Petroleum and Coal

Article **Open Access**

Kinetic Model of FAME Oxidation by Air Oxygen on the $TiO_2/MoO_3/Al_2O_3$ Catalyst

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Received November 16, 2021; Accepted March 25, 2022

Abstract

In this article, on the basis of the obtained experimental data, a proposed kinetic model of the oxidation of FAMEs with atmospheric oxygen using a $TiO_2/MoO_3/Al_2O_3$ catalyst is described. Also shown is a diagram of the experimental setup used in the work. The dependences of the consumption of unsaturated compounds contained in FAME and the rate of formation of compounds containing active oxygen are considered.

Keywords: *Fatty acid methyl esters (FAME); Epoxidation; Biodiesel; Infrared spectroscopy.*

1. Introduction

Oxygen-containing compounds of fatty acid methyl esters (FAME) are represented by several groups: hydroperoxides, epoxides, aldehydes, ketones, alcohols. All of these compounds are derivatives of the starting FAMEs obtained as a result of partial oxidation with atmospheric oxygen. Of greatest interest for practical use are epoxies and hydroperoxides, since these groups of compounds are well compatible with various paints and varnishes and can be functional additives to compositions consisting mainly of alkyd compounds. The binder for alkyd materials is an alkyd resin. Alkyd resins are mainly made by cooking vegetable oils [1-5] - linseed, tall oil, soybean, etc. - together with alcoholic and organic acids or acid anhydrides. Like oils, alkyd resins dry out by oxidation. The higher the fat content (oil percentage) of the alkyd resin, the more elastic the paintwork. The drying speed of alkyd resins is regulated by special additives - desiccants. Oxygenated FAME derivatives can be desiccants. The production of such driers is an urgent task, since the additives allowing to obtain improved qualities of the main product are high-margin products.

It was previously studied [6] that the selective oxidation of FAME to epoxy products is catalyzed by compounds containing transition metals such as molybdenum. With this catalysis, selectivity values for epoxy compounds of 30-33% were achieved. The conversion of the initial unsaturated FAMEs was 45-55%. A deeper analysis of the literature data [7–10] showed that titanium compounds, in particular TiO_2, can significantly contribute to the rearrangement of hydroperoxide compounds into epoxy ones. In view of the fact that all previously obtained results described experiments carried out on a homogeneous catalyst, there was a need to describe the kinetics of oxidation on a heterogeneous catalyst. In this work, we studied the oxidation of FAME with atmospheric oxygen on a heterogeneous catalyst containing molybdenum and titanium compounds.

2. Experimental part

2.1. Description of the experiment

FAME from sunflower oil, produced by OOO AVK-Khim, was used as a raw material. The initial composition of the FAME is presented in Table 1. The oxidizing agent in the process of the study was air oxygen. Before air was supplied to the reactor, the air was preliminarily dried using an OAA gas dryer (JSC "Promkataliz", Ryazan). The synthesis was carried out in a bubble-type reactor (Fig. 1).

Table 1. Fatty acid composition of FAME

FAME	Fatty acid composition of FAME, wt%				
	C16	C18/0+1	C18/2	C18/3	C20
Sunflower	6.5	35.8	56.3	1.4	0.9

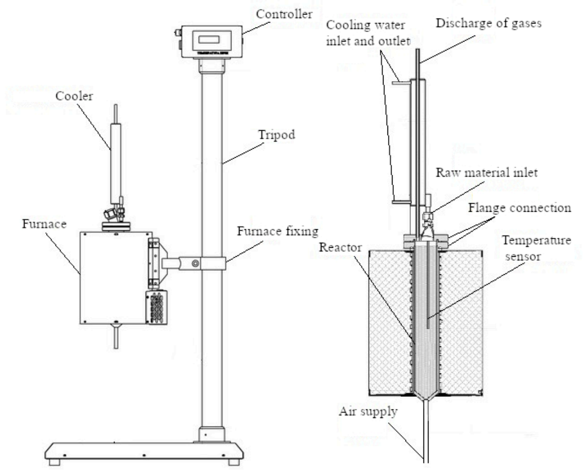


Figure 1. Schematic of the experimental setup

A ceramic foam filter was installed in the reactor for better air dispersion in the volume of FAME. An air supply tube from the compressor was connected to the lower part of the apparatus to supply the oxidizer to the system.

