The process intensification in the last reactor of the unit with repeated-batch catalyst regeneration is achieved by reducing the pressure (to 0.7 to 1 MPa at the inlet of the last reactor); by maintaining moderate temperatures (not above 500°C) at the inlet of the main reactors with a bed of stationary catalyst KR-108; by raising the temperature at the inlet of the last reactor to 530 to 540°C; by maintaining constant catalyst activity in the last reactor by periodic regeneration in a separator regenerator; and by substituting the extruded catalyst in the last reactor by spherical catalyst.

Table 1 shows the process indexes before and after modernization of the unit. The approximate cost of modernization was 4 to 5 million rubles and the amortization period 2 to 2.5 years.

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MARINE FUELS FROM PRODUCTS OF DEEP PETROLEUM REFINING

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UDC 665.63.048:541.182

The development of commercial ship building in the USSR and the exploitation of ship's diesel engines abroad [1] is tightly related to the widening use of high-end-point distillate fuels in high-speed diesel engines (HSD) and of residual petroleum fuels in medium- (MSD) and low-speed diesel engines (LSD). Changes in the composition and structure of the petroleum fuels, noticed during the last ten years, related to the increasing depth of petroleum refining and its rational utilization [2], have created the need for the development of a standardized low-viscosity marine fuel (LMF) and a high-viscosity marine fuel in three grades, a light (HML), heavy (HMH), and superheavy (HMS) fuel, from the residues of the processing of crudes and middle distillates by thermodestructive processes, keeping the addition of straight-run products at a minimum.

The requirements placed before the standard grades of petroleum fuels for all types of modern marine diesel engines at a universal (world) standard level, are given in Table 1. The main fuel quality parameters for marine diesel engines are: the viscosity, which provides normal atomization of the fuel in the burners; the carbon residue, which characterizes the coking tendency of parts of the fuel-handling equipment; the ash content, which predicts the appearance of deposits in the fuel supply system.

In comparison with the L-0.5 diesel fuel according to GOST [All-Union State Standard] 305-82, intended mainly for high-speed diesel engines on land, the requirements placed before the low-viscosity marine fuel with respect to cetane number, sulfur content and mechanical impurities, carbon residue, ash content, and other parameters are less severe. Thus, the cetane number of the LMF fuel must not be lower than 40, while for the L-grade diesel fuel it must not be lower than 45; the sulfur content of the developed marine fuel can be as high as 1.5% instead of 0.5% in the case of the commercial diesel fuel.

Industrial samples of heavy residues were selected and thoroughly tested at the refineries of the "Bashneftekhimzavody" association; they were taken from atmosphere-vacuum pipestills, visbreaking, and propane deasphalting units: heavy resids from medium- and high-sulphur crudes, cracking resids and vacuum distillation concentrates, asphalts. Straight-run middle distillates and products of secondary processes (delayed coking, catalytic and thermal cracking) were used as diluents and structure and property modifiers of the petroleum resids.

According to the model in [3, 4] the petroleum fractions consist of complex structural units (CSU) with a nucleus consisting of supermolecular structures, surrounded by solvate shells and distributed in the liquid dispersion medium; the blending composition of the

TABLE 1

Index	Marine fuel, grade			
	LMF	HML	HMH	HMS
Nominal [Engler] viscosity, °E, not higher than				
at 20 °C	2	—	—	—
at 50 °C	—	5	—	—
at 80 °C	—	—	8	16
Cetane number, not lower than	40	—	—	—
Ash content, %, not higher than	0,01	0,05	0,12	0,15
Mass fraction, %, not higher than				
of mechanical impurities	0,02	0,1	0,3	0,6
of sulfur	1,5	2,5	3,5	5
Carbon residue, %, not higher than	0,2	7	15	22
Flash point, °C, not lower than				
closed-cup	62	61	—	—
open-cup	—	—	80	110
Solid point, °C, not higher than	—10	+5	+10	+25
Density at 20°C, kg/m³, not higher than	890	950	995	1015
Vanadium, mass %, not higher than	—	0,015	0,03	0,06

marine fuels was therefore based on the study of their colloidal structure by low-angle x-ray diffraction, optical microscopy, and the experimental determination of the most important physicochemical and performance properties of the fuels [5, 6].

