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Introduction of heavy diesel fractions of primary and secondary refining processes in the production of light oil products

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Abstract: *In order to increase the yield of light oil products, it is proposed to use the following heavy fractions obtained by JSC Angarsk Petrochemical Company in the course of oil refining as components for low-viscosity marine fuel: light coker gas oil, heavy diesel fractions removed from vacuum columns of primary-oil-refining units, heavy diesel fractions obtained from atmospheric columns and vacuum distillates of various fractional compositions. The results of tests conducted according to standardised procedures showed that an introduction of depressor (VES-410D) and depressor-dispersing (VES-410DDP) additives into the components of low-viscosity marine fuel significantly depresses the pour points of these components. In this article, the authors propose depressor and depressor-dispersing additives, as well as determine their optimal concentrations for high depression rates allowing the pour point to be reduced to a standardised value for the compound composition using heavy diesel fractions of primary and secondary refining processes. In addition, the authors determined the optimal basic formulation of the low-viscosity marine fuel including products of primary and secondary oil processing with heavy fractional composition. A number of commercial depressor-dispersing additives were tested using this basic formulation in order to explore alternatives and study the additives market. Five of these commercial additives provide good chemmotological indicators for low-viscosity marine fuel (including low-temperature characteristics, filterability and sedimentation stability) and can be recommended for further industrial use. The optimal composition of the mixtures was modelled on the basis of the obtained data, allowing a determination of the most rational technology for producing low-viscosity marine fuel in conformity with regulatory requirements.*

Keywords: *low-viscosity marine fuel, pour point, heavy diesel fractions, diesel fraction of delayed coking, light catalytic gas oil, depressor and depressor-dispersing additives*

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Вовлечение тяжелых дизельных фракций первичного и вторичного происхождения в производство светлых нефтепродуктов

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Резюме: *С целью увеличения выхода светлых нефтепродуктов в качестве компонентов топлива маловязкого судового предложено использовать тяжелые фракции переработки нефти АО «Ангарская нефтехимическая компания»: легкий газойль замедленного коксования, тяжелые дизельные фракции с вакуумных колонн установок первичной переработки нефти, утяжеленные дизельные фракции с* *атмосферной колонны и вакуумные дистилляты различного фракционного состава. По результатам испытаний, проведенным по стандартизированным методикам, установлено, что введение депрессорной (ВЭС-410Д) и депрессорно-диспергирующей (ВЭС-410ДДП) присадок в компоненты топлива маловязкого судового значительно снижает температуру застывания компонента и дает высокие, положительные показатели депрессии. Предложены депрессорные и депрессорно-диспергирующие присадки, найдены их оптимальные концентрации, позволяющие снизить температуру застывания до нормируемой величины и получить высокие, положительные показатели депрессии для компаундируемого состава с применением тяжелых дизельных фракций первичного и вторичного происхождения. Подобрана оптимальная рецептура базовой основы топлива маловязкого судового с вовлечением продуктов первичной и вторичной переработки нефти утяжеленного фракционного состава. На данной базовой основе в рамках повышения альтернативности выбора и изучения рынка присадок был испытан ряд товарных депрессорно-диспергирующих присадок, пять из которых позволяют достигнуть хороших химмотологических показателей для топлива маловязкого судового, в том числе по низкотемпературным характеристикам, коэффициенту фильтруемости и седиментационной устойчивости, и могут быть рекомендованы для их дальнейшего промышленного использования. Полученные данные позволяют моделировать оптимальный состав смесей и определять наиболее рациональную технологию получения топлива судового маловязкого, соответствующего нормативным требованиям.*

Ключевые слова: *топливо судовое маловязкое, температура застывания, тяжелые дизельные фракции, дизельная фракция коксования, легкий газойль каталитического крекинга, депрессорные и депрессорно-диспергирующие присадки*

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INTRODUCTION

One of the most urgent problems facing the modern oil refining industry consists in the need to increase refining depth. The technical level of most oil refineries in the Russian Federation currently fails to comply with the most advanced contemporary global standards. The main problem here consists in the low refining depth achieved by its domestic refining industry (Russia – 72%, Europe – 85%, USA – 96%). In recent years, research interest has been directed towards the use of petroleum products of secondary refining processes as fuel components, since the technological development of these chemical processes will significantly improve the key economic indicators of oil refineries, such as the Nelson index, sales profitability and refining depth[1] [1].

Low-viscosity marine fuel (LMF) is one of the high-volume products of JSC Angarsk Petrochemical Company (JSC APCC) produced in accordance with TU 38.101567-2014 "Low-viscosity marine fuel. Technical requirements".

LMF intended for use in ship power plants is produced from fractions obtained via straight-run distillation as well as secondary oil and gas condensate refining processes[1] [1, 2]. Unlike diesel fuel, LMF has a lower cetane number and is characterised by fewer restrictions on density, viscosity, sulphur mass fraction and iodine number. However, LMF has similar requirements to diesel in terms of its low temperature properties (Table 1). In accordance with the approved technology of JSC APCC, the following components were used in LMF production until 2016:

1. Straight-run middle-distillate fractions, including distillates of heavy fractional composition, obtained in the process of atmospheric distillation of desalted crude oil;
2. Light gas oil, obtained in the course of catalytic cracking of a mixture of vacuum distillates;
3. Hydrotreated middle-distillate fractions, obtained by hydrotreating a mixture of diesel fractions of different origin and coker gasoline;
4. Distillation residues obtained in the process of atmospheric-and-vacuum distillation of the hydrogenated product collected from units for hydrogenating primary and secondary heavy middle-distillate fractions;

[1] Элверс Б., Альфке Г. [и др.]. Топлива. Производство, применение, свойства: справочник / пер. с англ. под ред. Т.Н. Митусовой. СПб.: Профессия, 2012. 416 с. / Elvers B. *Handbook of Fuels. Energy Sources for Transportation*. Weinheim, 2008 (Russ. Ed.: Elvers B., Al'fke G. [et al.]. *Fuels. Production, application and properties*. St. Petersburg: Professiya Publ., 2015. 416 p.)

5. A middle-distillate fraction of slop oil (MDF-SO) obtained via atmospheric distillation;6. A diesel fraction obtained in the process of delayed coking (DF-DC) of a mixture of tar, heavy catalytic gas oil and heavy pyrolysis pitch.

