УДК 665.65

E. I. Grushova, A. Yu. Yurkevich, A. I. Yusevich, N. N. Malevich, A. S. Sharif
Belarusian State Technological University

ADDITIVES-MODIFIERS FOR INTENSIFICATION OF OIL STRAIGHT-RUN DISTILLATION AND HEAVY PETROLEUM RESIDUES OXIDATION

Native oil atmospheric vacuum distillation in presence of the heavy pyrolysis tar (0.5–5.0 wt %) allows increasing the distillate fractions screening. Structural-group composition of the resulting residual oil product differs from the composition of the residue obtained by fractional distillation of the oil without the additive mostly due to aromatic structures content increase. The modified residue oxidation runs more slowly and the product with lower melting point is formed.

Key words: oil, additive, pyrolysis tar, fractional distillation, distillate, yield, residual oil product, oxidation, bitumen.

Introduction. At the present stage of the petroleum-refining industry development the main objective is to improve the quality of manufactured products by efficient processing of hydrocarbon raw materials. For this reason, systematic research aimed at improving technologies of manufacturing oil products of different nature seems to be very important. Analysis of the results of the previous work [1–5] has shown that a very promising way to intensify the processes of crude oil direct distillation and oxidation of tars to bitumen is to affect oil disperse systems by additives-modifiers. Various additive were investigated in the processes concerned, which in case of realization of such methods of processing hydrocarbon raw materials industrially would require to increase 2–3 times not only the amount of reagents used in technological processes, but also cost of their storage, preparation etc. Therefore, it was of interest from both scientific and practical points of view to develop such an additive-modifier, which at one-fold addition to hydrocarbon raw materials (oil) would have a positive effect on a number of refining processes.

The aim of the work involved was to develop an additive-modifier of “prolonged” action, which when added to oil would increase the yield of distillates in atmospheric-vacuum oil distillation and improve the quality of crude oil subjected to oxidation for producing bitumen.

Main part. According to the data given in [6, 7], positive effect on the distillation of crude oil, fuel oil is achieved by introducing additives with high content of aromatic structures, and the process of oxidation of native liquid asphalt is affected by pyrolysis heavy tar. Thus, for the intensification of oil distillation and the subsequent oxidation of the residue from the distillation of liquid asphalt, pyrolysis heavy tar obtained at JSC “Lesohimik” (Borisov) was used as an additive. Its properties are given in Table 1.

The additive was introduced into the oil in the amounts of 0.5; 1.5; 3.0; 5.0 wt %. Oil distillation was carried out according to [3, 5]. At atmospheric pressure fractions of D. K.–180 and 180 to 250°C were drawn off. Further distillation was carried out at the residual pressure of 5 mbar and the fractions of 250–350°C, 350–440°C and 440–480°C were extracted. After atmospheric and vacuum distillation the residue obtained was oxidized during 8 h by common method at the temperature of (245 ± 2)°C, air consumption being 10 dm^3/min · kg. Table 2 shows the results of the atmospheric-vacuum distillation of crude oil.

Table 3 deals with the fractional composition of the resulting gasoline fractions, determined by the method of limited distillation [8].

Analysis of the data in Tables 2 and 3 shows that when introducing the additive the yield of distillates is substantially changed. But the refractive index of the distillates from atmospheric distillation decreases to some extent, which testifies to the petroleum system components redistribution under the influence of the additive introduced.

Table 1

Properties of heavy pyrolysis tar

Index	Value
Relative density, d_4^{20}	1.3006
Initial boiling point, °C	185
Fractional composition, wt %: B. K.–250°C	48.35
250–350°C	8.74
350–440°C	8.74
440–480°C	19.09
Higher than 480°C	15.08

Table 2

The results of crude oil atmospheric-vacuum distillation with pyrolysis heavy tar

Index	Additive: heavy pyrolysis tar, wt %				
	0	0.5	1.5	3	5
Initial boiling point, °C	48	45	40	38	36
Fractions yield, wt %: D. K.–180°C	12.57	8.18	8.27	8.74	7.06
180–250°C	8.06	12.93	9.42	11.57	11.09
250–350°C	15.91	17.92	19.79	20.95	20.71
350–440°C	15.17	17.92	19.79	20.95	20.71
440–480°C	8.06	7.33	7.17	8.34	7.15
Residual mineral oil	40.23	36.03	37.63	32.11	36.08
Refractive index of the fractions: D. K.–180 (nD20)	1.4170	1.4071	1.4050	1.4145	1.4190
180–250 (n_D^{20})	1.4468	1.4405	1.4330	1.4398	1.4428
250–350 (n_D^{50})	1.4543	1.4545	1.4565	1.4582	1.4618
350–440 (n_D^{50})	1.4675	1.4856	1.4861	1.4868	1.4820
440–480 (n_D^{50})	1.4732	1.4920	1.4895	1.4967	1.5068

Table 3

Fractional composition of gasoline

Index	Gasoline drawn off from oil containing the additive, wt %				
	0	0.5	1.5	3	5
Initial boiling point, °C	55.5	55.6	55.3	55.5	56.4
$t_{10\%}$, °C	61.2	61.4	61.1	61.3	64.4
$t_{50\%}$, °C	85.7	86.7	88.8	89.5	99.4
$t_{90\%}$, °C	139.7	140.8	133.2	145.8	153.3

However, even small changes in the distillates output reduce the output of residual mineral oil by more than 2 wt %.