As a result of the large volume of scientific research work in this field, carried out at the Ufa Petroleum Institute in collaboration with the New-Ufa Refinery, the All-Union Scientific-Research Institute for Petroleum Processing, the I. M. Gubkin MING, the TsNII MF, and other organizations, the LMF fuel was admitted for use on vessels of the sea and river fleets and on ships of the fishing industry of the Soviet Union with HSD, MSD, and gas turbine units, following the approbation of the results obtained in practice by the State Interdepartmental Commission. Besides the not hydrotreated straight-run diesel fraction boiling between 180-420° the fuel contains high-end-point middle distillates boiling up to 400-420° without preliminary desulfurization.

The significant content of products of secondary provenience in the fuel which contain polycyclic aromatic hydrocarbons, resins, and organic sulfur compounds intensifies the intermolecular interactions (IMI) and the formation of CSU and an interfacial layer on the metallic surfaces of the fuel-handling equipment and the engine, as well as at the interface between the phases in the fuel itself which affect the performance of the latter. Changes in the intensity of IMI and in the dimensions of CSU in real fuel dispersions with an optimum blending composition create the conditions for "liquid–solid" and "liquid–hydrocarbon vapor" phase transitions at the operating temperature in the fuel preparation system and in the engine.

Thus, the presence of cracking distillates together with straight-run fractions gives the fuel excellent lubricating, protective, anticorrosion, and low-temperature properties [7, 8]; it also gives the developed fuel significant technical and economical advantages over the diesel fuel according to GOST 305-82, used at present on the ships. The production of the LMF fuel on the industrial scale was organized at the New-Ufa refinery for the first time in the Soviet Union. The quality parameters of its first batches from serial production according to TU 38.101567-87 and some performance characteristics are given in Table 2. The production of this fuel releases hydrotreating capacities, increases the selection of light petroleum products, and expands the resources of diesel fuels. As a result of this the depth of petroleum processing can be increased by more than 3%.

On the other hand, the high-viscosity marine fuels approach, according to their main quality parameters, the DT, DM, and DTp motor fuels, the F-5 and F-12 fleet fuels, and the exported M-2.5 boiler fuels and grade 40 and 100 heating fuels, used in ship's power units. Due to the introduction into the composition of high-viscosity marine fuels of resids from deep petroleum processing, including those from secondary processes, the principles of compounding of heavy resids with a distillate diluent, which in this case acts as a structure modifier, have changed. Besides this, the need arose of studying the mechanism of structure formation in dispersed petroleum systems (DPS). According to [5-12], the change in the number and dimensions of CSU and the modification of the colloid-chemical properties of DPS when heavy resids are added to distillates is attributed to the adsorption of surfactant molecules at the interface and to their association when a critical surfactant concentration in the solution is reached.

In the region of low resid concentrations in the mixture asphaltenes are mainly adsorbed at the interface between the nuclei of the wax crystals in the gas oil fraction; as a

TABLE 2

Index	Sample of low-viscosity marine fuel		
	1	2	3
Viscosity at 20°C			
nominal [Engler], °E	1,2	1,45	1,54
kinematic, mm^2/sec	3	5,7	6,6
Cetane number	48	46	43
Sulfur content, %			
total	1,23	1,45	1,5
mercaptan	0,0069	0,0084	0,014
Carbon residue, %	0,13	0,18	0,2
Mechanical impurities, %	0,017	0,020	0,018
Ash content, %	0,007	0,008	0,01
Flash point (closed-cup), °C	70	74	88
Solid point, °C	—12	—10	—10
Density at 20°C, kg/m^3	876	879	887
Iodine number, g I_2/100 g	10,4	12,6	18,7
Lubricating properties (on four-ball tester): P_{cr}, N	400	500	540
Corrosion (at water condensation, GOST 18597-73), g/m^2	0,5	0,9	1,1

result of this, the IMI between the wax crystals is weakened significantly. When the critical saturation concentration of the asphaltenes in the solution is reached, they start to form associates [10-12]. At concentrations above the critical concentration, aggregation of the asphaltene structural units takes place which, due to the increase in size, are desorbed from the interface between the phases to form structures in the bulk of the solution, creating a microheterogeneous system [5, 6, 10-12]. This is confirmed by a decrease in the number and an increase in the size of CSU nuclei (Figs. 1 and 2), as determined by low-angle x-ray diffraction analysis, and also by deep changes in the colloidal properties of the discussed systems.