However, the need to increase refining depth and marginal profits drives the interest in developing new fuel compositions on the basis of existing petroleum feedstocks.

Such oil refinery products as:

7. Light coker gas oil (LCGO);

8. Heavy diesel fractions obtained from vacuum columns (HDF-VC) of primary processing units;

9. Heavy diesel fractions obtained from atmospheric columns (HDF-AC);

10. Vacuum distillates of different fractional composition were not used in LMF production prior to our research [3].

In this connection, the present work was aimed at studying the possibility of using diesel fractions of primary and secondary refining processes as components of light oil products. On the basis of this study, the optimal formulation of the LMF base, including heavy fractions obtained in the course of oil refining and depressor-dispersing additives, was determined.

EXPERIMENTAL PART

In this research, we studied LMF along with heavy fractions obtained in the course of oil refining as components for its preparation.

The hydrocarbon composition of components was calculated using data collected when determining:

– the aniline point (according to GOST 11065);

– the combined mass fraction of unsaturated and aromatic hydrocarbons (according to GOST 6994-74), obtained by treating the oil product under test with 98.5–99.0% H_2SO_4;

– the iodine number (in accordance with GOST 2070, method A), expressed in grammes of iodine absorbed by 100 grammes of an oil product in the course of titrating free iodine with a sodium thiosulphate solution following treatment of the oil product with an iodine alcoholic solution.

The density of the samples was determined in accordance with GOST 3900 using a TLC-3 thermostatic apparatus by immersing a hydrometer in the test product at a temperature of 20 °C. The sulphur content was assessed according to GOST R 51947 using a Lab-X3500 XRF analyser by placing the test sample in a cone of rays emitted by an X-ray source; measuring the excitation energy; and comparing the resulting impulse counter readings with the counter readings taken when testing calibration samples prepared in advance. Kinematic viscosity was determined in accordance with GOST 33 as a product of the viscometer constant and the flow time of a certain volume of an oil product under the influence of gravity at a known and continuously monitored temperature using a VIS-T-09-3 liquid thermostat and a VPZH-4 capillary glass viscometers. The closed-cup flash point was determined according to GOST R EN ISO 2719 as the lowest temperature at which the ignition source causes the vapours of the oil product to ignite and spreads the flame over the surface of the liquid using a Pensky Martens HFP 339 Flash Point Analyzer.

Low-temperature properties of the fuel and its components were determined as follows:

– the pour point was established by preheating the oil test sample, followed by cooling at a given rate to a temperature at which the sample loses its flow characteristics using an LZN-75 apparatus (according to GOST 20287). The resulting temperature was defined as the pour point;

– the cloud point was established using an LTZ unit, in which the fuel test sample was cooled with the help of cooling mixtures, as well as by visual comparison of the cooled sample with the reference sample, followed by registration of the cloud point (according to GOST 5066);

– the cold filter plugging point (CFPP) was established by gradually cooling the fuel test sample at intervals of 1 °C using an apparatus in which the sample was drawn through a wire mesh filter at a vacuum of 1961 Pa. This process of determination continued until the quantity of paraffin crystals released from the solution onto the filter caused stoppage or slowing down of the fuel flow to the extent that pipette filling time exceeded 60 s or the flow of fuel back into the measuring vessel ceased completely (according to GOST 22254).

The LMS was also assessed according to filterability (according to GOST 19006) and sedimentation stability parameters (according to STR 11605031-041-2010, developed by VNII NP). The filterability factor was estimated on the basis of a change in the filter capacity when a certain amount of fuel was passed through it (using a PFDT-2M apparatus). Sedimentation stability was estimated on the basis of a visual assessment of the distribution of paraffin in the fuel layer as well as the difference between the upper and lower parts of the fuel sample in terms of the cloud- and cold filter plugging points as compared to the initial data. If the cloud- and cold filter plugging points of the upper and lower parts of the fuel sample do not differ by more than ±2 °C as compared to the initial data, then the fuel is considered stable and the use of a depressor additive can be recommended [4–9].

RESULTS AND DISCUSSION

The possibility of using heavy fractions obtained in the course of oil refining as LMF components (items 7–10) is demonstrated. A comparison of the physical and chemical properties of the above-mentioned LMF components (items 7–10) with those of the currently used components (items 1–6) allowed us to identify key parameters exceeding the requirements for LMF (Table 1).

Table 1

Physical-chemical and chemmotological parameters of LMF and its components

Таблица 1

Физико-химические и химмотологические показатели ТМС и компонентов, используемых в рецептуре его приготовления

Component			Density at 15 °C, kg/m^3	Mass fraction of sulphur, %	Pour point, °C	Closed-cup flash point, °C	Kinematic viscosity at 20 °C, mm^2/s	Combined mass fraction of hydrocarbons, reacted with H_2SO_4, %	Iodine number, grammes of iodine per 100 g of liquid	Aniline point, °C	Calculated content of unsaturated hydrocarbons, %	Calculated content of aromatic hydrocarbons, %
LMF (according to TU 38.101567-2014)			not more than 893	type I – ≤ 0.5 type II – ≤ 1.0	not more than -10	not less than 61	not more than 11.4	not specified	not more than 20	not specified	not specified	not specified
Components for preparing LMF, used according to technology until 2016	1	straight-run middle-distillate fractions:										
	–	GK-3 unit	851	0.31	-19	82	5.3	24.0	1.1	66.0	0.9	23.1
	–	ELOU-AVT-6 unit	869	0.49	-3	85	11.4	25.0	1.4	71.1	1.3	23.7
	2	light catalytic gas oil	946	1.16	-46	71	2.8	79.0	12.1	–	9.8	69.2
	3	hydrotreated middle-distillate fractions	841	0.0009	-17	60	4.5	0.4	0.5	67.6	0.4	0
	4	distillation residue	833	0	0	146	10.8	2.0	0.7	92.3	0.7	1.3
	5	MDF-SO	829	0.25	-59	47	1.8	31.0	5.8	46.5	4.5	26.5
	6	DF-DC	852	0.59	-50	59	1.9	43.2	45.3	48.8	43.2	0
Components proposed for preparing LMF	7	LCGO	899	1.03	-4	109	11.0	54.0	24.2	56.2	23.1	30.9
	8	HDF-VC	870	0.50	-4	91	11.8	25.0	1.4	71.1	1.4	23.6
	9	HDF-AC:										
	–	GK-3 unit	861	0.37	-27	85	4.5	32.0	2.3	59.2	2.2	29.8
	–	ELOU-AVT-6 unit	892	0.67	13	132	26.8	28.0	3.3	73.1	3.5	24.5
	10	vacuum distillate	903	0.71	11	169	28.7	32.0	3.0	72.8	3.2	28.8

