EFFECT OF THE NATURE OF THE STARTING MATERIAL

ON THE PHYSICOCHEMICAL PROPERTIES OF COKE

R. Kh. Sadykov, N. E. Filippovich,
M. E. Levinter, and M. F. Galiakbarov

In this paper we report the results of a study on the relationship between the nature of the material to be coked and the physicochemical properties of the coke.

The following three types of materials were studied: residue of resins produced by pyrolyzing gaseous hydrocarbons at 830°C, a hydraulic resin produced by pyrolysis of a ligroin-kerosene fraction at 760°C, and fuel oil from crude Sakhalin oil (Table 1).

Figure 1 shows the infrared spectra of the hydraulic resin and the Sakhalin fuel oil; these spectra were taken in a UR-10 spectrophotometer. The infrared spectra contain absorption bands in the range between 3100 and 3000 cm^{-1} which are typical of CH valence vibrations of aromatic rings, between 2920 and 2850 cm^{-1} which are typical of the CH valence vibrations of CH_2- and CH_3-groups of paraffin chains, bands at 1600 and 1500 cm^{-1} produced by deformation vibrations of the ring, bands at 1380 and 1460 cm^{-1} produced by deformation vibrations of CH_2- and CH_3-groups, and bands between 700 and 900 cm^{-1} produced by CH deformation vibrations of various substituted aromatic rings [1]. From the ratio between the intensities of the characteristic absorption bands it follows that Sakhalin fuel oil is a residue with a high content of paraffins and a low content of aromatic structures, whereas the hydraulic resin has a high content of aromatic compounds.

The oil fractions were coked: the residue of resins produced by pyrolysis of gaseous hydrocarbons at high temperature was coked in an industrial slow-coking unit; the hydraulic resin in coking cells (with production of KNPS coke); and the Sakhalin fuel oil in a laboratory equipment which constitutes a model of an industrial slow-coking unit. The raw coke samples thus produced were heated in graphite crucibles placed in a metal container. The thermal treatment was carried out at a constant temperature between 500 and 950°C in a 99.9% pure nitrogen atmosphere for 3 h.
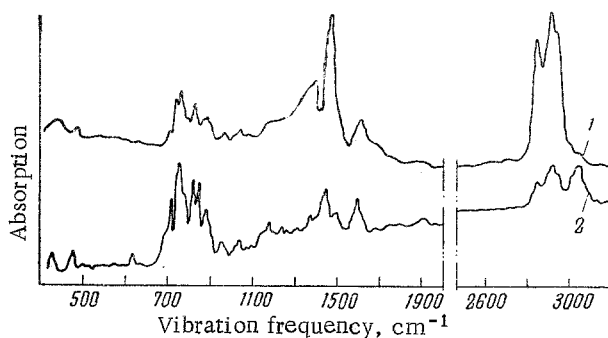

Fig. 1. Infrared spectra of starting materials to be coked:
1) fuel oil from crude Sakhalin oil; 2) residue of resins
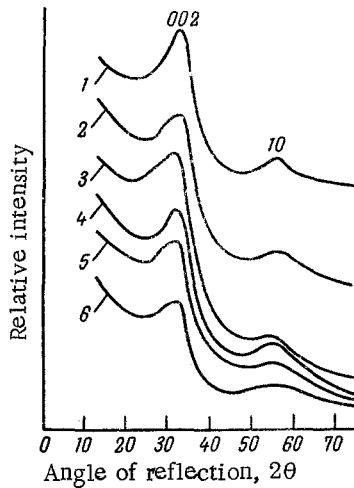produced by pyrolysis of a ligroin-kerosene fraction.

Fig. 2

Fig. 3

Fig. 2. Photometrically determined intensities of the diffraction patterns of coke treated at various temperatures and prepared from the residue of resins produced by pyrolysis of gaseous hydrocarbons: 1) 950°C; 2) 900°C; 3) 800°C; 4) 700°C; 5) 600°C; 6) 500°C.
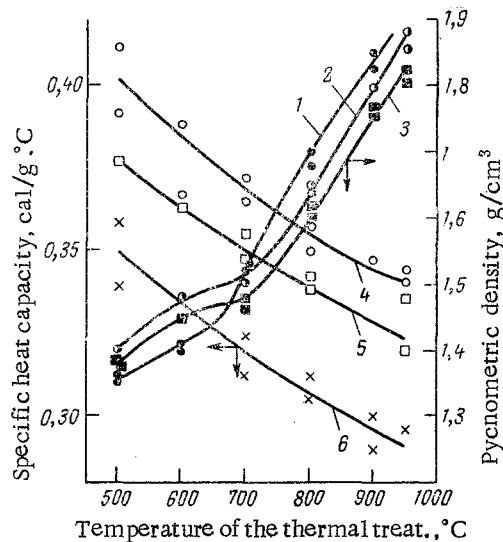
Fig. 3. Pycnometric density and specific heat capacity plotted versus the temperature of the thermal treatment: 1, 4) coke from Sakhalin fuel oil; 2, 6) coke from the residue of resins produced by pyrolysis of gaseous hydrocarbons; 3, 5) coke from the residue of resins produced by pyrolysis of a ligroin-kerosene fraction [KNIS].

