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Abstract

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On the Chemical Composition of Gasolines from Thermal and Catalytic Cracking*

Knowledge of the nature of unsaturated and other groups of hydrocarbons entering into the composition of cracking products is of great interest. At present, the question of the influence of the chemical composition of the initial feedstock, used in various methods of thermal processing, on the composition and structure of the unsaturated and other groups of hydrocarbons formed in these processes is insufficiently clear. Clarification of this question will bring us closer to the rational selection of feedstock for obtaining light petroleum products of specified quality and will open up a number of possibilities for petrochemical synthesis. The investigation of the composition of cracking products encounters specific difficulties.

For the first time, to study the detailed group chemical composition of cracked gasolines, N. D. Zelinskii and R. Ya. Levina proposed a combined method combining sulfuric-acid treatment with hydro- and dehydrogenation catalysis ([1,3]).

For selective hydrogenation of unsaturated hydrocarbons under hydrogen pressure in the presence of aromatic hydrocarbons (not containing sulfur compounds), we proposed a copper catalyst ([4–6]). Subsequently, this method was applied by Glusheva and Nepryakhina to investigate the chemical composition of gasolines from oxidative cracking ([7,8]).

G. M. Mamedaliev ([9]), for the above-mentioned purpose, proposed nickel on kieselguhr as a catalyst. Hydrogenation of unsaturated compounds was carried out at atmospheric pressure and at various temperatures, depending on the boiling point of the fraction.

In the present investigation a combined method was used, including: 1) the sulfuric-acid method for determining the total content of unsaturated and aromatic compounds (sulfonation was carried out with Katwinkel reagent**, cooled with ice water); 2) determination of the percentage content of unsaturated hydrocarbons in the fractions from the iodine number and molecular weight; 3) selective hydrogenation of unsaturated hydrocarbons at a hydrogen pressure of 80 atm and at 280–300° in a laboratory installation in test-tube autoclaves ([10]); 4) dehydrogenation catalysis, to establish the nature of cyclanes (both unsaturated and saturated); 5) the aniline-point method, to determine the group composition of fractions not containing unsaturated hydrocarbons. The objects

of the present investigation were predistillates of thermal and catalytic cracking, obtained from the same Grozny paraffinic crude oil at the Grozny petroleum refinery.

For determining iodine numbers, the Kauffmann-Galpern method ([11]) was used in all cases.

* The experimental part of the work was carried out with the participation of E. G. Iskhakova, T. V. Fedorova, T. N. Buturlova, and N. N. Chekalova.
** 30 g P_2O_5 + 100 ml H_2SO_4, $d = 1.84$.

Study of thermal-cracking gasoline. After drying, the plant gasoline was distilled into standard fractions on a column with an efficiency of 30 theoretical plates, in a weak stream of nitrogen.

Table 1 gives the yields and characteristics of the fractions. A charge of 605,0 g was taken for distillation.

The fractions obtained for investigation were divided into two parts; one part was investigated by the sulfuric-acid method, while the second part was first subjected

Table 1

Fraction No.	Temperature, °C	Yield, g	Yield, %	n_D^{20}	d_4^{20}	A. p. max.	Iodine number	$MW_{\text{avg.}}$
0	23–60	31,7	5,3	1,3740	0,6512	51,5	163,2	–
1	60–95	66,3	10,9	1,4038	0,7089	41,5	134,5	91,0
2	95–122	74,3	12,3	1,4200	0,7475	40,9	120,1	105,0
3	122–150	85,5	14,1	1,4330	0,7706	42,5	97,9	116,0
4	150–200	144,5	23,6	1,4505	0,8044	46,5	70,9	144,0
5	above 200	181,0	29,9	–	–	–	–	–
6	losses	21,9	3,9	–	–	–	–	–
Total		**605,0**	**100,0**					
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to selective hydrogenation of unsaturated compounds over a copper catalyst. After sulfonation and distillation from the polymers, the naphthenoparaffinic residue was subjected to exhaustive dehydrogenation over a platinum-iron catalyst ([12]), prepared by the method described earlier ([13]).

The content of aromatic (primary), hexamethylene (after dehydrogenation), and

pentamethylene hydrocarbons was determined by the aniline method; the paraffin content was determined by difference.

Table 2

Fraction No.	Temperature, °C	Yield, %	Unsaturated: hexamethyl	Unsaturated: pentamethyl	Unsaturated: aromatic	Unsaturated: acyclic	Saturated: naphthenic	Saturated: hexamethyl	Saturated: pentamethyl	Saturated: paraffinic
1	60–95	18	$\frac{4,6}{0,8}$	$\frac{11,8}{2,1}$	–	$\frac{34,1}{6,1}$	$\frac{4,7}{0,8}$	$\frac{5,1}{0,9}$	$\frac{5,9}{1,1}$	$\frac{33,8}{6,1}$
2	95–122	20	$\frac{7,2}{1,4}$	$\frac{16,7}{3,3}$	$\frac{1,2}{0,2}$	$\frac{24,5}{4,9}$	$\frac{9,3}{1,9}$	$\frac{10,4}{2,1}$	$\frac{6,4}{1,3}$	$\frac{24,3}{4,9}$
3	122–150	23	$\frac{8,3}{1,9}$	$\frac{13,0}{3,0}$	$\frac{2,3}{0,5}$	$\frac{21,3}{4,9}$	$\frac{13,3}{3,0}$	$\frac{8,7}{2,0}$	$\frac{7,4}{1,7}$	$\frac{25,7}{5,9}$
4	150–200	39	$\frac{8,1}{3,1}$	$\frac{9,0}{3,5}$	$\frac{1,8}{0,7}$	$\frac{21,4}{8,3}$	$\frac{13,9}{5,4}$	$\frac{8,8}{3,4}$	$\frac{6,4}{2,5}$	$\frac{30,6}{11,9}$

Note. Above the line—the content of hydrocarbons in wt.%; below the line—in wt.% relative to the whole 60—200° gasoline.