These parameters include density at 15 °C, mass fraction of sulphur, kinematic viscosity at 20 °C for LCGO, HDF-AC and vacuum distillates. However, according to the requirements, the LMF pour point must not exceed -10 °C. The use of the components specified in items 7–10 will undoubtedly lead to inconsistencies. The solution to the problem lies in the use of depressor and depressor-dispersing additives, aimed at lowering the pour point, improving the mobility of oil products at low temperatures and ensuring sedimentation stability[2] [10–15].

In order to ascertain the effectiveness of depressor and depressor-dispersing additives for LMF, two additives produced by the Angarsk Plant of Catalysts and Organic Synthesis – VES-410D depressor additive and VES-410 depressor-dispersing additive – were added in the amount of 300 ppm to each of the studied components (Table 2). It was established that the introduction of depressor and depressor-dispersing additives into the fuel components significantly reduces their pour points (Table 2) and supports high positive depression rates (Fig. 1). The highest responsivity to both additives is observed for heavy straight-run fractions (straight-run middle-distillate fractions from GK-3

[2] Папок К.К., Рагозин Н.А. Словарь по топливам, маслам, смазкам, присадкам и специальным жидкостям; 4-е изд., перераб. и доп. М.: Химия, 1975. 392 с. / Papok K.K., Ragozin N.A. *Slovar' po toplivam, maslam, smazkam, prisadkam i spetsial'nym zhidkostyam* [Dictionary of fuels, oils, lubricants, additives and special liquids]. Moscow: Khimiya Publ., 1975. 392 p.

and ELOU- AVT-6 units; HDF-AC from GK-3 and ELOU-AVT-6 units; HDF-VC; vacuum distillates), whereas the lowest responsivity was ascertained for fractions resulting from secondary processes (light catalytic gas oil, distillation residue, MDF-SO, LCGO) [3].

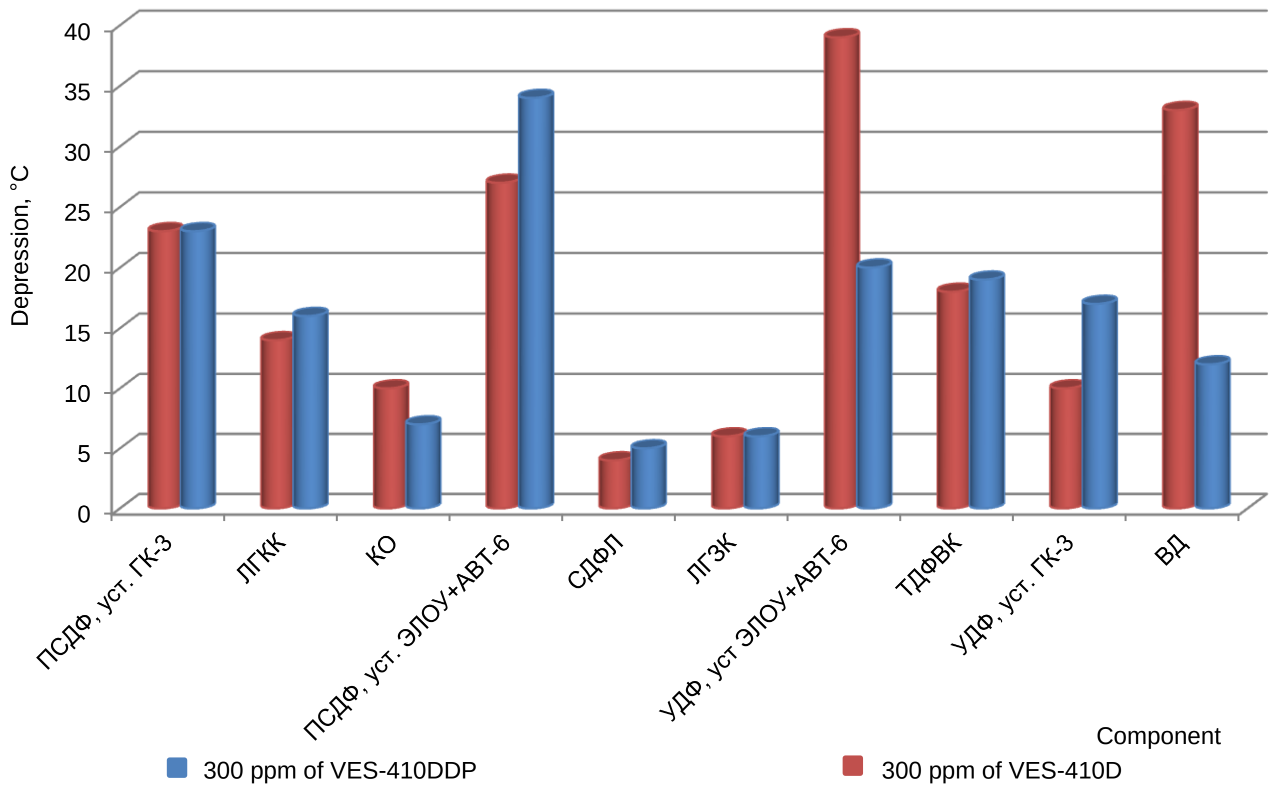
Table 2

Pour point of components with or without additives

Таблица 2

Температура застывания компонентов исходного и при введении присадок

Component No. according to Table 1	Component	Pour point, °C		
		initial	depressor additive VES-410D	depressor-dispersing additive VES -410DDP
1	straight-run middle distillate fractions:			
–	GK-3 unit	-19	-42	-42
–	ELOU-AVT-6 unit	-3	-30	-37
2	light catalytic gas oil	-46	-60	-62
4	distillation residue	0	-10	-7
5	MDF-SO	-59	-63	-64
7	LCGO	-4	-10	-10
8	HDF-VC	-4	-22	-23
9	HDF-AC:			
–	GK-3 unit	-27	-37	-44
–	ELOU-AVT-6 unit	13	-26	-7
10	vacuum distillate	11	-22	-1



ПСДФ, уст ГК-3 – straight-run middle-distillate fractions, GK-3 unit light catalytic;
ПСДФ, уст. ЭЛОУ+АВТ-6 – straight-run middle-distillate fractions, ELOU-AVT-6 unit;
УДФ, уст. ЭЛОУ+АВТ-6 – HDF-AC, ELOU-AVT-6 unit;
ТДФВК – HDF-VC;
ЛГКК – gas oil;
КО – distillation residue;
СДФЛ – MDF-SO;
ЛГЗК – LCGO;
УДФ, уст ГК-3 – HDF-AC, GK-3 unit;
ВД – vacuum distillate.

