

The most common are monometallic molybdenum- or tungsten-based precursors formed in the hydrocarbon medium in the presence of sulfiding agents such as MoS<sub>2</sub> or WS<sub>2</sub>. In practice, 90–95% of the catalyst is returned to the process as filtration residues. Only part of this flux is removed in the system so as to prevent the accumulation of toluene-insoluble solid products from the initial tar.

Refining of coal and heavy hydrocarbons (coal distillates, heavy petroleum components, bitumen, and petroleum residues) by hydrogenation in the presence of molybdenum disulfide synthesized in situ from aqueous solutions of the precursor has been thoroughly investigated. Considerable information has been obtained regarding the morphology and promotion of the catalyst; the composition of the emulsion has been optimized [8–10].

The activity of nickel compounds is investigated in the hydrogenation of individual organic materials. Good results are obtained when using highly dispersed nickel with a developed surface (Raney nickel). Metallic nickel is used on an industrial scale for the hydrogenation of plant-based fats to produce margarine [11]. Nickel sulfide is less often used for the hydrogenation of organic compounds. There are examples of the hydrogenation of coke-plant benzene derived from coal tar in the presence of NiS [12].

In the present work, we investigate the catalytic properties of unsaturated nickel sulfide catalysts in the hydrogenation and desulfurization of coal tar from the semicoking of Shubarkol coal (Kazakhstan). The results may be used to intensify tar processing, increase the yield of needle coke, and improve its quality.

The starting material is tar without preliminary dehydration (moisture content 3.4%). It is distilled with a 1 : 1 (by mass) mixture of specially prepared catalyst and the distillation residue (>320°C fraction) from Kumkol petroleum (Kazakhstan). The characteristics of Shubarkol semicoking tar are as follows:

Moisture content, %	3.4
Density (at 20°C), g/cm <sup>3</sup>	1.071
Ash content, wt %	0.11
Onset of boiling, °C	112–120
Fractional composition in distillation, wt %:	
<180°C	2.4
180–330°C	19.0
>330°C + losses	78.6
Content, wt %:	
polyaromatic hydrocarbons	60.0
toluene-insoluble component	1.3
quinoline-insoluble component	0.2
Flash point in closed crucible, °C	121
Conradson carbon residue, %	2.5–3.5

Sulfur content, wt %	0.35
Content of tar + asphaltenes, %	27.0

The petroleum residue has the following characteristics: density (at 20°C) 0.8077 g/cm<sup>3</sup>; viscosity 9.69 mm<sup>2</sup>/s; naphthalene content 14.73 wt %; asphaltene content 1.52 wt %; and tar content 8.2 wt %. Its elemental composition is as follows: 83.85 wt % C, 11.27 wt % H, 1.81 wt % S, 0.80 wt % N, and 2.27 wt % O.

The catalyst is prepared by adding an aqueous solution of nickel nitrate to the tar (3.0 wt % of the initial material) and also elemental sulfur in powder form (0.03 wt % of the catalyst). The Ni concentration is 0.025% wt % (of the initial material). The resulting mixture is dispersed in a homogenization unit at 130°C, with plate rotation at 1500 rpm.

Experiments are conducted with a high-pressure laboratory system including a 0.25-dm<sup>3</sup> reaction chamber and a mixer. The mixture of tar with the catalyst and added sulfur is heated to 70–80°C and charged in the chamber, which has been previously purged with argon and filled with hydrogen at an initial pressure of 2–3 MPa. The reactor is heated and, at 150°C, mixing begins. The temperature is measured by a thermocouple and automatically maintained within ±2°C. The working hydrogen pressure is 5.0 MPa; the temperature is 350–450°C; and the reaction time is 15 min.

These parameters are selected after preliminary research on the refining of coal tar from the semicoking of Shubarkol coal by hydrogenation in the presence of nanoheterogeneous molybdenum sulfide catalyst synthesized in situ from an aqueous solution of ammonium paramolybdate [13]. This research shows that the optimal parameters for deep processing of tar are 5 MPa and 400°C.

Table 1 presents the results for tar hydrogenation. We see that the quantity of liquid products formed is very similar for Ni-based catalyst and the Mo-based catalyst adopted as an example. The total yield of motor-fuel fractions in the presence of molybdate catalyst takes a maximum value of 76.8% at 400°C. For nickel catalyst in analogous conditions, the yield of liquid products is somewhat higher: 78.3%.

To produce raw material for coke production, the tar hydrogenates are filtered at 180°C under a pressure of 1.0 MPa, through belting fabric with two layers of filter paper, at a rate of 14–15 kg/min m<sup>2</sup>. The filtrates are distilled to obtain a fraction boiling below 280°C and a residue boiling above 280°C (the raw material for electrode-coke production). A laboratory reactor is used for coking of the residue at a final temperature of 620°C.

The filtrate yield is 90% in the case of molybdenum catalyst and 94.5% for nickel catalyst. The content of solids in the filtrate is 1.7 and 1.3%, respectively, while the content of solids in the residue is 34.7 and 50.9%.