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Academician A. V. Topchiev, I. A. Musaev, E. Kh. Isakova,

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Abstract

Full Text

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Academician A. V. Topchiev, I. A. Musaev, E. Kh. Isakova,
N. M. Sardanashvili, A. N. Kislinskii, and G. D. Gal' pern

STUDY OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF CRACKING GASOLINES FROM SURAKHANY SELECTED CRUDE OIL

In our previous communication (^1) a combined method was described for studying the detailed group chemical composition of three samples of gasoline fractions 60–175°, obtained by thermal and catalytic cracking of distillates from Surakhany selected crude oil: catalytic-cracking gasoline of the kerosene–gas-oil fraction (B-12); thermal-cracking gasoline of fuel oil (B-2) and thermal-cracking gasoline of the kerosene–gas-oil fraction (B-11).

In the present work we report the results of studying the individual hydrocarbon composition of the fractions of these gasolines, taken up to 60°, and of the aromatic hydrocarbons present in the 60–175° fractions of the same gasolines.

S t u d y o f t h e c o m p o s i t i o n o f f r a c t i o n s u p t o 60°. The fractions taken up to 60° on a 45 t. t. column were separated into narrow fractions. The characteristics of the fractions are given in Table 2. Fractions boiling up to 26.5° were studied on a gas-liquid chromatography apparatus (^2), and the composition of the 26.5–60.0° fraction was determined from combination-scattering spectra (^3).

Table 1

Content of aromatic hydrocarbons in the 60–175° fractions of cracking gasolines (in weight percent)

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Fraction temperature (°C)	Hydrocarbons	Gasoline-12: in aromatic fraction	Gasoline-12: in gasoline up to 150°	Gasoline-12: in gasoline up to 175°	Gasoline-2: in aromatic fraction	Gasoline-2: in gasoline up to 150°	Gasoline-2: in gasoline up to 175°	Gasoline-11: in aromatic fraction	Gasoline-11: in gasoline up to 150°	Gasoline-11: in gasoline up to 175°
60–95	Benzene	100	1.44	1.14	100	0.27	0.21	95	3.45	2.76
95–122	Toluene	100	6.86	5.42	85	1.21	0.94	97	5.77	4.57
122–150	Ethylbenzene	25	3.75	2.98	25	0.94	0.73	30	1.76	1.39
122–150	*p*-Xylene	20	3.02	2.38	15	0.56	0.43	15	0.88	0.70
122–150	*m*-Xylene	35	5.29	4.17	35	1.32	1.02	30	1.76	1.39
122–150	*o*-Xylene	20	3.02	2.38	20	0.75	0.58	20	1.18	0.93
150–175*	1-Methyl-2-ethylbenzene	10	—	1.26	5	—	0.15	20	—	0.82
150–175*	1-Methyl-3-ethylbenzene	tr.	—	tr.	15	—	0.44	10	—	0.41
150–175*	1-Methyl-4-ethylbenzene	tr.	—	tr.	5	—	0.15	5	—	0.20
150–175*	Mesitylene	15	—	1.89	10	—	0.29	5	—	0.20
150–175*	*n*-Propylbenzene	tr.	—	tr.	10	—	0.29	10	—	0.41
150–175*	Pseudocumene	65	—	8.19	30	—	0.87	30	—	1.22
150–175*	Hemimellitene	5	—	0.63	15	—	0.44	10	—	0.41
150–175*	sec-Butylbenzene	tr.	—	tr.	tr.	—	tr.	—	—	—
150–175*	tert-Butylbenzene	—	—	—	tr.	—	tr.	—	—	—

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* The aromatic hydrocarbons from the 150–175° fractions of B-2 and B-11 contain about 10% of unsaturated hydrocarbons that could not be identified. The concentrations of aromatics given in the table represent only a first approximation for these fractions.

