasolines. The evaluation of resin formation was carried out in terms of actual resin content. The resin formation of different nature gasoline mixtures with different contents of actual resins is studied. It is proved that the resin formation mixture of gasolines is of non-additive character. The introduction of oxygenates to gasoline composition of different nature reduces their resin formation. A large positive synergistic effect is exhibited by low molecular weight alcohols and amines as well as esters.

Key words: Gasoline, oxygenates, synergy effect, additivity, reformate, catalysate, isomerate, mixing, resins, induction period

INTRODUCTION

Modern trademark gasolines are the multicomponent mixture composed of hydrocarbons and other organic and inorganic materials (Safonov *et al*., 2002; Anisimov *et al*., 1999). Primarily, the composition of motor gasolines involve oxygenates (alcohols and ethers) with a high detonation resistance and improved environmental properties. And, their share in the composition of gasolines increases more and more. Earlier, the share of oxygenates in the composition of gasoline did not exceed 3-5% of vol. but now the share of oxygenates may exceed 50% of vol. First of all, the thing is not about alcohols, ethers and amines. For example, the gasoline of E-85 grade contains at least about 85% of ethanol and the rest is presented by gasoline fractions.

However, the effect of oxygenates and amines in the processes of gasoline gumming of different group composition formed from a variety of components (straight-run naphtha, gasoline fractions of secondary processes, "catalytic cracking, reforming, isomerization"), containing different amounts of resin forming components is not clear (ICATS, 2011; Anonymous, 2000; Sharifullin *et al*., 2004).

MATERIALS AND METHODS

In this study, we evaluated the resin formation of gasoline fraction mixed compositions containing the alcohols, esters and amines of different molecular weight. These substances are often used as the additives to the commercial gasolines. The evaluation of resin formation was carried out in terms of actual resin content index (according to Budarov). We studied the trade components of gasolines with different contents of actual resins and different storage periods.

Corresponding Author: L.R. Baibekova, Kazan Federal University, Kremlevskaya Str. 18, 20008 Kazan, Russia

Table 1: Physical and chemical properties of used gasolines

Gasoline type	Actual resins (mg 100 cm^{-3})	Density (g cm^{-3})	Content (wt%)	
			Aromatic hydrocarbons	Unsaturated hydrocarbons
Reformate (RB)	1447.00	0.7917	77.72	7.27
Isomerizate (IB)	13.75	0.7144	4.96	0.34
Straight-run (PB)	11.50	0.7917	1.16	0.46
Catalytic cracking catalyst (KB)	1225.20	0.7885	30.16	5.19

The physicochemical properties of gasolines used in the studies are listed in Table 1.

RESULTS AND DISCUSSION

The results of the analysis show that the resin formation of mixed gasoline compositions formed from various commodity components has a nonadditive character (Fig. 1). It shows a positive synergistic effect of actual resin reduction in the gasoline mixtures.

At that the mixture of gasolines with a high resin content provides less deviation from the additive value (Fig. 2) by actual resins than the mixture of gasolines with the initial low content of resins and high resin gasiolines (Fig. 2). It turns out that at a sufficiently high resin content in gasoline, excessively contained resins inhibit the process of subsequent gumming.

In order to assess the impact of oxygenates and amines the gasoline was introduced with the alcohols of various molecular weights, amines and esters at the amount of 10% wt.:

- Alcohols: Ethanol (EA), Isopropyl Alcohol (IPA), Ethylene Glycol (EG), Diethylene Glycol (DEG), Triethylene Glycol (TEG)
- Esters: Methyl Tert-Butyl Ether (MTBE)
- Amines: Mono Ethanol Amine (MEA)

The analysis results of the experiments show that the introduction of alcohols, esters and amines at the amount of about 10% reduces the content of actual resisns in respect of pure mixed compositions (Fig. 1). A positive synergistic effect is observed (Sharifullin *et al*., 2008); (Sharifullin, 2011).

In order to assess the effect of oxygenates on the actual content of resins in mixed contents the concentration dependences for the compositions RB+PB were determined containing 10% of oxygenates and amine. The mixture of RB+PB gasolines is selected for study since the deviations from an additive value is the maximal one. In order to assess the resin content in the presence of oxygenates used the maximum deviations by actual resins from the values of mixed compositions were used (Fig. 1).