Fig. 1. Depression of the pour points of components upon introduction of depressor and depressor-dispersing additives

Рис. 1. Депрессия температуры застывания компонентов при введении ДП и ДДП

The effectiveness of depressor additives is largely determined by the composition and other characteristics of the fuel [16]. The unsaturated and aromatic hydrocarbon contents of the fuel were estimated according to the iodine number and the combined mass fraction of hydrocarbons that reacted with H_2SO_4 (Table 1). Straight-run fractions (straight-run middle-distillate fractions, HDF-AC, HDF-VC, vacuum distillates) have a more constant composition with the unsaturated hydrocarbon content comprising between 1% (straight-run middle-distillate fractions, HDF-VC) and 3.5% (HDF-AC, vacuum distillates), whereas the aromatic hydrocarbon content comprised between 23% (straight-run middle-distillate fractions, HDF-VC) and 30% (HDF-AC, vacuum distillate). This compares with fractions of secondary processes (DF-DC, LCGO, light catalytic gas oil, distillation residue and MDF-SO), where the content of unsaturated hydrocarbons varies from 0% (hydrotreated middle-distillate fractions, distillation residue) to 45% (DF-DC), and the content of aromatic hydrocarbons ranges from 0% (hydrotreated middle-distillate fractions, DF-DC) to 70% (light catalytic gas oil).

The addition of VES-410D to straight-run fractions (straight-run middle-distillate fractions, GK-3 and ELOU-AVT-6 units; HDF-AC, GK-3 and ELOU-AVT-6 units; HDF-VC; vacuum distillates) results in an exponential dependence of pour point depression of components on their physico-chemical characteristics such as kinematic viscosity and density. At the same time, the addition of VES-410DDP to the same fractions does not allow a correlation between depression and these physico-chemical characteristics to be obtained (Fig. 2, 3).

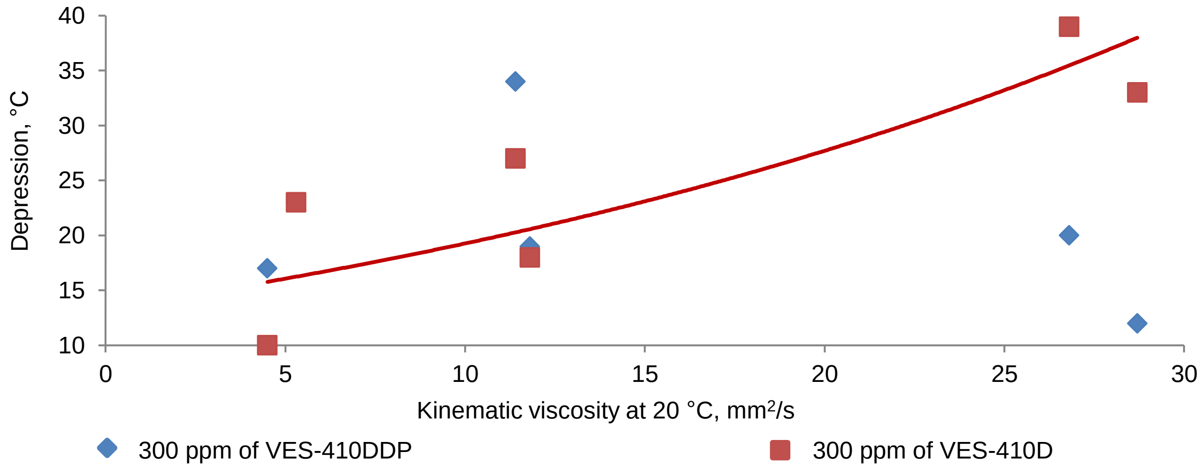


Fig. 2. Dependence of pour point depression of components on kinematic viscosity with introduction of depressor and depressor-dispersing additives

Рис. 2. Зависимость депрессии температуры застывания компонентов от вязкости кинематической при введении ДП и ДДП

