PRODUCTION OF ELECTRODE COKE BASED

ON DISTILLATE FEEDSTOCK

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The demand for petroleum coke will approximately double over the period 1967-1970 and will more than quadruple by 1975 [1]. The problems of selecting coking feedstock which will ensure the production of high-quality coke are acquiring special importance.

The main types of feedstock for coking are petroleum residues from straight distillation and from cracking. However, it is known that all the petroleum components detrimental to coke are concentrated in the residues, particularly inorganic impurities which transfer completely into the coke in the form of ash.

However, it is possible to use distillate feedstock of secondary origin for coking. These include heavy, aromatics-containing gas oils from catalytic cracking, coking, and other destructive processes. For example, the coking power of the heavy gas oil fraction from catalytic cracking, known as decanted oil, is approximately 6%, its density is greater than unity, and its aromatic hydrocarbon content is higher than 60%, i.e., this is a feedstock whose chemical structure is suitable for coking [2]. There is some foreign experience in the production of coke from distillate feedstock. For example, at a new plant at Immingham in the United Kingdom [3] equipment has been installed for delayed coking to produce normal and "premium" coke. The latter is obtained from products from thermal cracking of distillate origin.

We have conducted an experimental study on the coking of certain samples of distillate coke and determined the quality of the coke obtained.

Low-sulphur distillate products of secondary origin were used as feedstock, viz. a heavy gas oil from delayed coking selected at an industrial plant of the Fergana refinery, and heavy gas oils from catalytic cracking from a plant of the Krasnovodsk refinery and from the test station of the All-Union Scientific Research Institute for the Petroleum Industry (VNII NP).

The plant at the Fergana refinery processes residues from mixtures of Fergana and Turkmen crudes consisting of 76% asphalt and 24% bitumen from deasphaltatization. The heavy gas oil from the Krasnovodsk refinery was obtained from a plant which processes lightened feedstock (90% up to 350°) from Koturtepinsk crude. The catalytic gas oil from the test station of VNII NP is also produced from Koturtepinsk crude (350-500°C fraction).

To determine the fractional composition of the feedstock, fractions boiling up to 400°C were distilled from the initial gas oils. Part of the residue from the coking gas oil was treated with furfural to increase the concentration of aromatic hydrocarbons. This was carried out at 100°C using a solvent: feedstock ratio of 1.5 : 1. The yield of extract was 26% of the residue.

The physicochemical properties of the residues obtained by vacuum distillation of coking and catalytic cracking gas oils, and those of the extract obtained from furfural treatment are shown in Table 1.

Table 2 shows the group chemical composition of the coking feedstock. As may be seen, the heavy gas oil from the Krasnovodsk refinery is a highly-aromaticized product containing 72.2% of predominantly heavy aromatic hydrocarbons.

TABLE 1. Physicochemical Properties of Distillate Feedstock for Coking

Coking feedstock	Yield on initial gas oil, wt. %	Density ρ_4^{20}	Refractive index n_D^{20}	Coking power, wt. %	Mol. wt.	Viscosity, cS		Solidification point, °C	Sulfur, wt. %	Ash content, wt. %	Iodine value, mg I/100 g
						at 50°C	at 100°C				
Residue (above 400°C) from heavy coking gas oil	42.0	0.913	1.5122	0.70	386	—	8.3	42.0	0.65	0.005	27.0
Extract of residue (above 400°C) of heavy coking gas oil	10.9	1.0140	1.5580	4.00	370	—	17.8	30.5	0.90	0.034	47.2
Residue (above 400°C) of heavy catalytic cracking gas oil, from the Krasnovodsk refinery	16.8	1.0135	1.6254	6.75	278	52.17	7.3	32.0	0.27	Traces	40.9
Residue (above 400°C) of heavy catalytic cracking gas oil from VNII NP test station	65.2	0.9065	1.5120	2.10	341	27.00	5.5	38.0	0.30	0.053	7.4

TABLE 2. Group Chemical Composition of the Coking Feedstock (wt. %)

