PETROLEUM COKE PROPERTIES AS INFLUENCED BY PARTICLE SIZE AND CALCINATION TIME AND TEMPERATURE

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In the immediate future, it is planned to build coker units in a complex with calcination blocks; i.e., the calcination of petroleum coke will be performed directly in the petroleum refineries. All carbonaceous materials, including petroleum cokes, that are used as fillers in manufacturing electrode products must have sufficiently high electrical conductivity and density, low yield of volatile products, and optimum porosity. These properties are imparted to the raw coke by calcining at 1200-1300°C.

Another major factor in electrode manufacture is the selection of the optimum particle size for the filler.

The effect of calcination temperature and holding time on the electrical conductivity of petroleum cokes has been described in [1, 2]. However, there is no adequate information in the literature on the effect of these factors and of the coke particle size on the yield of voltatile components, apparent density, and true density of petroleum cokes. If these relationships can be established, they will provide a more rational basis for selecting process conditions in the high-temperature upgrading of petroleum cokes.

We have investigated coke samples (5-7 mm fractions) from commercial units at three refineries—Novo-Ufa (NUNPZ), Fergana (FNPZ), and Volgograd (VNPZ). Included as a standard raw material for anode paste was pitch coke. The characteristics of the original raw coke samples are listed in Table 1.

Samples 1, 2, 4, and 5 were obtained by screening unclassified commercial coke, sample 3 by crushing 10-25 mm nut coke.

The samples were calcined in closed crucibles at temperatures from 500 to 1500°C in steps of 100°C (to 1000°C in a muffle furnace, at 1000°C or higher in a Tamman furnace). The samples were held 30 min at the test temperature. The time to bring to the given regime was about 5-10 min. The samples were weighed before and after calcining to determine the losses. The true density γ_t and the apparent density γ_a of the calcined cokes were determined, and the porosities calculated from the formula

$$P = \frac{\gamma_t - \gamma_a}{\gamma_a} \cdot 100\%$$

The apparent density of the coke was determined by a method described in [3]. The results of the experiments are presented in Figs. 1 and 2.

The nature of the change in true density as a function of calcination temperature is approximately the same for all petroleum cokes (see Fig. 1): Up to 1300-1400°C, γ_t increases, then decreases at higher temperatures. The true density of the pitch coke is essentially unchanged with calcination temperatures of 600-1000°C. This is explained on the basis that this particular coke was produced at 950-1000°C, so that all processes of structurization that take place under these conditions had been almost completely effected during the coking process. When the calcination temperature of the pitch coke is increased to 1300°C, the coke density also increases, and then remains practically constant over a temperature range of 1300-1500°C. Of all the test samples, the highest values of true density at ~ 1300°C are those of the low-sulfur petroleum cokes.

Novo-Ufa Petroleum Refinery (NUNPZ). Ufa Petroleum Institute (UFI). Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 4, pp. 20-23, April, 1973.

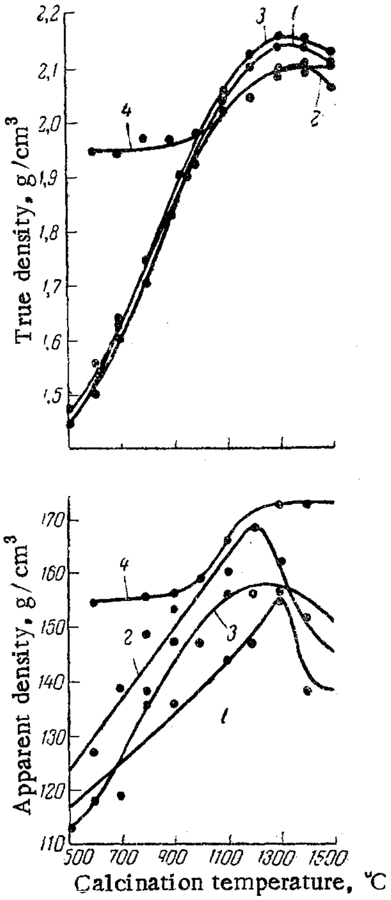

Fig. 1

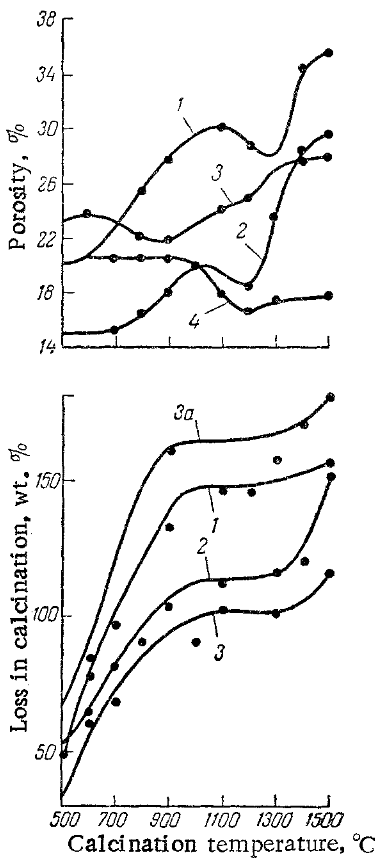

Fig. 2

Fig. 1. True and apparent densities as functions of calcination temperature for cokes produced in units of: 1) VNPZ; 2) NUNPZ; 3) FNPZ; 4) pitch.

Fig. 2. Porosity and losses as functions of calcination temperature for cokes from: 1) VNPZ; 2) NUNPZ; 3a) FNPZ; 3) FNPZ; 4) pitch.

The nature of the change in apparent density as a function of calcination temperature is approximately the same as for the apparent density (the curves pass through maxima, as shown in Fig. 1). However, the low-sulfur cokes have somewhat lower values of γ_a. The pitch coke has a higher density at all temperatures, and the sulfurous coke from the Novo-Ufa refinery is intermediate in density up to 1300°C.

The maximum in the curve of γ_a vs t is not at the same point for the sulfurous and low-sulfur cokes. For the sulfurous coke produced in the NUNPZ unit, the value of γ_a reaches its maximum at a temperature some 50-100°C lower than for the low-sulfur coke. With further increase in temperature, all of the test samples behave differently: γ_a for the pitch coke is almost unchanged over the temperature range of 1200-1500°C; for the sulfurous coke containing 4% sulfur, γ_a drops very sharply over this temperature range, from 1.68 to 1.45 g/cm^3; for the cokes produced in the units of the Fergana and Volgograd refineries, containing 0.98 and 1.95% sulfur respectively, γ_a decreases to a lesser extent. Here there is observed a dependence of the amount of reduction in γ_a on the sulfur content – evidently explained by a retarding action of sulfur on the process of consolidating the carbon networks. Apparently the removal of volatile substances and ash must have an analogous effect on the structurizing process.

It can be seen from Fig. 2 that the porosity of the test specimens depends on the sulfur content and on the yield of volatile components.

The highest porosity is that of the coke from the Volgograd refinery, which is distinguished by a high yield of volatile components (10%). At 1000-1500°C, the porosity for the pitch coke is the lowest and is practically unchanged by temperature.