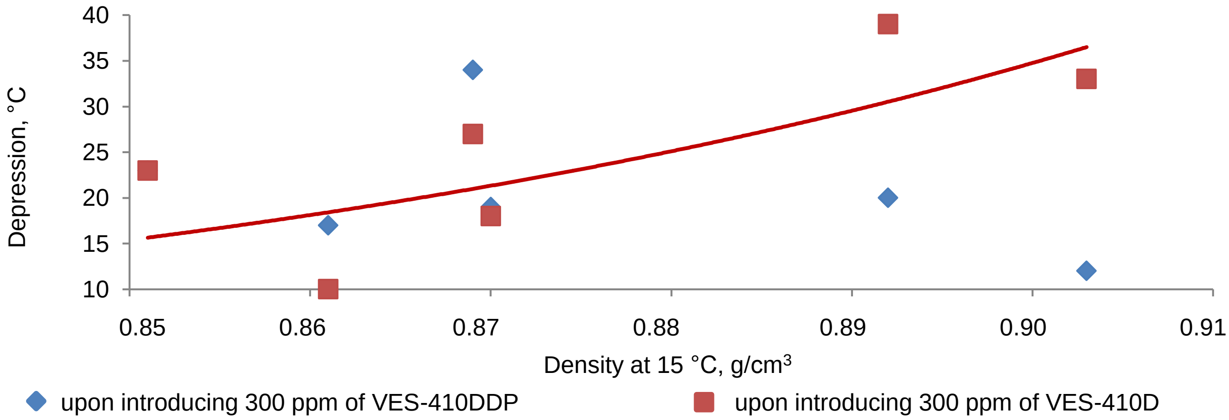
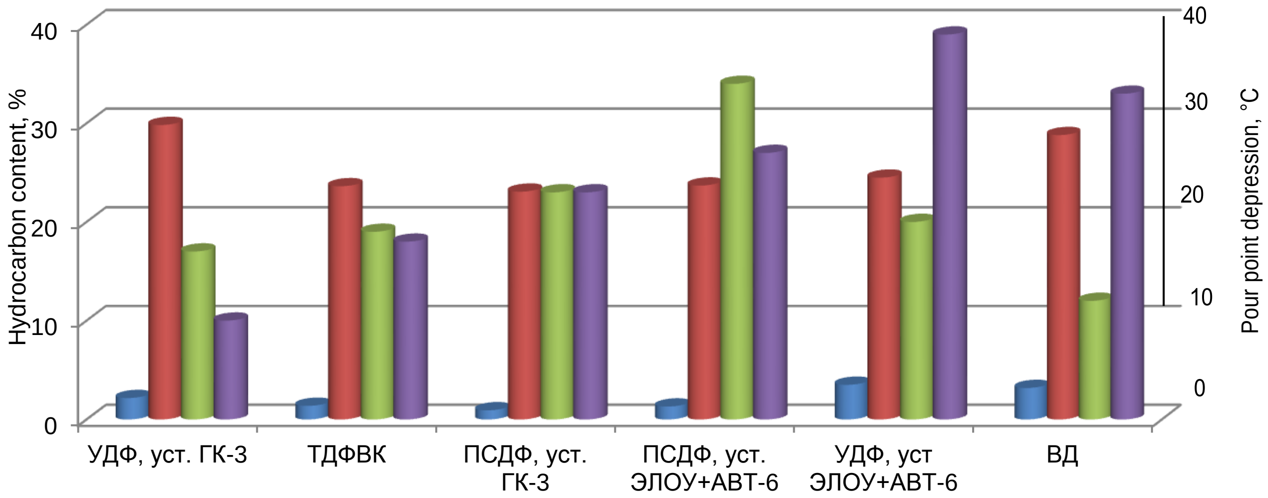


Fig. 3. Dependence of pour point depression of components on density with introduction of depressor and depressor-dispersing additives

Рис. 3. Зависимость депрессии температуры застывания компонентов от плотности при введении ДП и ДДП

For fractions of secondary refining processes (MDF-SO, LCGO, distillation residue, light catalytic gas oil), no correlation between the pour point depression and physico-chemical characteristics is observed.

It is shown that straight-run fractions have the highest responsivity to both additives, whereas fractions of secondary refining processes exhibit the lowest responsivity (Fig. 4, 5).

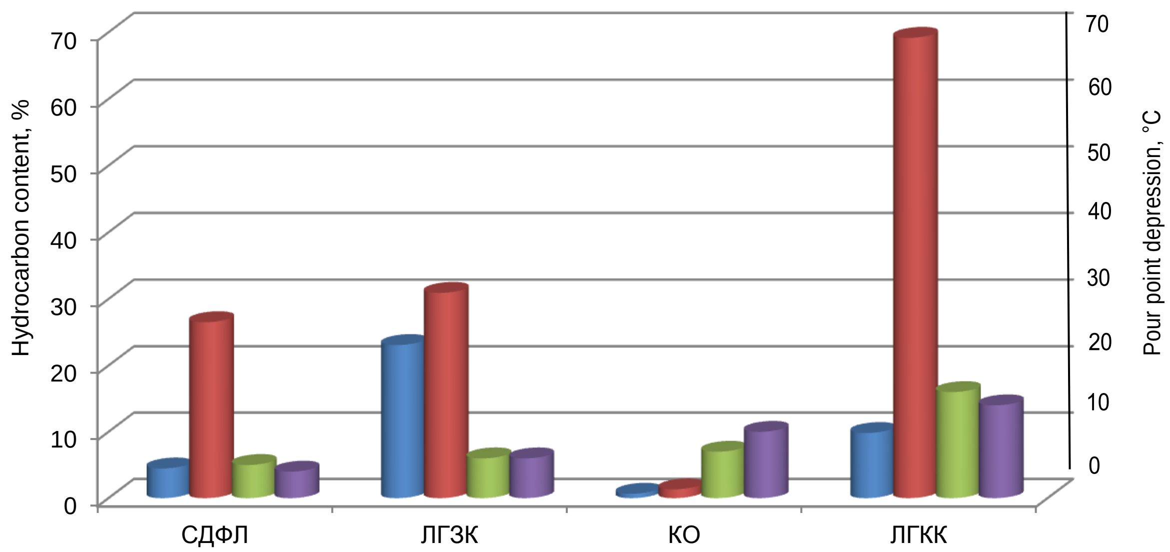


unsaturated hydrocarbon content
romatic hydrocarbon content
pour point depression upon introducing 300 ppm of VES-410DDP
pour point depression upon introducing 300 ppm of VES-410D

УДФ, уст ГК-3 – HDF-AC, GK-3 unit
ТДФВК – HDF-VC
УДФ, уст. ЭЛОУ+АВТ-6 – HDF-AC, ELOU-AVT-6 unit
ВД – vacuum distillate
ПСДФ, уст ГК-3 – straight-run middle-distillate fractions, GK-3 unit
ПСДФ, уст. ЭЛОУ+АВТ-6 – straight-run middle-distillate fractions, ELOU-AVT-6 unit

Fig. 4. Dependence of responsivity to depressor and depressor-dispersing additives on the nature of straight-run fractions

Рис. 4. Приемистость ДП и ДДП от природы прямогонных фракций



unsaturated hydrocarbon content
romatic hydrocarbon content
pour point depression upon introducing 300 ppm of VES-410DDP
pour point depression upon introducing 300 ppm of VES-410D

СДФЛ – MDF-SO
ЛГЗК – LCGO
КО – distillation residue
ЛГКК – light catalytic gas oil

Fig. 5. Dependence of responsivity to depressor and depressor-dispersing additives on the characteristics of secondary refining processes

Рис. 5. Приемистость ДП и ДДП от природы вторичных фракций

Against the background of a relatively constant hydrocarbon composition, pour point depression for straight-run fractions lies in the range of 10–40 °C. For the fractions of secondary refining processes, pour point depression ranges from 4 to 16 °C. While the low responsivity of MDF-SO to the specified additives is associated with lighter fractional composition, for LCGO this responsivity results from the high unsaturated hydrocarbon content relative to other fractions. The specific hydrocarbon composition of distillation residue has a significant paraffinic and naphthenic hydrocarbon content, which is formed in the course of hydrogenating aromatic raw materials at elevated temperatures and pressures. The best responsivity exhibited by light catalytic gas oil is due to the low unsaturated hydrocarbon content and heavy fractional composition.

