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IMPROVEMENT OF THERMAL OXIDATIVE CHARACTERISTICS OF DIESEL FUELS WITH ESTERS OF CYCLIC POLYATOMIC ALCOHOLS

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A number of symmetric, asymmetric and complex esters of 2,2,5,5-tetramethylolcyclopentanol and 2,2,6,6-tetramethylolcyclohexanol were synthesized, their physicochemical, viscosity-temperature and thermo-oxidative properties were studied. With the addition of these esters to hydrotreated diesel fuels 0.004% it was possible to significantly improve the operational properties of fuels: to increase thermal oxidative stability, flash point and lower pour point. Proceeding from these results, the esters of cyclic polyatomic alcohols are recommended as complex additives to diesel fuels.

Keywords: *esters of cyclic polyols, lubricating oils, diesel fuel, operational characteristics, complex additives.*

doi

Introduction

To improve environmental characteristics the removal of sulfur- and nitrogen-containing heterocyclic compounds from diesel fuels (DF) is required, which leads to a decrease in oxidative stability, since sulfur and nitrogen compounds are natural antioxidants and contribute to the inhibition of the oxidation of DF. Following from this, the most effective and cost-effective way to protect DF from oxidative degradation is the use of various antioxidant additives.

Currently, extensive research is underway on the thermo-oxidative transformations of DF and the search for new effective antioxidants. It is required to select such compounds which stabilize a DF, at the same time without interacting with its components responsible for the main operational indicators.

At present, to increase thermal oxidative stability (TOS), antioxidant additives are used (added to the fuel in an amount (0.04–0.05)%), which are a composition of 2,6-di-*tert*-butyl-4-methylphenol (ionol), nitrogen- or a sulfur-containing derivative of shielded phenol, up to 100 mass% by weight of an organic solvent [1]; the composition of 2,2-methyl-bis (4-methyl-6-*tert*-butylphenol), an oil solution of alkenyl succinimide, *bis*-(3,5-di-*tert*-butyl-2-hydroxybenzylidene) ethylenediamine etc. [2, 3]. However the-

se additives and their compositions at their application the operational properties of fuels is improve insufficiently. For instance, using ionol in an amount of 0.04%, the precipitate is 1 mg/100 ml of fuel. This figure currently does not meet the requirements of Euro-4 and Euro-5.

Therefore, the creation of new effective fuel additives is a very relevant scientific, practical and environmental problem. From this point of view, the synthesis of new esters of cyclic polyatomic alcohols of various structures and their study as additives to diesel fuels has is of certain scientific and practical significance.

Since the synthesized esters have symmetric, asymmetric, complex structures, five and six membered cyclic fragments, most polar ester groups should has is of a positive effect on the properties of fuels [4–6].

Experimental part

The starting cyclic polyatomic alcohols – 2,2,5,5-tetramethylolcyclopentanol (TMCP) and 2,2,6,6-tetramethylolcyclohexanol (TMCH) were synthesized by the aldol condensation of cyclopentanone and cyclohexanone with formaldehyde according to the Cannizzaro–Tishchenko reaction according to the following scheme:

Symmetric esters were obtained by esterification of TMCP and TMCH with caproic acid, taken in a molar ratio of alcohol:acid of 1:5.5 in the presence of a catalyst of *para*-toluenesul-

fonic acid (PTSA) taken in an amount of 1% of the mass of the reaction mixture, until the release of reaction water is stopped [4,5].

Asymmetric esters were obtained in 2 stages: in the first, diesters with enanthic acid

were obtained, then in the second stage free hydroxyl groups were esterified with caproic acid:

The complex esters of TMCP and TMCH were obtained in three stages: at the first stage, tetraesters were obtained by esterification of alcohols with caproic acid, at the second stage, the

free hydroxyl group was esterified with pimelic acid, and at the third stage, the free carboxyl group of the acid was esterified with hexyl alcohol:

The structure of the synthesized esters is proved by elemental analysis, IR spectroscopy and method NMR, as well as determination of acid and ether numbers.

Results and discussion

Physico-chemical properties of esters are given in Table 1.

The viscosity-temperature and thermo-oxidative properties of the synthesized esters were also determined (Tables 2, 3). The acid number is determined according to GOST 5895-79, thermo-oxidative stability (TOS) according to GOST 23797-79, volatility according to GOST 20354-74.

As can be seen from Table 2, the symmetric, asymmetric, and complex esters of TMCP in comparison with analogous esters of TMCH have low viscosity levels at 100°C and 40°C, low pour points, high flash points and viscosity index.