The study of DPS by low-angle x-ray diffraction allowed us to determine the dimensions of the CSU and to establish the exponential character of their distribution with respect to size in actual fuel formulations. The data obtained indicate the presence of structural units with different degrees of dispersion and, consequently, the occurrence of complex competing processes of the formation and destruction of microstructures in such systems. Curves were obtained representing the relative content and the mean size of the CSU nucleu as function of the resid concentration in the DPS (see Figs. 1 and 2), calculated from the experimental distribution curves.

The distribution of CSU according to size in real fuel compositions is determined not only by the concentration and structure of the high molecular components of petroleum resids (asphaltenes, resins, and solid paraffinic hydrocarbons), but also by the hydrocarbon composition of the dispersion medium of the resids and distillates. The surface tension of model and petroleum asphaltene-containing dispersed systems at the interface with air shows the presence of two inflection points on the interfacial tension isotherm $\sigma = f(\log C)$ and consequently of two critical concentrations, at which phase transitions of the high molecular compounds take place.

At the saturation concentrations the surface and bulk properties of DPS change sharply, due to associate formation and due to a change in the size of the CSU nuclei and in the thickness of the absorbed-solvated layer [5-12]. Thus, an increase in the relative content of CSU with nuclei of 10, 30, and 60 nm in dilute solutions (10-20% resid in the mixture) indicates weak IMI of the asphaltene structural units with similar structures; the decrease in the surface tension and the solid point of middle distillates (Fig. 3) manifests an adsorption-surface mechanism of the modification of the microstructure and properties of DPS in the presence of small amounts of heavy resids. The appearance of a second extremum on the curve, showing the dependence of the solid point of the distillate on the amount of resid added (more than 20%), is evidently due to an increased dissolving power of the dispersion medium and to a partial dispersion of the nucleus, leading to the formation of smaller CSU.

According to the concepts in [7, 12] the formation of an interfacial protecting layer on the metallic surfaces of the fuel-handling equipment and the engine is also caused by surface phenomena. The thickness and properties of this layer change radically under the influence of external effects. In spite of the higher sulfur content (from 1.5 to 5%) the marine fuels have better anticorrosion properties than the hydrotreated commercial diesel fuel with 0.5% sulfur; this is due to the concentration and structure of the resins, sulfur compounds, and polycyclic aromatic hydrocarbons, as well as to the thickness and composition
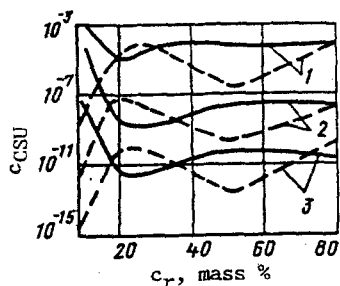
Fig. 1. Relative CSU content c_{CSU} in mixtures of a gas oil cut from delayed coking with a residue as function of the residue content c_r: ---) vacuum resid; —) cracking resid; 1, 2, 3) CSU with a nucleus having a radius of 10, 30, and 60 nm respectively.
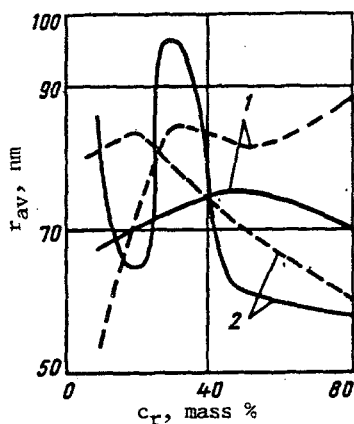

Fig. 2. Mean radius r_{av} of the CSU nucleus in mixtures of a straight-run diesel oil fraction from West-Siberian crude (solid curves) and a gas oil fraction from delayed coking (broken curves) with a residue as function of the residue content c_r: 1) vacuum resid, 2) cracking resid.

of the boundary layer and, consequently, to the size and number of its structural units. Thus, a synergistic effect has been achieved by the proper selection of the fuel composition. The proposed mechanism for the modification of the microstructure and properties of DPS is also confirmed by investigations of the structural and mechanical properties of fuel formulations with heavy resids in a wide interval of temperatures and loads. An analysis of structurization in real DPS [12] by means of rheological and thermodynamic activation parameters of viscous flow (ΔH, ΔG, ΔS) showed that heavy resids and their high molecular components (asphaltenes and resins) modify the paraffinic structure of the fuel and thus suppress the anomalous non-Newtonian flow of its distillate component in the whole temperature interval, to form a coagulation structure with different strength and binding energy.

