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Synthesis and investigation of ethylene glycol diester based on oxidate

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Abstract
The article is devoted to synthesis and research of a method of production of ethylene glycol diester based on oxidate (oxidized reaction mixture) in the presence of heterogeneous catalyst ZnO. The influence of the ZnO catalyst quantity, reaction temperature, mole ratio of oxidate and ethylene glycol has been studied with the aim of selecting the optimal synthesis condition of ethylene glycol diester. In the optimal mode found, ethylene glycol esterification reactions were carried out and the final product with the maximum yield was obtained. The synthesized diester was characterized by analytical and spectral methods and the material balance of the process for producing ethylene glycol diester was compiled. The purpose of further research was to study the plasticizing properties of diester in the manufacture of the composition based on polyvinyl chloride and testing as antioxidant and depressant additive for diesel fuel.

Keywords: Ethylene glycol, oxidate, esterification, diester, catalyst, plasticizer, antioxidant, depressant

Introduction

Complex esters of aliphatic-, alicyclic- and aromatic carboxylic acids of single- and diatomic alcohols can be used as plasticizers - one of the most important classes of polymer additives, the introduction of which into polymers leads to structural changes and, properties: elasticity, frost resistance, reduction of processing temperature [1-3], and antioxidants and depressant additives to improve thermo-oxidant and low temperature properties of diesel fuels.

As a rule, carboxylic acid esters are produced in two or more stages in an acidic medium [4] with a low yield, because the reaction mechanism follows the homogeneous mechanism [5] and this mechanism requires high temperatures for the thermal activation of one of the reagents. A recent review of the literature [6] identified Zn(II) ion as a highly effective catalyst for esterification of acids with medium/long-chain alcohols. The work [7] describes the use of simple zinc salts (II) ($ZnCl_2$, $ZnCO_3$, ZnO, $Zn(ClO_4)_2$, $Zn(BF_4)_2$) as catalysts for fatty acid esterification with long-chain alcohols. The results showed that catalytic activity depends on the nature of the gegenion: the most effective salts are those containing basic Brensted anions (oxide, acetate and carbonate).

Representatives of chemistry and chemical engineering defined green chemistry, shifting the focus from waste treatment to pollution prevention [8].

In view of the above, the development of an advanced method of producing esters from available raw materials in the presence of a heterogeneous catalyst, a single-stage method – without stages of neutralization, washing, drying is topical.

Authors of scientific research [9] synthesis of mixed propylene glycol esters based on natural petroleum and fatty acids in the presence of a ZnO catalyst and preliminary evaluation of the possibility of using synthesized diesters as a plasticizer for polyvinyl chloride and antioxidant diesel fuel. Optimal conditions for esterification were found: the ratio of acids and alcohol - 2.0:1.3, the amount of catalyst - 1.2-1.6 mass. %, the temperature is 110-120ºC, the reaction time is 3.5-4 h.

Depending on the fatty acid taken, the output of mixed diesters ranged from 88-90%. Structural-group composition of the obtained mixed diesters was determined by spectral methods (IR- and NMR-spectroscopy).

Work [10] focuses on the reception and study of 1.4-butanediol mixed (asymmetric) diesters of synthetic petroleum and aliphatic fatty acids (C_6-C_8). A high yield of the target product (90.3%) is found under the following conditions: temperature - 110-120°C, catalyst quantity - 1.3 mass. % (by acid), mole ratio of components - acid: alcohol - 2:1.4. Physico-chemical indicators and structure of synthesized products have been determined. It is shown that 1.4-butanediol mixed diesters have good compatibility with polyvinyl chloride, forming colorless elastic plastics. Synthesized esters have been tested as antioxidant, improving the thermooxidative stability of diesel fuel. It has been determined that the precipitation formed as a result of oxidative polymerization and polycondensation of diesel fuel due to the presence of heteroatomic compounds in its composition decreases at the addition of 0.004 mass.% of synthesized diesters from 4.6 mg/100 ml to 1.0 mg/100 ml of diesel fuel.

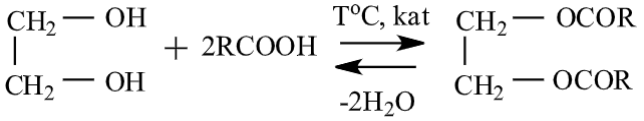
The recent trend is a constant increase in the cost of raw materials, which leads to higher prices for final products. There are a number of industries that justify the use of plasticizers, antioxidants with indicators that are slightly different from existing, but at the same time cheaper. The aim was to - develop an improved method for producing ethylene glycol diester based on the available raw material, the laboratory oxidate.

