Study of the laws of oxidation of biodiesel

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Abstract. The paper discusses in detail the first stage of the catalytic oxidation of fatty acid methyl esters with atmospheric oxygen. According to the data obtained as a result of processing the kinetic data, it was concluded that the reactivity of the components of biodiesel. It is established that polyunsaturated and monounsaturated compounds have different reactivity from each other. The kinetic pattern of consumption of unsaturated components of biodiesel was set up and kinetic constants were calculated, which are equal to: oxidation of C18/1 $k_1 = 0.106 \pm 0.008$ h^{-1}, and oxidation of C18/2 $k_2 = 0.269 \pm 0.005$ h^{-1}, respectively

1. Introduction

In the world there is a growing need for obtaining products from renewable raw materials. One of the main sources of raw materials are fats of plant origin [1–3]. From vegetable fats, a product is obtained that is in demand both on the energy market and on the market of raw materials for chemical technology of organic chemistry products (plasticizers, stabilizers, corrosion inhibitors, etc.). Such a product is methyl esters of fatty acids (FAME) or biodiesel (BD).

The main direction of use of FAME is the fuel direction. In the countries of the European Union and the United States, FAMEs are used as an environmentally friendly additive to diesel fuel. But there are a number of ways to obtain modified FAMEs [4–6]. Modification of FAME involves the introduction of functional groups in the fatty acid residue. Basically, the modification is carried out through several stages, the first of which is the formation of an epoxy cycle at the location of the double bond in the fatty acid residue. There is a method for producing epoxy compounds through radical aerobic oxidation. The radical mechanism of oxidation implies a static expenditure of components, but in our experiments it was established that the rate of consumption of components depends on the reactivity and stability of the radicals.

2. Experimental

To obtain FAME used commercial refined sunflower oil (GOST 1129-2013). The initial FAMEs were obtained by the standard method of alkaline transesterification of sunflower oil [7–10] in the laboratory of the Department of Chemical Technology of the Basic Organic and Petrochemical Synthesis of the Mendeleev University of Chemical Technology of Russia. The obtained FAME - crude was distilled at the molecular distillation unit KDL 1 BASIC VERSION 2007, manufactured by UIC GmbH at 170–175°C and pressure 0.2 bar. Analysis of distilled chromatograph chromatograms showed that they represent a mixture of esters of acids: palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), linolenic (C18:3) and arachidic (C20:0), in the ratio 6.5: 6.0: 29.0: 53.2: 1.4:

1.9 mass%, respectively. The kinematic viscosity of the obtained product at 40°C was 4.6 mm^2 / s, determined in accordance with GOST 33-2000 (ISO 3104-94) "Oil products. Transparent and opaque liquids. Determination of kinematic viscosity and calculation of dynamic viscosity". Dry compressed air was used as an oxidizer.

A. Oxidation of methyl esters of fatty acids

The bubbling reactor was loaded with biodiesel of 50 ml, after which the supply of dry compressed air was switched on, its flow rate was 2÷5 ml/sec and the reaction system was heated. After reaching the reaction mass of the desired temperature (110°C), a catalyst was added to the solution (0.12 g MoO_2PrGl_2, the molybdenum concentration in the reaction mass is 0.12 mmol. Mo/l). The process was followed by the analysis of the samples taken from the reactor for the content of hydroperoxides, unreacted remaining and formed epoxides. The duration of the experiments was 15 hours. After the end of the experiment, a sample was taken for analysis – gas chromatography.

B. The method of preparation of catalyst (MoO_2PrGl_2)

In a three-neck flask with a volume of 50 ml, 0.1766 g of ammonium molybdenum acid was placed. Dissolved in 10 ml of distilled water at 50–70°C. After complete dissolution, the liquid was heated to 90°C. Then 3 g of purified propylene glycol was added dropwise to the reaction mass. Then the solution was heated to 105°C. With intensive stirring, within 10 minutes the solution acquired a blue-green color. After that, another 7 ml of propylene glycol was added. After 1.5 hours with intensive stirring and a temperature of 105°C, the mixture acquired a dark green color.

Then the water was driven away, 1.5 hours were intensively mixed at 120°C. the Reaction mixture acquired a green color. Under vacuum (6÷10 mm Hg art.) drove propylene glycol, after which the solution began to acquire a dark green color, and then – green-brown. The total mass of the catalyst was 8.06 g.

C. Methods of analysis of the reaction mixture

The analysis of raw materials and reaction products was carried out by various methods of instrumental analysis, firstly, on the gas-liquid chromatograph "Crystal 4000 Lux" with a flame ionization detector on a capillary column 1 m long, 3 mm in diameter, phase – SE-30 (5%)

Chromatographically conditions: flow rate of nitrogen is 25 ml/min, hydrogen flow of 50 ml/min, airflow of 450 ml/min, T detector – 250°C, T appetites – 275°C, T speakers – 170°C – 200°C, analysis time – 40 min the Volume of injected sample was 0.1 µl. The device and the method of analysis was controlled by the concentration of the components of raw materials and products in the course of the experiments.