Table 2 contains the final data on the content of hydrocarbons of different groups in thermal-cracking gasoline in standard fractions, recalculated to the whole 60 –200° gasoline.

Study of catalytic-cracking gasoline. Fractions of catalytic-cracking gasoline were investigated by an analogous method. Table 3 gives the characteristics of the initial fractions. A charge of 1262 g was taken for distillation.

On the basis of the sulfuric acid-aniline method of selective hydrogenation of unsaturated hydrocarbons and dehydrogenation of six-membered naphthenes, the detailed group chemical composition of catalytic cracking gasoline (60-200°) and its fractions was established. The final results are given in Table 4.

Table 3

Fraction No.	Temperature, °C	Yield, g	Yield, %	n_D^{20}	d_4^{20}	A.p. max.	Iodine number	$MB_{\text{avg.}}$
0	up to 60	249.3	19.6	1.3649	0.6383	46.0	30.2	–
1	60-95	222.5	17.7	1.3990	0.7094	51.0	33.9	98.3

Fraction No.	Temperature, °C	Yield, g	Yield, %	n_D^{20}	d_4^{20}	A.p. max.	Iodine number	$MB_{\text{avg.}}$
2	95–122	125.8	9.9	1.4249	0.7592	41.8	28.7	99.6
3	122–150	130.0	10.5	1.4499	0.7978	26.5	17.0	103.2
4	150–200	258.0	20.4	1.4709	0.8324	24.5	13.0	140.7
5	above 200	254.0	20.1	–	–	–	–	–
6	losses	22.4	1.8	–	–	–	–	–
Total ...		1262.0	100.0					

By the combined method, a refined group composition was investigated for thermal and catalytic cracking gasolines obtained from the same paraffinic Grozny crude oil. It was shown that the 60-200° fractions of thermal cracking gasoline are characterized by a high content of unsaturated hydrocarbons (44.7%), with a predominance of acyclic–

Table 4

Fraction No.	Temperature, °C	Yield, %	Unsaturated: hexamethyl	Unsaturated: pentamethyl	Unsaturated: aromatic	Unsaturated: acyclic	Unsaturated: cyclic	Saturated: hexamethyl	Saturated: pentamethyl	Saturated: paraffins
1	60–95	30	0.4 0.1	6.5 1.9	–	9.1 2.7	5.1 1.5	4.7 1.4	18.3 5.5	55.9 16.8
2	95–122	17	–	7.0 1.2	2.5 0.4	3.3 0.5	16.5 2.8	16.8 2.9	15.0 2.6	38.9 6.6
3	122–150	18	–	5.3 1.0	–	6.3 1.1	42.6 7.7	12.7 2.3	7.7 1.4	25.4 4.5
4	150–200	35	2.0 0.7	1.2 0.4	0.7 0.2	3.1 1.1	60.3 21.1	6.8 2.4	4.4 1.5	21.5 7.5

Note. Above the line–the hydrocarbon content in wt. %; below the line–in wt. %, relative to the whole 60-200° gasoline.

cyclics (24.2%). Unsaturated hydrocarbons of the cyclohexene series (7.2%) and cyclopentenes (11.9%) were found in appreciable concentration.

The comparatively high content of paraffins (28.8%) in all fractions is close to the content of acyclic unsaturated hydrocarbons. The catalytic cracking gasoline investigated in the same way showed that the 60–200° fractions are characterized by a low content of unsaturated hydrocarbons, represented almost equally by acyclic (5.4%) compounds and compounds with a five-membered ring (4.5%), with an almost complete absence of unsaturated compounds with six-membered rings (0.8%). The content of paraffinic hydrocarbons considerably exceeds the olefin content; the content of aromatic hydrocarbons increases sharply with increasing distillation temperature and reaches 60% for the 150–200° fraction.

In both gasolines studied, diene hydrocarbons with conjugated bonds are absent. Research on the development of a combined method for studying the structural-group and individual hydrocarbon composition of cracking products is continuing.

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REFERENCES

1. N. D. Zelinskii, R. Ya. Levina, ZhPKh, **6**, 20 (1933).
2. N. D. Zelinskii, R. Ya. Levina, *Neft. khoz.*, No. 9, 47 (1934).
3. R. Ya. Levina, *Uch. zap. MGU*, vol. 3, chemistry, 241 (1934).
4. I. A. Musaev, G. D. Gal' pern, ZhPKh, **7**, No. 4, 572 (1939).
5. I. A. Musaev, DAN, **96**, No. 6, 1097 (1949).
6. I. A. Musaev, DAN, **80**, No. 5, 759 (1951).
7. V. E. Glushnev, A. V. Nepryakhina, *Tr. Inst. nefti AN SSSR*, **4**, 31 (1954).
8. V. E. Glushnev, A. V. Nepryakhina, ibid., **4**, 38 (1954).
9. G. M. Mamedaliev, Kh. D. Rzaeva, *Izv. AN AzerbSSR*, No. 7, 3 (1952).
10. I. A. Musaev, G. D. Gal' pern, *Tr. Inst. nefti AN SSSR*, **1**, 244 (1950).
11. G. D. Gal' pern, *Tr. Inst. nefti AN SSSR*, **4**, 116 (1954).
12. B. A. Kazanskii, G. S. Landsberg, *Determination of the Individual*

Composition of Straight-Run Gasolines (Instruction). Institute of Organic Chemistry, Academy of Sciences of the USSR, 1951 (collections).

13. I. A. Musaev, G. D. Gal' pern, DAN, **88**, No. 1, 71 (1953).

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

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