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INFLUENCE OF DISPERSING ADDITIVES AND BLEND COMPOSITION ON STABILITY OF MARINE HIGH-VISCOSITY FUELS

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The article offers a definition of the stability of marine high-viscosity fuel from the point of view of the colloid-chemical concept of oil dispersed systems. The necessity and importance of the inclusion in the current regulatory requirements of this quality parameter of high-viscosity marine fuel is indicated. The objects of the research are high-viscosity marine fuels, the basic components of which are heavy oil residues: fuel oil that is the atmospheric residue of oil refining and viscosity breaking residue that is the product of light thermal cracking of fuel oil. As a thinning agent or distillate component, a light gas oil was taken from the catalytic cracking unit. The stability of the obtained samples was determined through the xylene equivalent index, which characterizes the stability of marine high-viscosity fuel to lamination during storage, transportation and operation processes. To improve performance, the resulting base compositions of high-viscosity marine fuels were modified by introducing small concentrations (0.05 % by weight) of stabilizing additives based on oxyethylated amines of domestic origin and alkyl naphthalenes of foreign origin.
Keywords: marine fuels, additives, mazut, viscosity breaking residue, light gas oil, oil dispersed systems, xylene equivalent

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Introduction. The main regulatory document for the production of marine fuels worldwide is ISO 8217, and in Russia it is GOST 32510-2013 «Marine Fuels», developed on the basis of ISO 8217. In addition, since 1990 in the Russian Federation there are fuels TU 38.1011314 «High-viscosity marine fuel» and TU 38.101567 «Low-viscosity marine fuel»(developed by the Ufa Oil Institute, VNII NP and the Central Scientific Research Institute of Maritime Transport, St.Petersburg). Low-viscous and highly viscous marine low-pressure fuel have undergone state tests in bench and operating conditions and are approved for use in ship power plants. In their qualities they are not inferior to the requirements of ISO 8217, and for a number of indicators even exceed the requirements of the foreign standard.

Since July 2017, a new version of the ISO 8217 standard has come into force, while the requirements for ship residual fuels remained practically unchanged. However, the number of problems with their quality have not decreased in recent years [12]. With advancements in oil processing, the resources of fuel oil are reduced, which necessitates its replacement in the composition of ship residual fuels with tar or residues of thermodestructive processes. On the ships there were problems related to the high content of tar-asphaltene in fuel, high values of coking ability, instability of fuels, resulting in the formation of sediments in tanks and the fuel system. The combustion of fuels has worsened, the deposits in the combustion chamber and the exhaust path have increased [1, 13].

In this regard, a number of international oil companies have been working on the creation of marine fuels with improved environmental and operational properties, with the use of hydrocatalytic processes, in addition to thermodestructive ones. Such companies, for example, include Shell (USA) with the technology of obtaining low-sulfur ship high-viscosity fuel based on mazut (from 50 to 90 %) and distillate diluents with ultra-low sulfur content [9].

In 2016, ExxonMobil company proposed a method for producing ship bunker fuels, which contains 50-70 % of the hydrotreated vacuum residue in a mixture with diesel distillates [10], and the French Petroleum Institute in 2015 proposed mixing vacuum distillates and residues that had passed successive hydrotreatment processes and «hybrid» hydrocracking [11].

There are some papers devoted to the generalization of technologies for oil processing using various combinations of processes of thermodestructive and hydrocatalytic processing [2, 5].

The fuel mixture obtained by the technology of thermodestructive and hydrocatalytic processing must have a finely dispersed structure and be stable. Stability characterizes the ability of marine fuel to maintain its composition and basic properties during storage, transportation without delamination and use without precipitation. The loss of stability of the mixture is manifested in the formation and precipitation (sedimentation) of the sediment. The main reason for the loss of stability is the incompatibility of the components of the mixture used for fuel preparation. Loss of stability is also observed with prolonged storage of the fuel mixture.

According to the colloid-chemical concepts, ship fuel is a multicomponent mixture, it depends on the set of external factors and properties of the disperse system, where the resinous asphaltene substances, paraffins or specially introduced synthetic additives act as dispersed phase, and the dispersion medium is the set of other non-polar or low-polar hydrocarbons [7].

The stability of these colloidal systems is determined by the thickness of the solvation shell of asphaltenes, which is a structural-mechanical barrier that prevents the association of asphaltenes [3]. In the straight-run residues, the adsorption layer is the tar and aromatic hydrocarbons assigned to the unit of asphaltenes, which is 16 % in fuel oil and 9 % in tar oil, which makes the structure unstable. Asphaltenes are solids that are readily soluble in aromatic hydrocarbons. Depending on the hydrocarbon composition of the fuel, they are either in a colloidal-dispersed state (suspended) or precipitate in the form of a solid phase (sediment). In highly aromatic media, asphaltenes form stable and finely dispersed stable systems [6, 8]. Therefore, when obtaining ship fuels in oil refineries (refineries) or mixing their components with bunkering vessels, it is necessary to regulate the aggregate stability.

However, the ISO 8217 and GOST 32510-2013 standards do not regulate the issue of indicators responsible for stability (xylene equivalent) and compatibility (stain method) of mixtures, but ship fuel suppliers cannot but pay attention to these two important quality indicators. In this regard, special methods are needed to assess the stability of marine fuels.

Objects of research. Straight-run fuel oil, viscosity breaking residue from the light thermal cracking unit and light gas oil from the catalytic cracking unit were taken objects of research. Based on these components, taken in a certain mass ratio, four samples of high-viscosity fuel were prepared.