LMF formulations were experimentally selected on the basis of the physico-chemical and chemmotological characteristics of their components, as well as on the assessment of their responsivity to the additives. The laboratory samples were prepared by introducing heavy fractions and products of secondary refining processes (Fig. 6).

The samples were tested according to previously defined key parameters (Table 3).

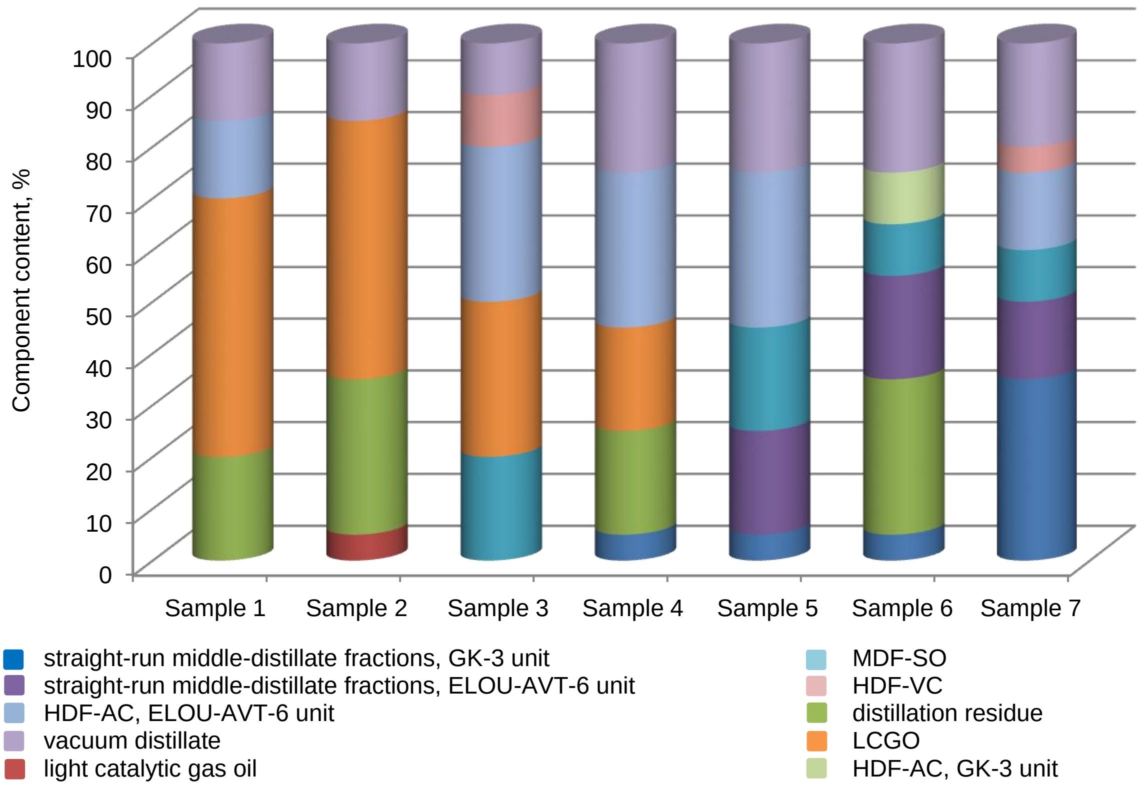


Fig. 6. Composition of laboratory samples

Рис. 6. Состав лабораторных образцов

Table 3

Test results for LMF laboratory samples

Таблица 3

Результаты испытаний лабораторных образцов ТМС

Parameter	Norm for LMF according to TU	Samples						
		1	2	3	4	5	6	7
Density at 15 °C, g/cm^3	not more than 893	871.2	871.7	867.4	875.4	870.0	868.1	889.9
Pour point, °C	not more than -10	4	4	1	6	0	1	-5
Closed-cup flash point, °C	not less than 61	85	92	80	116	115	107	82
Mass fraction of sulphur, %	type I – ≤ 0.5 type II – ≤ 1.0	0.51	0.52	0.48	0.53	0.47	0.46	0.67
Kinematic viscosity at 20 °C, mm^2/s	not more than 11.4	12.9	15.4	9.5	15.9	11.2	11.1	6.52
ASTM D 1500 colour	not specified, determination is required	1.5	2.5	1.0	1.5	1.0	2.0	1.0

According to the test results, Samples 1, 2 and 4 do not correspond to TU 38.101567-2014 in terms of the mass fraction of sulphur (for Type I) and the kinematic viscosity at 20 °C. Moreover, with the introduction of LCGO into the LMF composition (21/10-3M unit), a change in the colour of the product is observed. According to ASTM D 1500, the colour value of the second sample equals 2.5 colour units. It is shown that the introduction of this fraction to LMF in an amount of 5% leads to an increase in the colour value by up to 1.5 colour units, whereas introduction in an amount of 50% results in an increase in colour value by up to 5,5 colour units. Following 7 days of storage, the colour value of the laboratory samples increased by 1–2.5 colour units. This phenomenon can be explained by the high content of unsaturated hydrocarbons in the LCGO and their oxidation propensity.

Samples 3, 5, 6 and 7 were used for further studies, due to their conformity with the LMF requirements in terms of main quality indicators, with the exception of the pour point value (No. 3, 5, 6 as LMF of the first type; No. 7 as LMF of the second type).

In order to bring the pour point parameter to the values specified for LMF, domestically-produced depressor and depressor-dispersing additives, as well as a Dodiflow-4971 depressor-dispersing additive (Clariant), were introduced into the test Samples 3, 5, 6, 7 (Table 4). Upon the introduction of additives, a significant depression of the LMF pour point was observed (Fig. 7).