Table 2

Yield and characteristics of narrow gasoline fractions selected up to 60°

Fraction No.	Boiling temperature of fraction (°C)	Benzine-12: yield on gasoline up to 60°	Benzine-12: yield on gasoline up to 150°	Benzine-12: n_D^{20}	Benzine-12: d_4^{20}	Benzine-12: iodine number	Benzine-2: yield on gasoline up to 60°	Benzine-2: yield on gasoline up to 150°	Benzine-2: n_D^{20}	Benzine-2: d_4^{20}	Benzine-2: iodine number	Benzine-11: yield on gasoline up to 60°	Benzine-11: yield on gasoline up to 150°	Benzine-11: n_D^{20}	Benzine-11: d_4^{20}	Benzine-11: iodine number
1	Up to 26.5	39.7	10.7	—	—	—	24.7	2.7	1.3581	—	176	20.2	1.9	1.3625	—	221.6
2	26.5–32	20.3	5.4	1.3855	0.6258	40	13.5	1.5	1.3660	0.6352	42	10.5	1.0	1.3670	0.6432	84
3	32–39	19.9	5.4	1.3828	0.6255	24.2	34.9	3.8	1.3698	0.6441	69.7	33.8	3.1	1.3727	0.6471	92.4
4	39–46	1.8	0.5	1.4111	0.7398	25	2.7	0.3	1.4026	0.7152	42.4	6.5	0.6	1.4150	0.7512	98
5	46–56	2.7	0.7	1.3903	0.6722	2.5	12.7	1.4	1.3870	0.6812	21.4	21.1	1.9	1.3891	0.6842	24.5
6	56–60	15.6	4.3	1.3753	0.6594	6.2	11.5	1.2	1.3770	0.6619	7.0	7.9	0.7	1.3780	0.6627	5.0
1–6	B.p. up to 60°	100	27.0				100	10.9				100.0	9.2			

Data on the hydrocarbon composition of the front fractions of gasolines are compared in Table 3. The investigation established that in each of the three gasolines (fractions up to 60°) there are up to thirty individual hydrocarbons. Quantitative analysis revealed large differences in the concentrations of individual components. In the fraction up to 60° of catalytic-cracking gasoline (B-12), four hydrocarbons are present in concentrations exceeding 5%: 2-methylbutane (36.4%), 2-methylbutene-2 (15.1%), 2-methylpentane (8.6%), and *n*-butene (sum of 1- and 2-, 6.5%).

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In the fractions of thermal-cracking gasolines (B-2 and B-11), up to eight hydrocarbons occur in concentrations >5%, and six hydrocarbons in concentrations >7%. In B-2 these are: *n*-pentane (25.0%), 2-methylbutane (11.1%), 2-methylbutene-2 (7.9%), 2-methylpentane and 4-methylpentene-1 (7.5% each), and pentene-1 (7.2%). In B-11: *n*-pentane (19.9%), 4-methylpentene-1 (12.0%), 2-methylbutene-2 (10.0%), pentene-1 (7.7%), 2-methylbutane (7.4%), and cyclopentane (7.2%). If one takes into account that B-11 and B-12 were obtained from the same feedstock and that the yield of the fraction up to 60° in B-12 is considerably higher (27% versus 9.2 in B-11), the differences in the nature of the gasolines, depending on the method by which they were processed, become especially clear.

The front fractions of catalytic-cracking gasoline apparently may be regarded as potential feedstock for petrochemical synthesis based on isopentane, 2-methylbutene-1, and 2-methylpentane.

From the front fractions of thermal-cracking gasolines it is relatively easy to obtain *n*-butane, *n*-pentane, and such α-olefins as *n*-pentene-1, 2-methylbutene-1, and 4-methylpentene-1.

Investigation of the composition of the aromatic fractions. Aromatic hydrocarbons isolated by chromatography on silica gel from the 60–175° fractions were distilled over metallic sodium and then studied fraction by fraction by the method of combination-scattering spectra. The results of the analysis are given in Table 1.

From the data obtained it is evident that the total yield of aromatic hydrocarbons in B-12 is twice as high as in B-11 and five times as high as in B-2.

The principal aromatic hydrocarbons of B-12 are: pseudocumene (27% of the sum of aromatics and 8.2% in the gasoline up to 175°), toluene (respectively 18 and 5.4%), *m*-xylene (14 and 2%), ethylbenzene (10 and 3.0%), and *p*-xylene (7.8 and 2.4%). For B-11 these are: toluene (30 and 4.6%), benzene (18 and 2.8%), *m*-xylene (9 and 1.4%), and ethylbenzene (9%). And, finally, for B-2: *m*-xy-

Table 3

Hydrocarbon composition of fractions up to 60° of cracked gasolines (in weight percent)

