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INFLUENCE OF FEEDSTOCK ORIGIN AND DISTILLATION

RANGE ON YIELD AND SULFUR CONTENT OF COKE

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Along with recently published studies directed toward the reduction of sulfur content in coke by heat treatment [1], information is being reported on the production of coke with lower sulfur contents by the use of selected medium-sulfur feedstocks that have been appropriately pretreated [2, 3].

In this article we are presenting results from a study of the coking characteristics of medium-sulfur feedstocks from various sources and with various distillation ranges, to obtain data on the coke yield and on the sulfur content of the coke.

The feedstocks used in this work were (a) straight-run residues from mixed Romashkino crudes distilling above 350, 450, and 500°C; (b) residues from a catalytic gas oil produced from

TABLE 1. Physicochemical Properties of Coker Feedstocks

	Residues from mixed Romashkino crudes, distilling above			Residues from catalytic gas oil, distilling above			Residues from thermal gas oil, distilling above		
	350°C	450°C	500°C	350°C	400°C	450°C	350 C	400°C	450°C
Yield of residue on original feedstock, mass%	48,0	30,5	20,4	87,0	41,5	14,3	95,1	58,1	28,1
Density ρ_4^{20}	0,9627	0,9976	1,0184	1,0037	1,0451	1,1356	1,0845	1,1467	1,2073
Sulfur content, mass %	2,38	2,93	3,23	2,39	2,40	2,33	3,09	3,36	3,82
Hydrocarbon group composition, mass%									
Paraffinic/naphthenic	24,7	19,1	17,2	26,7	22,5	10,9	6,4	4,6	2,0
Aromatic									
light	13,9	10,2	8,5	4,0	3,9	3,2	2,5	1,2	0,8
medium	23,3	18,9	15,3	4,5	3,2	2,8	4,5	1,6	1,4
heavy	22,7	28,9	31,6	60,2	64,5	71,3	72,0	70,3	59,5
Resins	9,5	13,3	14,6	3,6	4,9	6,0	5,0	4,7	3,7
Asphaltenes	5,9	9,6	12,5	1,0	1,9	5,8	9,1	17,6	32,6

Moscow Institute of the Petrochemical and Gas Industry (MINKh i GP). Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 8, pp. 5-8, August, 1978.

TABLE 2. Coke Yield on Crude and S_c/S_f Ratio in Relation to Yield of Residue (coker feedstock) on Crude

Feedstock	Sulfur content, mass%	Sulfur content, mass%, in		Coke yield, mass% on crude	S_c/S_f
		feedstock (S_f)	coke (S_c)		
Mixed Romashkino crudes	48,0	2,38	3,04	9,4	1,28
	30,5	2,93	3,16	8,8	1,07
	20,4	3,23	3,44	7,0	1,07
Yusupovsk crude (Bashkiriya) [5]	60,0	4,28	5,65	12,5	1,32
	50,0	4,40	5,81	12,0	1,32
	40,0	4,64	5,87	11,6	1,26
Sernovodsk crude (Kuibyshev Oblast*) [5]	60,0	3,83	6,30	10,1	1,64
	50,0	4,05	6,32	9,8	1,56
	40,0	4,16	6,28	9,1	1,51
Sultangulovsk crude (Orenburg Oblast*) [5]	60,0	4,35	5,76	5,3	1,33
	50,0	4,43	5,70	5,3	1,29
	40,0	4,60	6,22	5,6	1,35
Karachaelginsk crude (Bashkiriya) [5]	60,0	5,03	5,79	10,5	1,15
	50,0	5,05	5,71	10,8	1,13
	40,0	5,17	5,96	10,1	1,15

the same crude, distilling above 350, 400, and 450°C; and (c) residues from a thermal gas oil (carbon-black feedstock) produced from mixed West Siberian crudes, also distilling above 350, 400, and 450°C.

The part of the investigation of the medium-sulfur gas oils of secondary origin was an extension of work reported in [3, 4], which showed that a feedstock containing a considerable quantity of heavy aromatic hydrocarbons, obtained by thermal cracking of distillates gave the most favorable S_c/S_f (i.e., the ratio of sulfur content in the coke to sulfur content in the coker feedstock was less than unity).

The influence of the distillation range of straight-run medium-sulfur residues (obtained from a given crude) on the coke yield and coke sulfur content has been discussed in a limited number of publications.

In Table 1 we have listed the physicochemical properties of the coker feedstocks investigated.

These feedstocks were coked in a laboratory still at a temperature of 420°C and a gauge pressure of 2 kgf/cm² (in order to avoid partial vaporization of the distillate feedstock).

After evolution of distillate and gas ceased, the coke was calcined at 500-510°C for 1 h.