3. Results and discussion

The feedstock in its composition has methyl esters of oleic and linoleic acids. These esters have an increased reactivity in oxidation reactions to hydroperoxides, since they have double bonds in their composition. Previously, the reactivity of these compounds in different ratios in the feedstock was not studied. In the presented systems, oxidation reactions are presented in Figure 1.
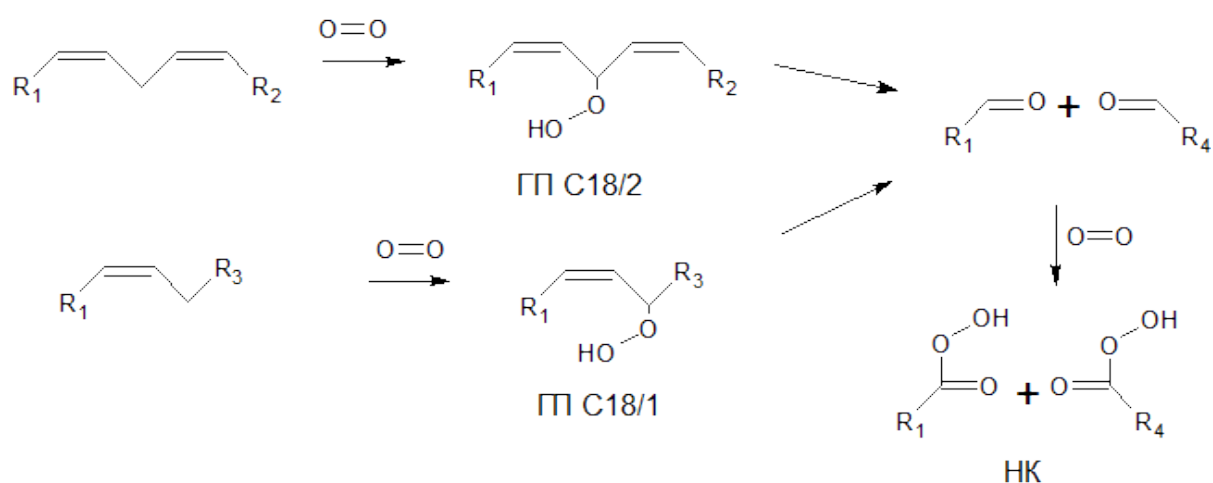
Figure 1. Oxidation scheme.

Aerobic oxidation of compounds, having in its composition of olefinic sites, such as methyl esters of oleic and linolevoy acids occurs by a radical chain mechanism. In the study of oxidation on different types of raw materials, it was found that the oxidation of methyl ester of linoleic acid (C18/2) occurs at a higher rate than the oxidation of methyl ester of oleic acid (C18/1) and does not depend on the initial ratio of acids in the raw material. To determine this pattern, a number of experiments were conducted on 6 different types of raw materials presented in Figure 2.
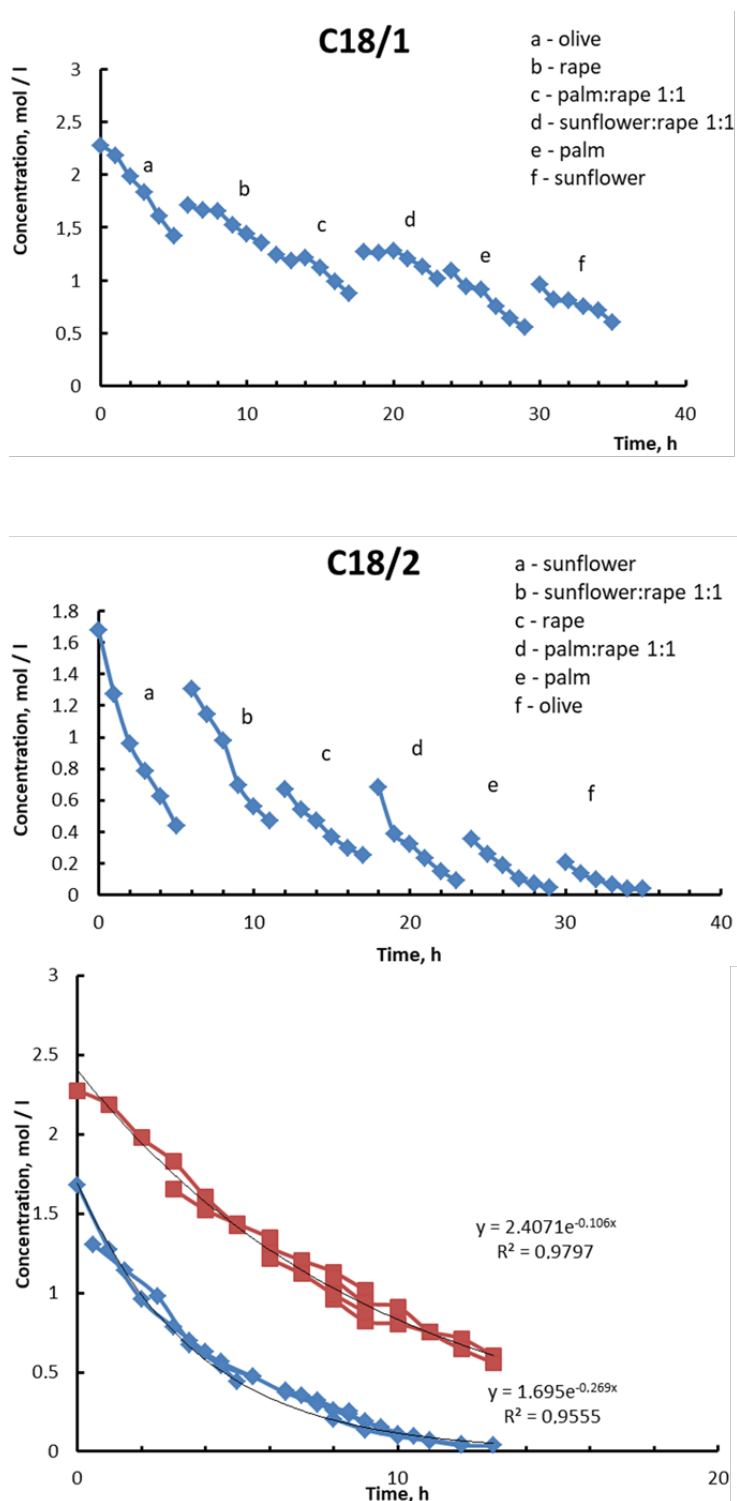
Figure 2. Kinetic curves of consumption of initial components of various raw materials

