SÍNTESE DE CICLOCARBINOL E CICLOCARBINOLATO DERIVADOS DO CIANTRENO E SUA EFICÁCIA ANTIFUMOS PARA OS COMBUSTÍVEIS DIESEL

SYNTHESIS OF CYCLOCARBINOL AND CYCLOCARBINOLATE DERIVATIVES OF CYMANTRENE AND THEIR ANTI-SMOKE EFFECTIVENESS FOR DIESEL FUELS

СИНТЕЗ ЦИКЛОКАРБИНОЛЬНЫХ И ЦИКЛОКАРБИНОЛЯТНЫХ ПРОИЗВОДНЫХ ЦИМАНТРЕНА И ИХ АНТИДЫМНАЯ ЭФФЕКТИВНОСТЬДЛЯ ДИЗЕЛЬНЫХ ТОПЛИВ

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RESUMO

Os resultados do desenvolvimento da técnica de síntese dederivados de ciclocarbinol do ciantreno e a produção de relevantes complexos de metais de ciclocarbinolato de bário - novos aditivos antifumos avançados, foram apresentados. Dados comparativos sobre a eficácia antifumo de compostos sintetizados e aditivos antifumo conhecidos para combustíveis diesel também foram apresentados. Estabelecidos, os resultados do desenvolvimento de um método de síntese de um único estágio de derivados de ciclocarbiol do ciantreno podem ser considerados como um processo básico para a produção de aditivos antifumo altamente eficazes para combustíveis diesel que atendam às exigências ecologicas na operação de veículos a diesel.

Palavras-chave: cimantreno, eficácia anti-fumaça, ciclocarbióis, ciclopentanona, ciclohexanona, cimantreno de lítio, complexos de metal carbinolato.

ABSTRACT

The results of the development of synthesis technique of cyclocarbinol derivatives of cymantrene and the production of relevant barium cyclocarbinolate metal complexes – new, advanced anti-smoke additives were presented. Comparative data on the anti-smoke effectiveness of synthesized compounds and known anti-smoke additives for diesel fuels were also presented. Established, results of the development of a single-stage synthesis method of cyclocarbinol derivatives of cymantrene can be assumed as a basic process for producing high-effective anti-smoke additives to diesel fuels that comply with the requirements of ecology in operation of diesel vehicles.

Keywords: cymantrene, anti-smoke effectiveness, cyclocarbinols, cyclopentanone, cyclohexanone, lithium cimantrene, carbinolate metal complexes.

АННОТАЦИЯ

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В работе приведены результаты разработки технологии синтеза производных циклонабинолацимантрона и производства соответствующих комплексов циркокарбинолата бария – новых, современных противодымных добавок. Также были представлены сравнительные данные о противодымной эффективности синтезированных соединений и известных противодымных добавок для дизельных топлив. Установлено, что результаты разработки метода одностадийного синтеза производных циклокарбинолацимантрена можно считать основным процессом получения высокоэффективных противодымных добавок к дизельным топливам, которые соответствуют требованиям экологии во время эксплуатации дизельных транспортных средств.

Ключевые слова:цимантрен, антидымная эффективность,циклокарбинолы,циклопентанон,циклогексанон, литий-цимантрен,комплексы карбинолатных металлов.

INTRODUCTION

Man-made impacts of vehicular transport on environment increases steadily and at present nearly 40% of toxic substances and soot are fed into the atmosphere with exhaust gases of the internal combustion engine. It should be also noted that growth of diesel transport, expectations on which were related to decreasing the level of harmful emissions into the atmosphere, resulted in sharp aggravation of the problem since diesel fuels throw out up to 1 percent soot in the form of solid particles (SP) of total fuel consumption (Tartakovsky and Sheintuch, 2018; Boot *et al.*, 2017; Zhao *et al.*, 2015).

Improvement and usage of ecologic clean, matching to world standards, automotive and diesel fuels is one of the most important tasks of modern fuel-energetic complexes (Zakharova *et al.*, 1995; Zakharova *et al.*, 2004a).

Development and usage of ecologic clean additives that improve detonation resistance and anti-smoke quality of motor fuels, improving wherein its ecologic characteristics can be attributed to such factors.

Additives that improve cetane number of diesel fuels have important meaning for them (Kuznetsov, 2007; Han and Yao, 2015). Cetane increasing additives accelerate the initial pre-burning reactions and promote the formation of new active centers of reaction. As lower cetane number, as higher the rigidity of works of diesel. The cetane number of euro diesel working in Euro-3 and Euro-4 standards is regulated by Europe E № 590-1999 and 590-2004 standards respectively, require minimal cetane number 51. Also, other engine performance indicators are depending on the meaning of cetane number: its squeak, average effective combustion pressure, specific fuel consumption, exhaust gas temperature, engine build-up, smoke and odor of exhaust gases.