Experimental part

For the production of ethylene glycol diester were used as raw materials: oxide, ethylene glycol (EG) (99%, Alpha Aesar, A11591), ZnO (98%, Alpha Aesar, A16188), toluene (99%, Alpha Aesar, L967). Oxidate was produced under laboratory conditions, by liquid-phase oxidation of naphthene-paraffin hydrocarbons extracted from oil distillate T-1500 in the presence of a Mn dibrombenzoate catalyst in a bubble reactor at a temperature of 140°C

(physico-chemical indicators of oxidate: acid number - 60 mg KOH/g; molecular mass calculated on acid number - 935 g·mol^{-1}; ρ_4^{20} - 0.9555 g/cm^3; n_D^{20} - 1.4695).

The synthesis of ethylene glycol diester in the presence of the ZnO catalyst was carried out in a single step in a three-way glass flask equipped with a mechanical mixer, thermometer, refrigerator and Dean-Stark water separator in the following way:



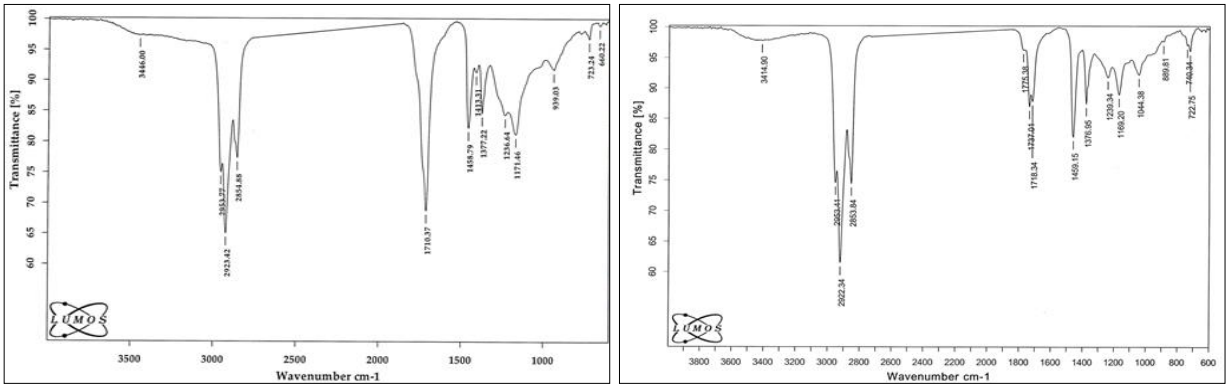
where R is the radical of oxidate.

The synthesis of the target ester is described below: 467.5 g oxidate, 23.25 g ethylene glycol, 0.93 g ZnO and 345.0 g toluene (taken in the amount of 70% of the total mixture of components as azeotrope generator). The reaction continued for 6 hours. The end of the reaction was determined by the amount of water emitted and the acid number (0.1-1.0 mg KOH/g). At the end of the reaction, the contents of the bulb were cooled to room temperature, after which the mixture was separated from the catalyst by filtering. It should be noted that when using ZnO, processing of raw ester takes place without neutralization, washing, drying. After the distillation of the solvent - toluene, the raw ester was subjected to atmospheric and vacuum distillation, as a result of which the target ester was obtained and physico-chemical indicators were determined: boiling temperature - 150-200ºC/6.65 10^{-4} MPa, acid number - 0.5 mgKOH/g, ρ_4^{20} - 0.9478 g/cm^3, n_D^{20} - 1.4700, mass fraction of volatile substances - 0.6%, freezing temperature – - 44-46°C, output - 88% (in theory). The material balance of ethylene glycol diester has been compiled and is shown in table 1.

Table 1: Material balance of ethylene glycol diester production process

Raw material			Products		
Name	Amount		Name	Amount	
	g/mole	%		g/mole	%
Oxidate	467.5	55.88	Water	8.9	1.06
EG	23.25	2.78	EG	7.4	0.88
ZnO	0.93	0.11	ZnO	0.75	0.09
Toluene	345,0	41.23	Toluene	338.0	40.40
Total	836.68	100.0	Ethylene glycol diester	474.0	56.65
			Wastage	7.63	0.92
			Total	836.68	100

The structural-group composition of the oxidate and synthesized ethylene glycol diester are determined on the Fourier spectrometer of the model «ALPHA» (BRUKER) in a set with the attachment of a broken full internal reflection with a prism of diamond, which is designed for the analysis of solid, Liquid and powdery samples in scanning range 4000-400 sm^{-1} and shown in Figure 1.



