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Abstract

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UNSATURATED HYDROCARBONS OF THERMAL-CRACKING GASOLINE

In our previous studies we reported on the chemical composition of the fraction up to 60° of thermal-cracking gasoline obtained from Grozny paraffinic crude oil ([1]), and on the development of a chromatographic method for separating mixtures consisting of naphthene-paraffin, olefinic, and aromatic hydrocarbons ([2]). By means of the method proposed, we separated the 60–150° fraction of the same gasoline into naphthene-paraffin, olefinic, and aromatic hydrocarbon groups. The composition of the aromatic and hexamethylene portions of the gasoline isolated from the 60–150° fraction was also reported earlier ([3]).

In the present communication, data are given on the hydrocarbon composition of the olefinic portion of the fraction. The olefinic fraction on a 45 t.t. column was distilled into 10 narrow fractions, the characteristics of which are given in Table 1.

Table 1

Fraction Nos.	Collection temperature (°C/760)	Fraction yield (g)	Fraction yield (%) on olefin fraction	Fraction yield (%) on gasoline fraction 60–150°	Fraction yield (%) on gasoline up to 150°	n_D^{20}	d_4^{20}	Iodine number	Mol. wt.	Max. aniline point
1	60–66	15.07	6.97	2.67	2.44	1.3939	0.6902	295.9	82.9	22.5
2	66–80	20.99	9.91	3.72	3.40	1.4100	0.7196	305.0	84.1	15.1
3	80–90	9.39	4.34	1.66	1.52	1.4098	0.7225	272.3	95.8	24.9
4	90–98	32.78	15.16	5.81	5.31	1.4118	0.7232	274.0	96.4	25.7
5	98–110	18.66	8.63	3.30	3.02	1.4387	0.7868	305.0	94.9	8.4
6	110–120	16.51	7.63	2.92	2.67	1.4249	0.7538	261.0	107.4	25.2

Fraction Nos.	Collection temperature (°C/760)	Fraction yield (g)	Fraction yield (%) on olefin fraction	Fraction yield (%) on gasoline fraction 60–150°	Fraction yield (%) on gasoline up to 150°	n_D^{20}	d_4^{20}	Iodine number	Mol. wt.	Max. aniline point
7	120–123	17.81	8.24	3.15	2.88	1.4230	0.7462	283.5	109.1	28.9
8	123–137	27.60	12.76	4.89	4.47	1.4370	0.7803	285.0	111.3	22.5
9	137–144	17.52	8.10	3.10	2.84	1.4347	0.7751	270.2	122.4	29.8
10	144–150	23.81	11.01	4.22	3.86	1.4360	0.7786	245.0	122.5	31.1
Residue	150	16.1	7.45	2.85	2.61	–	–	–	–	–
Total		216.24	100.0	38.29	35.02	–	–	–	–	–
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Note. Fractions Nos. 1, 2 –C_6; Nos. 3, 4, 5 –C_7; Nos. 6, 7, 8 –C_8; Nos. 9, 10 –C_9.

The molecular-weight values (Table 1) showed that the fractions were divided into 4 groups according to the number of carbon atoms in the molecule.

The 5th fraction, judging from its characteristics, apparently consists mainly of cycloolefins. The detailed group composition of the fractions was investigated by a combination of sulfuric-acid, hydrogenation and dehydrogenation catalysis methods, and the aniline method.

As can be seen from Table 2, the content of cyclopentene hydrocarbons considerably predominates over that of cyclohexene hydrocarbons in all fractions (fractions Nos. 1, 2, 4, and 7 contain practically no cyclohexene hydrocarbons).

The cyclenes were distributed unevenly among the fractions. Thus, in fractions Nos. 8 and 10 the content of cyclenes exceeds the content of alkenes; the percentage of cyclenes in these fractions is respectively 69 and 55. Fraction 5 is especially rich in cyclenes, where their content is 90%.

