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Petrochemistry

**SYNTHESIS OF A DIESTER ON THE BASIS OF SYNTHETIC PETROLEUM ACIDS
AND DIPHENYLOLPROPANE PROPYLENE OXIDE MONOETHER IN THE
PRESENCE OF NANO - TiO_2 (PC-500) CATALYST AND INVESTIGATION OF THE
DIESTER ANTIOXIDANT PROPERTIES**

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In the paper presented the synthesizing of diester from naturally occurring petroleum acids and monoether of diphenylolpropane propylene oxide taken at ratio 2:1mol, temperature range 110-120 °C, for 8-9 hours in the presence of 1wt.% of nano- TiO_2 (PC-500) has been described. Physical-chemical rates of the diester obtained have been determined by chemical analytical and spectral means. It has been revealed several advantages due to use of such type of nanocatalyst. One of them is environmental admissibility of the process. The synthesized diester may be applied as an impactful antioxidant for diesel fuels.

Keywords: nano- TiO_2 catalyst, synthetic petroleum acids, diphenylolpropane propylene oxide monoether, esterification, diesel fuel, ecological process

For the first time the authors have studied the synthesis and characteristics of alkyl ethers of tetracyclo[6,2,1^{1,8}, 1^{3,6}, 0^{2,7}] dodes-9-en-4 carboxylic acids. The reaction was performed at 80-90 °C, for 3-4 hours in the presence of nano- TiO_2 (PC-500) and was distinguished by high yield [1].

The alkyl esters of bicyclic and methyltetracyclocarbon acids have been synthesized and described in the presence of the same catalyst [2, 3].

Monoether of natural petroleum acids (NPA) and trimethylolpropane, diether and butyl ether of α -naphthyl ethanoic acid and ethylene glycol have been synthesized by researchers from the Liquid-Phase Oxidation Laboratory in the presence of nano- TiO_2 (PC-500) and the esters applied as an antioxidant to learn whether such additives are suitable or not for the purposes [4].

Conditions of the production of esters on the base of NPA and trimethylolpropane conducted in the presence of nano- TiO_2 (PC-500)

as well as the esters physical-chemical rates have been determined. The authors also undertook investigations to study a behaviour of the esters as softeners for polyvinylchloride PVC S39-71. It has been found out that the samples tested have some higher indices than those for commercial softener dioctylphthalate [5].

From [6,2,1^{1,8}, 1^{3,6}, 0^{2,7}]-dodes-9-en-4 carboxylic acid and trimethylolpropane and in the presence of nano- TiO_2 (PC-500) the novel ester has been synthesized, the influence of some basic parameters on the ester yield determined [6].

In the presence of nano- TiO_2 (PC-500) the ester from synthetic petroleum acids (SPA) and dihydrodicyclopentadiol has been synthesized with high yield, the optimum conditions of the reaction, the ester physical-chemical rates and general engineering scheme of the process have been proposed by the researchers [7].

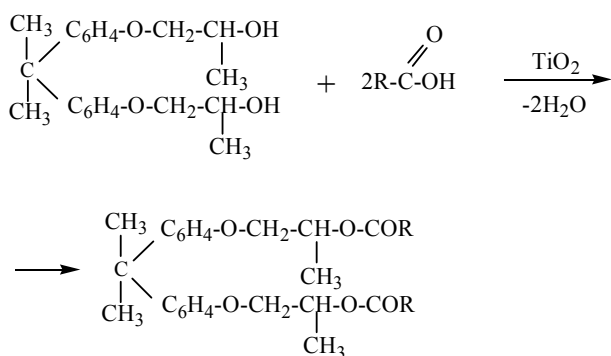
Physical-chemical data of initial reagents used in experiments are given in table 1.

Table 1

The indices of the initial reagents

Substance name	Boiling temperature, $8 \cdot 10^{-4}$ MPa, °C	ρ_4^{20} , kg/cm ³	Refraction index, n_D^{20}	Acid Number, mgKOH/g
SPA	80-200	987.2	1.4620	255.0
Monoether of diphenylolpropane propylene oxide	–	1031.5	1.4902	0.050

The esterification reaction on SPA and monoether of diphenylolpropane propylene oxide based synthesis was conducted in the presence of nano-TiO₂ (PC-500) catalysts, the optimal conditions of a diester synthesis have been determined:



here, R is radical of SPA.

The synthesis was accomplished at the following conditions:

- electric heating device, thermometer, in three-necked flask equipped by Dean-Stark type water trap 44g(0.2mol) of SPA, 105.0g(0.105 mol) of monoether of diphenylolpropane propylene oxide (the monoether is taken over 0.05 mol more). 0.44g of nano-TiO₂ catalyst (1 wt.% to the acids) and 100 ml of toluene are placed. The reaction was conducted for 8-9 hours, consequently 3.6 g of water was isolated.

- after the reaction mixture stirring has been completed the catalysts was separated from the other components and the solvent was distilled by a water pump. Yield of the ether obtained is near 90%. The ether is a liquid of yellowish colour.

