

УДК 665. 61. 033. 28

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INFLUENCE OF POLAR SOLVENTS ON THE STRAIGHT DISTILLATION OF CRUDE OIL

It is offered to use for activation of oil raw materials of an additive of polar organic solvents. It is shown that for a preliminary estimate of activating action of additives it is possible to use results of the comparative analysis of properties of asphaltenes, allocated of the samples of oil not containing and containing an additive, before distillation.

Introduction. As it is known [1], oil and virtually all residual oil products, heavy, and under certain conditions, the lighter fractions of oil are dispersed systems. To regulate colloidal and dispersed properties of petroleum feedstock, and hence more fully realize its potential in the recycling process, you can use a simple but effective method – activation of petroleum feedstock by additives of compounds of different nature.

Traditionally, to assess the impact of activating additives for petroleum distillation process results to the material balance of atmospheric-vacuum distillation explore structural-group composition of selected distillates, residues from the distillation (oil, tar), and separated from residual oil asphaltenes [1–4]. The effect of additives on the oil dispersion is associated with changes in the properties of the dispersion medium – increase of its solvent power, polarity [5].

Currently as additives modifying the oil before direct distillation a wide range of substances of different chemical nature was investigated [3–9]. This is oil with a high content of aromatic structures (Selective refined oil extracts, various fractions of gas oil of catalytic cracking process, coal tar fraction, etc.), hydrocarbons (paraffin wax), compounds with the functional groups $-\text{NH}_2$; $-\text{OH}$; $-\text{COOH}$, etc.

By the nature of the impact of these substances on oil dispersions additives can be divided into three groups. The first group contains substances that may act as new nuclei of dispersed phase. They form new complex structural units (CSU) by reducing the size of solvation shells and even same supramolecular structures of CSU in the initial oil. As a result of reducing the particle size of the dispersed phase viscosity of distilled petroleum feedstock decreases and more favorable conditions for the selection of the distillate fractions are formed.

The second group contains substances that reduce the viscosity of the dispersion medium, i.e. diluents. Presumably, this result is achieved by mixing oils of different viscosity.

The third group consists of agents that affect the polarity of the dispersion medium, its solvent power. This leads to the destruction of the adsorption – CSU solvate layers of CSU and corre-

spondingly increases the selection of distillate fractions in the distillation of oil.

However, so far due to lack of sufficient data of systematic studies it is difficult to imagine the impact of these mechanisms of the oil additive dispersion system will determine the quantitative and qualitative indicators of straight distillation of crude oil.

In connection with the above, the task of this paper was to investigate the possibility of expanding resources of additives, as well as to develop a method of assessing their activating effect in the process of direct distillation of crude oil.

Main part. Objects of study in this paper were two groups of asphaltenes. The first group of asphaltenes was isolated from tar – residual product of atmospheric and vacuum distillation of crude oil processed at “Naftan” (Novopolotsk). Direct distillation of crude oil was carried out by a known method without activating additive, as well as with additives in an amount of 1.5 wt % on oil of polar solvents – caprolactam (CL), N-methylpyrrolidone (N-MP), sulpholane, ethylene glycol (EG) [8].

The second group of asphaltenes was isolated from the initial oil and oil in which the listed additives of solvents were introduced in an amount of 1.5 wt % per oil.

In both cases, the isolation of asphaltenes is carried out according [10] – by processing raw oil sample by 40 times taken the amount of n-heptane, holding the resulting system within days and filtering the precipitate. Table 1 shows the temperature of the beginning of distillate petroleum distillates by the atmospheric distillation of crude oil ($t_{b,b}$).

Table 1

Initial boiling points of the petroleum feedstock at atmospheric pressure

Oil raw	$t_{b,b}, ^\circ\text{C}$
Crude oil	75
Crude oil + 1,5 wt % CL	80
Crude oil + 1,5 wt % N-MP	70
Crude oil + 1,5 wt % sulpholane	80
Crude oil + 1,5 wt % EG	70

Asphaltene samples were analyzed by infrared spectroscopy. IR spectra were recorded on a Fou-

rier spectrometer NEXUS (Thermo Nicolet, USA) in KBr pellets with data processing on a computer. The assignment of the absorption bands in the IR spectra was carried out [11]. The relative intensity of the absorption coefficients of aromatic hydrocarbons and paraffinic hydrocarbons of normal structure were determined by the ratio $A_1 = D1600 / D720$, of polysubstituted aromatics and paraffins - $A_2 = D750 / D720$, coefficient of branching was determined by the ratio of the absorption intensity of methyl and methylene units: $P = D1380 / D720$; coefficient of relative intensity of the absorption of trisubstituted and polysubstituted aromatic hydrocarbons were determined by the ratio $A_3 = D815 / D750$; conditional content of paraffinic structures was found in terms of the $P = D720 + D1380 / D1600$.

