

## KINETICS ON BIODIESEL OXIDATION BY AIR OXYGEN CATALYZED BY MOLYBDENUM COMPLEX

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### Abstract

The proposed method of processing fuels derived from bio-raw materials allows for obtaining products of organic synthesis. The simplified scheme of reactions occurring in the system of oxidizing biodiesel and mathematic description were developed, and they are suitable for non-catalytic as well as Mo-catalyzed oxidation of biodiesel by air oxygen. Kinetic regularities of the process of biodiesel aerobic oxidation were studied by using this kinetic model. It has been found out that Mo-catalyst accelerates formation of all final products including epoxides by means of interaction with peroxy radicals, i.e. the traditional Sharpless epoxidation mechanism doesn't match to this case. General parameters of the process, such as air supply speed and temperature do not impact on the character of components concentration curves. Influence of the composition of FAME on the epoxidation selectivity was revealed. The growth of epoxide formation selectivity (up to 85% at 50% – conversion of C-C – double bonds) is observed when mono-/poly-unsaturated compounds ratio is increasing. Thus, fatty acid methyl esters with different unsaturation degree demonstrate tendency to interact in various types of reactions.

**Keywords:** *Mathematical modeling; Epoxidation; Fatty acid methyl esters; Hydroperoxides.*

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## 1. Introduction

Due to the complicated ecological situation, especially in point of environmental pollution by slowly decomposing materials of petrochemical origin, it is of current interest to search biodegradable alternative chemicals, produced from vegetable resources. For example, the different transformations of vegetable oil derivatives are attractive routes for obtaining monomers and polymers [1-2] lubricants, [3-4] plasticizers and stabilizers of polymers [5-6]. Epoxidation of fatty acids or their esters can provide chemical industry by some intermediates for organic syntheses, such as monomers for epoxide resins [7] as well as other widely used products. In fact, epoxidized soybean oil has already been widely used as a polyvinylchloride additive.

According to the principles of Green Chemistry [8-11], environmentally friendly raw materials and products of organic synthesis are not enough to satisfy present ecological requirements. Scientists are also obliged to develop safety process for production necessary chemicals with applying non-toxic reagents and generating minor quantity harmful wastes. Consequently, present technologies on epoxidation of vegetable oil derivatives are to be altered, because they are based on using hazardous organic hydroperoxides [12] or peracids [13] as epoxidizing agents. The method, proposed by a number of scientists with hydrogen peroxide using to form epoxide rings [11] are not suitable in view of rather explosive properties of concentrated hydrogen peroxide solutions. At this research, we investigate the oxidation of fatty acid methyl esters (FAME) of a row of vegetable oils with different fatty acid (FA) composition. It has supposed within the approach we use, that air oxygen is an epoxidizing agent without adding other organic reagents.

Taking to account all the problems related to free radical oxidation, in the course of the present work the molybdenum complex has been chosen as the catalyst due to its epoxidation

ability concerning to olefin substances by Sharpless mechanism [14-15]. Unlike the industrial epoxidation, the hydroperoxides forming *in-situ* are directed to epoxidize olefin bonds of FAME. Here we presented a kinetic model of the process of FAME epoxidation catalyzed by Mo-complex in comparison with non-catalytic oxidation, and general directions of the reaction. In addition, the evidence for our conclusions has been shown by means of calculations as well as graphical interpretation based on our kinetic model.

## 2. Experimental section

### 2.1. Materials and methods

According to the literature, biodiesel preparing was carried out by the reaction of vegetable oil with methanol catalyzed by NaOH. Four types of biodiesel with different percentages of mono- and di-unsaturated esters were used in the experiments (Table 1).