With the increasing of cetane number of engines, engine starting is facilitated and increases the medium pressure of combustion, decreases other indicators, at all engine performance improves (Han and Yao, 2015).

In the whole world demand for high-quality diesel fuels is increasing in connection with the growth of the increase in production of cars with diesel engines. Along with this the question about the necessity of development of anti-smoke additives, increasing the quality of diesel fuels, which is a topical problem of modern energy complexes raises.

One of the prospective directions of decreasing emission of solid particles (SP) with exhaust gases is the introduction of antismoke, multifunctional additives, particularly, barium containing compounds of different nature into fuel which allows reaching targeted goals without changing the construction of diesel and system of their feed system (Li *et al.*, 2013).

However, it is known that despite prevalence of using barium antismoke additives in diesel fuels, for a number of reasons the last, such as growth of ash-content, filtration coefficient of fuel, higher content in fuels and the presence of excessive oxide and barium carbonate in gas emissions, do not also completely meet all requirements of ecology (Mitusova *et al.*, 2015; Kolobova *et al.*, 1978; Kulchitsky, 2004; Suleimanov *et al.*, 2007; Napolitano *et al.*, 2018).

In this connection additives based on

organo-metal compounds which contain barium and easily ionizable metals of variable valency of IV period of Periodic System of elements are of great interest and they show a synergetic catalytic effect in burning process of soot in fuel combustion at low concentrations.

The target of these researchers in the development of available synthesis techniques of mono-, and binuclear cycloalkylcarbinol derivatives of ferrocene and cymantrene (cyclopentadienyl manganese tricarbonyl), as well as the study of their properties as more effective nanocomposite additives to diesel fuels.

MATERIALS AND METHODS

The basis of experimental researches are composed:

X-ray and thermogravimetric analysis of substances of additives, researching of the surface tension of clean fuel and fuel with additive, toxicity studies, effectivity and economy of a full-size diesel, working on different pressure and speed modes on clean fuel and fuel with the additive.

In order to study the peculiarities of the occurrence of exothermic reactions during the thermal decomposition of the developed additives to fuel, their laboratory-chemical studies were carried out (Safarov *et al.*, 2018; Meißner *et al.*, 2016).Elemental analyses of chemical compounds gained compounds were performed by X-ray and microanalytical method. The X-ray diffraction pattern was obtained with a DRON-3M diffractometer.The thermogravimetric diagrams of the complexes are shown in Figure 1

For the researching of phase transformations and chemical reactions, accompanied by thermal effects, a thermogravimetric analysis of the obtained compounds on the OD-112 derivato graph was carried out.

Bench tests of the diesel 4h11/12.5 on standard fuel and fuel with anti-smoke additives were carried out in the engine testing laboratory of the FGBOU VPO in accordance with GOST 18509-88 at the rolling-brake stand KI-5543 GOSNITI (GOST 18509-88).

For measuring the concentrations of main toxic components (CO, CH, NO) and the smokiness of OG diesel, working on fuel with different anti-smoke additives, the gas analyzer META AVTO-TEST was used. The cetane number of diesel was found by IDN method. The smoke opasity of the exhaust gases is measured on the modes of the external speed characteristic from the maximum speed of rotation to the greater of two: 0.45 n_{max} or 16.7s^{-1}, and the smoke opasity is measured at least six times at equal intervals of rotation frequencies, including maximum torque, and free acceleration. The measurements are carried out on diesel fuel of grade L according to GOST 305-82, density at 20 °C 820 - 830 kg / m^3 (GOST 305-82). The excess pressure of exhaust gases in the chamber of the measuring device during the measurement was in the range of 490 N / m^2 (50 mm Hg) - 585 N/m^2 (60 mm Hg). The temperature of the gas in the measuring chamber of the device must be at least 343 K (70 °C) and not higher than the maximum permissible value specified by the device manufacturer. Smoke opasity in each mode was measured three times, while the difference in the measurement results did not exceed 4% in units of the instrument scale. The interval between consequental measurements did not exceed 1 min. The arithmetical average of the three measurements is taken as the result of the measurement.

RESULTS AND DISCUSSION

It is known that cymantrene and its many derivatives have properties of antiknock additives for engine fuels which substitute ecologically harmful tetraethyllead (TEL) (Suleimanov *et al.*, 2007).

