

Hydrogenation of the Semicoking Tar of Coal from the Shubarkol Deposit

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Abstract—The results of the hydrogenation processing of the semicoking tar (AO Sary Arka Spetskoks, Karaganda, Republic of Kazakhstan) of coal from the Shubarkol deposit in the presence of Mo- and Ni-containing pseudohomogeneous catalytic systems for the production of motor fuel components and chemical substances are reported. It was established that the yield of a gasoline fraction at a temperature of 400°C (5.0 MPa, a 0.015% S additive) was 18.7% with the use of a molybdenum catalyst or 10.6% with a nickel catalyst; therefore, the coal tar can be considered as a potential raw material for obtaining motor fuel components.

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In Kazakhstan, Russia, and abroad, chemical products from coals are mainly obtained with the use of the thermal degradation of coals—coking and semicoking processes. Coal (coke) tar, which mainly consists of condensed aromatic hydrocarbons and other high-molecular-weight compounds, is the most difficult to process raw material. In spite of the high temperature of its production (900°C or higher), the tar contains a considerable amount of reactive compounds, which undergo further condensation upon heating to 350–400°C according to a traditional primary distillation procedure. On the one hand, this decreases the yield of light distillate fractions (raw materials for obtaining valuable chemical products) and, on the other hand, prevents the production of high-quality pitch, so-called needle coke, at the stage of coking [1–3]. In order to apply the tar as a potential raw material for the production of chemicals and motor fuel components, it is important to know the chemical composition and yield of distillate fractions.

Here, we report the results of the hydrogenation processing of the semicoking tar (AO Sary Arka Spetskoks, Karaganda, Republic of Kazakhstan) of coal from the Shubarkol deposit in the presence of Mo- and Ni-containing pseudohomogeneous catalytic systems for the production of chemical substances and motor fuel components. Table 1 summarizes the characteristics of the initial tar.

A petroleum paste-forming agent (in a ratio of 1 : 1) and catalysts as the water-soluble salts of Mo (ammonium paramolybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$) and Ni (nickel nitrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$) in an amount of

Table 1. Characteristics of the coal tar

Characteristic	Value
Density at 20°C, kg/m ³	1071
Fractional composition, wt %:	
initial boiling point	130
boiled away to 180°C	2.4
180–330°C	19.0
above 330°C + losses	78.6
Elemental composition, wt %:	
C	91.11
H	5.50
S	0.35
N	1.46
O (by difference)	1.58

Table 2. Effect of the Mo- and Ni-containing catalysts on the hydrotreating of coal tar (5.0 MPa; 0.015% S; laboratory high-pressure flow system)

Catalyst	Metal concentration in the catalyst, wt %	Temperature, °C					
		350	400	450	350	400	450
		Total yield of liquid products, wt %			Yield of a fraction with a boiling point to 180°C, wt %		
With no catalyst	—	28.9	47.1	30.8	5.2	7.8	10.3
Mo	0.025	23.9	45.2	30.8	4.2	10.7	10.3
	0.05	33.9	65.2	31.6	6.4	18.7	7.6
	0.12	32.0	60.1	25.0	5.2	20.6	6.3
Ni	0.025	29.2	44.4	38.0	6.3	9.6	7.3
	0.05	32.0	60.1	22.0	5.2	10.6	6.3
	0.12	33.9	58.0	25.0	4.2	9.3	5.3

0.025–0.12% on a metal basis were added to the tar with a water content of 3%. The distillation residue (with a boiling point higher than 350°C) of petroleum from the Kumkol oil field (Republic of Kazakhstan) was used as the paste-forming agent with a density of 0.83 g/cm³ and a viscosity of 9.69 mm²/s. It had the following hydrocarbon group composition, wt %: paraffins, 14.73; asphaltenes, 1.52; and tars, 8.2. Elemental composition, wt %: C, 83.85; H, 11.27; S, 1.81; N, 0.80; and O, 2.27.

A mixture of the tar with the petroleum paste-forming agent and catalyst additives was dispersed in a homogenizer at a temperature of 130°C; the rotational velocity of plates was 1500 rpm. The resulting mixture was heated to 70–80°C and loaded into a reactor, which was blown with argon three times and filled with hydrogen at an initial pressure of 2–3 MPa. The reactor heating was turned on, and the stirrer was turned on as a temperature of 150°C was reached. The reactor was heated by a detachable electric furnace. The temperature was measured with a thermocouple and automatically maintained at a specified level to within ±2°C. The operating pressure of hydrogen was 5.0 MPa, and the temperature was 350–450°C. After an exposure under the experimental conditions, the heating was turned off and the reactor was cooled. Electrolytic hydrogen of 99.98 vol % purity (the rest being nitrogen with oxygen and argon impurities) was used in the experiments. Elemental sulfur (0.015 wt %) was added to the reaction mixture.

