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Abstract

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Production of Aromatic Hydrocarbons by Catalytic Processing of Thermal-Cracking Kerosene in the Presence of Light Oil from the Pyrolysis of Petroleum Feedstock

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In our studies ([1–5]) it was shown that, in the process of catalytic processing of various petroleum distillates in the presence of benzene and toluene over aluminosilicates, deep aromatization of the hydrocarbons of the initial distillate takes place, and that the medium of the aforementioned aromatic compounds favors the course of this reaction.

As a development of the above-mentioned works, the study of the process of catalytic aromatization of petroleum distillates in the presence of light oil from the pyrolysis of petroleum feedstock is of considerable practical interest. Such a process, along with deep stabilization of the light oil, provides for the production of an additional amount of low-molecular-weight aromatic hydrocarbons, which acquire exceptionally great importance for the development of modern processes of petrochemical synthesis.

In the present work the principal results are given of investigations of the process of catalytic aromatization of thermal-cracking kerosene in the presence of light pyrolysis oils over synthetic aluminosilicates.

Thermal-cracking kerosene and light oil from various pyrolysis operations were used as the starting products. The characteristics of these products are given in Table 1.

Cracking kerosene boils within the range 125–310°; its iodine number is 50.5. The yield of the fraction up to 205° is 32.2%. The weight content of unsaturated, paraffinic, naphthenic, and aromatic hydrocarbons in it was, respectively, 31.1, 45.6, 16.9, and 6.4%. In studies ([6,7]) it was shown that the unsaturated hydrocarbons of thermal-cracking kerosene are chiefly compounds of cyclic structure.

Light oil from the pyrolysis tar of the ethane–propane fraction contains practically no paraffinic or naphthenic hydrocarbons. The amounts of aromatic and unsaturated compounds in it were, respectively, 73.8 and 26.2%. It was established that the unsaturated hydrocarbons of this light oil consist mainly of

styrene, indene, and their homologs. Spectral investigation of the 140–145° fraction isolated from the light oil showed the presence in it of about 90% styrene. The 175–185° fraction is distinguished by a high content of indene (181).

Light pyrolysis oil from mixed heavy distillate feedstock, obtained from the Baku Neftgaz plant, boiled within the range 42.5–232°. The amount of unsaturated compounds in it is usually 31–33%, aromatics 60–65%, and the sum of paraffinic and naphthenic hydrocarbons 5–9%. The experiments were carried out in a laboratory flow-reactor unit, the scheme of which was given in works ([1,4]). The characteristics of the initial ···

mixtures, the obtained catalyzates and their principal aromatic fractions is given in Tables 2 and 3.

Table 1

Characteristics of thermal-cracking kerosene and light oils from pyrolysis of petroleum feedstock

Characteristic	Thermal-cracking kerosene: fraction yield, wt.%	Thermal-cracking kerosene: n_D^{20}	Light oil from ethane-propane fraction pyrolysis: fraction yield, wt.%	Light oil from ethane-propane fraction pyrolysis: n_D^{20}	Light oil from heavy distillate feedstock pyrolysis: fraction yield, wt.%	Light oil from heavy distillate feedstock pyrolysis: n_D^{20}
Fractional composition, initial boiling point, °C	125,0	–	40,0	–	42,5	–
up to 50°	–	–	0,58	1,4675	0,65	1,4355
50–76	–	–	1,57	1,4845	2,58	1,4372
76–78	–	–	0,80	1,4942	0,90	1,4762
78–83	–	–	**53,82**	1,4999	**17,80**	1,4870
83–88	–	–	0,50	1,4959	0,90	1,4800
88–95	–	–	0,30	1,4951	0,95	1,4770
95–103	–	–	0,45	1,4930	1,00	1,4750
103–108	–	–	0,40	1,4930	0,93	1,4762

Characteristic	Thermal-cracking kerosene: fraction yield, wt.%	Thermal-cracking kerosene: n_D^{20}	Light oil from ethane-propane fraction pyrolysis: fraction yield, wt.%	Light oil from ethane-propane fraction pyrolysis: n_D^{20}	Light oil from heavy distillate feedstock pyrolysis: fraction yield, wt.%	Light oil from heavy distillate feedstock pyrolysis: n_D^{20}
108–113	–	–	**15,88**	1,4962	**30,20**	1,4890
113–118	–	–	0,50	1,4941	1,05	1,4760
118–125	–	–	[[unclear: 0,4?]]	1,4945	1,15	1,4740
125–132	4,07	1,4175	0,90	1,4992	2,00	1,4732
132–136	0,52	1,4232	0,52	1,5030	1,48	1,4740
136–144	**1,60**	1,4283	**6,38**	1,5260	**17,48**	1,4890
144–149	0,95	1,4316	0,70	1,5240	0,62	1,4925
149–160	3,18	1,4345	1,00	1,5290	2,30	1,4929
160–165	1,00	1,4382	1,81	1,5310	2,95	1,4952
165–175	3,67	1,4400	1,30	1,5420	1,45	1,5030
175–180	2,70	1,4435	1,05	1,5540	3,01	1,5100
180–185	2,85	1,4453	1,50	1,5541	0,85	1,5170
185–final boiling point	11,70	1,4493	5,01	1,5546	5,05	1,5472
Final boiling point, °C	205,0		200,0		232,3	
Total yield, %	32,24		95,4		95,3	