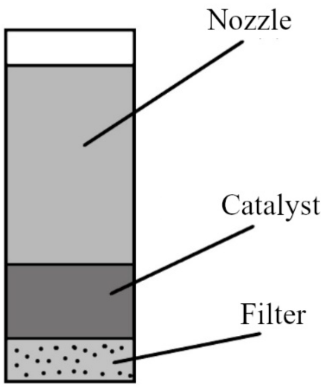


Figure 2. Catalyst loading scheme

The reactor was placed in an oven and secured. The reflux condenser was bolted to the flange. A reactor loaded with a catalyst (Fig. 2) was filled with FAME with a volume of 100 to 125 mL. The feed of the oxidizing agent was switched on at a constant flow rate of 26 L/h. The air flow was controlled using a calibrated rotameter. The synthesis temperature is 120°C. The temperature was controlled and maintained by a PID controller included in the installation. After reaching a predetermined temperature throughout the experiment, samples were taken for analysis every hour.

As a heterogeneous catalyst, we used granular mixtures of oxides of molybdenum, aluminum, and titanium in a mass ratio $TiO_2/MoO_3/Al_2O_3$ equal to 5/15/80. A homogeneous catalyst MoO_2PrGl_2 was also used as a reference catalyst [11-12].

2.2. Analytical tools

The analysis of the selected samples from the reaction mass was carried out by instrumental methods using an FSM-2202 IR Fourier spectrometer (OOO Infraspek). The error in determining the concentrations of reagents and reaction rates did not exceed 12%.

The analysis of the kinetic features of the interaction of FAME with air oxygen and the modeling of the kinetic curves of the consumption of reagents and the accumulation of target compounds was carried out using the KINET program, version 0.8 (November 02, 2012).

3. Discussion of results

The kinetics of FAME oxidation is a complex nonlinear process. The process path consists of complex sequential and parallel stages. Without taking into account the diffusion of oxygen into the reaction mass, the transformation scheme can be represented by the reaction equations shown in Figure 3.