In Table 2 and in Fig. 1 we present the results obtained in coking straight-run residues from the Romashkino crudes, along with data reported in [5] from the batch coking of residues from high-sulfur crudes, each crude being reduced to residues of 60, 50 and 40% by mass.

Both for the Romashkino residues and for those from the high-sulfur crudes (data of [5]), a linear relationship was obtained between the coke yield and the bottoms yield in reducing the crude (see Fig. 1).

The content of sulfur in the feedstock was found to increase for the heavier feedstocks. The content of sulfur in the cokes produced from residues of a given crude oil varied over rather narrow limits (see Table 2).

The ratio between the sulfur contents in the coke and in the feedstock ranged from 1.07 to 1.64, the lowest value being obtained in coking the heavy residues.

The yields of coke (calculated on the original crude oil) decreased slightly or remain almost constant as the coker feedstock became heavier. Thus we see that, for these types of straight-run residues, the degree of reduction (yield of residue on crude) does not have any basic importance from the standpoint of coke yield.

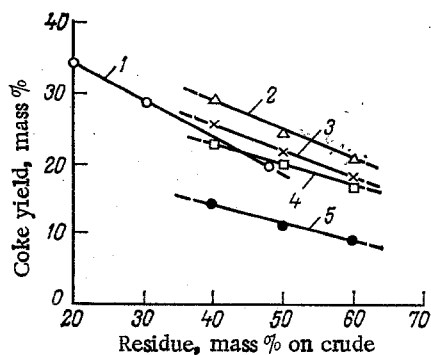


Fig. 1. Coke yield from residues taken to various degrees of reduction, from indicated crude oil: 1) Romashkino; 2) Yusupovosk [5]; 3) Karachaelginsk [5]; 4) Sernovodsk [5]; 5) Sultanovsk [5].

As regards the content of sulfur in the coke, we find that the use of heavier feedstocks had an adverse effect on this property index, i.e., the content of sulfur in the coke increased.

However, for certain crude oils, the content of sulfur in the cokes remained practically constant (see Table 2, Sernovodsk crude), this difference in behavior being due to the differences in thermal stability of the sulfur compounds in the different crudes.

In Table 3 and Fig. 2 we present data on the coke yields and the sulfur content in the coke when using feedstocks of secondary origin. Coking of the residues from either type of gas oil gave considerably higher coke yields than were obtained by coking the straight-run residues; this is explained by the differing contents of coke-forming components in the residues under comparison, and also by differing influence of the elevated pressure that was used in the coking.

For the residues from the catalytic gas oil, we find, much the same as for the straight-run residues, a linear relationship between coke yield and the residue yield in reducing the gas oil.

For the thermal gas oil residues, an increase in initial boiling point from 400 to 450°C gave only an insignificant increase in coke yield on feedstock. This points up the decisive role of polycyclic aromatic compounds in coke formation: The residue distilling above 450°C is distinguished by a lower content of aromatic compounds and a high content of asphaltenes.

TABLE 3. Coke Yields on Initial Gas Oil and Sulfur Content in Coke, in Relation to Distillation Range of Catalytic and Thermal Gas Oils

Feedstock	Sulfur content in coke, mass%	Coke yield on original gas oil, mass%	S_c/S_f
Residue from catalytic gas oil			
>350°C	2,54	31,1	1,06
>400°C	2,55	22,3	1,06
>450°C	2,50	9,6	1,07
Residue from thermal gas oil			
>350°C	2,36	42,1	0,79
>400°C	2,30	35,1	0,68
>450°C	2,13	17,9	0,56

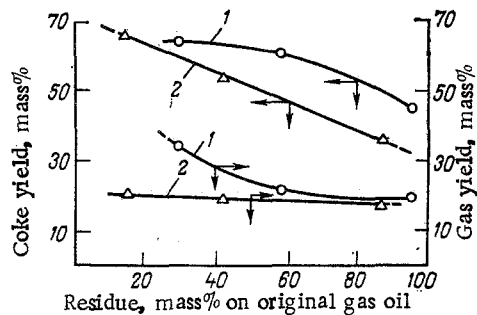


Fig. 2. Coke and gas yields from residues obtained by reducing secondary feedstocks to various degrees: 1) thermal gas oil; 2) catalytic gas oil.

Here the yields of coke on the original gas oil drop off very greatly as the coker feedstock becomes heavier, by factors of more than 2 and 3 (respectively) for the residues from thermal and catalytic gas oil. Thus, from the standpoint of coke yield, it is not advisable to reduce such feedstocks to such a degree that their initial boiling point is above 350-370°C.

