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Identification of Oxygen-containing Compounds in Benzine and Kerosene Oil Fractions and Determination of Sulfur and Halogen Content in Them

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Abstract—A procedure based on X-ray fluorescence and inductively coupled plasma with mass spectrometric recording was developed for express determination of the content of sulfur and halogen-containing compounds in benzine and kerosene oil fractions. Oxygen-containing compounds in gasolines and reforming products were identified by chromatography-mass spectrometry.

The requirements to the quality of motor fuels (in particular, to gasoline) become increasingly stringent [1]. Heteroatomic compounds (S-, O-, N-, and chlorine-containing products) strongly affect the gasoline quality. The major part of these compounds is removed by hydrofining, but their certain fraction is retained in the final product.

In this study we developed reliable procedures for quantitative determination of heteroorganic compounds in raw materials and benzine components, and also in reforming products from the Ryazan Oil Refining Plant, Joint-Stock Company (RORP).

EXPERIMENTAL

The samples of the initial raw materials, catalyzates, and stable and unstable hydrogenizates were taken from installations for primary (AT-6) and secondary oil refining [hydrofining of benzine, kerosene, diesel oil, and other reforming products, namely, L-35/8-300 (benzene), L-35/5-300 (xylene), L-35/11-300 (12/1, benzine)] and for hydrofining of kerosene (24/600) at the Ryazan Oil Refining Plant. The contents of sulfur and organic chlorine were determined by X-ray fluorescence analysis (RF) [2] using a Spectroscan spectrometer and by the method of inductively coupled plasma with mass spectrometric recording (ICP-MS). The comparative study of products from the entire cycle of production of high-octane gasolines was performed by IR Fourier spectrometry (IR-FS) [3] on an FSM 1201 unit.

The oxygen- and nitrogen-containing compounds in the samples were identified by gas chromatography-mass spectrometry (GC-MS) according to the procedure given in [4], using the MassLab and Amdis software and databases.

The highest content of sulfur was determined in the feed of the 24/600 installation. The 105-140 (feed of L-35/5-300) and 115–180°C fraction contain 0.0353 and 0.0487 wt % sulfur, respectively. The feed of the installation for benzene reforming, (62–85°C, L-35/8-300) and 85–105°C fraction (feed of L-35/6-300) contain 0.0128 and 0.0184 wt % sulfur, respectively.

The content of sulfur in the wide benzine fraction, 85–180°C, supplied to benzine reforming and in benzine from the K-8 fractionating column (AT-6 installation) varies from 0.054 to 0.062 wt %.

Due to hydrofining, the content of sulfur in stable hydrogenates and catalyzates obtained from the above installations decreases to 0.0005 wt%, whereas in imported gasoline, its content is as high as 0.0098 wt %.

The IR spectrum of the straight-run naphtha from the K-8 column (AT-6) exhibits a broad strong absorption band of the methylene groups of alkanes and naphthenes at 2850–2980 cm^{-1}. The presence of methylene groups in alkanes and in paraffins and cyclic compounds (C_5–C_6) is confirmed by a doublet at 1365–1395 and a singlet at 750 cm^{-1}, respectively. The content of arenes in naphtha is low, which is confirmed by a weak band at 1580 cm^{-1}. The carboxy and hydroxy

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Table 1. Content of chlorine, bromine, and iodine in feed, hydrogenizates, and catalyzates from various installations at the RORP Join-Stock Company