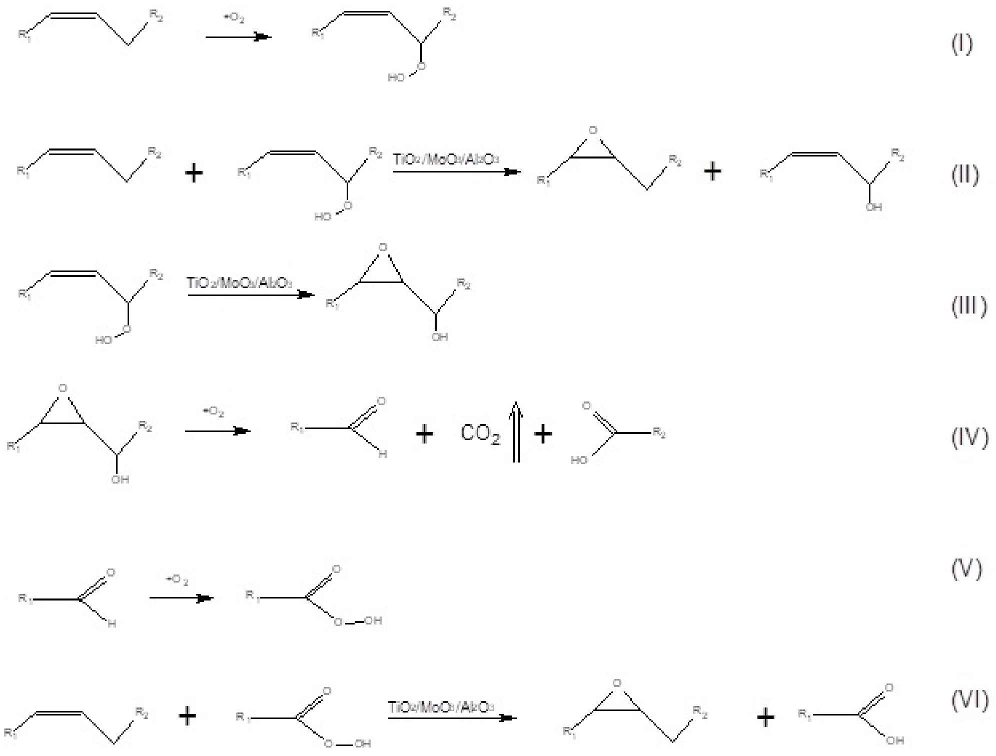
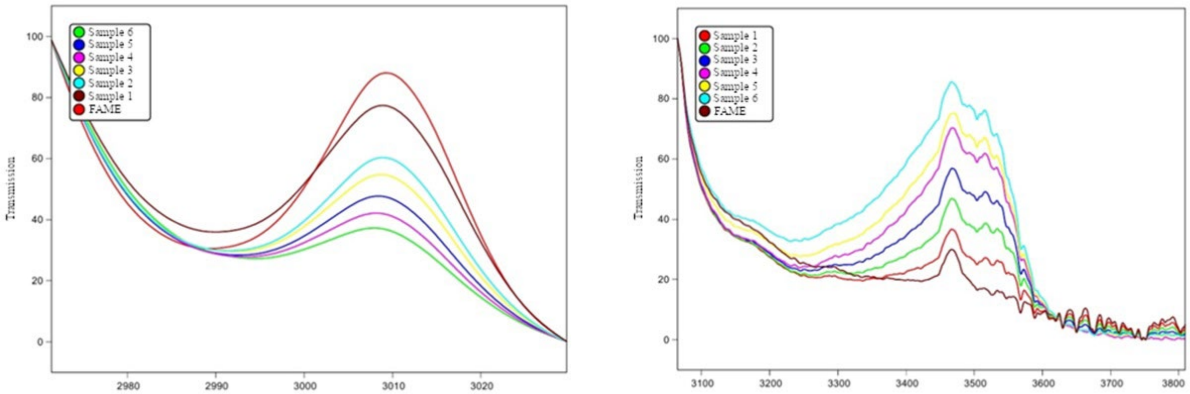


Figure 3. Scheme of transformations of the FAME oxidation process

According to this scheme, at the first stage, oxygen is added to the unsaturated fragments of the FAME hydrocarbon chain, forming the main epoxidizing agent FAME hydroperoxide. Upon further oxidation, this group of compounds forms FAME cleavage products. The main epoxidizing agent enters into the epoxidation reaction, forming the target oxygen-containing compounds - epoxies and alcohols. The presented diagram reflects the main path of the process, without delving into its radical mechanism.

The key starting components in this process are compounds containing unsaturated fragments ($-CH_2 = CH_2-$), since they are reactive. The reaction products contain active oxygen (-O-). To determine the kinetic dependences, the change in the intensity of the characteristic peaks of the above functional groups in the IR spectrum was evaluated. In the region of 2900 - 3050 cm^{-1}, a decrease in the intensity of the peak was observed, proportional to the decrease in the concentration of unsaturated functional groups, and in the region of 3100 - 3700 cm^{-1}, an increase in the signal intensity proportional to the increase in the concentration of active oxygen (Fig. 4).



