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UDC 547.431.5:621.892

ESTERS OF CYCLIC POLYATOMIC ALCOHOLS AS ANTIOXIDANTS TO DIESEL FUELS

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A number of esters of cyclic polyatomic alcohols - 2,2,5,5-tetramethylolcyclopentanol and 2,2,6,6-tetramethylolcyclohexanol with normal, iso- and neo-monocarboxylic acids were synthesized and their physicochemical, viscosity-temperature and thermo-oxidative properties were studied. A number of compositions were prepared with the addition of 0.004% of esters to hydrotreated diesel fuels, determined their operational characteristics. It was found that with the addition of esters of cyclic polyatomic alcohols with normal, iso- and neo-acids to hydrotreated diesel fuel, it leads to significant increases in TOS - the sediment decreases to 0-1.32 mg/100 ml, the flash point increases from 76°C to 87°C and the pour point decreases from minus 19.2°C to minus 28°C. Therefore, these esters can be recommended as complex additives to diesel fuels.

Keywords: esters of cyclic polyol, diesel fuel, thermo-oxidative stability, complex additives

Intensive development of modern technology increases the requirements for lubricating oils and fuels. Increasing quality requirements for diesel fuels leads to the use of a large number of additives to diesel fuels. Compliance with the Euro-4 and Euro-5 standards is impossible without the use of substances that, in small quantities, significantly improve the operational properties of diesel fuels: their thermo-oxidative stability (TOS), pour point, flash point, etc..

Hydrotreated diesel fuels do not contain natural antioxidants (sulfides, pyridines and alkyl phenols) and are easily oxidized by atmospheric oxygen dissolved in the fuel. Such fuels without antioxidant additives have low chemical stability and are unsuitable for long-term storage [1].

In the present, antioxidant additives are used to increase the TOS of fuels: such as spatially hindered derivatives of alkyl phenols- 2,6-di-tert-butyl-4-methylphenol (ionol) [1], compositions based on 2,2-methylene bis (4-methyl-6-tert-butylphenol), an oil solution of alkenyl succinimide, bis (3,5-di-tert-butyl-2-hydroxybenzylidene) ethylenediamine [2-3] and etc.. The disadvantage of these additives and their composi-

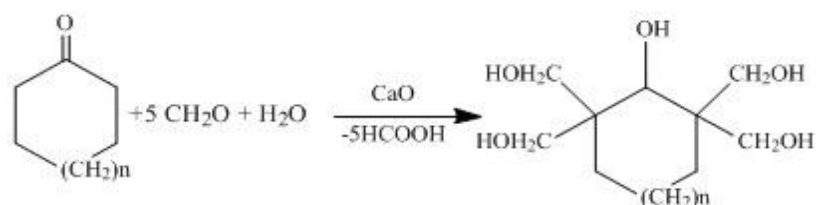
tions is that with their use, TOS of fuels improves slightly. For example, using ionol in an amount of 0.04% the sediment is 1 mg/100 ml of fuel. This figure currently does not meet the requirements of Euro-4 and Euro-5.

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

It should be noted that the synthesized esters have a cyclopentane and cyclohexane ring, normal, iso- and neo-acid radicals of many polar ester groups should have a positive effect on the properties of fuels [4-5].

