

Refining of Coal Tar by Hydrogenation in the Presence of Nanoheterogeneous Nickel Sulfide Catalyst

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Abstract—The refining of coal tar by hydrogenation is considered. In this process, nanoheterogeneous Ni-based catalysts may expediently be produced in situ from precursors in the reaction medium. The yield of needle coke in complete coal processing with recirculation of the residue at the coking stage is found to be 50–55%. That is 1.5 times the industrial yield in the coking of pitch.

Keywords: coal tar, hydrogenation, refining, nanoheterogeneous nickel sulfide catalysts, needle coke

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Coal tar, a coking byproduct formed in the pyrolysis of coal at 800–900°C, contains numerous reactive compounds, which undergo condensation after distillation at 350–380°C, with the formation of pitch fractions that do not boil below 380°C.

The pitch fractions of tar that boil above 350–380°C are used directly as binder in electrode production or are first oxidized to increase their softening temperature and the yield of pitch coke. The coke obtained from high-temperature pitch is predominantly of isotropic structure and may be used to produce anodes and artificial graphite for the construction industry. However, they are unsuitable for the production of graphitized electrodes and cathode modules in aluminum electrolysis tanks. Those components are produced from anisotropic needle coke [1].

Coal pitch may be divided into four main fractions, in terms of solubility

1. The γ fraction, which is soluble in isooctane, determines the liquidity of the whole system, as well as the viscosity and wettability of pitch.

2. The β fraction, which is insoluble in isooctane but soluble in benzene and toluene, determines the binding and sintering properties of the pitch.

3. The α_2 fraction, which is insoluble in toluene but soluble in quinoline, determines the sintering and coking conditions of the pitch, as well as its susceptibility to graphitization.

4. The α_1 fraction, which is insoluble in quinoline and unreactive, may be a gas or a liquid. In either case,

it prevents the formation of block structures in graphitization, thereby constraining the formation of anisotropic needle coke in pitch coking.

To obtain anisotropic (needle) coke, the coking batch must have a minimal content (no more than 1.0%) of the α_1 fraction. Its content in pitch depends on the method of batch preparation [2].

By varying the content of the quinoline-insoluble fraction in the pitch, the properties of pitch coke may be adjusted over a wide range. Likewise, the microstructure of the coke may be regulated. That is accomplished at Japanese plants, which supply not only isotropic coke for the production of high-strength construction-industry graphite but also needle coke for graphitized electrodes, as well as anodic coke of intermediate quality, with structural components that differ greatly in size. Note that the specifics of the production of needle coke from purified coal tar are the commercial property of the manufacturers; practically no information is available in the literature.

The reactive compounds in tar may be stabilized before its preparation (heating for distillation, pitch coking, etc.) by hydrogenation in the presence of finely crystalline nanocompounds of metals such as Mo, Ni, Fe, and W, comparable in size with the tar molecules [3, 4]. In terms of effective dispersion, nanoheterogeneous catalysts produced in situ from precursors in the reaction medium are most promising [5].

The precursors employed may be water-soluble [3, 6] and oil-soluble [7] transition-metal compounds.

The most common are monometallic molybdenum- or tungsten-based precursors formed in the hydrocarbon medium in the presence of sulfiding agents such as MoS_2 or WS_2 . 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^3	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) $0.8077 \text{ g}/\text{cm}^3$; viscosity $9.69 \text{ mm}^2/\text{s}$; 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^3 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 $\pm 2^\circ\text{C}$. 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 $\text{kg}/\text{min m}^2$. 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%.

Table 1. Results for tar hydrogenation (5.0 MPa, $\tau = 15$ min, 1 : 1 tar–petroleum mixture, high-pressure laboratory system)

Characteristic	Temperature, °C	Yield (wt %) of liquids boiling at			Total yield of distillates, %	Gas + H ₂ O, wt %	Slurry, wt %	Losses, wt %
		<180°C	180–250°C	250–320°C				
No catalyst or sulfur	350	5.3	11.4	13.2	29.9	36.0	16.2	17.9
	400	7.8	15.3	24.0	47.1	36.3	9.1	7.5
	450	10.3	7.6	12.9	30.8	36.0	19.3	13.9
With nanoheterogeneous Ni- and Mo-based catalysts								
0.025%Ni + 0.03% S	350	2.3	15.8	43.4	61.5	15.5	14.1	8.9
	400	2.7	23.2	52.4	78.3	8.7	9.0	4.0
	450	2.8	17.0	48.4	68.2	15.5	13.3	3.0
0.025%Mo + 0.03% S	350	2.3	15.2	42.0	58.5	22.8	14.5	4.2
	400	2.7	22.8	52.3	76.8	8.2	9.2	5.8
	450	2.8	11.5	38.8	51.5	26.4	14.2	7.9

Table 2. Results for the coking of >280°C distillation fractions from tar hydrogenation in the presence of Ni-based catalyst

Yield, wt %			Coke characteristics, wt %		
coke	liquids	gas + losses	A^c	S^{tot}	V_{daf}
46.0	41.3	12.7	0.13	0.16	8.4

Table 3. Characteristics of coke roasted at 1300°C

Effective density, g/cm ³	CLTE at 200–400°C, K ^{−1}	ER, Ω m	S_{me}
2.11	$(1.42–1.84) \times 10^{-6}$	43	5.0

In other words, the product obtained when nickel catalyst is used is better suited to filtration.

The Mo content is 0.0003% in the filtrate and 1.3% in the filtration residue; the corresponding figures for Ni are 0.0013% and 0.8%. That indicates that most of the catalyst is concentrated in the solid residue and may be returned to the process simply by adding the residue to the new tar portion.

Table 2 presents the results of laboratory coking for distillates boiling above 280°C, as well as the characteristics of the coke produced. The liquid products contain 80–85% of fractions boiling above 280°C and may be returned for coking. The fractions boiling below 280°C consist mainly of monocyclic and bicyclic aromatic hydrocarbons (including up to 15% naphthalene and up to 7% monomethylnaphthalenes) and must be sent for processing together with the hydrogenation products of the tar.

To determine the characteristics of the coke sample, it is roasted at 1300°C with 5-h holding, in accordance with State Standard GOST 22898–78. Table 3 presents the results. We see that the effective density of the coke matches that of regular anisotropic coke. It has low values of the coefficient of linear thermal expansion (CLTE) and electric resistivity (ER), as is typical of highly textured coke.

The mean microstructure score for the coke according to State Standard GOST 26132–84 is $S_{me} = 5.0$, with 95.8% distribution of the structural components. That corresponds to lobed coke with large fibers (35–70 μ m), without any orientation of the structural elements.

After heat treatment at $2000 \pm 30^\circ\text{C}$, we determine the parameter $\sin^2\alpha$, which characterizes the susceptibility of the coke to graphitization. We know that, for Conoco SP needle coke, $\sin^2\alpha = 0.95–0.97$; for KNPS isotropic coke, $\sin^2\alpha = 0.81–0.83$.

For the coke produced from hydrogenated coal tar, we obtain $\sin^2\alpha = 0.93 \pm 1$. That result falls between needle coke and isotropic coke, somewhat closer to needle coke.

Thus, we find that hydrogenated coal tar from the coking of Shubarkol coal is a potential source of coke with improved structure (anisotropic coke). In complete processing of the tar with recirculation of the residue (its addition to the coking batch) and hydrogenation of the tar using nanoheterogeneous nickel sulfide catalyst, the yield of such coke is 50–55%. That is 1.5 times the yield in the industrial coking of pitch.

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