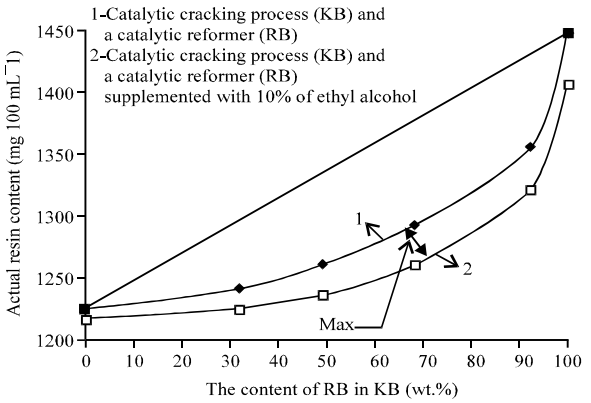

Fig. 1: The content of the actual resins in the mixtures of various nature gasolines

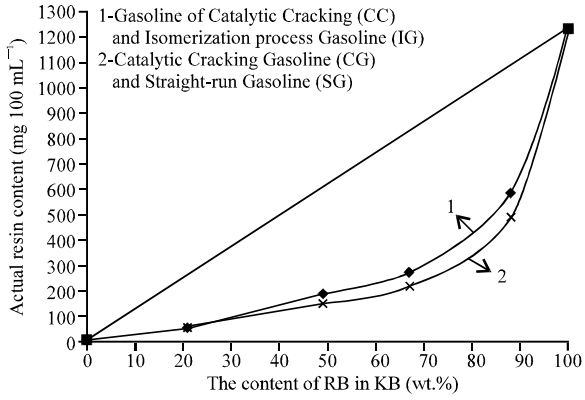

Fig. 2: The content of the actual resins in gasoline mixtures of different nature

The analysis of the data shows (Fig. 3) that with the decrease of alcohol molecular weight, the deviation degree from the additive increases (there is a positive synergistic effect), respectively, the actual content of resins is reduced respectively. Therefore, the low molecular weight alcohols and amines largely inhibit resin formation process in mixed formulations than polyols. MTBE and MEA also has a high positive synergistic effect of resin actual content reduction in mixed contents of Reforming process Gasolines (RG) and Straight-run Gasoline (SG) (Fig. 3).

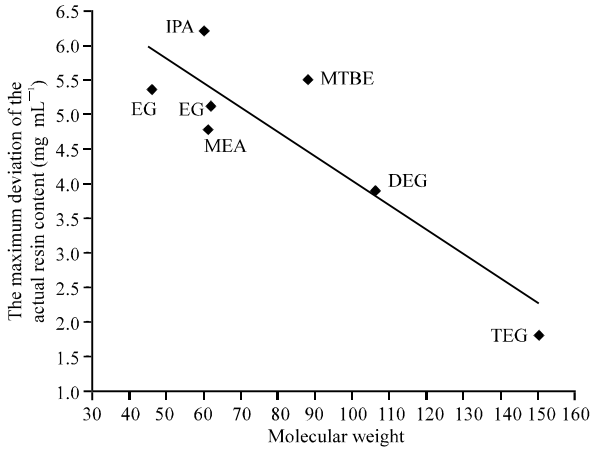

Fig. 3: The dependence of maximum deviation from the content of actual resins in mixed formulations RB+PB, which do not contain or containing about 10% of oxygenates, amines from their molecular weight. EA: Alcohols ethanol; IPA: Isopropyl Alcohol; EG: Ethylene Glycol; DEG: Diethylene Glycol; TEG: Triethylene Glycol; MTBE: Esters Methyl Tert-Butyl Ether; MEA: Amines Monoethanolamine

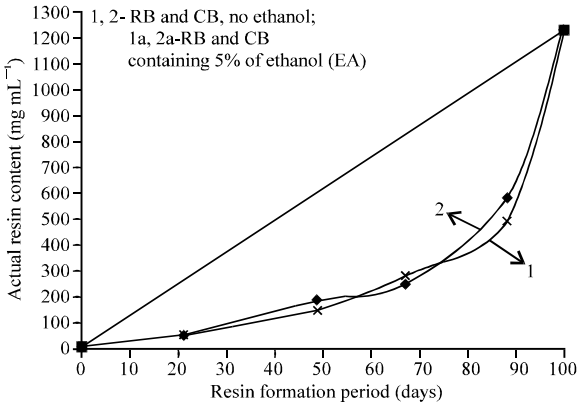

Fig. 4: The kinetics of gasoline resin formation within the process of Reformate (RB) and catalytic cracking (KB), containing: 1, 2-RB and CB; 1a, 2a-RB and CB, containing 5% of ethanol (EA)

