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Obtaining Petroleum Sintering Additives

R. R. VALINUROV, A. SH. FAZILOV, D. F. OSIPENKO, A. F. AKHMETOV, V. P. ZAPORIN, V. P. LOSEV

Ufa State Petroleum Technological University,
Ufa, Russia

E-mail: v_radim@mail.ru

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Abstract

The methods of manufacturing the sintering additives to coal charges from the vacuum residues of visbreaking tar, one of the most widespread and large-tonnage products, are considered. The starting raw material was subjected to deep vacuum distillation on a laboratory unit and thermal oxidation in a batch reactor. Experimental samples of sintering additives were obtained, and the possibility to produce sintering additives of petroleum origin on this basis was investigated. The physicochemical characteristics of the obtained products were determined; the possibility of their transportation, crushing, mixing and use instead of sintering coal grades in coal coking charges was assessed. A comparison of the obtained sintering additives was carried out for different production methods: an increase in the extent of tar conversion in visbreaking, deep vacuum distillation of the visbreaking residue, and oxidation of the visbreaking vacuum residue. The possibility of the industrial production of sintering additives from visbreaking residues was evaluated on the basis of research results.

Keywords: visbreaking, oil refining, oil sintering additives, oxidation, coal charge, vacuum distillation of oil residues, sintering capacity

INTRODUCTION

The main directions in processing heavy oil residues may be divided into two groups: the first one involves the use as fuel (the production of furnace and marine bunker oil, sponge coke as fuel for cement kilns and thermal power plants), while the second includes the manufacture of special products (components of coal charges for blast-furnace processes, needle coke for nonferrous metallurgy, synthesis gas, and nanomaterials) [1].

The use of heavy oil residues and oil processing products as components of coal charges for obtaining blast-furnace coke has been known long ago; some works consider the application of petroleum coke breeze as mineral fillers, oil coke as coking additives, petroleum sintering additives (PSA) instead of fat coal [2–9].

Attempts of the industrial production and use of PSA and coking additives were accompanied by difficulties limiting their application: inhomogeneity of the characteristics of semi-coke over the height and diameter of the coking chamber during PSA production by means of coking under soft conditions; low sintering ability and softening temperature during PSA production in visbreaking installations; long manufacturing time for the production of PSA from a mixture of pitches with plastics [10, 11]. Nevertheless, investigation of the possibility to use petroleum products after additional treatment as the raw material for coke chemical industry remains a promising direction.

The goal of this work is to evaluate the possibility to obtain PSA in the processes of vacuum distillation, oxidation and visbreaking.

The following tasks were formulated:

1. To analyze the effect of the depth of raw material conversion in visbreaking on the characteristics of the formed vacuum residues, and to evaluate the possibility to use vacuum residue of increased conversion degree as PSA to coal charges.

2. To analyze the effect of the extent of vacuum distillation on the characteristics of the industrial samples of visbreaking residues and to evaluate the possibility of the application of the residues of deep vacuum distillation (RDVD) as PSA.

3. To carry out oxidation of the industrial residues of visbreaking, to evaluate the possibility to use the obtained products as PSA;

4. To compare the characteristics of the obtained products, to estimate the possibility of large-scale production of PSA using the methods under investigation.

EXPERIMENTAL

Three methods were studied for use in the production of sintering additives from the residue of heavy oil visbreaking – the most widespread and large-scale product of petroleum industry: 1) change of the depth of thermal cracking of the heavy oil residue during visbreaking; 2) vacuum distillation of visbreaking residue; 3) oxidation of the vacuum residues of visbreaking.

Due to the principal differences between the methods of the production of sintering additives, the problem was put forward to obtain the products with the ring-and-ball softening point (GOST 32054 "Determination of softening temperature using the ring and ball method") ~115 °C, because sufficient breakability of petroleum product is provided at this temperature. Evaluation of the possibility to obtain sintering additives was carried out over the physicochemical and performance characteristics of the obtained products shown in Table 1.

The ability of a petroleum product to bind coal particles during heating (sintering ability) was determined according to Roga test (GOST 9318). The stability of finely crushed particles of agglomerating additive against coalescence during transportation and storage was evaluated on the basis of penetration factor (GOST 32154). Other parameters were determined using the following procedures: initial boiling point (i.b.p.) – according to GOST 2177, conventional (Engler) viscosity – GOST 6258, open-cup flash point – GOST 4333, density – GOST 3900, sulphur content – GOST 32139, component composition – according to the USSR Authors' Certificate No. 520541.

The raw material for obtaining PSA by means of deep vacuum distillation and oxidation was industrial vacuum residue from visbreaking installation, sampled from one batch with the same physicochemical characteristics presented in Table 2. The raw material for the studies of the possibility to obtain PSA by enhancing the depth of cracking was straight-run tar of the mixture of West Siberian and Bashkir oils from the installations of primary petroleum distillation.