Table 4

Pour point of LMF samples with additives

Таблица 4

Температура застывания (°C) лабораторных образцов смесей ТМС при добавлении присадок

Sample number	Without additives	Amount of additive, ppm								
		Dodiflow-4971			Depressor-dispersing additive VES-410DDP			Depressor additive VES-410D		
		100	150	300	100	150	300	100	150	300
3	1	-9	-9	-12	-7	-8	-13	-8	-10	-12
5	0	-6	-7	-9	-4	-6	-7	-8	-11	-13
6	1	-2	-4	-7	0	-1	-5	-4	-6	-8
7	-5	-11	-12	-12	-10	-12	-12	-13	-13	-13

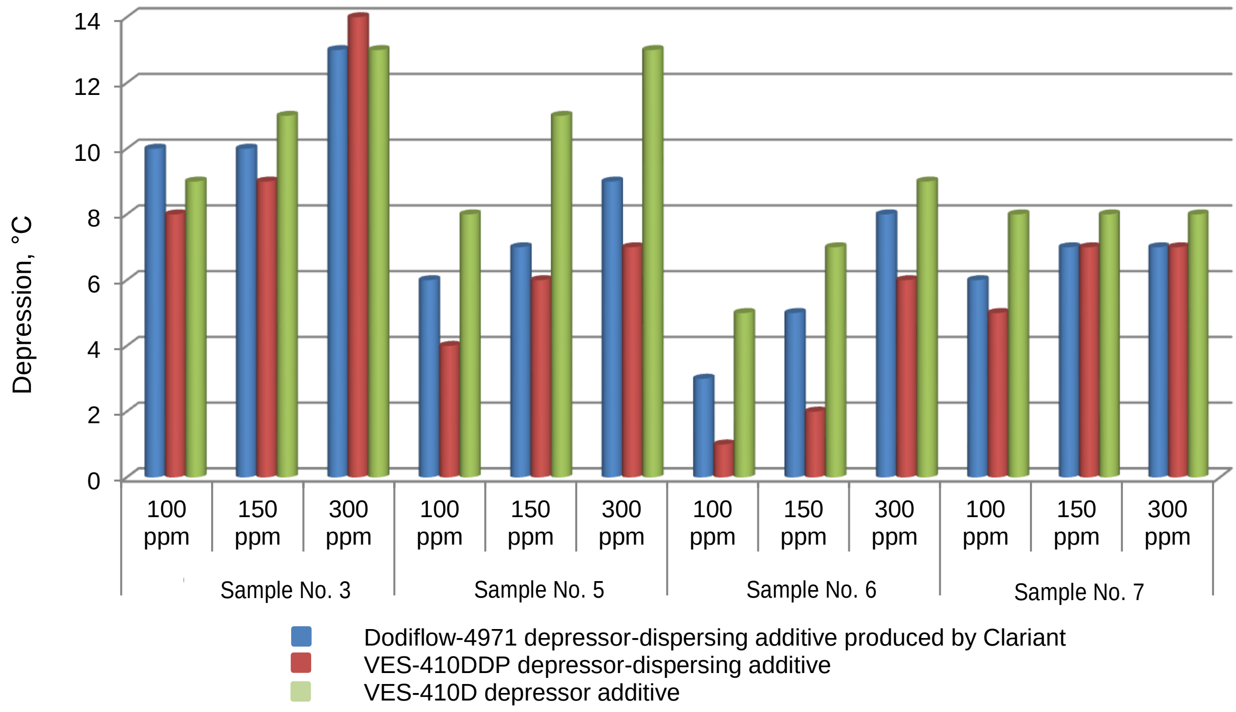


Fig. 7. Pour point depression of LMF upon introduction of depressor and depressor-dispersing additives

Рис. 7. Депрессия температуры застывания композиций ТМС при введении ДП и ДДП

In order to ascertain the cost-effectiveness of replacing straight-run diesel fractions with heavy fractions in LMF preparation with the use of depressor and depressor-dispersing additives, as well as converting straight-run diesel fractions into a commercial product, calculations were made on the basis of laboratory test results using PIMS software (Aspen Tech[3])and the optimal component composition for the LMF base (Table 5) complying with the requirements given in TU 38.101567-2014, except for the pour point parameter equal to +2 °C (Table 6).

Table 5

Components of LMF and their formulation

Таблица 5

Компоненты образцов ТМС и рецептура приготовления

Component	Content, wt%
Straight-run middle-distillate fractions, including distillates of heavy fractional composition, obtained in the process of atmospheric distillation of desalted crude oil	47
Vacuum distillate	35
Heavy diesel fractions obtained from vacuum columns of the ELOU-AVT-6 unit	12
Heavy diesel fractions obtained from vacuum columns of the GK-3 unit	2
Light gas oil obtained in the course of catalytic cracking	4

Table 6

Physical-chemical and performance parameters of LMF base

Таблица 6

Физико-химические и эксплуатационные показатели базовой основы

Parameter	Normative document on the test method (document number)	Norm according to TU 38.101567-2014	Test result
Kinematic viscosity at 20°C, mm^2/s	GOST 33	not more than 11.4	9.7
Closed-cup flash point, °C	GOST R EN ISO 2719	not less than 61	83
Pour point, °C	GOST 20287	not more than -10	2
Mass fraction of sulphur, %	GOST R 51947	not more than 0.5	0.4
Mass fraction of sour sulphur, %	GOST 17323	not more than 0.025	0.002
Mass fraction of water	GOST 2477	traces	none
Coking ability,%	EN ISO 10370	not more than 0.2	0.03
Content of water-soluble acids and alkalis	GOST 6307	none	none
Ash content, %	GOST 1461	not more than 0.01	none
Mass fraction of mechanical impurities, %	GOST 6370	not more than 0.02	none
Density at 15 °C, kg/m^3	GOST R 51069	not more than 893	869
Density at 20 °C, kg/m^3	GOST 3900	not more than 890	865
Lodine value, gramme of iodine per 100g of fuel	GOST 2070 (method A)	not more than 20	3

In order to explore alternatives and study the additives market, 14 commercial depressor-dispersing additives from various manufacturers (Altai Additives, CLARIANT, Offo-Trade, Ferrospin Eco, Dorf Ketal, Nalko-Element, Multisol, Angarsk Plant of Catalysts and Organic Synthesis, Innospec Rus) were tested using this LMF base.