Target cymantrene– cycloalkylcarbinol derivatives were synthesized on the basis of two basic reactionary directions. (Equation1)

The first was based on the interaction of organolithium derivative (Equation 2) of cymantrene,$(OC)_3MpC_5H_4Li$with corresponding cyclic ketones, where=4-6.

The reaction of the reciprocal interaction of cyclopentyl and ketone at temperatures of $30 \div 35^0$C but with the reaction yield of 20–30% resulted in the production of an intertype complex of simantrenyl lithium carbinolate. Conversely, the reaction at temperatures of 0^0C ÷ -13^0C resulted in a variation in the yield of the desired product dimantrenylpentylcarbinol in the range of 70÷82%. (Equation3)

It should be noted that according to the same rule with the reaction yield of 68–75% was received simantrenylcyclohexylcarbinol complex.(Equation 4).

The second direction includes the direct oxyalkylation of cymantrene with cycloalkylketons in phase-transfer catalysis. Earlier under these conditions, we have obtained cymantrenyl-carbinols of linear structure (Korchagin and Filonenko, 1997).

On the example of cyclopentanone transformation, as well as cyclohexanone according to the first reactionary direction it was established that independent of reaction temperature and polarity of reaction medium different cycloalkylcarbinolate and ether derivatives and carbine complexes of Fischer are formed as basic products which after relevant neutralization of reaction medium (Equation 5) are converted to target products (Equation 6)p=4 (I); p=5(II) with yield not exceeding 10-14 % on cymantrene.

This fact suggests that the synthesis of derivatives I and II by the first reactionary direction cannot be considered perspective, due to the low yield of target products, multiple stages and large losses of components of the reaction mixture in their isolation.

In development plan of a single-stage synthesis method of I and II, the second reaction of direct oxyalkylation of cymantrene during the interaction both with cyclopentanone and cyclohexanone under interphase-transfer catalysis is more effective.

Water (inorganic phase creator) and petroleum ether – a light fraction of petroleum $T_{N.к}$ 40°C-$T_{K.к.}$ 80°C (organic phase creator) were used in the oxyalkylation process as phrase creators.

Reactionary components (cymantrene and relevant cyclic ketones) were added into the organic phase, but acid catalyst (92-94 % H_2SO_4) was added into inorganic phase. Quaternary ammonium salt – diethyl ammonium naphthenate(Equation 7)was used as an interphase transfer catalyst.

When developing synthesis technique the fact of the possible addition of cymantrene into both aliphatic and aromatic aldehydes and ketones only under high acidity of reaction medium (pK - 21-22) was considered.

When choosing optimum conditions for oxyalkylation of cymantrene relevant cyclic ketones complied with not only volume ratio of organic and inorganic phases equal to 20:1, but also weight ratio of acid catalyst *(H_2SO_4),* both to ketones and interphase- transfer catalyst (DEANaf), correspondingly (1:1).

Conditions of producing cymantrenylcyclopentyl-(hexyl-) carbinols by oxyalkylation of cymantrene with cyclopentanone or cyclohexanone using H_2SO_4 - DEANaf of catalytic system are given in Table 1.

Studies on the dependence of yield of target products on the oxyalkylation temperature of cymantrene with cyclic ketones showed that even at room temperature decomposition of metal complexes occurs due to the impact of daylight. Thus, upon absorption of energy of light photons, decarbonylation of complexing metal (*Mn*) occurs initially with the further complete decomposition of the compound.

Oxyalkylation of cymantrene is to be conducted in complete isolation from the impact of light flux at a temperature, not higher than-10°C. When following synthesis conditions indicated in table 1, the yield of relevant cymantrenecyclopentyl-(hexyl-) carbinols, I and II for cymantrene makes 86-89%.

Method of isolating target products I, II from reaction mixture was reduced to the following sequence of procedures.

First, the reaction mixture was neutralized with 5 % solution of$NaHCO_3$, the organic layer was removed and after dehydration, the solvent was completely evaporated, and the oily residue was extracted twice with diisopropyl ether. The extracts were combined together and after evaporation of diisopropyl ether derivatives, I and II were extracted in pure form.

Their elemental composition that corresponds to chemical formulas $C_{12}H_{13}MpO_4(1)$ and $C_{14}H_{15}MpO_4(P)$was established using microanalysis method.

It appears that unlike cymantrene its derivatives I and II are liquid products with density of d^{20} =1,257g/cm^3(1); d^{20} = 1,269 g/cm^3 (II).

It was established that in the interaction with *LiOH(NaOH)* in alkali medium*(pH*=8-9) derivatives I and II form relevant alkoxides(III, IV), but in aqueous-(Equation8; Equation9) alcoholic medium in the interaction with $Ba(OH)_2$disolvate salt of barium alkoxides are

formed, where π =4,5 (V-VI).Cymantrenecyclopentyl(hexyl) carbinols and their barium derivatives are well soluble both in different sorts of gasoline and their fractions and in diesel fuels.