Installation, product	Cl	Br	I
	$c \times 10^{-4}$, wt %		
AT-6, desalinated oil	16.0	3.9	6.4
24/600, feed	13.0	1.8	5.5
24/600, hydrofined kerosene	1.8	0.7	2.4
Å™-6, naphtha from K-8	11.0	2.5	5.6
L-35/5-300, feed	10.0	2.1	5.8
L-35/5-300, catalyzate	2.1	0.75	3.2
L-35/5-300, unstable hydrogenizate	1.5	0.6	3.0
L-35/5-300, stable hydrogenizate	1.2	0.5	2.9
L-35/11-300, feed	9.0	1.8	4.6
L-35/11-300, stable catalyzate	3.0	1.0	3.2
L-35/11-300, unstable hydrogenizate	1.7	1.0	0.9
L-35/11-300, stable hydrogenizate	1.3	0.75	0.84
L-35/8-300, feed	8.0	2.5	5.1
L-35/8-300, catalyzate	1.7	1.0	0.9
L-35/8-300, unstable hydrogenizate	1.3	0.65	2.2
L-35/11-300, stable hydrogenizate	1.0	0.6	2.1
12/1, 62–70°C fraction	1.1	0.8	0.9
12/1, 70–115°C fraction	5.0	1.8	1.3
L-35/11-1000, feed	8.0	1.3	1.4
12/1, 115–180°C fraction	7.0	2.0	1.6

groups in naphtha are almost absent; the absorption bands corresponding to these groups are very weak.

As can be seen from the IR spectrum of the catalyzate (L-35/11-300 installation), it is enriched in arenes (1580 cm^{-1}), whereas the content of alkanes is smaller than that in the initial naphtha (180°C dry point).

According to the IR spectra, there are no arenes in light benzine from the E-201 tank (L-35/11-300 installation). The intensity ratio of the absorption bands in the IR spectra of unstable catalyzate sampled from the S-1 separator (L-35/11-300 installation) and hydrogenizate differ from that in the feed. The IR spectrum of the stable catalyzate from this installation exhibits strong absorption bands of arenes at 700–740, 1580, and 3080 cm^{-1}.

The IR data indicate that the 62–70 and 70–115°C fractions contain almost no arenes; these fractions predominantly consist of alkanes, isoalkanes, and naphthenes (strong absorption band at 750 cm^{-1}).

Organic halogens were determined by combustion of the oil product sample, with subsequent absorption of the combustion products with soda and analysis by ICP-MS.

As can be seen from Table 1, the content of organic halides in the feed supplied for secondary oil processing is higher than that in the final products from installations for hydrofining and reforming. The content of chlorine in unstable hydrogenizate is higher than that in the stable product. The chlorine content increases with increasing dry point of the fraction.

It should be noted that, in some cases, the iodine content is much greater than that of bromine. Organic compounds of iodine, bromine, and chlorine strongly accelerate corrosion of installations and pipelines, especially in the presence of water.

The data on the content of organic chlorine in oil and some petroleum products from installations for benzene and benzine reforming at the KINEF Limited Liability Company processing West-Siberian crude oil well agree with the results of an analysis of the feed and products from the RORP installations using the same crude oil.

A typical chromatogram of the 85–180°C fraction, used as the feed at the L-35/11-300 reforming installation, consists of 42 peaks; most of them belong to the compounds listed in Table 2. Nearly 40 and 10 oxygen-containing compounds were iden-

Table 2. Oxygen-containing compounds identified in benzine and its components prepared at the RORP Joint-Stock Company

