Fuel additive production via oxidative modification of fatty acid methyl esters

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Keywords: fatty acid methyl esters, oxidation with atmospheric oxygen, formation of esters, separation and analysis of reaction products, peroxides, ignition promoter for diesel fuel.

Relevance of the research topic. Vegetable oils and their derivatives are promising renewable raw materials for industrial organic synthesis. For example, fatty acids (FA) and fatty acid methyl esters (FAME) have found application in the production of lubricants, surfactants, in the fuel, agrochemical, cosmetic and paint industries. In turn, epoxidized oil derivatives can be used in the synthesis of epoxy resins, as well as a stabilizer and plasticizer for polyvinyl chloride.

As is known, FAMEs have found wide application in the fuel industry of a number of developed countries: they are used as an alternative fuel for diesel engines either in pure form (grade B100) or as an additive to petroleum diesel fuel. In Russia, according to GOST 32511-2013, the introduction of up to 7% vol. of FAMEs into diesel fuel is allowed. However, new environmental standards imply stricter requirements for fuel combustion characteristics, namely, a reduction in the permissible emission limits of unburned particles and nitrogen oxides. The development of new additives and additives to fuels based on renewable raw materials in order to increase the purity of exhaust gases and improve the fuel combustion process in the engine is a very urgent task in the fuel industry.

To increase the cetane number, special cetane-enhancing additives are added to fuels. The most common additives for increasing the cetane number are nitrate-type additives, such as 2-ethylhexyl nitrate (2-EHN). However, obtaining this compound is a multi-stage process: obtaining n-butanal from propylene, aldol condensation of n-butanal, hydrogenation to obtain 2-ethylhexanol, nitration of 2-ethylhexanol. It should be noted that some stages require the use of explosive

(hydrogen/hydrogenation) or toxic and corrosive reagents (mixture of sulfuric and nitric acids/nitration).

As is known, organic peroxides can also be used as a cetane booster. Currently, research is being conducted in Russia to develop additives of this type, but at the moment they have not found wide application. In addition to the advantages associated with more environmentally friendly synthesis, peroxides have a number of operational advantages compared to alkyl nitrates: lower explosion hazard, stability during storage, do not affect the anti-wear properties of fuel, have good compatibility with anti-wear additives, low corrosion activity, are low-toxic and do not contain nitrogen (i.e. do not affect NOx emissions during combustion). However, as a rule, they are less effective and poorly compatible with sealing substances.

The goal of the research is to develop theoretical basic principles for the process of obtaining environmentally friendly diesel fuel ignition promoters by oxidizing fatty acid methyl esters with atmospheric oxygen.

The tasks of the research.

To achieve this goal, it was necessary to solve the following tasks:

1. To study the composition of the products of cleavage of FAME fatty acid chains;
2. To separate a multicomponent mixture of FAME oxidation products using column chromatography;
3. To analyze and establish the structure of compounds with "new" ester groups;
4. To study the effect of an additive based on FAME oxidation products on the efficiency of a diesel engine;
5. To establish the features of the FAME hydroperoxides synthesis process both non-catalytically and in the presence of N-hydroxyphthalimide;
6. To study the decomposition of FAME hydroperoxides and calculate the rate constants of the process;
7. To study the effect of factors affecting the stability of FAME hydroperoxides.

The scientific novelty of the research includes separating the multicomponent products of FAME oxidation by atmospheric oxygen, which have a high affinity. The structure of esters formed during aerobic oxidation of fatty acid esters was established. For the first time, a fraction of substances containing "new" esters was isolated, with a concentration sufficient for their analysis using NMR spectroscopy. The possibility of FAME hydroperoxides using as an ignition additive to diesel fuel in a full-size four-cylinder engine was studied and demonstrated.

The theoretical significance of the research is determined by the need to study the oxidation processes of unsaturated compounds. The structure of substances increasing the concentration of ester groups in the reaction mixture has been established. The possibility of targeted catalytic and non-catalytic synthesis of FAME hydroperoxides with the achievement of a high concentration of target compounds has been demonstrated.

The practical significance of the research lies in the synthesis of an environmentally friendly promoting additive to diesel fuel based on renewable plant raw materials, which improves the environmental friendliness of the fuel combustion process.

The main provisions for the defense:

- structure and formation pathways of esters during oxidation of vegetable oil FAMEs with atmospheric oxygen both in the light fraction of products and in the main part of the reaction volume;
- potential use of FAME hydroperoxides as an ignition promoter for diesel fuel combustion;
- features of the synthesis and decomposition of FAME hydroperoxides, as well as the influence of various substances on these processes.