The hydrocarbon composition and its effect on the physical-chemical quality indices of light gas oil catalytic cracking were considered by the authors in [4].

Methods of research. The method for determining the xylene equivalent makes it possible to evaluate the stability against sedimentation for marine high-viscosity fuels, mazut and bitumen, and consists in dissolving the test residual fuel in a mixture of xylene and normal heptane with consequent research of drop of this mixture on a paper filter.

The xylene equivalent is the minimum volume fraction of xylene in a solution of normal heptane that does not form a ring in the center of the spot when the test fuel is dissolved.

The xylene equivalent is written in the form of a fraction, the numerator is the minimum xylene concentration in n-heptane, at which a ring appears inside the spot, and the denominator is the minimum xylene concentration in n-heptane, at which the ring inside the spot disappears. The xylene equivalent of not more than 25/30 is one of the criteria for the straight-run of residual fuels.

The tests were carried out in accordance with GOST 33288-2015 «Residual fuels. Definition of straight-run qualities. Method for determination of xylene equivalent» developed by JSC «VNII NP».

Experimental part. Stability of mixtures of straight-run fuel oil and viscosity breaking residue with a light gas oil of catalytic cracking compiled in a weight ratio (Table 1) were studied for stability.

Studies of mixtures of straight-run heavy fuel oil and a viscosity breaking residue with a light catalytic cracking gas oil containing 80 % aromatic hydrocarbons have shown that viscosity breaking-based mixtures, in contrast to straight-run fuel oil, are extremely unstable. The xylene equivalent is increased from 20/25 to 100, and the total precipitate is from 0.01 to 0.6 %. The use of flavored petroleum fractions, for example light catalytic cracking gas oil, as a thinning agent, gives positive results (Table 2).

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Table 1

Component composition of ship fuel samples

Components	Ratio of components, %			
	Sample 1	Sample 2	Sample 3	Sample 4
Straight-run mazut	50	–	50	–
Viscosity breaking residue	–	50	20	80
Light gas oil catalytic cracking	50	50	30	20

Table 2

Stability of samples of marine fuels based on the viscosity breaking residue and straight-run fuel oil with a light gas oil catalytic cracking

Quality indicators	Norm for stable fuel, not more than	Sample			
		1	2	3	4
Xylene equivalent, % by volume	25/30	20/25	< 100	40/45	60/65
Spot method	2	–	5	–	–
Total sediment, %	0.1	0.01	0.6	–	–

Table 3

The effect of dispersant additives on the stability of marine fuel

Xylene equivalent of fuel without additives, % by volume	The xylene equivalent of fuel with 0.05 % additive, % by volume	
	VNII NP 200 (Russia)	Bunkersol D (Amerod, USA)
30/35	25/30	25/30
35/40	35/40	30/35
55/60	50/55	45/50

Note. The norm for stable fuels not more than 25/30.

Table 4

Stability of mixed marine fuel

Components	Xylene equivalent of mixtures, %			
Straight-run mazut	70	55	50	40
Viscosity breaking residue	–	15	20	30
Distillate of secondary processes	30	30	30	30
Xylene equivalent, % by volume	25/30	35/40	40/45	55/60

Note. The norm for stable fuels is not more than 25/30.

According to expectations, mixtures of fuel oil of straight-run and light gas oil of catalytic cracking are stable – the xylene equivalent is 20/25, while mixing of the viscosity breaking residue with a light catalytic cracking gas oil leads to the formation of sediments.

The improvement of fuel stability can be achieved by adding stabilizing additives that keep tar-asphaltene substances in suspension state (Table 3).

Dispersing additives, sorbed on particles of tar-asphaltene substances, prevent their association and maintain these substances in a finely dispersed state, thereby increasing the physical stability of marine fuels.

Two dispersing additives were studied in the paper: foreign – Bunkersol D (Amerod, USA) and domestic fuel – VNII NP 200. The active substance of the foreign additive is nonionic surfactants based on oxyethylated amines, the main active ingredient of the domestic additive are alkylnaphthalenes.

However, if the fuel contains a significant amount of unstable components (xylene equivalent 55/60), then the use of an additive will not give a positive result. Additives of this type, along with stabilizing ones, contain a detergent component, so the initial concentration of the planned additive should be minimal. Otherwise, when introducing the increased amount of additive, the deposits will be washed out and build up on the filters, which can lead to a complete blockage of the latter.

To obtain a stable fuel, along with the introduction of an additive, it is necessary to select the optimum component ratio, the main rule of which is not to mix the straight-run components with heavy residual fractions having different densities. Table 4 shows the effect of such mixing on the stability of marine fuel.

Conclusion. The stability of marine ship high-viscosity fuels is determined with the help of the xylene equivalent index. According to the analysis results, mixtures of fuel oil of straight-run and light gas oil of catalytic cracking are stable and the xylene equivalent is 20/25, respectively, while mixing of the viscosity breaking residue with light catalytic cracking gas oil leads to the formation of sediments.

The effect of stabilizing additives, which active component is a nonionic surfactant based on oxyethylated amines, as well as alkylnaphthalenes, was determined. It was found that with the introduction of 0.05 % additive, the xylene equivalent of fuel mixtures with different content of catalytic cracking distillates is reduced, which indicates an increase in the stability of fuels

When mixing high-viscosity marine fuels, it is necessary to regulate their stability by selecting the nature and composition of the initial components and the concentration of the stabilizing additive introduced, taking into account the xylene equivalent values for the samples under study.

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