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Hydrocarbons	Gasoline-12: per fraction up to 60°	Gasoline-12: per fraction up to 150°	Gasoline-2: per fraction up to 60°	Gasoline-2: per fraction up to 150°	Gasoline-11: per fraction up to 60°	Gasoline-11: per fraction up to 150°
Ethane + ethylene	tr.	tr.	0.13	0.01	0.29	0.03
Propane + propylene	0.12	0.03	0.32	0.04	not found	not found
2-Methylpropane	4.59	1.23	0.48	0.05	0.16	0.01
n-Butane	1.49	0.40	5.86	0.63	2.45	0.23
2-Methylpropene	3.46	0.93	4.51	0.49	3.10	0.28
n-Butene	6.59	1.76	4.51	0.49	3.10	0.28
3-Methylbutene-1	tr.	tr.	tr.	tr.	1.62	0.15
2-Methylbutane	36.4	9.78	11.1	1.20	7.36	0.68
Pentene-1	0.54	0.14	7.15	0.77	7.69	0.71
2-Methylbutene-1	1.69	0.46	5.23	0.55	6.14	0.56
Isoprene	not found	not found	0.14	0.01	0.32	0.03
Ethylcyclopropane	not found	not found	tr.	tr.	tr.	tr.
n-Pentane	0.32	0.09	25.0	2.68	19.9	1.83
Methylcyclobutane	not found	not found	tr.	tr.	not found	not found
trans-Pentene-2	2.57	0.69	2.23	0.24	3.76	0.35
cis-Pentene-2	2.37	0.64	1.75	0.19	2.01	0.19

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Hydrocarbons	Gasoline-12: per fraction up to 60°	Gasoline-12: per fraction up to 150°	Gasoline-2: per fraction up to 60°	Gasoline-2: per fraction up to 150°	Gasoline-11: per fraction up to 60°	Gasoline-11: per fraction up to 150°
2-Methylbutene-2	15.1	4.06	7.93	0.85	10.0	0.92
1-Methylcyclobutene-1	not found	not found	tr.	tr.	not found	not found
3,3-Dimethylbutene-1	0.09	0.02	not found	not found	not found	not found
Piperilene	not found	not found	not found	not found	tr.	tr.
Cyclopentene	1.16	0.31	0.82	0.09	3.66	0.34
Cyclopentane	tr.	tr.	3.98	0.43	7.23	0.67
2,2-Dimethylbutane	not found	not found	not found	not found	tr.	tr.
4-Methylpentene-1	tr.	tr.	7.53	0.81	12.0	1.11
3-Methylpentene-1	tr.	tr.	0.58	0.06	0.40	0.03
2,3-Dimethylbutene-1	tr.	tr.	0.58	0.06	0.39	0.04
cis-4-Methylpentene-2	not found	not found	0.57	0.06	not found	not found
1,3-Dimethylcyclobutane	not found	not found	not found	not found	tr.	tr.
2,3-Dimethylbutane	4.7	1.86	3.05	0.32	3.55	0.33
trans-4-Methylpentene-2	tr.	tr.	1.78	0.19	0.79	0.07
2-Methylpentane	8.6	2.32	7.48	0.81	5.53	0.51
Total C_2–C_6	**100.0**	**26.88**	**100.0**	**10.77**	**100.0**	**9.24**

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Hydrocarbons	Gasoline-12: per fraction up to 60°	Gasoline-12: per fraction up to 150°	Gasoline-2: per fraction up to 60°	Gasoline-2: per fraction up to 150°	Gasoline-11: per fraction up to 60°	Gasoline-11: per fraction up to 150°
Paraffins C_2–C_6	56.20	15.11	53.39	5.74	39.24	3.62
Of these: normal structure	1.93	0.52	31.29	3.36	22.64	2.06
Of these: branched	54.27	14.59	22.10	2.38	16.60	1.53
Of these: cycloparaffins C_5	+	+	3.98	0.43	7.23	0.67
Olefins C_3–C_6	32.35	8.70	39.98	4.28	51.84	4.44
Of these: normal structure	13.71	3.23	11.66	1.26	16.56	1.53
Of these: branched	18.64	5.47	28.32	3.02	31.62	2.91
Of these: cycloolefins	1.16	0.31	0.82	0.09	3.66	0.34

lene (17 and 1.0%), toluene (14 and 0.94%), pseudocumene (13 and 0.87%), and ethylbenzene (11 and 0.23%).

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