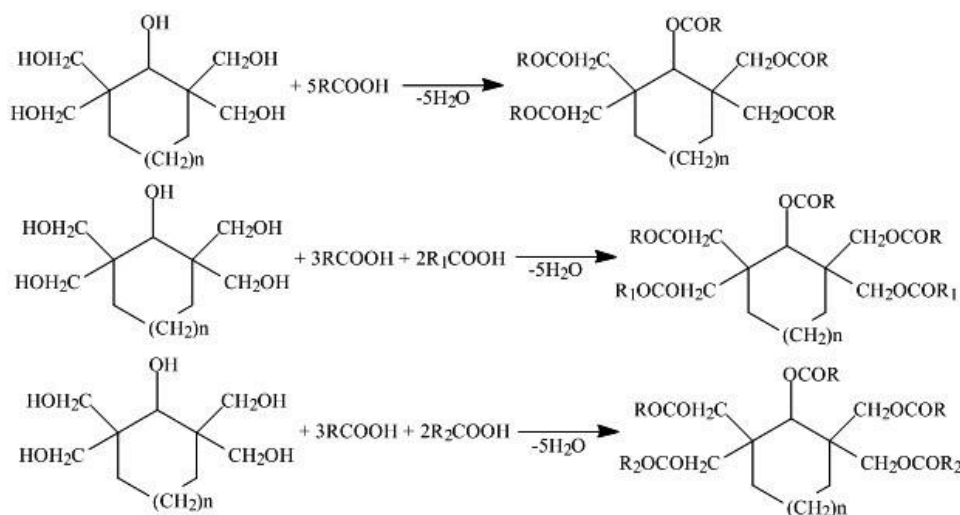
Experimental part

The initial cyclic polyatomic alcohols - 2,2,5,5-tetramethylolcyclopentanol (TMCP) and 2,2,6,6-tetramethylolcyclohexanol (TMCH) were synthesized by condensation of cyclic ketones (cyclopentanone and cyclohexanone) with formaldehyde by aldol condensation [6].



where, $n=0,1$

Next esterification by caproic acid with normal, iso- and neo-structures, the corresponding esters are synthesized:



where,

- $n=0$ ester I; R- radical of normal caproic acid $[\text{CH}_3-(\text{CH}_2)_4-\text{COOH}]$
- $n=0$ ester II; R_1 - radical of iso-caproic acid $[\text{CH}_3-\overset{\text{CH}_3}{\text{CH}}-(\text{CH}_2)_2-\text{COOH}]$
- $n=0$ ester III; R_2 – radical of neo-caproic acid $[\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{COOH}]$
- $n=1$ ester IV; R- radical of normal caproic acid $[\text{CH}_3-(\text{CH}_2)_4-\text{COOH}]$
- $n=2$ ester V; R_1 - radical of iso-caproic acid $[\text{CH}_3-\overset{\text{CH}_3}{\text{CH}}-(\text{CH}_2)_2-\text{COOH}]$
- $n=3$ ester VI; R_2 – radical of neo-caproic acid $[\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{COOH}]$

Цеокап-2 was used as an esterification catalyst. The effectiveness of the catalyst was evaluated by the quality and quantity of the esters. The physico-chemical, viscosity-temperature, thermo-oxidative properties of these esters are determined. The structure of the synthesized complex esters of TMHC was confirmed by IR and NMR spectroscopy, as well as the determination of molecular weight, acid and ester numbers. Acid numbers are determined according to GOST 5985-79, TOS according to GOST 23797-79, volatility according to GOST 20354-74.

Discussion of the results

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

Table 1

Physico-chemical characteristics of esters of cyclic polyols

Number of esters	Yield,% mas.	Boiling point, °C at 0.27 kPa	Refractive index, n_D^{20}	Density at 20°C, kg/m ³	Molecular mass	Empirical formula
					exper./calcul.	
I	86.2	230-233	1.4615	1010	691/696	C ₃₈ H ₆₈ O ₁₀
II	76.1	225-227	1.4604	1023	691/694	C ₃₈ H ₆₈ O ₁₀
III	68.9	220-223	1.4720	1017	694/695	C ₃₈ H ₇₀ O ₁₀
IV	90	270-272	1.0312	1457	710/712	C ₄₀ H ₇₀ O ₁₀
V	81.7	271-274	1.0301	1461	710/714	C ₄₀ H ₇₀ O ₁₀
VI	83.4	262-264	1.0421	1462	714/718	C ₄₂ H ₇₂ O ₁₀

Table 2

Viscosity-temperature properties of esters of cyclic polyols

Number of esters	Viscosity, mm ² /s, at tem. °C			Viscosity index	Temperature, °C	
	100	40	-30		flash point	pour point
I	7.90	34.2	26346	125	290	-53
II	8.95	36.48	20048	120	281	-56
III	21.05	225.2	-	23.8	322	-36
IV	10.20	42.23	26500	128	284	-47
V	10.90	46.12	21600	123	280	-51
VI	22.8	239.3	-	25.14	320	-33

As can be seen from table 1, the obtained esters are colorless liquids with high boiling points (220-274°C at 0.27 kPa); their yield is 70-90% of the mas. from theoretical. Data on molecular weights correspond to those calculated.