A **B**

Fig 1: IR spectra of oxidate (A) and ethylene glycol diester (B)

The purpose of further research is to study the plasticizing properties of ethylene glycol diesters in the manufacture of a polyvinyl chloride (PVC) based composition. The degree of compatibility was judged by the time of swelling in it PVC. For this purpose the composition was prepared - 100 mass of PVC, 30-70 mass of synthesized diester, 1 mass of stabilizer - calcium stearate $Ca(C_{17}H_{35}COO)_2$ (99%, Dansuk Industrial Co., Ltd). The composition was kept in the thermostat for a certain time, depending on the temperature (65, 75, 85ºC) to complete swelling of the composition. The chilled composition was then held under load to room temperature on the filter paper until there was no grease stain.

The synthesized diester has also been tested as an antioxidant for diesel fuel on the LSART machine at a temperature of 120°C and as a depressant to improve the low-temperature properties of diesel fuel according to the (ISO:3013-74) method.

Discussion of the results

To determine the optimal conditions for the production of ethylene glycol diester, the following reaction parameters were varied: the ratio of oxidate:EG within 2:(1.2-1.6) mole, the range of reaction temperature change – 80-140°C, the amount of catalyst – 1.6-2.2 mass.% (to the oxidate).

The highest yield of ethylene glycol diester (88%) is obtained by optimum mode of synthesis: temperature – 110-120°C, catalyst quantity – 2.0 mass.% (by oxidate), the ratio of oxidate:EG – 2.0:1.5 mole:mole, reaction duration – 6 h.

The IR oxidate's spectrum exhibits the following absorption bands: deformation (723, 1377, 1413, 1458 sm^{-1}) and valence (2854, 2923, 2953 sm^{-1}) oscillations of the C-H bond in CH_3 and CH_2 groups; valence (1710 sm^{-1}) oscillations of C=O bond of oxidate; valence (939, 1171, 1236 sm^{-1}) oscillations –COOH group of the O-H and C-O bonds of the oxidate; valence (3446 sm^{-1}) oscillations OH group of the O-H bond of the oxidate (Fig.1**A**). The spectra of the synthesized diester show absorption bands in the

following areas: 1717,1737,1778 sm^{-1} – C=O bond of the ester; 1080, 1134, 1169,1242 sm^{-1} – C-O bonds; 3452 sm^{-1} – valence oscillations of the O-H-bond of OH group; 2854, 2922, 2953 sm^{-1} – valence oscillations of C-H bond of CH_3- and CH_2-groups. The presence of functional groups in the spectrum of the above mentioned groups proves that the synthesized compound belongs to the class of esters (Fig.1B).

Usually plasticizers are combined with PVC at a temperature of 65-75°C within 30-40 mass. Given that the synthesized oxidate-based diester has a large molecular mass, therefore the optimal compatibility limit was 50 mass at 85°C.

The application of diesel fuels at low temperatures causes considerable difficulties, as crystals of high-melt hydrocarbons fall out of the fuel, resulting in loss of mobility and complete engine shutdown. It is difficult to use diesel fuels at low temperatures. Therefore, the development of low pour point fuels is an urgent problem. The resulting ethylene glycol diester has been tested as an antioxidant and a diesel depressant. The analysis of the data showed that the performance characteristics of diesel fuels are significantly improved: a sediment characterizing the thermooxidative stability of diesel fuel, with the addition of 0.004 mass.%. of the synthesized diester is reduced from 1.0 mg/100 ml to 0.2 mg/100 ml, and the floc and freezing temperature at the addition of 0.05 mass.% of diester drops from minus 2°C to minus 12°C and from minus 20°C to minus 22°C, respectively.

The synthesized ethylene glycol diester is a light yellow oily liquid with a specific smell, insoluble in water, but well soluble in organic solvents.

Conclusion

The proposed method for producing an oxidate-based diester in the presence of a heterogeneous catalyst makes it possible to simplify the process technology, thereby ensuring environmental purity.

According to the obtained data, the possibility of using a synthetic ethylene glycol diester as a secondary plasticizer of polymer materials and an effective antioxidant additive and a depressant additive to fuels has been identified.

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