Structure of the diether obtained on the base of SPA and monoether of diphenylolpropane propylene oxide was studied by "ALPHA" IR- Fourier spectrometer. There the following absorption bands have been observed:

1373, 1455, 2869 cm⁻¹ – deformation and valence vibrations of CH₃- and CH₂- groups
 1089 cm⁻¹ – vibrations of the ether groups C-O-C
 1244, 1295, 1728 cm⁻¹ – vibrations of the ester C-O-C and C=O bonds
 1605 cm⁻¹ – C=C bond vibrations of benzene structure
 1508 cm⁻¹ – vibrations of benzene structure core

In addition, the diester chemical structure was studied by other physical-chemical means. It has been shown by investigations that the procedure used for the diester synthesis has a definite advantage and may be used in the future as a promising way from economical and ecological point of view. The diester obtained from SPA and monoether of diphenylolpropane propylene oxide was tested as an antioxidant in hydrorefined diesel fuel. To make this, 0.004 wt.% of the diester was added to the diesel fuel and the sample was subjected to the heat treatment in the LSART apparatus at 120 °C for 4 hours over copperplate, according to the GOST-2397-79. The thermo-oxidative stability is defined according to an amount of deposit in mg being formed at heat treatment of 100ml of diesel fuel for 4 hours. Results of impact of the diester on thermo-oxidative stability of diesel fuel are presented in table 2.

Table 2

Data on thermo-oxidative stability of diesel fuel containing the diester additions

No	Sample	Thermo-oxidative stability, amount of a deposit formed in the fuel, mg/100 ml	Density, kg/m ³	Content of total sulfur, %	Cetane number
1.	Hydrotreated diesel fuel (D/F)	4.6	850.0	0.0141	45.0
2.	Diester of SPA diphenylpropane oxide (0.004 wt. %)+ D/F	1.0	844.0	0.0083	44.2

As it is seen from table 2, 0.004 wt.% additions of the diester to the hydrotreated diesel fuel entail decrease of the sediment amount from 4.6 mg to 1.0 mg. According to the results obtained one may corroborate, that the diester can be applied in hydrotreated diesel fuels as an antioxidative agent.

Thus, for the first time, diester on the base of SPA and monoether of diphenylpropane propylene oxide has been synthesized using nano-TiO₂ catalyst, and their respective physical-chemical indices have been determined. Diester samples for further testing in the diesel fuel were prepared, their antioxidative ability and properties upon adding in the diesel fuel have been studied. It has been established that the tested diester samples may be used in a diesel fuel as effective antioxidative admixtures.

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NANO-TiO₂ (PC-500) KATALİZATORUNUN İŞTİRAKI İLƏ SİNTETİK NEFT TURŞUSU VƏ DİFENİLPROPANIN PROPİLEN OKSİDİNİN MONOEFİRİ ƏSASINDA DİEFİRİN SİNTEZİ VƏ ONUN ANTİOKSİDANT XASSƏSİNİN ÖYRƏNİLMƏSİ

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Nano-TiO₂ (PC-500) katalizatorunun iştirakı ilə miqdarı (1,0 kütlə %), təbii neft turşusu və difenilpropanın propilen oksidinin monoefiri 2:1 mol nisbətində, temperatur 110-120 °C, 8-9 saat müddətində yüksək çıxımla diefir sintez olunmuşdur. Sintez edilmiş diefirin fiziki-kimyəvi göstəriciləri təyin olunmuş və spektral üsulla identifikasiya edilmişdir. Bu katalizatorla alınan diefirin sintezi bir neçə üstünlüklərə malikdir. Belə ki, aparılan birləşmə reaksiyasını ekoloji cəhətdən əlverişli proses kimi qəbul etmək olar. Sintez edilən diefir dizel yanacağında antioksidant kimi istifadə oluna bilər.

Açar sözlər: nano-TiO₂ katalizator, sintetik neft turşusu, difenilpropanın propilen oksidinin monoefiri, efirləşmə, dizel yanacağı, ekoloji proses

СИНТЕЗ, ИССЛЕДОВАНИЕ ДИЭФИРА, ПОЛУЧЕННОГО НА ОСНОВЕ СИНТЕТИЧЕСКОЙ НЕФТЯНОЙ КИСЛОТЫ И МОНОЭФИРА ОКСИД ПРОПИЛЕНА ДИФЕНИЛОЛПРОПАНА В ПРИСУТСТВИИ НАНО-TiO₂ (PC-500) КАТАЛИЗАТОРА, А ТАКЖЕ ИЗУЧЕНИЕ ИХ АНТИОКСИДАНТНЫХ СВОЙСТВ

П.М.Керимов, Э.Б.Зейналов, О.М.Алескерова, Л.Г.Нуриев, Б.К.Агаев, С.Г.Алиева, Э.М.Гулиева

Был синтезирован диэфир с высоким выходом на основе моноэфира оксид пропилен дибензилпропана и синтетической нефтяной кислоты в соотношении 2:1,0 моль, в присутствии гетерогенного катализатора нано-TiO₂ (PC-500) в количестве 1,0 мас. %, при температуре 110-120 °C и продолжительности реакции 8-9 часов. Были определены физико-химические показатели синтезированного диэфира, а идентификация его была доказана спектральными методами. Использование нано-TiO₂ катализатора в реакциях этерификации приводит к следующему преимуществу, как суждение об экологически чистом процессе. Синтезированный диэфир может быть применен в качестве антиоксиданта к дизельным топливам.

Ключевые слова: нано-TiO₂, синтетическая нефтяная кислота, моноэфир пропилен оксида дифенилолпропана, этерификация, дизельное топливо, экологически чистый процесс