The chemical composition of the distillate fractions obtained was determined by gas–liquid chroma-

tography on a CHROMATEK chromatograph (Germany), and the sulfur content was determined on a POST LEKI P1437 instrument (Germany).

Tables 2 and 3 summarize the results of the studies. Table 2 indicates that the main characteristics of tar hydrogenation with the use of the above catalysts were similar. However, note that the yield of liquid products at 400°C with the use of the Mo-containing catalyst (0.05% on a metal basis) increased by 18.1%, as compared with that in the process without the catalyst, or by 12.1%, as compared with that in the process performed in the presence of the Ni-containing catalyst. The yield of a gasoline fraction at a temperature of 400°C was 17.7% with the use of the molybdenum catalyst or 10.7% with the nickel catalyst; therefore, coal tar can be considered as a potential raw material for the production of motor fuel components.

A comparative analysis of the effects of Mo- and Ni-containing catalysts on the chemistry of tar hydrotreating is of interest. Based on the data of Table 2, Fig. 2 shows the temperature dependence of the total yields of liquid products at the following three concentrations of Mo and Ni metals (Figs. 2a and 2b, respectively) in the catalysts: 0.025, 0.05, and 0.12 wt %. From Fig. 2, it follows that the yield of liquid products as a function of temperature has a maximum at *a* in the presence of either of the test catalysts. It is likely that the degradation reactions of tar macromolecules to radicals with smaller molecular weights are slowed down at low temperatures, and the reactions of radical recombination occur at higher temperatures to cause the condensation of products.

Table 3. Chemical composition (wt %) of coal distillates with a boiling point to 180°C obtained after the hydrotreating of tar (400°C; 5.0 MPa; 0.015% S; pseudohomogeneous Mo- and Ni-containing catalysts, 0.05 wt % on a metal basis; laboratory high-pressure flow system)

Compound	Catalyst		
	With no catalyst	(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	Ni(NO ₃) ₂ · 6H ₂ O
Aromatic hydrocarbons, including:	16.33	4.69	12.98
Benzene	—	2.12	5.26
Toluene	—	0.82	2.09
1,3,5-Trimethylbenzene	1.03	—	—
1,2,3,5-Tetramethylbenzene	1.61	—	—
1,2,4-Triethylbenzene	10.96	—	—
1,3-Diethylbenzene	1.20	—	—
1,4-Diethylbenzene	1.53	—	—
1,2-Naphthalene	—	1.07	1.51
2,6-Naphthalene	—	—	1.17
1,6-Naphthalene	—	0.42	2.35
1,6,7-Naphthalene	—	0.26	0.60
Paraffins, including:	56.39	10.22	12.06
Heptane	0.98	0.87	—
Nonane	10.50	4.63	3.77
Octane	8.50	2.71	2.95
Dodecane	0.57	0.92	—
Hexadecane	12.05	1.09	5.34
Octadecane	10.53	—	—
Nonadecane	13.26	—	—
Isoparaffins, including:	10.14	32.30	30.00
2,5-Dimethyloctane	—	—	2.77
3,3-Dimethyloctane	0.95	12.46	9.02
3,6-Dimethyloctane	0.23	12.07	1.09
2-Methylnonane	3.15	0.34	0.04
3-Methylnonane	0.65	1.01	1.57
2,2-Dimethylheptane	2.05	2.00	3.84
2,3-Dimethylheptane	—	1.99	6.32
2,4-Dimethylheptane	2.37	2.07	3.16
5-Methylnonane	0.74	0.36	2.19
Naphthenes, including:	1.22	0.68	1.55
Cyclohexane	0.44	0.26	0.60
Isobutylcyclohexane	—	0.42	0.48
1,1,3- <i>cis</i> -Trimethylcyclohexane	0.78	—	0.47
Olefins, including:	2.30	1.42	1.00
1-Decene	1.14	1.20	0.56
2-Methyl-2-octene	1.16	0.22	0.44
Cycloolefins, including:	0.48	—	1.24
3-Methyl-2-cyclohexene	—	—	0.62
2-Cyclooctene	0.48	—	0.62
Phenols	—	29.1	37.3