Table 2

Fraction Nos.	Boiling range (°C)	Content per fraction (wt. %): cyclohexenes	Content per fraction (wt. %): cyclopentenes	Content per fraction (wt. %): alkenes
1	60–66	0	29	80
2	66–80	4	38	58
3*	80–90	25	0	75
4	90–98	3	29	68
5	98–110	29	61	10
6	110–120	12	30	58
7	120–123	0	35	65
8	123–137	28	41	31
9	137–144	13	32	55
10	144–150	18	37	45
Sum	60–150°	13.2	32.3	54.5

* The content of cyclopentenes and cyclohexenes in fraction No. 3 was obtained by the optical method.

The individual hydrocarbon composition of the fractions was investigated by the method of combination light-scattering spectra. The procedure and apparatus used were the same as in determining the composition of the fraction up to 60° of the gasoline studied by us ([1]).

For a more complete interpretation of the fractions, both the spectra of the original olefin fractions and the spectra after their hydrogenation were investigated, and, beginning with fraction No. 7, also after dehydrogenation. In the interpretation, an atlas of combination light-scattering spectra ([4]) and other literature data ([5–11]) were used. With the aid of the above-mentioned method we succeeded in interpreting the individual hydrocarbon composition of the first five fractions (up to 110°). In the higher fractions (110–150°), only the molecular structure of the olefins was determined, without indicating the position of the double bonds in the molecule.

The final data on the interpretation of the hydrocarbon composition of the unsaturated part of the gasoline isolated from the 60–150° fraction of thermal-cracking gasoline are given in Table 3.

As can be seen from Table 3, the aliphatic olefins are represented mainly by unbranched and slightly branched olefins, while the cyclenes are mono- and disubstituted. Diolefins and olefins with quaternary carbon atoms were not found. Apparently, they are absent from the gasoline studied, or their amounts lie beyond the limits of spectral analysis. Saturated hydrocarbons were not detected in any of the olefin fractions.

Table 3

Unsaturated hydrocarbons found in thermal-cracking gasoline, and their concentration in gasoline up to 150°

Olefins	Content in gasoline up to 150° (wt. %)	Cycloolefins	Content in gasoline up to 150° (wt. %)
Hexene-1	1.71	3-Methylcyclopentene-1	0.37
2-Methylpentene-2	1.38	1-Methylcyclopentene-1	1.02
3-Methylpentene-2	0.17	Cyclohexene	0.55
Hexene-2 (cis-, trans-)	1.02		
Total C_6H_{12}	**4.28**	**Total C_6H_{10}**	**1.94**
2-Methylhexenes	0.90	Methylcyclohexenes	1.47
Heptenes-1 and -2 (predominantly heptene-1)	2.69	1,2-Dimethylcyclopentenes	2.19
Unidentified	1.14	1,3-Dimethylcyclopentenes	1.06
		Ethylcyclopentenes	0.15
Total C_7H_{14}	**4.73**	**Total C_7H_{12}**	**4.87**
2-Methylheptenes	1.65	1,1-Dimethylcyclohexenes	0.27
2,2- and 3,4-Dimethylhexenes	0.26	1,2,3-Trimethylcyclopentenes	3.58
n-Octenes	2.04	1,2,4-Trimethylcyclopentenes	3.58
		Ethylcyclohexenes	0.59
		1,2-Dimethylcyclohexenes	0.42
		1,3-Dimethylcyclohexenes	0.54
		1,4-Dimethylcyclohexenes	0.22
Total C_8H_{16}	**3.95**	**Total C_8H_{14}**	**5.62**
C_9-olefins (C_9H_{18})	3.75	1,2,4-Trimethylcyclohexenes	0.23
		1-Methyl-2-ethylcyclohexenes	0.46

Olefins	Content in gasoline up to 150° (wt. %)	Cycloolefins	Content in gasoline up to 150° (wt. %)
		1,1,3-Trimethylcyclohexenes	2.40
Total C_6–C_9 alkenes	**16.71**	**Total C_9H_{16}**	**1.14**
Of these:		**Total C_6–C_9 cyclenes**	**13.57**
normal olefins	7.46	Of these:	
with one substituent	4.10	without substituents	0.55
with two substituents	0.26	with one substituent	3.77
C_9-olefins	3.75	with two substituents	5.30
		with three substituents	2.70
		unidentified	2.40

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Note: Figure translations are in progress. See original paper for figures.