Table 1. The composition of raw materials

Plant oil – biodiesel feedstock	Components weight %					
	C16*	C18/0*	C18/1*	C18/2*	C18/3*	C20*
Sunflower	6.8	3.1	22.4	67.7	0	0
Rapeseed	4.1	1.6	64.8	19.3	8.2	2
Olive	11.3	2.4	79.4	5.6	0.6	0.7
Palm olein	7.5	0	92.5	0	0	0

\*C16 -methyl palmitate; C18/0 - methyl stearate; C18/1 - methyl oleate; C18/2 - methyl linoleate; C18/3 - methyl linolenate; C20 - methyl arachidonate.

Oxidation process has been performed in the glass column reactor, where the air flow was being bubbled through the bottom. The reaction was investigated at different temperatures (80-110°C), air supply speed (5-25 mL/s) and concentration of catalyst ( $3,3 \cdot 10^{-5}$  –  $1,2 \cdot 10^{-3}$  mol/L).

Molybdenum complexes with propylene glycol were used as the homogeneous catalysts. The complexes have been prepared by dissolving of MoO<sub>3</sub> powders in the mixture of ammonia and 1,2-propanediol. The synthesis of catalysts was carried out in two-necked round bottom flask at 150-160°C and atmospheric pressure for 3 hours. Propylene glycol has been added to the mixture immediately after the total dissolution of oxide in ammonia. Then the reaction mixture was gradually heated to 150-160°C. After the synthesis the reaction mixture undergoes vacuum distillation to remove water and excess propylene glycol.

Peroxide value was measured by iodometric titration using 0,1 N aqueous solution of sodium thiosulfate, 50 wt % potassium iodide, and acetic acid. Concentrations of methyl esters and epoxides during the process were determined by means of GLC on the Kristall 4000 Lux chromatograph with flame ionization detector and capillary column (DB-23 30 m×0,25 mm×0,25 μm). The chromatography conditions applied were 275°C for evaporator, 250°C for detector; the carrier-gas was nitrogen (90 mL/s).

## 3. Results and discussion

### 3.1. Non-catalytic process

Firstly, we have obtained some general regularities for aerobic oxidation of different mixtures of FAME. Hydroperoxides concentration curve always has a maximum, but it doesn't exceed 25 wt%; a beginning point of intensive HP consumption matches to autoacceleration of the processes leading to the formation of by-products through FA-chain cleavage, oligomerization and other possible reactions except epoxidation (Figure 1).