Characteristic	Thermal-cracking kerosene: fraction yield, wt.%	Thermal-cracking kerosene: n_D^{20}	Light oil from ethane-propane fraction pyrolysis: fraction yield, wt.%	Light oil from ethane-propane fraction pyrolysis: n_D^{20}	Light oil from heavy distillate feedstock pyrolysis: fraction yield, wt.%	Light oil from heavy distillate feedstock pyrolysis: n_D^{20}
Residue, %	66,93		4,1		4,1	
Losses, %	0,83		0,5		0,6	
n_D^{20}	1,4560		1,5102		1,4915	
d_4^{20}	0,8120		0,8888		0,8592	
Sulfurizability, %	35,6		100,0		95,4	
Molecular weight	157		94,0		118,2	
Iodine number						
Group chemical composition, wt.%	50,5		**70,5**		66,9	
paraffins	45,6		–		4,0	
naphthenes	16,9		–		4,0	
unsaturated	31,1		26,2		31,2	
aromatic: benzene	–		51,5		17,4	
aromatic: toluene	–		15,0		29,0	
aromatic: C_8	–		2,5		13,0	
aromatic: C_9 and higher	6,4		4,8		4,4	

The weight ratio of cracking kerosene to the light oil of pyrolysis of the ethane-

propane fraction in the mixture was 1 : 2. The content of benzene, toluene, and xylene fractions in it was 34,9; 8,5 and 4,1%. The iodine number of the mixture was 65,2; that of the fractions: benzene 14,7, toluene 17, xylene 145.

At a temperature of 525°, a pressure of 15 atm, and a space velocity of 0,5 l/l · h, as a result of single-pass processing of the mixture, complete chemical stabilization of the unsaturated hydrocarbons is achieved. Deep aromatization of the thermal-cracking kerosene takes place. The iodine number of the product decreases to 0,2. The sulfurizability of the catalyzate is 92,3%. The content of benzene, toluene, and xylenes, respectively, is 41,5; 15,1 and 9,2% based on the catalyzate. The bromine numbers of the target aromatic hydrocarbons vary within the range 0,08–0,2; sulfurizability is 94–97%. The yield of catalyzate is 91%, gas 3,8%, and coke 4,6%.

Table 2

Characteristics of the products of catalytic processing of a mixture of thermal-cracking kerosene and light oils from petroleum pyrolysis. Temperature 525°C; pressure 15 atm; space velocity 0.5 l/l · h; cycle duration 30 min.

Fractional composition, b.p., °C	Feedstock: cracking kerosene and light oil of gas pyrolysis (wt. ratio 1:2), fraction yield, wt.%	Feedstock: cracking kerosene and light oil of gas pyrolysis (wt. ratio 1:2), n_D^{20}	Catalyst, experiment No. 75, fraction yield, wt.%	Catalyst, experiment No. 75, n_D^{20}	Feedstock: cracking kerosene and light oil of pyrolysis of gas-oil fraction (wt. ratio 1:2), fraction yield, wt.%	Feedstock: cracking kerosene and light oil of pyrolysis of gas-oil fraction (wt. ratio 1:2), n_D^{20}	Catalyst, experiment No. 81, fraction yield, wt.%	Catalyst, experiment No. 81, n_D^{20}
Initial b.p.	40.0	–	36.0	–	42.0	–	36.1	–
to 50°C	0.13	–	3.26	1.3761	0.30	1.3711	0.63	1.3920
50–76	0.53	1.4520	1.00	1.4416	1.96	1.4733	1.93	1.4185
76–78	0.50	1.4860	0.60	1.4800	1.20	1.4825	0.50	1.4675