In the residues from the catalytic gas oil, the sulfur content varied hardly at all with the degree of reduction (see Table 1). It is known from material reported in the literature and also from production data that light catalytic gas oils from a medium-sulfur feedstock contain approximately the same or even greater quantities of sulfur than do the heavy gas oils. According to data reported in [6], for example, in the cracking of a vacuum gas oil from Romashkino crude in a staged-counter-current pilot-plant cracking unit using synthetic aluminosilicate catalyst with an activity index of 33-35, the contents of sulfur in the light and heavy gas oils were practically identical, amounting to 2.26 and 2.22% respectively.

It is of interest that the cokes obtained from the catalytic gas oil residues (see Table 3) had essentially identical sulfur contents (2.5%), which is not much greater than the sulfur content of the feedstock.

In accord with data reported in [4], we find that the cokes obtained by coking the thermal gas oil residues contained less sulfur than was present in the feedstock ($S_c/S_f = 0.56-0.79$). Here the most favorable results were obtained with the heaviest feedstock, which could be processed to give a coke product with a 2.13% sulfur content, i.e., little more than half that of the feedstock sulfur content (3.82%).

In the coking of the heaviest residue, practically no liquid products were obtained, almost all of the feedstock being converted to coke and gas (see Fig. 2). This is explained on the basis that this residue contains a large amount of asphaltenes, the decomposition of which is usually accompanied by gas formation due to splitting of the side chains from the highly condensed structures.

We see that the coking of all fractions of the thermal gas oil can give cokes with sulfur contents lower than that of the feedstock by factors of 1.3-1.8, thus confirming the feasibility of producing cokes with lower sulfur contents from medium-sulfur feedstocks of secondary origin.

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OPERATING EXPERIENCE WITH TOWERS IN PRODUCTION OF OXIDIZED ASPHALTS

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The use of towers without internals in the large-scale production of oxidized (blown) asphalts goes back many years [1-3]. Along with the recent trend toward larger asphalt-unit capacities, these towers are being used more and more extensively in USSR asphalt production practice. Almost 50% of the entire production of oxidized asphalts is obtained with the use of towers, including almost 30% by direct oxidation in towers and about 20% by two-stage oxidation schemes in which other types of oxidation apparatus (such as stills or tubular reactors) are used along with the towers. In view of this situation, the experience that has been accumulated in tower operation should be analyzed and correlated.

Originally, oxidation towers were used in existing asphalt units [4, 5] for preliminary oxidation of the feedstock, the oxidation then being finished in other types of oxidation apparatus such as stills or tubular reactors.

It was established through commercial tests that oxidation towers are capable of reliable operation as independent apparatus for the production of commercial asphalt, in both paving and construction grades [6].

When towers are used, the oxidation scheme is simple. The feedstock is pumped to the upper part of the tower, up to a certain level. Air is fed from a compressor to the lower part of the tower through a manifold, in order to mix the reacting gas and liquid phases. The asphalt is pumped from the bottom of the tower (takeoff is located below the manifold), and the off-gas leaves the upper part of the tower from the gas space and is directed to "thermal decontamination" [combustion to remove pollutants]. The mixing of the gas and liquid phases with air equalizes the temperatures throughout the reaction zone of the tower, so that cold feedstock can be used; the fresh feed as it enters the tower mixes with the material being oxidized and is heated to the required temperature at the expense of the heat of the oxidation reaction. If the asphalt is to be highly oxidized (as in the production of construction-grade asphalts, or when a light feedstock is used), the cooling effect of the cold feed is supplemented by cooling through the injection of water into the gas space of the tower [3, 6, 7] or by circulating part of the asphalt through external heat exchangers or coolers. In some cases (Moscow refinery, Novokuibyshevsk refinery), the towers are left bare, without any heat insulation, in order to provide further cooling.

In order to stabilize the oxidation conditions, it is extremely important to maintain a constant liquid level in the tower. The level sensors may be thermocouples, pressure pickups, or floats. If the air flow rate is high, the float is located in a container (within the tower) to protect it from severe oscillations. The level is controlled either manually or automatically, the level meter being connected to either the product pump or the feed pump. Other instrumentation to monitor and control the oxidation process in towers includes feedstock and air flowmeters and thermocouples to measure the temperatures in the oxidation zone and in the separation zone (gas space). In certain cases, towers are equipped with oxygen meters [8]. When any undue increase in pressure occurs, part of the petroleum product is discharged from the tower through a relief valve into an emergency tank, thus preventing ignition of the petroleum product and contamination of the area [8].

In Table 1 we have listed the principal characteristics of the towers used in various refineries. As can be seen from these data, the oxidation is usually performed at tempera-

Bashkir Scientific-Research Institute for Petroleum Processing (BashnII NP). Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 8, pp. 8-12, August, 1978.