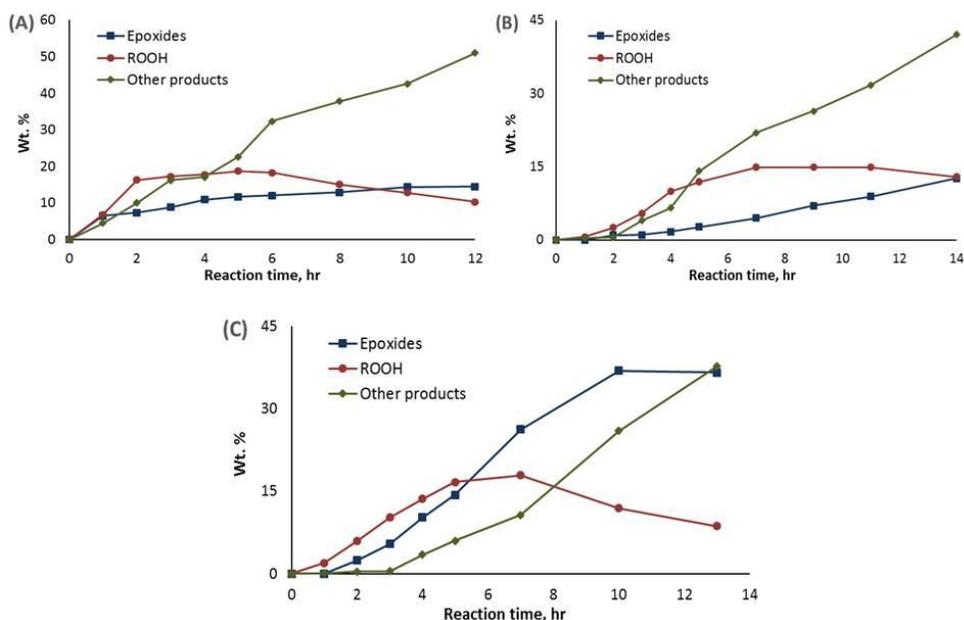


Figure 1. Changing of component’s concentrations during non-catalytic aerobic oxidation of (A) FAME of sunflower oil at 100°C and 20 mL/s air supply speed (B) FAME of rapeseed oil at 100°C and 20 mL/s air supply speed (C) FAME of olive oil at 110°C and 25 mL/s air supply speed

To describe the kinetics of biodiesel aerobic oxidation, we developed a simplified scheme of reactions occurring in the reaction mixture (Figure 2). All the rate constants are visible, and they may consist of several items; assumption on the 1<sup>st</sup> order of all the reactions except the last one ( $k_7$ ) was applied.

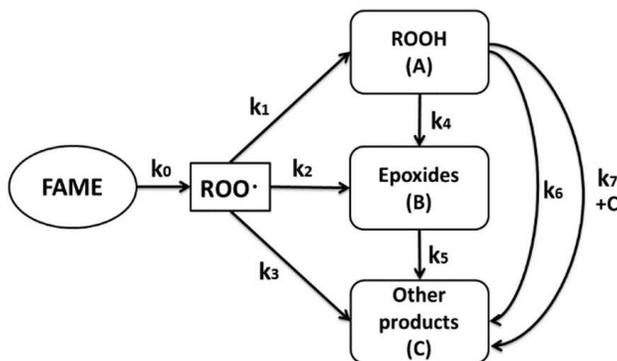


Figure 2. Simplified scheme of aerobic oxidation of FAME

Differential equations corresponding to the scheme are below:

$$\frac{d[RO_2 \cdot]}{dt} = k_0 \cdot [FAME] - k_1[RO_2 \cdot] - k_2[RO_2 \cdot] - k_3[RO_2 \cdot];$$

$$\frac{d[FAME]}{dt} = -k_0 \cdot [FAME];$$

$$\frac{d[A]}{dt} = k_1[RO_2 \cdot] - k_4[A] - k_6[A] - k_7[A] \cdot [C];$$

$$\frac{d[B]}{dt} = k_2[RO_2 \cdot] + k_4[A] - k_5[B];$$

$$\frac{d[C]}{dt} = k_3[RO_2 \cdot] + k_5[B] + k_6[A] + k_7[A] \cdot [C].$$

Due to the high reactivity of peroxy radicals  $RO_2$ , we could use the Bodenstein-Semenov method and presume the changing of peroxy radicals concentration is nil. Thus, the equations describing the components behavior in the system were derived:

$$k_0 \cdot [FAME] - k_1[RO_2 \cdot] - k_2[RO_2 \cdot] - k_3[RO_2 \cdot] = 0;$$

$$[RO_2 \cdot] = \frac{k_0}{k_1 + k_2 + k_3} [FAME];$$

$$\frac{d[A]}{dt} = \frac{k_0 k_1}{k_1 + k_2 + k_3} [FAME] - k_4[A] - k_6[A] - k_7[A] \cdot [C];$$

$$\frac{d[B]}{dt} = \frac{k_0 k_2}{k_1 + k_2 + k_3} [FAME] + k_4[A] - k_5[B];$$

$$\frac{d[C]}{dt} = \frac{k_0 k_3}{k_1 + k_2 + k_3} [FAME] + k_5[B] + k_6[A] + k_7[A] \cdot [C].$$

Excluding time from the process describing it could be possible to obtain the dependences between components concentrations and the amount of reacted esters. In this way, we get a range of relative rate constants (table 2) allowing to see the character of transformations in the reaction system.