For example, maximum solubility of derivatives I-V at 20°C in 95 RON varies in the range of 10 ÷ 24 g/l, but in diesel fuel, with a cetane number of 40, it varies in the range of 2÷8,7 g/l.

It was established that solubility of carbinols (I, II) in gasoline is better than cymantrene, but barium derivatives (V-VI) in diesel fuel are better soluble than in gasoline.

Study of antismoke effectiveness of both carbinols and barium carbinolate derivatives of cymantrene was performed relating to diesel fuel with a cetane number of 38 and density of d^{20}=0.856g/cm^3. Benzene was used as a standard to determine antismoke effectiveness.

Table 2 represents the motor test results of the antismoke effectiveness of synthesized carbinol and carbinolate derivatives of cymantrene.

These tests (in conformity with GOST 17.2.2.01-84) showed that after adding compounds I-II and V-VI into diesel fuels in the range of 0.02=0.035 g/l, the last show a rather high ability to reduce smoke emission at an average working load of engine, barium derivatives (V-VI) are more effective than carbinol derivatives and cymantrene (GOST 17.2.2.01-84).

Considerably lower concentrations of synthesized derivatives of cymantrene which were added into diesel fuel, also reduce the emission of barium compounds into the environment to a minimum that significantly differs them from known industrial antismoke barium additives.Some physico-chemical properties of the complexes obtained are shown in table 3.

It should be noted that when adding a large amount of antismoke additive ECO-1 and barium additive IChP-706 into the composition of diesel fuel, 0.4 and 0.5% (mass) correspondingly, amount of soot decreases only 30-40% in exhaust gases of diesel fuel at an average working load (Gladkov *et al*., 1984; Imanov, 2013).

Thus, results of the development of a single-stage synthesis method of cyclocarbinol derivatives of cymantrene can be assumed as a basic process for producing high-effective antismoke additives to diesel fuels that comply with the requirements of ecology in operation of diesel vehicles (Imanov *et al*., 2013; Emelyanov *et al*., 1998; Zakharova *et al*., 2004b).

CONCLUSIONS:

New anti-smoke additives made based on of zymantrene derivatives, for decreasing the smokiness during the burning of engine fuels were developed.

It was established out that additives made based on metal-organic compounds, that include barium and sodium, very effectively decrease the smokiness.

The comparison results of presenting and new-gained anti-smoke additives to diesel showed that they decrease smokiness on the average by 50-75%, by the content of mono-oxide of carbon and hydrocarbons by 20-40%.

Effectivity of developed additives was experimentally confirmed. It was shown that when the addition of 0.05 g / l of cymantrenylcyclohexylcarbinol to the fuel is effective, 68%, cymantrenylcyclopentyl sodium carbinol is 93%, and cymantrenylcyclohexyl sodium carbonylate is 95%.

It was found that nanocomposite solutions prepared on the basis of carbinol derivatives of ferrocene are more ecologically safe anti-smoke additives

The dependence between cetane number of diesel and anti-smoke effectiveness of composite material was established.

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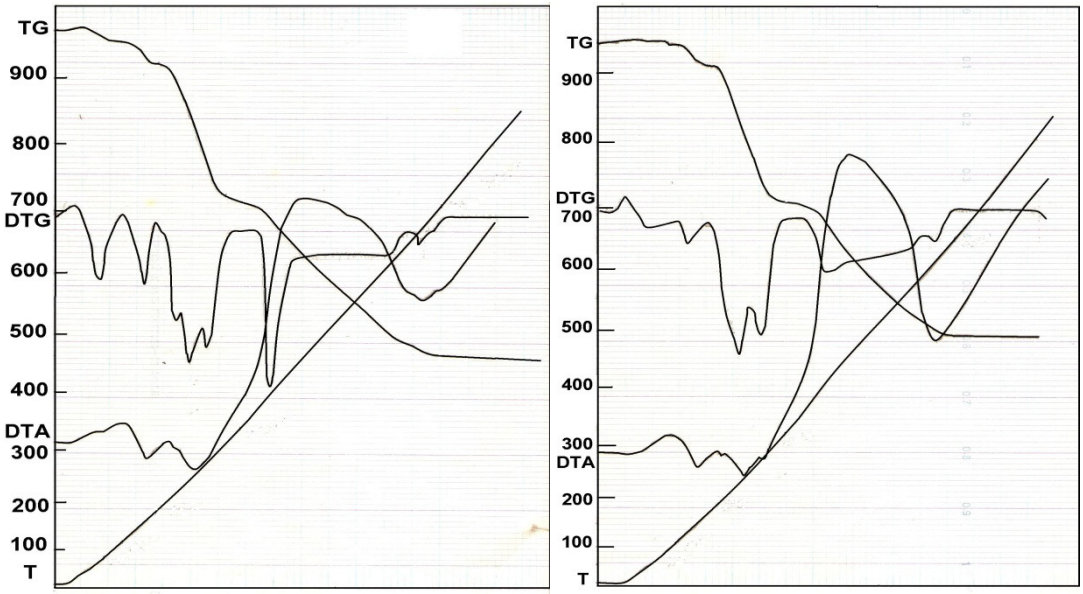