Fractional composition, b.p., °C	Feedstock: cracking kerosene and light oil of gas pyrolysis (wt. ratio 1:2), fraction yield, wt.%	Feedstock: cracking kerosene and light oil of gas pyrolysis (wt. ratio 1:2), n_D^{20}	Catalyst, experiment No. 75, fraction yield, wt.%	Catalyst, experiment No. 75, n_D^{20}	Feedstock: cracking kerosene and light oil of pyrolysis of gas-oil fraction (wt. ratio 1:2), fraction yield, wt.%	Feedstock: cracking kerosene and light oil of pyrolysis of gas-oil fraction (wt. ratio 1:2), n_D^{20}	Catalyst, experiment No. 81, fraction yield, wt.%	Catalyst, experiment No. 81, n_D^{20}
78–83	34.90	1.4940	41.50	1.4965	10.80	1.4894	17.30	1.4840
83–88	0.48	1.4960	0.20	1.4913	0.98	1.4760	0.28	1.4710
88–95	0.78	1.4942	0.35	1.4880	0.78	1.4835	0.30	1.4725
88–95	0.48	1.4930	0.28	1.4862	1.18	1.4833	0.48	1.4720
95–103	0.62	1.4938	0.45	1.4863	1.30	1.4832	0.45	1.4780
103–108	8.48	1.4956	15.10	1.4913	19.11	1.4852	24.43	1.4915
108–113	1.00	1.4941	0.48	1.4870	1.58	1.4778	0.60	1.4840
113–118	1.33	1.4942	0.50	1.4870	1.13	1.4768	0.33	1.4780
118–125	0.90	1.4980	0.53	1.4871	1.19	1.4770	0.40	1.4810
125–132	1.03	1.4990	0.38	1.4872	0.65	1.4780	0.40	1.4875
132–136	4.13	1.5110	9.20	1.4900	10.23	1.4866	17.83	1.4903
136–144	0.53	1.4995	0.43	1.4858	1.53	1.4812	0.33	1.4881
144–149	3.10	1.4973	3.25	1.4833	3.57	1.4770	5.00	1.4860

Fractional composition, b.p., °C	Feedstock: cracking kerosene and light oil of gas pyrolysis (wt. ratio 1:2), fraction yield, wt.%	Feedstock: cracking kerosene and light oil of gas pyrolysis (wt. ratio 1:2), n_D^{20}	Catalyst, experiment No. 75, fraction yield, wt.%	Catalyst, experiment No. 75, n_D^{20}	Feedstock: cracking kerosene and light oil of pyrolysis of gas-oil fraction (wt. ratio 1:2), fraction yield, wt.%	Feedstock: cracking kerosene and light oil of pyrolysis of gas-oil fraction (wt. ratio 1:2), n_D^{20}	Catalyst, experiment No. 81, fraction yield, wt.%	Catalyst, experiment No. 81, n_D^{20}
149–160	1.10	1.4830	2.60	1.4800	4.47	1.4760	2.30	1.4855
160–165	2.00	1.4815	1.21	1.4795	2.23	1.4766	3.73	1.4835
165–175	1.33	1.4800	0.85	1.4790	1.67	1.4741	1.83	1.4810
175–180	1.65	1.4810	1.15	1.4800	1.20	1.4718	0.75	1.4800
180–185	10.60	1.4880	4.53	1.4900	2.45	1.4722	6.70	1.4800
185–b.r.	–	–	–	–	–	–	–	–
End of distillation, °C	205.0	–	204.5	–	195.0	–	205.0	–
Total yield, wt.%	75.6	–	87.87	–	69.51	–	87.5	–
Residue, %	22.4	–	11.70	–	29.70	–	10.6	–
Losses, %	2.0	–	0.43	–	0.79	–	1.9	–
n_D^{20}	1.4919	–	1.4852	–	1.4802	–	1.4890	–

Fractional composition, b.p., °C	Feedstock: cracking kerosene and light oil of gas pyrolysis (wt. ratio 1:2), fraction yield, wt.%	Feedstock: cracking kerosene and light oil of gas pyrolysis (wt. ratio 1:2), n_D^{20}	Catalyst, experiment No. 75, fraction yield, wt.%	Catalyst, experiment No. 75, n_D^{20}	Feedstock: cracking kerosene and light oil of pyrolysis of gas-oil fraction (wt. ratio 1:2), fraction yield, wt.%	Feedstock: cracking kerosene and light oil of pyrolysis of gas-oil fraction (wt. ratio 1:2), n_D^{20}	Catalyst, experiment No. 81, fraction yield, wt.%	Catalyst, experiment No. 81, n_D^{20}
d_4^{20}	0.8603	–	0.8514	–	0.8447	–	0.8398	–
Sulfonatability, %	78.0	–	92.3	–	76.4	–	92.0	–
Iodine number	65.2	–	0.22	–	61.4	–	0.22	–
Material balance, wt.%: catalyst	–	–	91.0	–	–	–	91.4	–
Material balance, wt.%: gas	–	–	3.8	–	–	–	3.8	–
Material balance, wt.%: coke	–	–	–	–	–	–	–	–