Table 2. Relative rate constants for non-catalytic aerobic oxidation of FAME of sunflower and olive oils

FAME of	k <sub>0</sub>	k <sub>1</sub>	k <sub>2</sub>	k <sub>3</sub>	k <sub>4</sub>	k <sub>5</sub>	k <sub>6</sub>	$\frac{k_7, m_{mixture}}{m_{component}}$
Sunflower oil	5·10 <sup>-4</sup>	0,080	0,038	0,037	0	1,2·10 <sup>-4</sup>	2,0·10 <sup>-4</sup>	1,2·10 <sup>-5</sup>
Olive oil	5·10 <sup>-4</sup>	0,087	0,047	0,010	5·10 <sup>-4</sup>	1,5·10 <sup>-4</sup>	1,3·10 <sup>-4</sup>	3,0·10 <sup>-6</sup>

Important to note autoacceleration of by-processes that becomes obviously from the type of concentration curve for it's the inflection point. Furthermore, the correct mathematical description is reached only while the equation for accumulation of by-products ("C" on Figure 2) has the 4<sup>th</sup> addend matching the reaction of 2<sup>nd</sup> order.

### 3.2. Mo-catalyzed process

Several apparent features characterize the aerobic oxidation of FAME catalyzed by Mo-complex in comparison with the non-catalytic process: sharp decrease of hydroperoxides concentration, minor epoxidation rate enhancement, changing of by-products ("other products") accumulation curve type, i.e. disappearing of induction period (Figure 3).

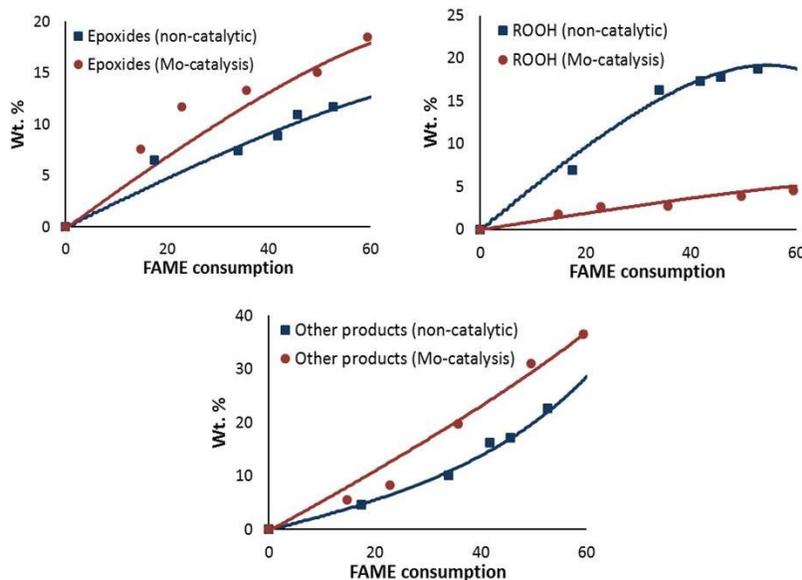


Figure 3. Concentration curves of non-catalytic and Mo-catalyzed aerobic oxidation of sunflower biodiesel at 100°C and 20 mL/s air supply speed

Investigation of the diffusion factor is realized through varying an air supply speed. The concentration curves corresponding to the different sparging intensity were superimposed on each

other by means of a transformation coefficient, which is a value modifying the reaction time. As it could be seen on Figure 4, the concentration curves matching to different air supply speed (5, 10, 15, 20, 25 mL/s) overlap each other that implies the relation of obtaining products as well as the types of concentration curves are in no way dependent on the bubbling velocity. Therefore, there is no matter whether we perform our experiments in diffusion, transitional or kinetic regime. The correlation between the transformation coefficient and air supply speed is shown in Figure 5, and it's derivation is based on the mass transfer coefficient equation in heterogeneous system "gas-liquid":

$$\frac{1}{\beta} = \frac{K_a}{\beta_g} + \frac{1}{\beta_l} \rightarrow \beta = \frac{\beta_g \beta_l}{K_a \beta_l + \beta_g}$$