An increase in the degree of tar conversion during visbreaking

The effect of conversion degree (the total yield of gas and petrol) of tar during visbreaking was studied using one of visbreaking installations at the Bashneft company.

The effect of conversion degree was evaluated by raising the temperature of raw material heating from 462 to 470 °C and varying the rate of raw material consumption in the reaction furnace from 44 to 58 m^3/h during tar visbreaking. The experimental run was performed with the constant composition of the raw material. To exclude the effect of the vacuum column operation mode, investigation was carried out at the constant re-

TABLE 1

Physicochemical characteristics to be met by petroleum sintering additives

Parameter	Optimal value
Sintering ability, units, not less than	50
Softening temperature, according to RaB, °C, not higher than	115
Penetration at 50 °C, mm, not more than	10

TABLE 2

Physicochemical characteristics of initial vacuum residue from visbreaking

Parameter	Value
Density, g/cm^3	1.03
Engler viscosity at 80 °C, °E	295
Open-cup flash point, °C	280
Sulphur content, wt. %	2.5
Initial boiling point, °C	305
Penetration at 50 °C, mm	250
Softening temperature according to RaB, °C	37

sidual pressure in the column (~40 mm Hg) and at the constant temperature in the still part of the column (~360 °C).

Deep vacuum distillation of visbreaking residue

The experimental samples of sintering additives were obtained by deep vacuum distillation of residues from visbreaking in the AutoMaxx 9400 laboratory installation (B/R Instrument, USA) according to the ASTM D5236 standard. Initial raw material was loaded into the still of the automated installation for vacuum distillation, then distillation was carried out until the residues with i.b.p. 500+ and 540+ °C were obtained, and the major physicochemical characteristics of the obtained RDVD were determined.

The hydrocarbon composition of the obtained products was determined to evaluate its changes during distillation under deep vacuum and its effect on the properties of the formed products.

Oxidation of the vacuum residues of visbreaking

The possibility to obtain sintering additives during the oxidation of vacuum residues from visbreaking was studied. The technology of obtaining bitumen through thermal oxidation of thermal cracking residues was taken as the basis [2].

Oxidation was carried out in a periodic laboratory set-up under the following parameters: temperature in the reaction zone 230 °C, air flow rate 5 L/min, the mass of the substance loaded into the reactor was 1.5 kg.

Oxidation degree was determined through intermediate sampling of the distillation residue and measurement of its softening point according to the ring-and-ball method (RaB). Oxidation of the products was carried out until residues with the RaB-determined softening point ~115 °C were obtained. The time of raw material residence in the reactor was variable.

RESULTS AND DISCUSSION

Result of an increase in the degree of raw material thermal cracking during visbreaking

The residues exhibiting physicochemical characteristics shown in Table 3 were obtained by rising the temperature of raw material heating in the furnace and decreasing the flow rate of the raw material in the furnace coil of visbreaking installation.

With an increase in cracking temperature and the time of temperature action, cracking reactions proceed with higher intensity, as well as the side reactions of polymerization and polycondensation. For instance, aromatic hydrocarbons are transformed into polycyclics, which are further on transformed into resins and then into asphaltenes. Their molecular masses increase in these processes; other physicochemical characteristics also change [2]. The data obtained in the studies provide evidence of the possibility to obtain PSA during visbreaking, because the values of softening temperature, sintering ability and penetration of some samples of the formed products correspond to the necessary PSA parameters.

Nevertheless, with an increase in temperature in the furnaces and with longer time of raw material residence in the coils, coke deposition on the inner walls of coils, pipelines and equipment increases, which may lead to shorter intervals between installation repairs [2].

Result of the deep vacuum distillation of visbreaking residues

Table 4 presents physicochemical characteristics of the initial raw residue obtained in the industrial

TABLE 3

Physicochemical characteristics of vacuum residues from different cracking depth

Parameter	Value				
Softening temperature according to RaB, °C	86	108	115	125	126
Sintering ability measured by Roga test at the mass ratio of the residue and anthracite, units:					
1 : 5	89.9	89.6	96.3	94.7	98.5
1 : 7	65.0	71.9	78.5	73.1	82.8
Density, g/cm^3	1.09	1.12	1.12	1.12	1.13
Sulphur content, mass %	4.06	4.21	4.34	4.40	4.51
Penetration at 50 °C, mm	16	5	1	1	0

TABLE 4

Physicochemical characteristics of visbreaking residues obtained with different vacuum distillation depth

Parameter	Visbreaking residue		
	Initial	Sample 1	Sample 2
Initial boiling point, °C	305	500+	540+
Density, g/cm^3	1.03	1.03	1.04
Softening temperature according to RaB, °C	37	43	52
Penetration at 50 °C, mm	250	78	27
Product yield*, %	100.00	92.37	81.22
Component composition:			
Paraffin-naphthene hydrocarbons	13.60	15.70	12.70
Aromatic hydrocarbons:			
light	10.80	13.40	13.00
medium	4.70	5.60	6.20
heavy	35.80	30.50	32.40
Resins 1	9.40	9.90	10.90
Resins 2	22.20	21.20	20.10
Asphaltenes	3.50	3.70	4.70

* Product yield was determined as the ratio of the mass of obtained residue to the mass of initial raw material.

visbreaking installation at the residual pressure 40 mm Hg in the vacuum column, and vacuum residues with i.b.p. 500+ °C (sample 1) and 540+ °C (sample 2), obtained under laboratory conditions with eth residual pressure in the column equal to 1.4 and 1.1 mm Hg, respectively.