Coking feedstock	Hydrocarbons				Resins	Total aromatic hydrocarbon content
	paraffinic-naphthenic	light aromatic	medium aromatic	heavy aromatic		
Residue (above 400°C) of heavy coking gas oil	56.1	10.8	9.2	18.1	5.8	38.1
Extract of residue (above 400°C) of heavy coking gas oil	27.7	9.4	9.5	44.3	14.1	63.2
Residue (above 400°C) of heavy gas oil from catalytic cracking at Krasnovodsk refinery	24.3	0.5	1.8	69.9	3.5	72.2
Residue (above 400°C) of heavy gas oil from catalytic cracking at VNII NP test station	68.7	4.5	1.0	21.0	4.8	26.5

TABLE 3. Material Balances for Coking Various Feedstocks

Coking feedstock	Autoclave pressure, atm	Coking yields, %		
		coke	distillate	gas and losses
Residue (above 400°C) of heavy coking gas oil	1.0	7.9	82.6	9.5
	2.0	14.8	73.0	12.2
	3.0	15.9	71.2	12.9
Extract of residue (above 400°C) of heavy coking gas oil	2.0	26.2	56.3	17.5
Residue (above 400°C) of heavy gas oil from catalytic cracking at Krasnovodsk refinery	1.0	47.8	36.7	15.5
	3.0	49.1	30.9	20.0
Residue (above 400°C) of heavy gas oil from catalytic cracking at VNII NP test station	1.0	12.8	78.9	8.3
	3.0	16.4	68.4	15.2

TABLE 4. Material Balances for Coking Two Types of Feedstock on a Flow Apparatus (in wt. %)

Coking products	Coking		Extracts of coking residue (above 400°C) at 450°C
	residue (>400°C) of hvy. coking gas oil at		
	450 °C	500 °C	
Coke	6,6	5,1	12,1
Distillate	87,9	85,7	78,3
Gas + Losses	5,5	9,2	9,6

TABLE 5. General Properties of Coke Samples

| Sample No.	Coking feedstock	Uncalcined coke			True density (in g/cm³) of coke calcined at 1300°C for 5 h
		yield of volatiles, wt. % (by GOST 3929-65)	ash content, wt. %	sulfur content, wt. %	
1	Residue (above 400°C) from coking gas oil (coking in autoclave at 1 atm)	4.43	0.07	1.09	2.09
2	The same at 3 atm	8.58	–	0.75	2.07
3	Extract from furfural purification of coking gas oil (coking on flow apparatus)	4.00	0.13	0.84	2.06
4	Residue (above 400°C) of gas oil from catalytic cracking at Krasnovodsk refinery (coking in autoclave at 1 atm)	2.20	0.06	0.13	2.13
5	The same at 3 atm	2.54	0.06	0.11	2.13
6	Residue (above 400°C) of gas oil from catalytic cracking at the VNII NP test station (coking in autoclave at 1 atm)	3.93	0.45	0.70	2.09
7	The same at 3 atm	1.03	0.29	0.32	2.12
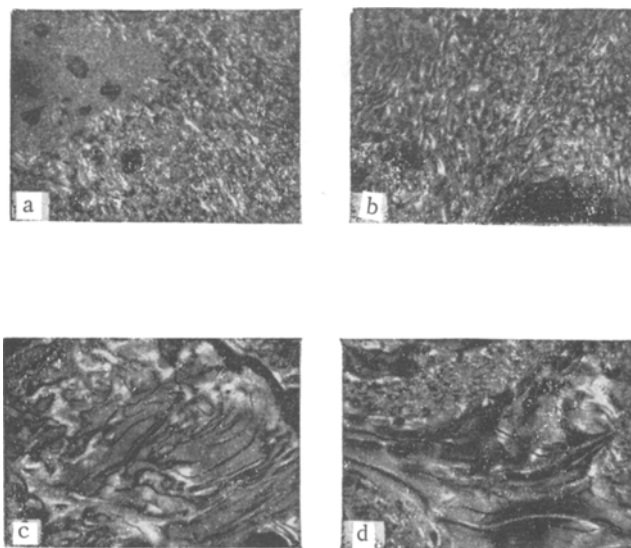
Fig. 1. Photographs of the microstructure of cokes obtained on coking: a) residue (above 400°C) of coking gas oil (in an autoclave at 3 atm); b) extract from furfural purification of coking gas oil (on a flow apparatus; c) residue (above 400°C) of a gas oil from catalytic cracking at the Krasnovodsk refinery (in an autoclave at 3 atm); d) residue (above 400°C) of gas oil from catalytic cracking at the test station of the VNII NP (in an autoclave at 3 atm).