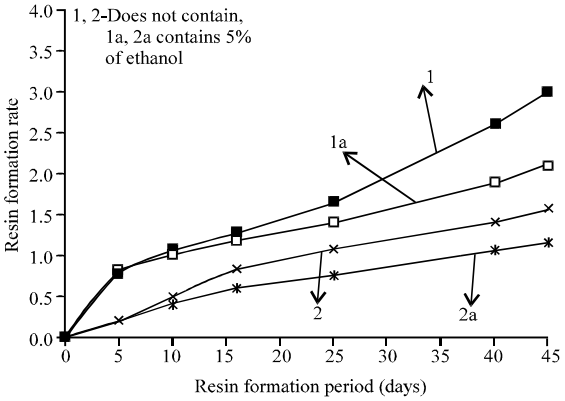

Fig. 5: Speed of gasoline gumming during catalytic reforming: (1) and catalytic cracking; (2) 1.2-does not contain, 1a, 2a-contains 5% of ethanol

In order to confirm the effectiveness of low molecular weight alcohol antioxidant properties the kinetics of low molecular alcohol mixture resin formation was studied for 45 days (Fig. 4) containing 5% of EA (Fig. 3). The analysis shows that the introduction of ethanol in gasoline composition reduces their resin formation degree. Although, the gasoline with a higher content of aromatic and unsaturated hydrocarbons (RB) has a high rate of gumming, the "braking" anti oxidation effect from the introduction of ethyl alcohol is more pronounced than for the gasoline with lower initial content of actual resins, aromatic and unsaturated hydrocarbons (KK). This may be assessed by determining the rate of gumming. Gumming rate calculated according to the Eq. 1:

$$\nu = \frac{F_1 - F_0}{t} \quad (1)$$

Where:

ν = Resin formation rate, mg 100 cm^{-3} of resins during t days of storage

F_1 = Actual resin concentration at the beginning of the experiment

F_0 = The concentration of actual resins after t days of storage, mg 100 cm^{-3}

The analysis of the Fig. 5 shows that the rate of gasoline resin formation with a higher resin content, of aromatic and unsaturated hydrocarbons is higher. At that ~within 10 day, the gumming speed of gasolines containing and not containing ethyl alcohol is about the same. With the further increase of storage rate time the gumming rate starts to differ materially. The gumming rate of gasolines containing no ethyl alcohol starts to grow and at the end of 45 days of storage exceeds the initial one ~1.3-1.5 times.

In order to confirm these regularities the induction period for the gasolines containing oxygenates was determined. The results are shown in Table 2. The results show that induction period is longer in the presence of oxygenates.

Summary: The share of oxygenates as the part of motor gasolines is more increasing. Earlier the composition of motor gasolines did not exceed the share of oxygenates within 3-5% of vol., now the share of oxygenates may

Table 2: Induction period

Gasoline type	Induction period (min)
Reformate (BR)	22
BR+5% of ethyl alcohol	24
Cat. cracking (KB)	27
KB+5% of ethyl alcohol	30
CB 5% of IPS	32

exceed 50% of vol. First of all, the thing is about alcohols, ethers and amines. For example, the gasoline of E-85 grade contains at least about 85% of ethanol and the rest is presented by gasoline fractions.

However, the effect of oxygenates and amines on the processes of gasoline gumming within different group composition formed from a variety of components is not clear (straight-run naphtha, gasoline fractions of "catalytic cracking, reforming, isomerization" secondary processes), containing different amounts of resin forming components.

It was proved that resin formation of gasoline mixture has a non-additive character. The introduction of oxygenates to gasoline composition of different nature reduces their resin formation rate. A large positive synergistic effect is exhibited by low molecular weight alcohols and amines as well as esters.

CONCLUSION

The resin formation index of mixed compositions formed from the gasolines of different nature with different content of resins has a nonadditive nature reducing the content of actual resins. At that the mixture of high resin gasolines provides less deviation from an additive value than the mixing of gasolines with an initial low content of resins and high resin gasolines.

The introduction of oxygenates into gasoline composition of different nature leads to the reduction of resin actual content. A strong positive synergistic effect was exhibited by low molecular weight alcohols, amines as well as by esters such as MTBE.

The "inhibitory" antioxidating effect from the introduction of ethanol is more pronounced for gasolines, containing a large number of aromatic and unsaturated hydrocarbons.

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