At low (5-10%) and high (higher than 20%) residue concentrations in the mixture a quasi-Newtonian flow is observed. It is caused in the first case by the adsorption of asphaltenes on crystals of paraffinic hydrocarbons, followed by weakening of the crystallization structure. In the second case it is caused by the formation of a coagulation-like three dimensional structure in the DPS. However, aggregation of asphaltenes leads to an in
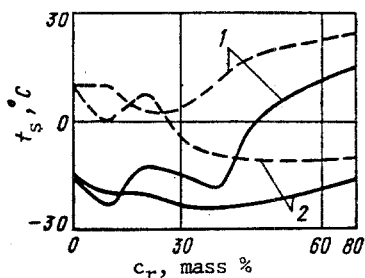
Fig. 3. Solid point t_s of mixtures of a straight-run diesel oil fraction (solid curves) and of a gas oil fraction from delayed coking (broken curves) with a resid as function of the resid content c_r; see Fig. 2 for denotations.
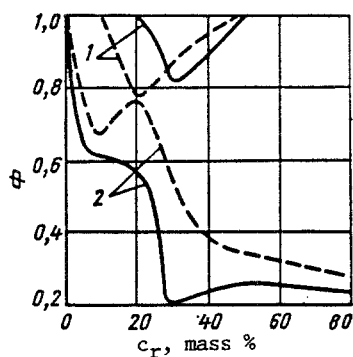

Fig. 4. Aggregate stability factor F of mixtures of a straight-run diesel fuel fraction (solid curves) and of a gas oil fraction from delayed coking (broken curves) with a resid as function of the resid content c_r; see Fig. 2 for denotations.

TABLE 3

Index	High-viscosity marine fuel		
	HML	HMH	HMS
Nominal [Engler] viscosity, °E			
at 50 °C	5	—	—
at 80 °C	—	7	15
Ash content, %	0,02	0,085	0,1
Content, %			
of mechanical impurities	0,05	0,14	0,3
of sulfur	2	2,5	3,6
of vanadium	0,005	0,012	0,02
Carbon residue, %	5	11	15
Flash point, °C			
closed-cup	61	—	—
open-cup	—	90	110
Solid point, °C	—5	0	+10
Density at 20°C, kg/m³	930	960	980
Stability factor	0,67	0,55	0,35
Corrosion (at water condensation) GOST 18597-73, g/m²	0,34	0,5	1,2

crease in size of the structural units, thickening of the system, and viscous flow. The change in the character of flow of the investigated DPS from non-Newtonian to quasi-

Newtonian, and then again to anomalous viscous flow when the temperature is increased from -20 to 100°C is also attributed to phase transitions in the fuel formulations.

The intensive phase formulation leads to a coarsely dispersed system with a characteristic tendency towards aggregate instability [4, 5]. The result is precipitation of the dispersed phase and layering (phase separation) of the system when the density of the newly formed phase is higher than the density of the initial phase. The stability of the fuel formulations obeys the general rules governing the formation of OSU in DPS, their structure, the size of the supermolecular structures, and the character of their change; this has been established experimentally.

The stability factor F of fuel formulations as function of the residue content is in good agreement with the change in the mean size of the CSU nucleus (Fig. 4). The size of the CSU nucleus is at a maximum and the stability to phase separation at a minimum for DPS containing 20-30% petroleum resid. The lower stability of fuels containing a cracking resid in comparison with fuels based on vacuum resids is due to differences in their colloidal structure and in the distribution of CSU according to size.

The colloidal structure of high-viscosity marine fuels, representing mixtures of a kerosene-gas-oil fraction KGF from delayed coking with a cracking resid, is based on particles, the nucleus of which is larger (8-17 nm) than in the case of formulations with a vacuum resid (1-8.5 nm). The number of such particles is higher than of particles with a nucleus having a radius of 60-80 nm by 6-7 orders of magnitude in the case of mixtures with a cracking resid and by 9-10 orders of magnitude in the case of mixtures with a vacuum resid.

Besides this, fuel formulations with a cracking resid, particularly those based on a straight-run diesel fraction, are characterized by a stronger dependence of the mean radius of the CSU nucleus on the resid concentration in the mixture (see Fig. 2). In the case of the corresponding mixtures with the vacuum resid the radius of the nucleus changes more uniformly. For instance, the mean size of the CSU nucleus at the extremum (at 30% cracking resid in a straight-run diesel fraction) is larger by almost a factor of 1.4 than at the same concentration of a vacuum resid in the mixture, while the stability factor is higher in the latter case by a factor of 4.