Table 2 shows the spectral coefficients of the two groups of asphaltenes, calculated from the optical density of the absorption bands in a particular area.

Using a scanning electron microscope HOL JSM 5610LV with a system of chemical analysis EDX JEOL 2201 JEOL (Japan) the content of asphaltene in the samples C and S was investigated (Table 3).

Analysis of the data presented in table 1 shows that the introduction of polar additives in the oil affects the structure of the resulting dispersions. In some cases (when introducing in the oil and CL and sulpholane is amplified) the intermolecular

interaction in the dispersion medium and the quantity $t_{b,b}$ petroleum feedstock increases, and in other cases (when introducing EG, N-MP in the oil), the opposite effect is observed. According to Table 2, the introduction of additives of solvents in oil provides an increase of the content of tar aromatic structures in asphaltenes, reduction of paraffinic structures. Consequently, in the presence of additives selection of distillate fractions runs better by changing the structure of the dispersed oil caused by the transition of molecules of solvent-adsorption shell of dispersed phase in the dispersion medium. Likewise, polar additives affect the composition of asphaltenes, extracted from oil.

Asphaltenes are extracted from crude oil (Table 3, Sample 1a) contain more carbon than the asphaltene, derived from tar oil (sample 1). Presumably, this is due to the transition of paraffinic hydrocarbon molecules out of the dispersed phase in the dispersion medium by diluting the last by n-heptane. In the asphaltenes – extracted from polar solvents of oil containing additives, the carbon content is less than in 2–6 samples of asphaltenes. It can be assumed, that increasing of the polarity of the dispersion medium reduces the solubility of hydrocarbon of paraffinic base included in CSU. To a large extent the carbon content of asphaltenes is reduced at introduction in oil of an additive of EG, which molecules are probably themselves embedded in the structure of CSU, which is consistent with their property to dissolve in the resin [12].

Table 2

Spectral coefficients of asphaltene extracted from crude oil and tar

Asphaltene extracted from tar	Spectral coefficients					Asphaltene extracted from crude oil	Spectral coefficients				
	A ₁	A ₂	A ₃	P	Π		A ₁	A ₂	A ₃	P	Π
Tar	0.98	0.98	0.91	1.95	3.0	Crude oil	1.72	1.03	1.05	1.91	1.7
Tar (CL)	0.97	1.08	1.0	2.0	1.21	Crude oil (CL)	1.81	1.07	1.02	2.04	1.26
Tar (N-MP)	–	–	–	–	–	Crude oil (N-MP)	1.82	1.04	1.07	1.98	1.22
Tar (sulpholane)	2.05	1.1	1.04	2.25	1.58	Crude oil (sulpholane)	1.84	–	–	1.82	1.62
Tar (EG)	1.89	1.06	1.05	2.0	1.61	Crude oil (EG)	1.77	1.06	1.02	1.89	1.64

Table 3

C and S content in asphaltenes

Sample number	Oil raw	Element	Content, wt %	Error, %	Sample number	Oil raw	Element	Content, wt %	Error, %
1	Tar (o)	C	81.14	1.19	1a	Oil (o)	C	85.05	1.61
		S	6.34	0.63			S	7.05	0.72
2	Tar (CL)	C	87.98	1.59	2a	Oil (CL)	C	86.94	1.54
		S	6.68	0.6			S	6.98	0.68
3	Tar (N-MP)	C	86.95	1.41	3a	Oil (N-MP)	C	85.81	1.15
		S	6.45	0.67			S	6.88	0.6
4	Tar (sulpholane)	C	88.78	1.65	4a	Oil (sulpholane)	C	87.32	1.42
		S	6.34	0.77			S	6.97	0.66
5	Tar (EG)	C	89.23	1.61	5a	Oil (EG)	C	74.16	1.10
		S	6.53	0.99			S	7.51	0.39

The content of sulfur (Table 3) in the asphaltenes of tar when polar additives are introduced in oil increases due to the destruction of solvation shells of CSU. Thus, in the asphaltens of oil the content of sulphur is more, than in the asphaltens of tars. It can be explained by the weakening of the molecular force field of the dispersion medium because of the introduction of n-heptane in oil. Thus, activation of oil by additives of polar organic solvents leads to change of structure of oil colloidal dispersion system.

Changes of the molecular force field in the composition of the dispersed phase will occur to a greater or lesser extent, depending on the nature of the introduced additive and its molecular force field. However, the direction of these changes is almost identical in nature for asphaltene products isolated from the residue of atmospheric crude oil of vacuum distillation of activated oil and asphaltenes, extracted from activated oil.

Conclusion. It is shown that additives of polar organic solvents can affect the intensity of intermolecular interactions in the dispersion medium of oil dispersion system. According to the results of the analysis of asphaltenes, obtained by solvent treatment of oil containing and not containing the additive, the effect of letter on the oil distillation process can be estimated.

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Received 27.02.2013