Compound	Feed, L-35/11-300	K-8 column Naphtha (AT-6)	Hydrogenizate, L-35/11-300
	wt %		
1-Butanol	0.05	0.14	0.07
2-Pentanone	0.02	0.38	
2-Pentanol	0.01	0.18	
2-Methyl-2-pentanol	0.08	0.27	
4-Methyl-2-pentanone	0.12	1.01	
3-Methyl-2-pentanone	0.20	0.44	
4-Methyl-2-pentanol	0.04	0.06	
4,4-Dimethyl-2-pentanone	0.10	0.20	
3-Hexanone,	0.32	0.60	0.07 (0.08)
2-Hexanone	0.59	0.70	0.09 (0.10)
2-Hexanol	0.22	0.13	0.02 (0.05)
Aliphatic alcohol C_6	0.33	0.07	0.01 (0.02)
2-Hexanol	0.32	0.18	0.03 (0.04)
3-Methyl-2-hexanone	0.23	0.27	
Aliphatic alcohol C_7	0.16	0.12	
5-Methyl-3-hexanone	0.16	0.18	0.01
2-Methyl-3-hexanone	0.21	0.22	
2,3-Dimethyl-3-pentanol	0.21	0.16	
3-Ethyl-2-pentanone	0.27	0.24	
4-Methyl-2-hexanone	1.11	1.21	0.01
5-Methyl-2-hexanone	0.15	0.14	
4-Heptanol	0.22	0.23	0.02
Aliphatic ketone C_7	0.23	0.30	0.02
Cyclohexanol	0.05	0.03	
3-Heptanone	0.69	0.61	
2-Heptanone	0.72	0.52	
Aliphatic ketone C_8	0.05	0.06	
Aliphatic ketone C_8	0.07	0.03	
Aliphatic ketone C_8	0.25	0.14	
4-Methyl-2-heptanone	0.48	0.49	
3,4-Dimethyl-2-hexanone	0.21	0.17	
Trimethylcyclohexanone	0.06	0.01	
6-Methyl-3-heptanone	0.09	0.02	
6-Methyl-2-heptanone	0.14	0.04	
Aliphatic ketone C_8	0.06	0.02	
Methyl cyclohexyl ketone	0.06	0.01	
4-Octanone	0.18	0.09	
3-Octanone	0.20	0.03	
Dimethylheptanone	0.43	0.13	
Aliphatic ketone C_8	0.14	0.07	
Cyclopentylpropanone	0.21	0.02	
Cyclohexylpropanone	0.10		
2,2,4-Trimethyl-1,2-dihydroquinoline	0.05		
Total $c \times 10^{-4}$, wt %	9.54	9.92	0.35 (0.37)

tified in the straight-run naphtha sampled from K-8 column (AT-6 installation) and in hydrogenizate of benzine reforming (L-35/11-300), respectively (Table 2).

The data on the content of oxygen-containing compounds in three samples taken from L-35/11-300 and AT-6 installations are also listed in Table 2. According to GC-MS data, the feed supplied to the L-35/11-300 installation (85–180°C) contains 42 compounds [41 oxygen-containing compounds and insignificant amounts of 2,2,4-trimethyl-1,2-dihydroquinoline (0.05 wt %)]. Aliphatic alcohols and ketones (C_4–C_9) were mainly identified, and the content of ketones is greater than that of alcohols by a factor of 3. The content of alicyclic alcohols is smaller by a factor of 32.4 – 48.0 than that of acyclic compounds. Similar trend is observed for ketones: the acyclic to alicyclic ketone ratio in the samples studied varies from 140 to 205.

As can be seen, aliphatic ketones with methyl substituents at different distance from the carbonyl group are predominant in the samples studied. The fraction of linear ketones C_6–C_8 is smaller. Among alcohols, the major fraction belongs to linear (primary and secondary) aliphatic alcohols.

CONCLUSIONS

(1) The content of sulfur and halogen-containing compounds in benzine and kerosene oil fractions from the RORP Joint-Stock Company was determined using the methods of X-ray fluorescence and inductively coupled plasma with mass spectrometric recording; oxygen-containing compounds were also identified. It was found that the content of ketones is greater than that of alcohols by a factor of 3.

(2) X-ray fluorescence procedure is the best method for express determination of sulfur in benzines and their components and in kerosene. For control of hydrofining and reforming (aromatization) of the benzine and kerosene fractions, the IR Fourier spectrometry is preferable. The method of inductively coupled plasma with mass spectrometric recording is the best for express analysis of halogens in organic compounds contained in oil and petroleum products.

(3) The higher the dry points of the fraction, the greater the content of bromine and iodine in it; in some cases the iodine content is much higher than that of bromine.

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