The results determining the thermo-oxidative stability of the esters also showed

that, according to all indicators, the TMCP esters have relatively better indicators than the TMCH esters: acid number $1.30 \div 2.91$ mg KOH/g versus $1.15 \div 3.18$, the precipitate is insoluble in isooctane $0.002 \div 0.141\%$ of the mass versus $0.004 \div 0.180$, volatility of $0.010 \div 0.50\%$ of the mass against $0.65 - 0.69\%$ of the mass.

The synthesized esters of cyclic polyatomic alcohols were investigated as antioxidant additives which improve the TOS of diesel fuels. By adding to diesel fuels in an amount of $0.1 - 0.004$ mass % of these ethers, a number of compositions were prepared and settled on the optimal option – 0.004 mass %. Studied all the indicators of the compositions of diesel fuels, the results of which are given in Table 4.

The TOS of the prepared samples was determined in an LSART apparatus at 150°C for 4 hours (GOST 9144-79), flash point in a closed crucible in the TVZ-LAB-11 apparatus according to GOST 6350, ASTM D 93/SD 2719.

Table 1. Physico-chemical properties of synthesized esters

№	Esters	Yield, mass %	Boiling point, °C at 0.27 kPa	Refractive index, n_D^{20}	Density, ρ at 20°C, kg/m ³	Molecular mass,	Empirical formula
						exp/cal	
1		80	238–240	1.4625	1012	691/694	C ₃₈ H ₆₀ O ₁₀
2		90	270–272	1.0312	1457	710/712	C ₄₀ H ₇₀ O ₁₀
3		75.1	256–258	1.4590	999	742/746	C ₄₂ H ₇₆ O ₁₀
4		83	290–297	1.0138	1465	766/765	C ₄₄ H ₇₈ O ₁₀
5		78	–	1.4620	1050	820/825	C ₄₅ H ₇₂ O ₁₂
6		80	–	1.4720	1118	838/840	C ₄₇ H ₇₄ O ₁₂

Table 2. The viscosity-temperature properties of the synthesized esters

Number of esters	Viscosity, mm ² /s, at temper. °C			Viscosity index	Temperature, °C	
	100	40	–30		flash point	pour point
1	7.90	34.20	26346	126	290	–53
2	10.28	42.23	26500	125	281	–47
3	8.61	36.28	26760	138	309	–50
4	10.47	44.51	24300	135	291	–44
5	17.90	56.23	–	136	320	–37
6	17.98	71.63	–	125	334	–31

Table 3. Thermo- oxidative stability of esters of TMCP and TMCH

Number of esters	Viscosity at 100°C, mm ² /s (after oxidation)	Acid number, mg KOH/g (after oxidation)	Precipitate insoluble in isooctane, mass %	Corrosion, mg/cm ²		Volatility, mass. %
				AK-4	ИИХ-15	
1	8.82	1.30	0.002	0.120	0.025	0.010
2	11.40	1.15	0.004	0.015	0.018	0.65
3	9.60	1.40	0.003	0.130	0.030	0.018
4	11.56	1.36	0.010	0.022	0.035	0.50
5	19.23	2.91	0.141	0.110	0.133	0.50
6	19.80	3.18	0.180	0.100	0.130	0.69

Table 4. Test results for diesel fuel with the addition of esters

Indicators	DF	Samples of diesel fuels with ethers					
		I	II	III	IV	V	VI
Density at 20°C, kg/m ³							
at 15 °C	845.8	846.5	846.5	847.2	847.6	845.9	846.1
at 20 °C	844.6	846.0	846.2	845.4	847.2	844.3	844.6
Kinematic viscosity at 20°C, mm ² /s	6.80	6.20	5.90	5.75	5.80	5.83	5.92
Pour point, °C	-18.2	-24.3	-22.6	-25.1	-21.8	-23.7	-22.4
Aromathydrocarbon content, %							
	17.6	17.3	17.1	17.8	18.0	18.2	17.9
Acidity, mg KOH/100 ml of fuel	0.0026	0.0026	0.0029	0.0030	0.0034	0.0030	0.0035
Thermo-oxidative stability, mg sediment/100 ml of fuel, (with esters in the fuel 0.004%)	8.6	0.6	1.9	2.2	3.0	3.2	3.6
Test on a copper plate, 3 hours at 50°C	r	e	s	i	s	t	s
Coking ability of 10% residue, %	0.0025	0.0020	0.0023	0.0021	0.0023	0.0020	0.0025
In closed cup flash point, °C	76	84	80	86	82	88	83
Fractional composition, °C							
Initial boiling point	206	202	204	200	203	210	213
50% distilled at temperature	275	275	270	277	272	280	281
96% distilled at temperature	350	352	354	352	356	360	362
End-boiling point	354	356	358	354	360	362	370
Mass fraction of sulfur, ppm	330	328	332	330	334	326	329
Cetane number	45	44.6	44.2	44.8	44.0	44.5	44.1

As a result of studies, it was found that the addition of ethers almost does not affect the fractional composition of diesel fuels, 96% are distilled in the range 350–362°C, the density of all samples is 845–847 kg/m³.