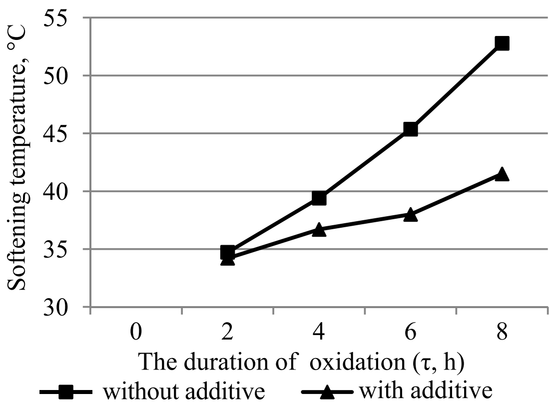
Structural-group composition of the residual oil product was studied by IR spectroscopy [8]. To assess the relative composition of hydrocarbon functional groups spectral coefficients were calculated according to [8]. The latter were used to determine the ratios of aromatic hydrocarbons to normal paraffins (A_1), aromatic hydrocarbons to paraffin ones (A_2), normal paraffins to paraffin hydrocarbons (P), naphthenic to paraffin hydrocarbons (N), the degree of paraffins branching (B) shown in Table 4.

The values of the spectral coefficients indicate that the introduction of the additive-modifier into original oil affects the composition of the residual oil product, small additions of pyrolysis heavy tar being the most essential in this respect.

Table 4

Spectral coefficients

Spectral coefficients	Oil	Residual oil product obtained from oil containing the additive, wt %			
		0	1.5	3	5
$A_1 = \frac{D_{1600}}{D_{720}}$	0.932	–	0.952	0.968	0.974
$A_2 = \frac{D_{1600}}{D_{1465}}$	0.225	0.238	0.295	0.340	0.365
$N = \frac{D_{970}}{D_{1465}}$	–	0.147	0.246	–	–
$B = \frac{D_{1380}}{D_{1465}}$	0.564	0.567	0.599	0.633	0.639
$P = \frac{D_{720}}{D_{1465}}$	0.215	0.247	0.310	0.343	0.374



The dependence of the oxidized residue softening temperature on the time of oxidation (τ) according to ring and ball method (GOST 11506–3)

But with the introduction of more than 3 wt % of the additive, structural-group composition of the residual oil product practically does not change. According to the data in the figure, the softening temperature of the oxidized residue obtained from the crude oil distillation without any additives introduced, is higher than that in the distillation of crude oil containing 3 wt % of the pyrolysis heavy tar. Apparently, according to Table 4 this is due to the predominance of aromatic structures that inhibit the oxidation process.

Conclusion. Thus, the results of the study involved confirm the possibility of controlling certain technological processes by single action of the additive-modifier on the structure of starting hydrocarbon raw materials and oil.

The use of pyrolysis heavy tar makes it possible to increase the extraction of distillate fractions, the proportion of aromatic structures in asphaltenes of the oxidized residue formed in the distillation of crude oil, the softening point of the residue being lower than that of the product obtained by the conventional method.

References

1. Shurbok A. O., Grushova E. I. Oxidized bitumen from the modified row materials. *Neftekhimiya* [Petroleum Chemistry], 2012, no. 5, pp. 383–389 (in Russian).

2. Yusevich A. I. Use of cyclohexanone effecting oxidized bitumen. *Neftepererabotka i neftekhimiya* [Refining and Petrochemical], 2012, no. 2, pp. 25–29 (in Russian).

3. Grushova E. I. Petroleum distillation activation by esters of rape oil. *Izvestiya VUZov. Neft' i gaz* [Bulletin of the Universities. Oil and gas], 2014, no. 1, pp. 84–89 (in Russian).

4. Grushova E. I. Effect of polar Organic Substances on the Distillates Yield in Atmospheric and Vacuum Distillation of Crucle Oil. *Petroleum Chemistry*, 2013, no. 3, pp. 225–228.

5. Grushva E. I., Sharif A. S. Petroleum crudest colloidal structure regulation by use of activating additives. *Voprosy khimii i khimicheskoy tekhnologii* [Question of Chemistry and Chemical Technology], 2013, no. 6, pp. 82–85 (in Russian).

6. Sharif A. S., Grushva E. I. Influence of polycyclic aren additives straight-run distillation of oil. *Trudy BGTU* [Proceeding of BSTU], 2011, no. 4: Chemistry Organic Substances Technology and Biotechnology, pp. 119–121 (in Russian).

7. Shurbok A. O., Grushva E. I., Pas'kova A. N., Krayko V. M., Yurkevich A. Yu. Oxidized bitumens from goudronmodifie with pyrolysis pitches. *Tezisy 78-y nauch.-tekhn. konferentsii professorsko-prepodavatel'skogo sostava* [Thesis of 78th Schentific and Technical Conference of Teaching Stuff]. Minsk, 2014, 38 p. (In Russian).

8. Shurbok A. O., Grushova E. I. Influence of polar solvents on straight-run distillation of oil. *Trudy BGTU* [Proceeding of BSTU], 2013, no. 4: Chemistry organic substances technology and biotechnology, pp. 25–27 (in Russian).

Information about the authors

Grushova Evgeniya Ivanovna – D. Sc. Engineering, professor, Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: Grushova.e@mail.ru

Yurkevich Anna Yur'evna – student. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: HannaYurkevich@ya.ru

YusevichAndreyIosifovich – Ph. D. Chemistry, associate professor, Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: usevich@mail.ru

Malevich Nikolay Nikolaevich – junior researcher. Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: jashhik87@rambler.ru

Sharif Ashraf – graduate student. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus).

Received 23.02.2015