A- decreasing signal of the consumption of double bonds;

B - increasing signal with an increase in the concentration of active oxygen

Figure 4. Areas of change in IR spectra

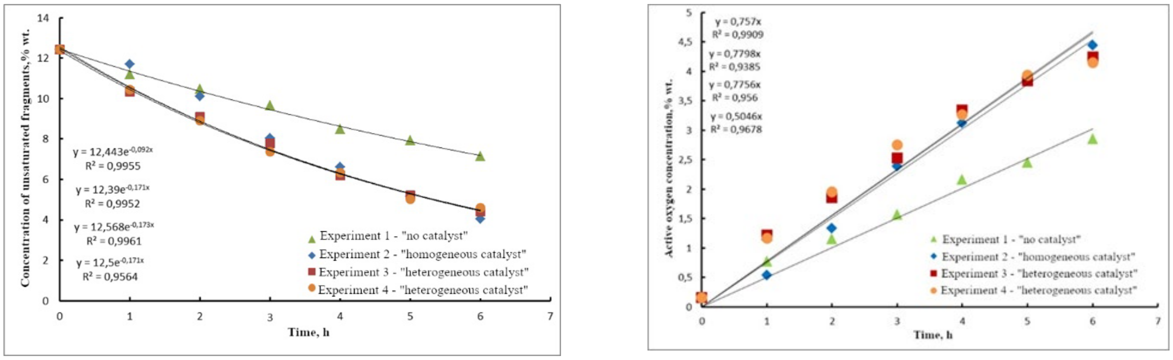
In the present study, a series of experiments were carried out in which the catalytic agents were varied. Four experiments were carried out, the kinetic curves of which are shown in Figure 5. The first experiment was carried out without a catalyst. It was noted that in the system the reactions are shown in Figure 3 in the absence of a catalyst. This fact is confirmed by previously presented studies [10]. Subsequent experiments were carried out using two types of catalysts: homogeneous (experiment 2) and heterogeneous (experiment 3 and 4). The homogeneous catalyst MoO_2PrGl_2 was introduced into the reaction mixture in an amount of 12 mmol at. Mo/L, this amount is sufficient so that the catalytic conversion to the target products does not limit the entire process. A heterogeneous catalyst ($TiO_2/MoO_3/Al_2O_3$) was poured into the reactor in an amount of 15.0 cm^3 (11.7 g). Since when a homogeneous catalyst is used in the system, there are no diffusion resistances, presumably the activity of heterogeneous catalysts should have been reduced; however, the experiments carried out showed that the activity of a homogeneous and heterogeneous catalyst is at the same level. This indicates that the stage of catalytic conversion on a heterogeneous catalyst is also not limiting in the entire process.

The presented scheme of transformations is supported by instrumental studies of the reaction mixture during the synthesis. The value of the rate constants for each reaction are presented in Table 2.

Table 2. Values of the rate constants of the individual stages.

Stage №	Speed constant, dimension	The value of constants			
		Experiment 1	Experiment 2	Experiment 3	Experiment 4
I	k_1, h^{-1}	0.0336	0.0753	0.0752	0.0753
II	k_2, $h^{-1}mole^{-1}l$	0.7247	0.0460	0.0461	0.0459
III	k_3, h^{-1}	6.2920	0.0010	0.0011	0.0012
IV	k_4, h^{-1}	0.2668	0.1978	0.1985	0.1967
V	k_5, h^{-1}	0	$1.367*10^6$	$1.386*10^6$	$1.375*10^6$
VI	k_6, $h^{-1}mole^{-1}l$	0	$4.055*10^5$	$4.026*10^5$	$4.037*10^5$

Analyzing the calculated values of the reaction rate constants, we can assume the following: the reactions proceeding without a catalyst are similar to the reactions proceeding in the presence of a catalyst, but differ only in the rate of occurrence; the rate constants of the individual stages proceeding on a homogeneous catalyst are equal to the analogous constants for heterogeneous catalysis, within an error of 5%. This is also confirmed by experimental data (Fig. 5).