The addition of esters of TMCP and TMCH leads to an increase in the TOS of all samples of the tested fuels, what is determined by the amount of precipitate formed. As can be seen from Table 4, on adding 0.004% of esters of various structures to diesel fuel in six samples, it decreases from 8.6 to 0.6–3.6 mg/100 ml. The coke ability of the 10% residue also decreases: from 0.0025 to 0.0020%. The flash point in a closed cup raises from 76 to 88°C, the pour point decreases from minus 18.2°C to minus 25.1°C. Among the given esters, the best indicators are symmetric and asymmetric esters of TMCP, which is directly related to the conformational state of the cyclopentane ring [7]. In comparison with complex esters (esters 5, 6), symmetric and asymmetric esters of these alcohols have a certain advantage, which are explained by the fact that they have simple molecular structures and, during oxidation, form

labile and stable peroxide compounds with different thermal stability and initiating ability.

There is scientific information [8] that the effect of esters on the quality of fuels occurs according to a radical mechanism. It is also suggested that two types of peroxide compounds – labile and stable, with different thermal stability and initiating ability are formed under ester oxidation conditions [9]. Labile peroxide compounds represent α - and β -acyloxyhydroperoxides and their products inside molecular isomerization. They decompose with high speeds without the formation of free radicals.

Comparison of esters of cyclic polyatomic alcohols – TMCP and TMCH with known antioxidant additives based on screened phenols (ionol) shows that these esters have significant advantages [2, 3]. In the case of adding 0.04% ionol, the precipitate makes up 1–1.5 mg/100 ml of fuel.

Conclusions

Relying on the results of the work performed, it was found that the addition of esters of cyclic polyatomic alcohols of various structures leads to significant increases in TOS, flash point, as well as lowering the pour point of diesel fuels.

Symmetric, asymmetric and complex esters of cyclic polyatomic alcohols – TMCP and TMCH can be recommended as complex additives to diesel fuels [10–11].

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TSİKLİK ÇOXATOMLU SPİRTLƏRİN EFİRLƏRİ İLƏ DİZEL YANACAQLARININ TERMOOKSİDLƏSMƏ XASSƏLƏRİNİN YAXŞILAŞDIRILMASI

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2,2,5,5-tetrametiloltsiklopentanol və 2,2,6,6-tetrametiloltsikloheksanolun bir sıra simmetrik, qeyri-simmetrik və kompleks efirləri sintez olunmuş, onların fiziki-kimyəvi, özlülük-temperatur və termooksidləşmə xassələri öyrənilmişdir. Bu efirlərin 0.004% miqdarında hidrotəmizlənmiş dizel yanacağına əlavə edilməsi ilə yanacaqların istismar xassələri xeyli yaxşılaşmışdır: termooksidləşmə stabilliyi, alışma temperaturu artır və donma temperaturu isə aşağı düşür. Bu nəticələrə əsasən, tsiklik çoxatomlu spirtlərin efirləri dizel yanacağına kompleks əlavələr kimi tövsiyə olunur.

Açar sözlər: tsiklik poliolların efirləri, sürükü yağları, dizel yanacağı, istismar xassələri, kompleks əlavələr

УЛУЧШЕНИЕ ТЕРМООКСИЛИТЕЛЬНОЙ ХАРАКТЕРИСТИКИ ДИЗЕЛЬНЫХ ТОПЛИВ ЭФИРАМИ ЦИКЛИЧЕСКИХ МНОГОАТОМНЫХ СПИРТОВ

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Синтезирован ряд симметричных, несимметричных и комплексных эфиров 2,2,5,5-тетраметилолциклопентанола и 2,2,6,6-тетраметилолциклогексанола, изучены их физико-химические, вязкостно-температурные и термоокислительные свойства. С добавлением этих эфиров к гидроочищенным дизельным топливам 0,004% удалось значительно улучшить эксплуатационные свойства топлив: повысить термоокислительную стабильность, температуру вспышки и снизить температуру застывания. Исходя из этих результатов эфиры циклических многоатомных спиртов рекомендованы в качестве комплексных добавок к дизельным топливам.

Ключевые слова: эфиры циклических полиолов, смазочные масла, дизельное топливо, эксплуатационные характеристики, комплексные добавки.