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APPLYING ADDITIVE-MODIFIERS IN DEWAXING RAFFINATE PROCESS

Dewaxing petroleum oil raffinates is carried out by low-temperature rectification in solvents acetone – toluene. To intensify the process as an additive-modifier we used ϵ -caprolactam. Analysis of structural-group composition dewaxed raffinate by infrared spectroscopy showed that in the presence of ϵ -caprolactam selectivity of dewaxing is increased due to smaller content slack aromatic, branched paraffins and oxygenates structures. However, if the content of ϵ -caprolactam > 1 wt % selectivity of separation is reduced, apparently by increasing solvent power system acetone – toluene (ϵ -caprolactam).

Key words: raffinate, dewaxing, acetone, toluene, additive-modifier, ϵ -caprolactam, crystallization, slack wax, dewaxed raffinate, IR spectroscopy, structural-group composition.

Introduction. When basic oils are obtained, most share of the cost covers the dewaxing process by selective solvents. Regarding that fact, the development of methods to increase efficiency of this process is a very important task.

Currently, different ways to improve the process of dewaxing are used: the use of more efficient crystallization, slow stirring of the cooled mass in the surge barrel, selection of effective ketone, the use of special additives-modifiers and so on [1–4].

However, the least expensive technology is that of dewaxing using additives-modifiers; its effectiveness is evaluated by the rate of filtration of the cooled solution, the yield, and the quality of deparaffinizing oil [2].

Modifying additives are used to dewax distillates of different composition obtained in the purification of oil fractions by selective solvents. According to [2] the additives reduce the solvent consumption, increase the filtration rate, deparaffinizing oil yield, and in some cases the temperature of the process. However, the use of such additives in industrial processes is limited for several reasons: for example, due to high cost, lack of industrial production, etc.

Taking into account the above mentioned, the aim of this work is to develop a cheap and effective additive modifier to dewax raffinates.

Main part. The early research [5] showed that using ϵ -caprolactam as additive to the modifier increases the deparaffinizing oil yield and paraffin hydrocarbons of normal structure in the slack wax.

This work continues the earlier performed research; it presents the results to assess the effect of ϵ -caprolactam on the structural-group composition of deparaffinizing raffinates. The method of IR spectroscopy is used; it is based on absorption, reflection and dispersion of infrared energy passing through matter [6–9].

Average molecules of deparaffinizing raffinates were evaluated by the contents of methylene groups (CH_2) in the absorption band of 720 cm^{-1} , methyl groups (CH_3) in the absorption band $1,380\text{ cm}^{-1}$, carbonyl groups (CO) in the area $1,720\text{--}1,700\text{ cm}^{-1}$, aromatic bonds C=C in the area $1,600\text{ cm}^{-1}$, relation to the methyl groups of paraffinic structures in the absorption band $1,465\text{ cm}^{-1}$, i.e. we used the spectral coefficients, which is the ratio of optical densities (D) at the corresponding wavelengths: aromaticity index $A_1 = D_{1,600} / D_{720}$ and $A_2 = D_{1,600} / D_{1,465}$; paraffinizing index $P = D_{720} / D_{1,465}$; branching index $B = D_{1,380} / D_{1,465}$; oxidation index $O = D_{1,700} / D_{1,465}$.

Raw material for dewaxing (raffinates) is extracted from oil distillate with a selective solvent (N-methylpyrrolidone) and VD-3 obtained at JSC “Naftan” by vacuum distillation of fuel oil.

Low temperature dewaxing of raffinates is carried out in the solvent media acetone – toluene (60 : 40), ϵ -caprolactam consumption is 0.5; 1.0 and 1.5 wt % for raw material.

Table 1 shows the results of the study of the structural-group composition of raffinates.

Assessment of changes in the hydrocarbon composition of deparaffinizing raffinates depends on the impact of the additive-modifier on the process of low-temperature crystallization; it is calculated according to [9, 10] group composition by optical densities. The latter is calculated according to IR spectra of the deparaffinizing raffinates samples for the absorption bands characterizing the deformation vibrations of C–H and C–C: $1,450$, $1,370$ and 720 cm^{-1} (alkanes); 970 cm^{-1} (naphthenes); $1,600$, 870 , 810 (arenes); $1,710\text{ cm}^{-1}$ (oxygenated compounds). The ratio of the sum of the optical densities of the bands characterizing the hydrocarbons to the sum of the total optical densities for all hydrocarbon and oxygen-containing compounds is used to calculate the content of aromatic and paraffin hydrocarbons (Table 2).

Table 1
The results of the study of the structural-group composition of the raffinates by the method of IR-spectrometry

ϵ -caprolactam consumption, wt %	Spectral coefficient				
	A ₁	A ₂	P	R	O
Raffinates extracted from oil distillates VD-2					
0	0.89	0.45	0.51	0.73	0.44
0.5	0.93	0.57	0.62	0.79	0.58
1	0.94	0.59	0.63	0.81	0.59
Raffinates extracted from oil distillates VD-3					
0	0.77	0.32	0.42	0.19	0.32
0.5	0.71	0.22	0.31	0.62	0.22
1	0.83	0.38	0.46	0.79	0.40

Table 2
Aromatic and paraffin hydrocarbons in the deparaffinizing raffinates

ϵ -caprolactam consumption, wt %	Raffinates contents from VD-2, %		Raffinates contents from VD-3, %	
	alcanes	arenes	alcanes	arenes
0	55.5	27.0	63.5	22.0
0.5	50.7	30.7	38.2	43.6
1	57.7	25.7	–	–
1.5	–	–	45.0	32.9

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A comparative analysis of the data presented in Tables 1 and 2 shows the following: the introduction of ϵ -caprolactam in the dewaxing process in the amount of 0.5 wt % allows reducing the aromatic hydrocarbons consumption from a slack wax; arenes concentrations in deparaffinizing raffinates are increasing; the raffinizing aromatic and/or branched structures contents are increasing. The latter is particularly evident in obtaining basic oil from distillate VD-3. However, if the consumption of ϵ -caprolactam (>1 wt %) is higher, the separation selectivity is reduced, apparently due to the increase in dissolving ability of the system acetone – toluene (ϵ -caprolactam) in relation to different structures.

As a result, when more viscous raffinate from VD-3 is dewaxed, the yield of the slack wax is somewhat reduced: from 9.1 to 8.9%; the raffinate yield from VD-2 increases from 12.4 to 15.2%.

Conclusion. Thus, the use of deparaffinizing raffinates when dewaxing ϵ -caprolactam as an additive modifier by the method of low-temperature crystallization of allows you to increase the efficiency of the process due to a more selective separation of paraffin hydrocarbons, the main component of the slack wax.

Improving the process does not require significant changes in the equipment design and significant cost of the additive, as its consumption does not exceed 1.5 wt % and it is produced in industrial scale at JSC “GrodnoAzot” (Grodno, Belarus).

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