Viscosity-temperature and TOS properties of esters were also determined (tables 2, 3). As can be seen from the table, 2 esters of TMHP and TMHC with iso- and neo-structures (II, III, V, VI) have a relatively high level of viscosity at positive temperatures. At negative temperatures, on the contrary, the viscosity of esters with normal acid residues (I, IV) is much higher than that of esters with iso-structure acids (II, V). As for the viscosity index and flash point, esters with iso-acid structures are inferior to esters with normal acids. In terms of flash

point, esters with neo-acids exceed all esters. When comparing esters with neo-acids (III, VI) with esters of normal and iso- acids, they have a high viscosity level at 40°C and 100°C, a low viscosity index (24-25 units), and a high flash point (320-322°C) and a relatively high pour point (minus 33 ÷ minus 36°C).

According to thermo-oxidative stability, esters of polyols with neo-acids (III, VI) have low volatility (0.18-0.25% by mas.), they are quite stable during oxidation in bulk. Slight corrosion was observed on the aluminum alloy AK-4 and steel IX-15. Upon completion of oxidation, a sediment insoluble in isooctane was not detected.

According to TOS, esters with iso-structure acids (II, V) are somewhat inferior to esters with normal and neo-structures (I, III, IV, VI).

Table 3

Thermal oxidative stability of esters of cyclic polyols

Number of esters	Viscosity at 100°C, mm ² /s (after oxidation)	Acid number mgKOH/g (after oxidation)	Sediment insoluble in iso-octane, % mas.	Corrosion, mg/cm ²		Volatility, % mas.
				AK-4	IIIX-15	
I	8.82	1.30	0.0020	0.120	0.025	0.010
II	10.23	1.85	0.0026	0.130	0.029	0.026
III	22.58	1.23	no sediment	0.150	0.300	0.180
IV	11.40	1.15	0.003	0.009	0.016	0.650
V	12.60	1.22	0.005	0.012	0.021	0.720
VI	23.92	1.12	no sediment	0.170	0.220	0.250

Table 4

Test results for diesel fuel with the addition of esters

Data	DF	Samples of diesel fuels with esters					
		I	II	III	IV	V	VI
Density at 20 ⁰ C, kg/m ³ at 15 ⁰ C at 20 ⁰ C	844.5 841.3	845.6 842.3	845.3 842.1	845.8 842.2	847.3 844.2	845.7 843.4	845.2 843.6
Kinematic viscosity at 20 ⁰ C, m ² /s	4.81	4.87	4.82	4.80	4.96	4.90	4.93
Aromatic hydrocarbon content, %	17.2	17.5	18.5	18.0	18.4	18.2	18.6
Acidity, mgKOH/100 ml of fuel	0.0021	0.0026	0.0029	0.0031	0.0027	0.0025	0.0030
Thermo-oxidative stability, mg sediment/100 ml of fuel, [with esters in the fuel (0.004%)]	6.0	0	0	0.9	0.92	1.03	1.32
Test on a copper plate, 3 hours at 50 ⁰ C	r	e	s	i	s	t	
Coking ability of 10% residue, %	0.0025	0.0022	0.0023	0.0021	0.0023	0.0021	0.0023
Temperature, ⁰ C flash point in the closed cup	76	84	82	82	80	87	84
cloud	-15.0	-20.8	-19.2	-21.6	-21.0	-19.8	-20.4
pour point	-19.2	-24.1	-22.6	-28.0	-26.1	-25.2	-23.8
Fractional composition, ⁰ C Initial boiling point	190	202	204	201	203	205	206
50% distilled at temperature	270	272	273	271	272	270	271
96% distilled at temperature	350	351	353	350	351	352	353
End-boiling point	354	360	361	356	358	355	356
Mass fraction of sulfur, ppm	330	333	336	332	331	330	332
Cetane number	45	44.4	44.3	44.2	44.1	44	44.6