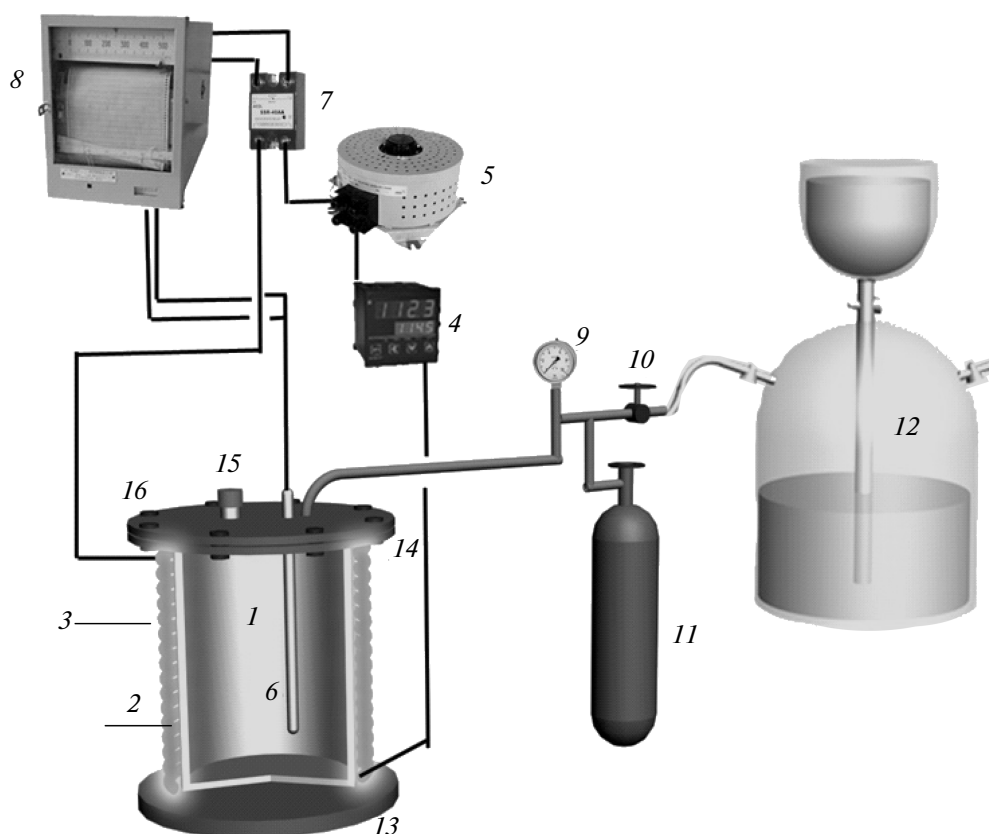


Fig. 1. Schematic diagram of the laboratory system: (1) reactor, (2) insert container, (3) electric furnace, (4) ammeter, (5) laboratory transformer, (6) thermocouple, (7) relay, (8) KSP-4 recorder, (9) manometer, (10) fine adjustment valve, (11) gas cylinder, (12) gas meter, (13) stirrer, (14, 16) sealing bolts, and (15) plug.

It is interesting to note that the yield of liquid products as a function of the concentration of Mo or Ni in the catalysts also has a maximum (in this case, at a metal concentration of 0.05 wt %). However, the explanation of this question requires additional experimental data on the particle sizes of the catalysts and the structure peculiarities of source materials. Note that, according to the above data, the molybdenum catalyst is more effective than the Ni-containing one under the conditions of a maximum yield of liquid products.

Figure 3a compares the hydrocarbon group compositions of distillate fractions with boiling points to 180°C obtained in the presence of the Mo- and Ni-containing catalysts. It can be seen that, in general, the yield of group composition components with the use of the molybdenum catalyst is higher than that with the use of the Ni-containing one.

It is well known that isoparaffins are more thermodynamically stable than corresponding paraffins [4]. On the other hand, isoparaffins are more reactive than paraffins. Therefore, the yield of isoparaffins in the

presence of the catalysts would be expected to be lower. Indeed, according to the data of Table 3, the isoalkane content of a fraction with a boiling point to 180°C with the use of both of the catalysts was greater than that in the uncatalyzed process, and the *n*-alkane content was smaller.

A comparative analysis of the yields of aromatic compounds with the use of Mo- and Ni-containing catalysts is of interest. Figure 3b compares the yields of toluene, phenol, benzene, 1,2-dimethylnaphthalene, 1,6-dimethylnaphthalene, and 1,6,7-trimethylbenzene. It is clear that, in general, the concentration of aromatic structures in the fraction with a boiling point to 180°C in the case of the Mo-containing catalyst was lower than that in an analogous fraction obtained in the presence of the Ni-containing catalyst.