Comparison of the physicochemical characteristics of the obtained products showed that visbreaking residues with i.b.p. 500+ and 540+ °C do not meet the required PSA quality parameters (see Table 1).

Result of the oxidation of vacuum residues from visbreaking

Tar oxidation involves many reactions resulting in densification: polycondensation, oxidative dehydrogenation, oxidative polymerization, dealkylation, cracking followed by densification of its products. Transformation chains are as follows: hydrocarbons → resins → asphaltenes → carbenes → carboides; hydrocarbons → acids → oxyacids → asphaltenic acids [12]. The main reactions proceeding during oxidation lead to an increase in the molecular mass, so oxidation of vacuum residues demonstrated encouraging results.

Depending on the depth of vacuum distillation which resulted in the formation of residues, and initial softening temperature, it took 6 to 6.5 h to bring them to the state with the required softening temperature (~115 °C). The difference in oxidation times is explained by a small difference in the component composition of the vacuum residues. Results of the product analysis are presented in Table 5.

Initial raw material and vacuum residues with i.b.p. 500+ and 540+ °C were subjected to oxidation. The sintering properties of oxidized residues were evaluated according to Roga test in order to determine preliminarily the possibility of application as the components of coal charges in the production of blast-furnace coke. Sintering ability was investigated according to GOST 9318 at the mass ratio of the sample under investigation and reference anthracite sample equal to 1 : 5. The values obtained for all the products under investigation turned out to be rather high, and differences between the values of sintering ability of the products were within the limits of method error. For this reason, it was decided to study the sintering ability of the obtained products at the ratio to reference anthracite equal to 1 : 7 in order to achieve higher accuracy and visibility. Results of investigations are presented in Table 6.

According to the data obtained, oxidized industrial vacuum residue from visbreaking and oxidized RDVD obtained under laboratory conditions correspond to the requirements to PSA.

It was established by comparing the oxidized RDVD that the sintering ability of oxidized residues increases with an increase in the extent of

TABLE 5
Characteristics of the products obtained through oxidation of different residues

Parameter	Oxidation time			
Initial substance				
Oxidation time, h	0	3	5	6
Softening temperature according to RaB, °C	37	72	95	115
Penetration at 50 °C, mm	250	47	11	7
Residue from deep vacuum distillation (i.b.p. 500+ °C)				
Oxidation time, h	0	4.5	5.5	6.25
Softening temperature according to RaB, °C	43	88	101	115
Penetration at 50 °C, mm	250	23	14	7
Residue from deep vacuum distillation (i.b.p. 540+ °C)				
Oxidation time, h	0	2	4.1	6.5
Softening temperature according to RaB, °C	52	77	97	115
Penetration at 50 °C, mm	250	28	21	8

TABLE 6
Physicochemical characteristics of oxidized products

Parameter	Residue of visbreaking after oxidation		
	Initial	i.b.p. 500+ °C	i.b.p. 540+ °C
Softening temperature according to RaB, °C	115	115	115
Sintering ability measured by Roga test at the mass ratio of the residue and anthracite, units:			
1 : 5	84.5	86.7	88.7
1 : 7	61.7	62.4	65.9
Penetration at 50 °C, mm	7	7	8

vacuum distillation of the residues before oxidation: for the 1 : 5 ratio – from 84.5 to 88.7, for 1 : 7 – from 61.7 to 65.9. It may be assumed that the highest value for oxidation is that of the medium aromatic hydrocarbons and resins. The larger is their amount, the faster and more efficient is the oxidation of the residue from visbreaking.

Taking into account a small difference in oxidation time and a relatively small difference in the sintering ability of oxidized vacuum residues, we may conclude that preliminary deep vacuum distillation of visbreaking residues is unreasonable.

The initial product, which is a component of boiler fuel, obtained at the industrial visbreaking installation, does not possess sintering properties because in the case of low conversion degree of tar during visbreaking cracking reactions dominate over densification processes.

The residue from deep vacuum distillation with i.b.p. 540+ °C, oxidized under laboratory conditions, exhibits the highest sintering ability.

CONCLUSION

The following conclusions were drawn on the basis of comparison of the studied methods of PSA production from visbreaking residue:

1. It is possible to produce PSA from visbreaking residues using two methods: an increase in the depth of tar conversion and oxidation of vacuum residues.

2. Without changing the depth of tar conversion during visbreaking, it is impossible to obtain sintering additives by means of deep vacuum distillation.

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