The synthesized esters of cyclic polyatomic alcohols with normal, iso- and neo-acid radicals were investigated as additives to diesel fuels in order to improve their operational properties. A number of compositions were prepared with the addition of 0.004% of esters to hydrotreated diesel fuels and all operational characteristics were determined, the results of which are given in table 4.

The TOS of the prepared compositions was determined in an JICAPT apparatus at 150°C for 4 hours (GOST 9144-79), the flash point in a closed cup is in the TB3-ЛАБ-11 apparatus according to GOST 6350, ASTM 93/SD 2719.

After determining the properties of the compositions, it was found that the addition of esters almost does not affect the fractional composition of diesel fuels, 96% is distilled in the range 350-353°C, the density of all samples is 844-847 kg/m³.

The addition of esters of TMHP and TMHC leads to an increase in the TOS of all samples of the tested fuels, which is determined by the amount of sediment formed. As can be seen from table 4, with the addition of 0.004% of esters of various structures to diesel fuel in all six samples the sediment decreases from 6.0 to 0-1.32 mg/100 ml. The coking ability of the 10% residue is also reduced: 0.0025 to 0.0021%. The flash point in the closed cup rises from 76°C to 87°C, the pour point decreases from minus 19.2°C to minus 28°C. Among the given esters by the amount of sediment, the best data are the esters of TMCP and TMHC with normal acid residues. The addition of esters of iso- and neo-acid radicals leads to a decrease in sediment to 0.9-1.32 mg/100 ml. Compared with iso- and neo-acid esters, esters with normal acids (I, II) reduce precipitation to zero, which is explained by the fact that they have simple molecular structures and easily form labile and stable peroxide compounds with different thermal stability and oxidation and initiating ability. Labile peroxide compounds are α - and β -allyloxyhydroperoxides and products of their intramolecular isomerization. They decompose at high rates without the formation of free radicals [7-8].

Comparison of the synthesized esters of TMCP and TMHC with known antioxidant additives based on screened phenols (ionol) and other additives [2,3] shows that these esters have great advantages. In the case of the addition of 0.01% of ionol the sediment is 1-1.5 mg/100 ml of fuel.

As a result of the work, it was found that the addition of esters of cyclic polyatomic alcohol with normal, iso- and neo-acids to hydrotreated diesel fuel leads to significant increases in TOS (sedimentation decreases to 0-1.32 mg/100ml), and an increase in flash point (from 76°C to 87°C) and lowering the pour point (from minus 19.2°C to minus 28°C) of diesel fuels.

Thus, as a result of the studies, it was found that the used series of esters of cyclic polyatomic alcohol - TMHP and TMHC has significant advantages with known additives to diesel fuel and therefore they can be recommended as complex additives to diesel fuels [9-10].