Fractional composition, b.p., °C	Feedstock: cracking kerosene and light oil of gas pyrolysis (wt. ratio 1:2), fraction yield, wt.%	Feedstock: cracking kerosene and light oil of gas pyrolysis (wt. ratio 1:2), n_D^{20}	Catalyst, experiment No. 75, fraction yield, wt.%	Catalyst, experiment No. 75, n_D^{20}	Feedstock: cracking kerosene and light oil of pyrolysis of gas-oil fraction (wt. ratio 1:2), fraction yield, wt.%	Feedstock: cracking kerosene and light oil of pyrolysis of gas-oil fraction (wt. ratio 1:2), n_D^{20}	Catalyst, experiment No. 81, fraction yield, wt.%	Catalyst, experiment No. 81, n_D^{20}
Material balance, wt.%: losses	–	–	} 5.2	–	–	–	} 4.8	–

Table 4

Material balance of the process

Product	Experiment No. 75, charged	Experiment No. 75, obtained	Experiment No. 81, charged	Experiment No. 81, obtained
Thermal-cracking kerosene	33.3	–	33.3	–
Light oil of gas pyrolysis	66.7	–	–	–
Light oil from pyrolysis of heavy distillate feedstock	–	–	66.7	–

Product	Experiment No. 75, charged	Experiment No. 75, obtained	Experiment No. 81, charged	Experiment No. 81, obtained
Stable fraction (initial b.p. 205°)	–	80.0	–	80.2
Including: benzene (78-83°)	34.9*	37.8	10.8*	15.0
Including: toluene (108-113°)	8.5*	14.7	19.1*	23.4
Including: xylenes and ethyl-benzene (136-144°)	4.1*	9.0	10.2*	16.3
Residue above 205°	22.4	10.6	29.1	9.7
gas	–	3.8	–	3.8
coke	–	} 5.6	–	} 6.5
losses	–	} 5.6	–	} 6.5

* Crude aromatic fractions.

The characteristics of the mixture of light oil from pyrolysis of heavy distillate feedstock with thermal-cracking kerosene and of the catalyst obtained in processing this mixture are also given in Tables 2 and 3.

Under optimal conditions, deep destruction of kerosene hydrocarbons occurs. The yield of the fraction boiling above 200° decreases from 30 to 10%, and, conversely, the yield of the fraction boiling up to 200° increases. The iodine number decreases from 61 to 0.2. A marked increase is observed in the yields of the benzene, toluene, and xylene fractions.

Spectral study of the xylene fraction of the catalyzates showed,

that the amounts of para-, ortho-, and meta-isomers and ethylbenzene in their mixture are, respectively, 22-25; 29-35; 37.5-46; and 2-5.7%.

Table 4 gives the material balance for representative experiments.

Table 3

Characteristics of the main aromatic fractions

	Fractions of raw cracking kerosene and light gas-pyrolysis oil (wt. ratio 1:2)	Catalyst fractions of experiment No. 75	Fractions of raw cracking kerosene and light oil from pyrolysis of heavy distillate fraction (wt. ratio 1:2)	Catalyst fractions of experiment No. 81
Fraction 78–83°yield based on catalyzate, %	34.9	41.5	10.8	17.3
n_D^{20}	1.4990	1.4965	1.4894	1.4840
d_4^{20}	0.8668	0.8659	0.8595	0.8511
Sulfonability, %	100.0	97.0	94.5	90.1
Bromine number	14.7*	0.2	48.7*	0.1
Fraction 108–113°yield based on catalyzate, %	8.48	15.10	19.11	24.43
n_D^{20}	1.4956	1.4913	1.4852	0.4915
d_4^{20}	0.8655	0.8601	0.8532	0.8630
Sulfonability, %	100.0	96.0	92.5	96.9
Bromine number	16.9*	0.08	18.9*	0.1
Fraction 136–144°yield based on catalyzate, %	4.13	9.2	10.23	17.83
n_D^{20}	1.5110	1.4900	1.4866	1.4903
d_4^{20}	0.8794	0.8601	0.8545	0.8606
Sulfonability, %	100.0	94.6	94	94.9
Bromine number	145.0*	0.08	87.5*	0.16

* Iodine number.

The yield of the broad fraction (b.p. 205°) is about 80% based on the initial mixture. In processing a mixture of cracking kerosene with light gas-pyrolysis oil, the yield of benzene was 37.8%, toluene 14.7%, and aromatic hydrocarbons C_8 –9.0%. In processing a mixture of light oil from the pyrolysis of heavy distillate feedstock with thermal-cracking kerosene, the yield of benzene is about 15.0%, toluene 23%, and xylenes and ethylbenzene 16.3 wt.% based on the feedstock processed.

The gaseous products of the experiments consisted of 86-87% methane and its homologues, 9-10% hydrogen, and 3-3.5% unsaturated hydrocarbons.

The proposed process for aromatizing products of thermal cracking and petroleum pyrolysis represents a promising direction in the development of the production of aromatic hydrocarbons, and its broad application will make it possible to substantially increase the resources of benzene, toluene, and xylenes.

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