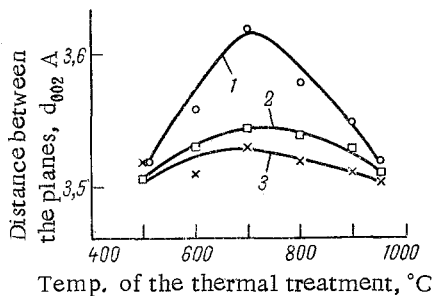Temp. of the thermal treatment, °C

Fig. 4. Distance between the lattice planes as a function of the temperature of the thermal treatment: 1) coke from Sakhalin fuel oil; 2) coke from the residue of resins produced by pyrolysis of a ligroin-kerosene fraction [KNIS]; 3) coke from the residue of resins produced by pyrolysis of gaseous hydrocarbons.

The preliminary heating of the muffle furnace was so adjusted that the time of the temperature rise was identical in all cases. After the experiment the container was cooled in air.

The effect the duration of firing has on the properties of coke was studied in a special series of experiments; it was thus established that even at the lowest temperature (500°C) a firing period of 2-3 h suffices for stabilizing the structure and properties of the coke (Table 2).

We determined the pycnometric density (GOST 3276-62) of the samples prepared, and measured the specific heat capacity by means of the mixing method [2]. The structure of the coke samples was studied from x-ray diffraction. The x-ray diffraction patterns were taken in a URS-60 apparatus (iron radiation) in RKD cells and measured in an MF-4 photometer.

The x-ray diffraction patterns contain the lines with indices 002 and 10, which are typical of coals [3, 4] and oil cokes [5, 6], and are more distinctly developed as the heating temperature is raised. The background of γ rays incoherently scattered around the exit aperture of

TABLE 1. Quality of the Material to Be Coked

Starting material	Density ρ_4^{20}	Yield of coke, weight %	Content of sulfur, weight %
Fuel oil from crude Sakhalin oil....................	0.942	4.6	0.58
Residue of resins produced by pyrolysis of gaseous hydrocarbons.................................	1.02-1.04	10.5	0.35
Residue of resins produced by pyrolysis of a ligroin-kerosene fraction	1.21	43.4	—

TABLE 2. Variation of the Properties of Coke Produced from Sakhalin Fuel Oil with Firing Time (firing temperature 500°)

Firing time of the coke, min	Pycnometric density, g/cm³	Specific heat capacity, cal/g·°C
10	1,36	0,430
30	1,38	0,400
60	1,37	0,392
120	1,38	0,383
180	1,41	0,392

the collimator characterizes the carbon fraction orderly arranged in aromatic layers. The position of the 002 line determines the distance between the planes of carbon orderly arranged in aromatic layers.

The distance d_{002} between the lattice planes was determined by applying Bragg's formula

$$2d_{002} \sin \theta = n\lambda \; ;$$

θ denotes the angle of reflection of the incident pencil of x rays; n the order of reflection; λ the wavelength of the x rays.

In Figs. 3 and 4 the specific heat capacity, the pycnometric density, and the lattice plane distance d_{002} are plotted versus the temperature at which the coke samples were heated. From Figs. 3 and 4 it is evident that the specific heat capacity and the lattice plane distance of the coke samples produced from Sakhalin fuel oil are highest throughout the temperature range examined (500-950°), and the pycnometric density of these samples is highest at temperatures above 700°C. The coke produced from the residue of resins obtained by high-temperature pyrolysis shows the lowest values for these properties in the temperature range considered. KNPS coke occupies an intermediate position.

A remarkable feature is that the pycnometric density of the coke produced from Sakhalin fuel oil increases steeply at temperatures above 700°C.

At this temperature the distance d_{002} between the lattice planes of all cokes and, in particular, of the samples produced from Sakhalin fuel oil attain a maximum.

These findings may be explained by the conversion of disordered carbon of the side chains during the heat treatment. Considering the physical meaning of the heat capacity, we may state that the variations of this property are due to the circumstance that the structure of the crystalline substance is more rigid than that of the amorphous (noncrystalline) part.

For example, as the firing temperature is raised, a larger fraction of carbon is transferred from paraffin chains to aromatic rings and layers, which reduces the number of degrees of freedom of the molecules and causes the heat capacity to decrease.

The relative position of the curves representing the heat capacity is explained by the circumstance that the coke containing the largest amount of paraffin chains has a less rigid structure and the highest heat capacity.

Exactly as the heat capacity curves, the curves representing the variation of the distance between the lattice planes are arranged in the sequence of the degree of ordering. The d_{002} curves show maxima near the temperature of 700°C, which decrease in the sequence coke from Sakhalin fuel oil, KNPS coke, and coke from the residue of resins produced by pyrolysis of gaseous hydrocarbons. The variation in the distance between the lattice planes is explained by the circumstance that as the firing temperature is raised, fine crystals with a degree of ordering lower than that existing at the coking temperature form from nonordered carbon. Therefore, the average distance d_{002} between the lattice planes increases [4], although the amorphous part of the substance is ordered. The increase of this distance is more pronounced as the starting material to be coked has a higher paraffin content.

The curves representing the variation of the pycnometric density confirm that the ordering of the structure is a continuous process resulting in the formation of densely packed aromatic layers from the nonordered carbon of side chains. The pycnometric density of all three cokes examined increases monotonically in the temperature range considered. However, the steep rise along the S-shaped pycnometric density curve for the coke from Sakhalin fuel oil is explained by the circumstance that paraffin chains retard the aromatization process at temperatures up to 700°, while the decomposition products of these chains accelerate the ordering process of the structure at higher temperatures.

CONCLUSIONS

1. It has been shown that the variations of the pycnometric density, specific heat capacity, and distance d_{002} between the lattice planes in coke samples heated at various temperature are related to the origin of the material coked.

2. The degree of ordering of carbon in coke from an aromatic starting material is higher and the specific heat capacity is lower than the corresponding parameters of coke produced from a paraffinic material.

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