a) b)

Figure 1.The thermogravimetric diagrams of the complexes: a) $(OC)_3MnC_5H_4C(CH_3)_2OH$

b) $(OC)_3MnC_5H_4–C(OH)–C_6H_4–CH_2$

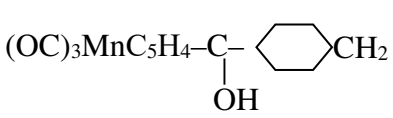
Table1.*Conditions of producing cymantrenylcyclopentyl-(hexyl-) carbinols by oxyalkylation of cymantrene with cyclopentanone or cyclohexanone using H_2SO_4 - DEANaf of catalytic system*

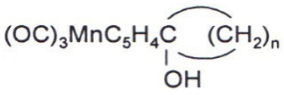
Phase	Phase creating components and their volume ratio	Reaction temperature,°C	Reacting components and their mole ratio	Products of oxyalkylation
Organic	Petroleum ether 20	-10÷ -20	Cymantrene, cyclopentanone (cyclohexanone) 1:1	Cymantrenyl-cyclopentyl-(cyclohexyl-) carbinols
Inorganic	Water 1	-10÷ -20	H_2SO_4: (DƏANaf) 1:1	Catalyst carrier

Table 2.*Smoke reducing effect in the series of cymantrene and its cyclocarbinol (I, II) and bariumcarbinol derivatives (V, VI) in diesel fuel (GOST 17.2.2.01-84) at an average load of engine*

№	Name of complex	Influence of cymantrene and its derivatives on smoke reducing effect, %			
		0.02 g/l	0.025 g/l	0.035 g/l	0.05 g/l
1	Cymantrene	18	33	47	48
2	Cymantrenylcyclopentylcarbinol	29	48	63	65
3	Cymantrenylcyclohexylcarbinol	31	52	67	68
4	cymantrenylcyclopentylcarbonylatesodium	69	84	92	93
5	cymantrenylcyclohexylcarbonilatesodium	71	88	94	95

Table 3.*Some physico-chemical properties of the complexes obtained*

Compounds	Results of elemental analysis					
	Found, %			Calculated, %		
	C	H	Mn	C	H	Mn
$(OC)_3MnC_5H_4C(CH_3)_2OH$	50.30	4.25	20.86	50.38	4.19	20.99
	55.70	4.88	18.30	55.62	4.96	18.21



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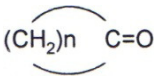

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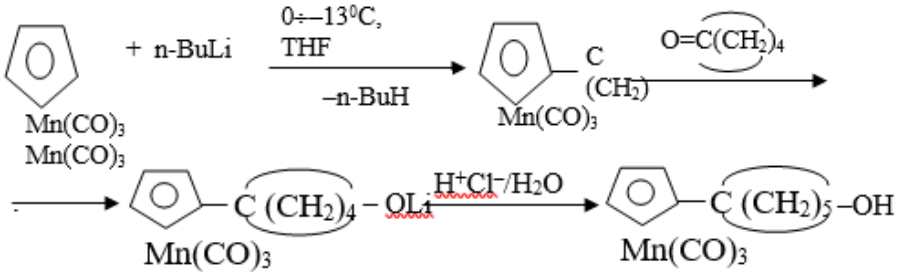

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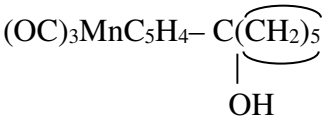

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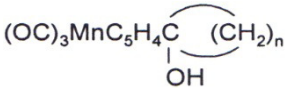

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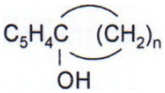

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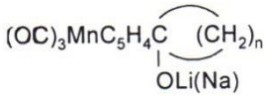

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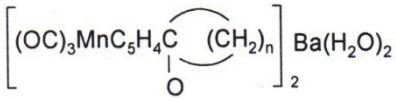

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