It is interesting to note that the residue from the catalytic gas oil from the Krasnovodsk refiner and decanted gas oil [2] are very close in physicochemical properties.

The feedstock was coked in an autoclave at 420°C, this temperature being reached over the course of 30 min; the coke was calcined at 510-550°C until the evolution of volatiles ceased completely. An increased pressure in the autoclave promoted an increase in the residence period of the product in the high-temperature zone.

Table 3 shows the material balances for the autoclave coking of all the types of feedstock listed.

For the same coking conditions the yield of coke from the gas oil derived from catalytic cracking at the Krasnovodsk refinery considerably exceeds that from the other forms of feedstock, which is explained by the higher content of heavy aromatic hydrocarbons in this gas oil.

It is interesting to note that the effect of pressure on the coke yield is less marked when coking a highly-aromatized feedstock. This is possibly explained by the nature of the polycondensation reactions of aromatic hydrocarbons which proceed with the evolution of hydrogen, i.e., without a decrease in volume. This is confirmed by the reduced density of the gases from the coking of aromatized feedstock (approximately 0.8 g/liter) compared with the density of the gases from the coking of other forms of feedstock (approximately 1.1 g/liter).

The residue from the heavy coking gas oil and its extract were subjected to coking on a laboratory flow apparatus simulating chamber coking. This was carried out at a space velocity of 0.1 h^{-1}, a pressure of 2 atm, and temperatures of 450 and 500°C (Table 4).

A comparison of the data in Tables 3 and 4 shows that high yields are obtained from the batch coking of feedstock in an autoclave. It is also evident that moderate temperatures and elevated pressures are required for the coking of distillate feedstock. Such conditions prevent the vaporization of unconverted feedstock and favor polycondensation reactions.

Characteristic of all the coke samples is the low ash content, which is hundredths of a percent in some cases (Table 5).

The yields of volatiles are not significant, because calcination was conducted under the conditions characteristic of the type of laboratory apparatus concerned.

In over-all properties (ash content, sulfur content, volatiles, and true density), the coke samples obtained satisfy the requirements of the GOST for electrode coke of petroleum origin.

Figure 1 shows photographs of the microstructure of samples of the "feedstock" cokes (uncalcined), whose general properties are given in Table 5. The photographs were taken with a horizontal MIM-8m microscope in polarized light at a magnification of 70. Photographs were taken of two samples of coke obtained from a coking gas oil (2 and 3 in Table 5) and two samples of coke obtained from catalytic gas oils (5 and 7 in Table 5). As may be seen from Fig. 1, the method of preparing the coke feedstock had an appreciable effect on the formation of structure in the coke formed.

All the coke specimens considered have a clearly defined fibrous microstructure, but they can be separated into two types according to the nature of the fibers: cokes obtained from coking gas oils and cokes obtained from catalytic cracking gas oils. The former (Fig. 1a and b) have a dense structure with very fine, thin skeletal fibers, and a great amount of interweaving. The orientation of the fibers is weak. The microstructure of the second type of coke (Fig. 1c and d) is characterized by large and medium dimensions for the fibers. The oriented fibers seem to form bundles, but no interbundle orientation is observed.

In cokes obtained from the catalytic gas oil from the VNII NP test station (sample 2), regions of the structure are found to be similar to the structure in Fig. 1a and b. However, these are small, fibers of large dimensions comprising the main mass. In its structure sample d is less uniform than all the remaining samples.

According to [4] a fibrous structural component has a high true density, i.e., it can be highly graphitized, which is an advantage in the production of graphitized electrodes.

The reactivity of cokes having a fibrous structure is lower than that of cokes with a point structure [5].

A coke with a fibrous structure has a low thermal expansion, which is particularly important for electrodes of high cross-sectional area [2, 5].

CONCLUSIONS

1. The coking of several samples of low-sulfur, distillate feedstock of secondary origin has been investigated.

2. It is shown that coking of distillate feedstock should be carried out at elevated pressure. The effect of pressure is shown to a lesser extent in the coking of highly aromaticized feedstock.

3. The coke specimens obtained are distinguished by low ash contents and a favorable microstructure.

Preference can be given to coke from highly aromaticized heavy gas oil derived from catalytic cracking.

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