A - Dependence of the concentration of unsaturated fragments on time

B - Dependence of active oxygen concentration on time

Figure 5. Kinetic curves

4. Conclusion

Based on the experimentally obtained dependences of the consumption of unsaturated compounds contained in the FAME and the rate of formation of compounds containing active oxygen at a temperature of 120°C, with $TiO_2/MoO_3/Al_2O_3$ catalysis, for a bubbling reactor, a kinetic model of the partial selective oxidation of FAME was developed, including 6 serial-parallel reactions. The rate constants were optimized based on the obtained concentration values. The model is based on the concentrations of functional groups, which allows describing the presented process with an accuracy of more than 95%.

It is shown in this work that the kinetics of oxidation on a heterogeneous catalyst coincides within the error with the kinetics of oxidation on a homogeneous catalyst. The present study will make it possible to continue work on improving the process of selective oxidation of FAMEs with atmospheric oxygen.

References

[1] OstrovskayA AV, Naumova VN, Budkin VA, Svetlakov NV, Liakumovich AG, Samuilov YD, Goldberg YuM. Method For Producing Alkydo Resin, Patent of Russia No. 2340631 C1 04/03/1992.

[2] Agafonov GI. Method for Producing Alkydo Resin. Patent of Russia No. 2340631 C1 26.12.2007.

[3] Sabirov RG. Method for Producing Alkydo Resin. Patent of Russia No. 2375382 C2 26.12.2007.

[4] Wei Y, Li G, Lv Q, Cheng Ch, Guo H. Epoxidation of Methyl Oleate and Unsaturated Fatty Acid Methyl Esters Obtained from Vegetable Source over Ti-Containing Silica Catalysts. Ind. Eng. Chem. Res. 2018; 57, 48, 16284–16294 2018.

[5] Kumar D, Ali A. Ti/SiO_2 as a Nanosized Solid Catalyst for the Epoxidation of Fatty Acid Methyl Esters and Triglycerides. School of Chemistry and Biochemistry, Thapar University, Patiala 147 004, India 2012

[6] Kulazhskaya AD, Sapunov VN, Udaev SA, Voronov MS. Epoxidation of Fatty Acid Methyl Esters of Vegetable Oils by Air. EuropaCat XII. Catalysis: Balancing the use of fossil and renewable resources. European Congress on Catalysis. Kazan (Russia) 30 Aug. - 4 Sept., 2015. [Electronic resource]: abstracts – Novosibirsk: Boreskov Institute of Catalysis, 2015. - P. 1969-1970, Kazan (Russia), 2015

[7] Meier MAR, Metzger JO, Schubert US. Plant oil renewable resources as green alternatives in polymer science. Chem. Soc. Rev. 2007;. 36: 1788–1802.

[8] Aguilera AF, Tolvanen P, Eranen K, Leveneur S. Epoxidation of oleic acid under conventional heating and microwave radiation. Chemical Engineering and Processing: Process Intensification. 2016; 102: 70–87.

[9] Ismail TNMT, Ibrahim NA, Noor MAM, Hoong SS, Palam KDP, Yeong ShK, Idris Z, Schiffman ChM, Sendijarevic I, Abd Malek E, Zainuddin N, Sendijarevic V. Oligomeric Composition of Polyols From Fatty Acid Methyl Ester: The Effect of Ring-Opening Reactants of Epoxide Groups. J. Am. Oil Chem. Soc. 2018; 95: 509–523.

[10] Vicente G, Martınez M, Aracil J, Esteban A. Ind. Eng. Chem. Res. 2005; 44(15): 5447–5454.

[11] Yudaev SA, Ivashkina EN, and others Chemical industry today, 2017; 1: 22–33 (Yudaev SA. Ivashckina E. N. et.al. Chem. Prom. Today. 2017. N. 1. P. 22–33).

[12] Sapunov VN, Yudaev SA, Cherepanova AD, Ivashkina EN, Voronov MS, Kozlovsky RA. Journal of Applied Chemistry, 2020; 93(5): 697-704.

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