However, the stability of DPS cannot by explained only by the geometrical dimensions of the CSU present; it also depends on the molecular structure, the chemical and hydrocarbon composition of the dispersed phase and of the dispersion medium, and their mutual solubility, which cannot be estimated by low-angle x-ray diffraction. Thus, the better dissolving power of the kerosene-gas-oil fraction from delayed coking than that of the straight-run diesel fraction is the cause of the partial dispersion of CSU and of the more uniform change in their size in the bulk of the fuel, i.e., of the higher aggregate stability of the mixture (see Fig. 4). The total decrease in the kinetic stability of DPS by almost a factor of 3 at cracking resid concentrations of 20-30% is caused not only by the CSU size and the asphaltene content (which is higher by almost a factor of 2 than in the vacuum resid), but also by a poorer solubility of the resids from secondary processes and of their high-molecular components which have undergone a deeper aromatization and condensation [10, 11].

By taking into account the correlations with one or more extrema of the relative content and size of CSU, and of the properties of DPS with the concentration of heavy resids in straight-run and secondary distillates, we have developed the compositions for standardized grades of high-viscosity marine fuels. Based on mixtures of middle distillates with 10-20% resid, HML-grade high-viscosity marine fuels can be obtained with a solid point not higher than 5°C, a nominal [Engler] viscosity at 50°C of not higher than 5°E, and a sufficiently high resistance to phase separation (F = 0.6-1). Mixtures with 20-50% resid are recommended for the blending of HMH and HMS grades: viscosity at 80°C not higher than 8 and 16°E; solid point not higher than 10 and 25°C respectively; the stability factor and the other characteristics satisfy the performance requirements.

The quality parameters of test batches of high-viscosity marine fuels, prepared at the New-Ufa refinery, are given in Table 3. The tests batches of fuels for medium- and low-speed diesel engines have passed with positive results the laboratory and pilot-plant tests, as well as the tests on ships of the Maritime Ministry of the USSR. Their commercial production is now being organized. The rational utilization of products from deep petroleum processing increases the efficient utilization of the fuel and energy resources of the national economy, renews the assortment and shortens the range of fuels used by the navy; it also increases the depth of crude processing at some refineries of the Branch by an average of 5% by reducing the fraction of heating resids in the general balance.

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STABILIZATION OF LIGHT CATALYTIC GASOIL

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UDC 665.7.035.5

The expanded role of catalytic cracking in the fuel balance has brought about an increase in the relative amount of middle distillates from secondary processing. These products, because of low octane number and unsatisfactory chemical and thermooxidative stability, are commonly used as components of furnace oils, marine fuels, and gas-turbine fuels; such use is never advantageous from the economic standpoint. Increasing emphasis is being placed on the utilization of light catalytic gasoil (LCGO) as a component of diesel fuel [1-3]. In this connection, it is of interest to investigate the stability of LCGO and its blends with straight-run diesel fuel (SDF).

The formation of precipitate and resins in unstable middle distillates very often fails to follow the laws of free-radical oxidation [4] that had been thoroughly studied in the example of gasolines and naphthas; from this point of view, the behavior of unstable middle distillates is a matter of independent scientific interest. Moreover, results obtained in studies of the stability of products obtained in destructive processing of petroleum feedstocks may be useful in investigating the extremely unstable hydrocarbon fractions obtained from nonpetroleum sources, for example by the liquefaction of coals and oil shales. Within the visible future, these products will find application as fuel components.

The stability of LCGO from the G-43-107 cat cracker at the Moscow Petroleum Refinery, alone and in blends with SDF, were investigated by heating fuel samples for 16 h at 100°C in air in the presence of a copper strip. This test method is included in the set of methods for qualification testing of diesel fuels [5]. After oxidation, the fuel sample is analyzed to determine the quantity of insoluble precipitate, acidity, existent gum content, and color (TsNT colorimeter).

Tests were performed on three samples of LCGO taken from the cat cracker at different times. The characteristics of these LCGO samples and the SDF sample are given in Table 1. A distinctive feature of the LCGO is its high content of aromatic compounds, amounting to 60-80%. At the same time, the concentration of unsaturated hydrocarbons, as determined by iodine number, is comparatively low. The LCGO differs from the SDF in content of bicyclic and tricyclic aromatic hydrocarbons. For example, the content of naphthalene derivatives in the