When preparing samples for testing low-temperature parameters, the depressor-dispersing additives under study were introduced in the amounts recommended by the manufacturers (Table 7).

The assessment was carried out not only on the basis of the pour point values, but also against such parameters as cloud point and cold filter plugging point (CFPP), evaluated within a complex of methods for qualification tests (CMQT) when engineering production. According to the data presented in Table 7, it is clear that not all additives in the recommended concentrations brought the CFPP values to the required level. In this connection, the depressor-dispersing additive amounts were adjusted for retesting (Table 8)

[3] Aspen PIMS program (Process Industry Modeling System). Available at: https://www.aspentech.com/en/resources/brochure/aspen-pims-family (accessed 04 April 2019).
PIMS – экономико-технологическая система моделирования нефтепереработки – инструмент построения методом линейного программирования (ЛП) моделей планирования процессов нефтепереработки для создания оптимальных планов, включая оценку альтернатив сырой нефти, промежуточного сырья, сырья, получаемого за границами рассматриваемой установки, технологий, продуктов и рынков / PIMS is a linear programming (LP) tool for constructing planning models of refining processes used to create optimal plans, including evaluation of alternatives to crude oil, intermediate raw materials, raw materials outwith the process unit, technologies, products and markets.

Table 7

Results of samples tested for low-temperature parameters

Таблица 7

Результаты испытаний на низкотемпературные показатели

Additive	Additive content, ppm	Pour point, °C	Cloud point, °C	CFPP, °C
Norm for LMF, type I	–	not more than -10	not specified	not more than -10 (CMQT)
Base	–	2	6	4
DD-08	500	-25	9	3
STM-F2	500	-22	7	-5
Dodiflow 4971	500	-35	6	3
Dodiflow 8112	500	-33	8	-4
Dodiflow 8022	500	-28	3	-9
Dipris 5416	500	-25	7	4
Anti - Wax	2500	-14	6	-2
Anti - Wax 2	2500	-15	5	3
SR-1677 CFPP	500	-29	3	5
EC5947A	800	-35	5	3
Infineum R707	500	-18	8	-6
Infineum IDN 10966	500	-30	6	-7
VES 410	500	-16	3	0
OFI 8863	500	-30	5	0

Table 8

Results of samples tested for low-temperature parameters

Таблица 8

Результаты испытаний на низкотемпературные показатели

Additive	Additive content, ppm	Pour point, °C	Cloud point, °C	CFPP, °C
Norm for LMF, type I	–	not more than -10	not specified	not more than -10 (CMQT)
Base	without additive	2	6	4
DD-08	1000	-30	6	-8
STM-F2	1000	-29	7	-4
Dodiflow 4971	1000	-42	7	3
Dodiflow 8112	1000	-42	7	-11
Dodiflow 8022	1000	-41	6	-12
Dipris 5416	1000	-29	6	6
Anti - Wax	3000	-29	7	-3
Anti - Wax 2	3000	-33	6	0
SR-1677 CFPP	1000	-34	6	-1
EC5947A	1000	-39	5	-1
Infineum R707	1000	-30	7	-7
Infineum IDN 10966	1000	-32	7	-8
VES 410	1000	-30	6	-5
OFI 8863	1000	-39	5	0

The obtained results show that the majority of tested additives change the pour point of the samples while having practically no effect on the cloud point or CFPP.

In the framework of qualification tests for engineering LMF production, the following parameters are of great importance: filterability factor and sedimentation stability. It is established that the difference in the filterability factor – both with and without additive – does not exceed three units. This indicates the absence of impurities in the tested depressor-dispersing additives that can cause clogging of fuel filters.

Only five of the fourteen tested depressor-dispersing additives meet the stated requirements for sedimentation stability: DD-08 (Altai Additives), Dodiflow 8022 (CLARIANT), Dodiflow 8112 (CLARIANT), Infineum R707 (Multisol) and Infineum IDN 10966 (Multisol).

[4] Митусова Т.Н., Хавкин В.А. Отчет по результатам квалификационных испытаний топлива маловязкого судового по ТУ 38.101567-2014, выработанного АО «АНХК» по измененной технологии с вовлечением депрессорно-диспергирующей присадки Диприс 8112. М.: ОАО «ВНИИ НП», 2016. 15 с. / Mitusova T.N., Khavkin V.A. *Report on the results of qualification tests of low-viscosity marine fuel according to TU 38.101567-2014, developed by SC «APCC» according to a modified technology with the introduction of a Dipris 8112 depressor-dispersing additive*. Moscow: SC «VNIINP», 2016. 15 p.

Although these results were taken into account when assessing the properties of the depressor-dispersing additives, they were not decisive, since, in our opinion, the method does not reproduce actual product life cycle conditions. Moreover, a series of tests was carried out under conditions close to actual product use involving a rapid cooling of the fuel, keeping it in a frozen state and then bringing it back to a normal temperature. The quality of the product did not change following the performed operations.

CONCLUSIONS

1. It was proposed to use the following heavy fractions obtained by JSC APCC in the course of oil refining as LMF components: LCGO, heavy diesel fractions obtained from the vacuum columns of a primary processing unit, heavy diesel fractions removed from an atmospheric column and vacuum distillates having various fractional compositions.

2. It is established that the introduction of depressor (VES-410D) and depressor-dispersing (VES-410DDP) additives into the components of the fuel significantly reduces the pour point of the component and produces high depression rates.

3. The optimal formulation of the LMF base including products of heavy fractional composition (no more than 30%) of primary and secondary refining processes and depressor-dispersing additives was determined.

4. In order to explore alternatives and study the additives market, 14 commercial depressor-dispersing additives from various manufacturers were tested using this LMF base. Five of the tested additives showed good results in terms of low-temperature characteristics, filterability factor and sedimentation stability. These five additives are recommended for further industrial use.

5. The obtained data allow the optimal composition of the mixtures to be modelled and help to determine the most rational technology for producing LMF in conformity with set requirements.

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Contribution

Zhanna N. Artemyeva, Igor I. Kuzora, Svetlana G. D'yachkova, Olga V. Starikova on the basis of the results summarized the material and wrote the manuscript. Zhanna N. Artemyeva, Igor I. Kuzora, Svetlana G. D'yachkova, Olga V. Starikova have equal author's rights and bear equal responsibility for plagiarism.

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