For processing the experimental data, a method of time kinetic curve shift was used. Found that the oxidation of the initial components of C18/1, C18/2 occurs according to independent kinetic laws. These laws are described by the first order kinetic reaction law. It was calculated that the oxidation rate constant C18/1 k_1 = 0.106 ± 0.008 h^{-1}, and the oxidation rate constant

C18/2 $k_2 = 0.269 \pm 0.005$ h^{-1}. the standard deviation of the calculated data from the experimental data is no more than 5%.

The increased consumption rate of C18/2 compared with C18/1 can be explained by the fact that the radical C18/2 formed when the hydrogen radical is detached has a more stable structure than the radical C18/1. The stability of the radical is determined by the number of carbon nuclei involved in stabilization, which is shown in Figure 3.

All the patterns shown demonstrate that the radical oxidation processes of various raw materials can be controlled. From a technological point of view, this makes the process controllable. Managed oxidation processes can form the basis of the industrial process for the oxidation of FAME.
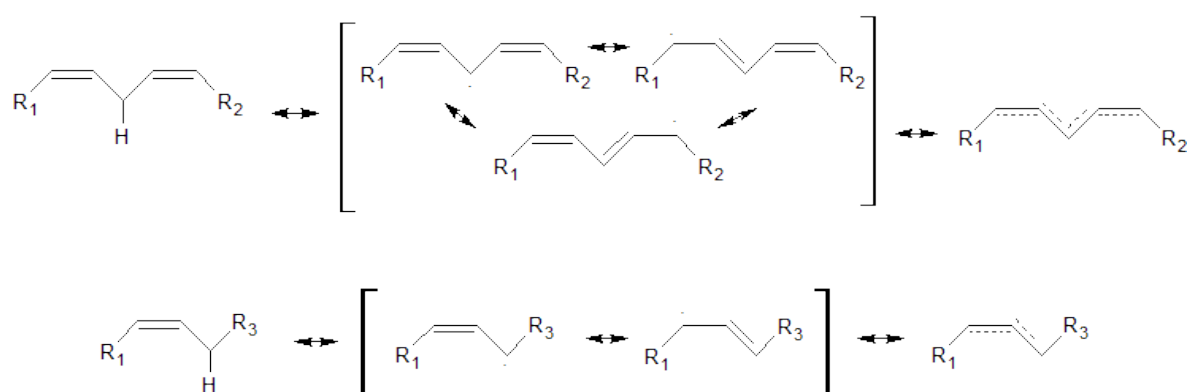
Figure 3. Stability of the radicals C18/2 and C18/1

4. Conclusions
As a result of the work done, it was established:

1.   Component C18/1 has a less stable radical than component C18/2. In this connection, this radical has a higher reactivity, which is proved by the behavior of kinetic curves;

2.   Oxidation rate constant C18/1 $k_1 = 0.106 \pm 0.008$ h^{-1}, and the oxidation rate constant C18/2 $k_2 = 0.269 \pm 0.005$ h^{-1}. The standard deviation of the calculated data from the experimental data is not more than 5%.

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