The results of the experimental studies were applied to the development of a new concept of coal (coke) tar utilization, according to which it was proposed to perform processing in the following manner: undehydrated crude tar is subjected to hydrorefining under a low pressure of hydrogen (4.0–5.0 MPa) in the

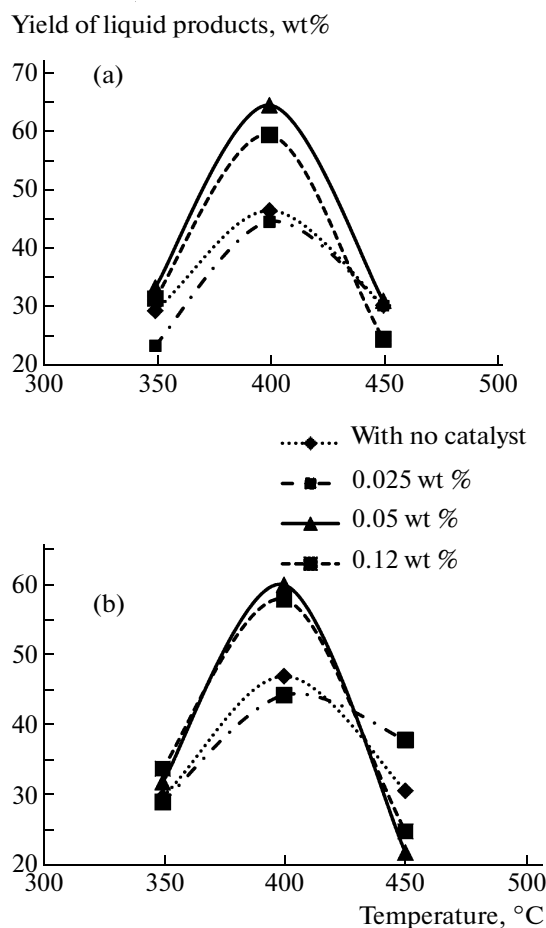


Fig. 2. The temperature dependence of the yield of liquid products in the hydrogenation of tar in the presence of (a) Mo- and (b) Ni-containing catalysts with different metal concentrations.

presence of pseudohomogeneous Mo- or Ni-containing catalysts; the resulting distillate fractions with boiling points of to 180 and 180–360°C are directed to further processing by well-known methods (hydrofining and reforming) for the production of motor fuel components; solid particles are separated from the low-viscosity tar hydrogenation products by usual separation methods with the production of low-ash (needle) coke from high-boiling fractions by coking; and chemical products (benzene, naphthalene, tetralin, 2,6-dimethylnaphthalene, etc.) and refined absorption oil for the recovery of crude benzene are obtained from the distillate fractions together with a fraction of crude benzene.

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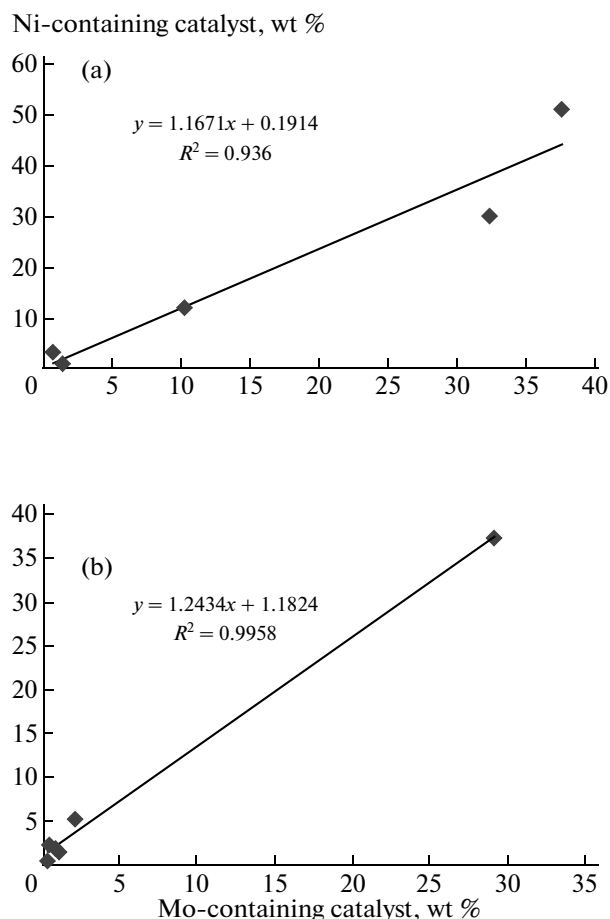


Fig. 3. Comparison of the group hydrocarbon compositions of (a) distillate fractions with a boiling point to 180°C and (b) the composition of a group of aromatic compounds (toluene, phenol, benzene, 1,2-dimethylnaphthalene, 1,6-dimethylnaphthalene, and 1,2,3-trimethylnaphthalene) obtained in the presence of the Mo- and Ni-containing catalysts.

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