REFERENCES

1. Kapustin V.M. Petroleum and alternative fuels with lubricants and additives. M.: Kolos, 2008, 234 p.
2. Patent 2372382 Russia 2002
3. Moikin A.A. Prospects for the development of the production of additives to oils, diesel fuels//World of Petroleum Products, 2006, No. 1, pp. 24-27
4. Mamedyarov M.A., Alieva F.Kh., Gurbanov G.N. Synthetic lubricating oils (structure and properties). Scientific world, 2017, 335 p.
5. Grishina I.N. Physicochemical fundamentals and patterns of synthesis, production and use of additives that improve the quality of diesel fuels. M.: Oil and gas, Russian State University of Oil and Gas named after I.M. Gubkina, 2007, 230 p.
6. Gurbanov G.N. Esters of cyclic neopolisols - the basis of synthetic lubricants // Processes of petrochemistry and oil refining, 2006, №1, pp. 31-47
7. Emanuel N.M., Zaikov G.E., Maisus 3.K. The role of the medium in radical chain reactions of oxidation of organic compounds. M.: Nauka, 1973, 279 p.
8. Denisov E.T., Kovalev G.I. Oxidation and stabilization of jet fuels. M.: Chemistry, 1983, 272 p.
9. Mitusova T.N., Polina E.V., Kalinina M.V. Modern diesel fuels and additives to them. M.: Technique, 2002, 64 p.
10. Mitusova T.N., Khavkin V.A., Gulyaeva L.A., Kalinina M.V., Vinogradova N.Ya. The current state of production of low-curing diesel fuels at Russian plants//World of Petroleum Products, 2012, №2, pp.6-8

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TSİKLİK ÇOXATOMLU SPİRTLƏRİN EFİRLƏRİ DİZEL YANACAQLARINA ANTIOKSİDANT ƏLAVƏLƏR KİMİ

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2,2,5,5-tetrametilolsiklopentanol və 2,2,6,6-tetrametilolsikloheksanolun normal, izo- və neo-monokarbon turşularla bir sıra mürəkkəb efirləri sintez olunmuş və onların fiziki-kimyəvi, özlülük-temperatur, termooksidləşmə xassələri öyrənilmişdir. Bu efirlərin hidrotəmizlənmiş dizel yanacaqlarına 0.004% əlavəsilə kompozisiyalar hazırlanmış, onların istismar xassələri öyrənilmişdir. Müəyyən edilmişdir ki, tsiklik çoxatomlu spirtlərin normal, izo- və neo-turşularla efirlərinin hidrotəmizlənmiş dizel yanacaqlarına əlavəsilə termooksidləşmə sabilliyində əhəmiyyətli dərəcədə yaxşılaşma halları baş verir – çöküntü 0-1.32 mq/100ml-ə qədər azalır, alışma temperaturu 76⁰C-dən 87⁰C-yə qədər artır və donma temperaturu mənfi 19.2⁰C-dən mənfi 28⁰C-yə qədər azalır. Buna görə də, bu efirlər dizel yanacağına kompleks əlavələr kimi tövsiyə edilə bilər.

Açar sözlər: tsiklik poliolların efirləri, dizel yanacaqları, termooksidləşmə sabilliyi, kompleks əlavələr

ЭФИРЫ ЦИКЛИЧЕСКИХ МНОГОАТОМНЫХ СПИРТОВ В КАЧЕСТВЕ АНТИОКСИДАНТОВ К ДИЗЕЛЬНЫМ ТОПЛИВАМ

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Синтезирован ряд сложных эфиров циклических многоатомных спиртов- 2,2,5,5 тетраметилолциклопентанол и 2,2,6,6 тетраметилолциклогексанол с нормальными, изо- и нео-монокарбоновыми кислотами и изучены их физико-химические, вязкостно-температурные и термоокислительные свойства. С добавлением этих эфиров к гидроочищенным дизельным топливам в количестве 0.004% масс. эфиров приготовлены ряд композиций, определены их эксплуатационные характеристики. Найдено, что добавление эфиров циклических многоатомных спиртов с нормальными, изо- и нео- кислотами к гидроочищенному дизельному топливу приводит к значительным повышениям ТОС- осадкообразование снижается до 0-1.32 мг/100мл, повышению температуры вспышки от 76⁰С до 87⁰С и снижению температуры застывания от минус 19.2⁰С до минус 28⁰С дизельных топлив. Поэтому эти эфиры можно рекомендовать в качестве комплексных добавок к дизельным топливам.

Ключевые слова: эфиры циклических полиолов, дизельное топливо, термоокислительная стабильность, комплексные добавки