where: ( $\beta$  – full mass transfer coefficient between gaseous and liquid phases;  $K_a$  – absorption constant;  $\beta_g$  – mass transfer coefficient between gas and interface;  $\beta_l$  – mass transfer coefficient between interface and liquid). Simultaneously, apparent reaction velocity is linearly dependent from mass transfer coefficient while a diffusion limits the process. Thereby, we have got the equation:

$$f = \frac{2 \cdot U}{16 + U}$$

( $f$  – transformation coefficient, proportionate to apparent velocity of the process;  $U$  – air supply speed, ml/s; 2 – value, proportionate to  $\beta_l$ ; 50 – value, proportionate to  $K_a \beta_l$ ).

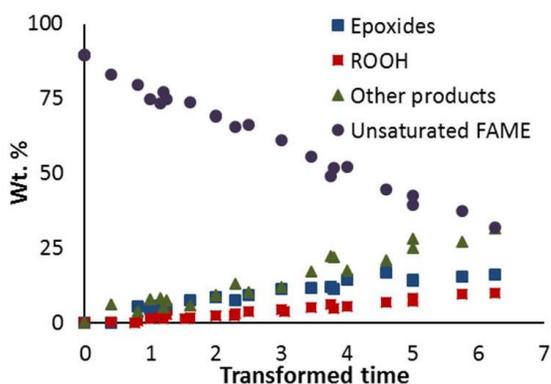


Figure 4. Superimposed concentration curves of sunflower biodiesel aerobic oxidation at 5, 10, 15, 20 and 25 mL/s air supply speed

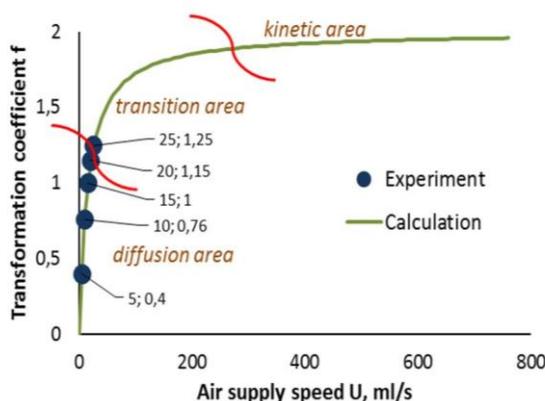


Figure 5. Oxidation process flowing areas (correlation between transformation coefficient and air supply speed)

The correlation we got demonstrates that our experiments at 5-15 mL/s air supply speed were performed in deeply diffusion area, whereas the oxidation regime at 20-25 mL/s becomes a transition. A kinetic area could be reached at extremely high bubbling speed, which is impossible in laboratory conditions. Nevertheless, it should be noted again that the character of concentration curves remains the same at different air supply speed and consequently at different regimes, that is the regularities of the oxidation do not change, and we can describe the kinetic. The intensity of air bubbling affects only on oxidation rate, which can be excluded by applying relative rate constants and correlation of components concentrations from quantity of reacted methyl esters as it has been showed above for non-catalytic process.

Increasing catalyst concentration leads to the changing of relative constants of oxidation process. If Mo-concentration in system is low then the process extremely resembles non-catalytic free radical oxidation, but enhancing of Mo content in the reaction mixture changes the mechanism of reactions. Substantial dropping down of hydroperoxides formation rate at high content of molybdenum is not caused by acceleration of their sequence conversion to secondary products, because of the constants  $k_6$  and  $k_7$  also have decreased. Thus, it could be claimed in case of FAME oxidation Mo-complex accelerates the reactions of peroxy radicals, and final products are forming directly from  $RO_2\bullet$  skipping the hydroperoxide formation stage.

In addition, it has been observed negligible epoxidation rate gain; the constant of C-C double bonds epoxidation by hydroperoxides  $k_4$  is nil even at the high catalyst concentration, i.e. the ratio of the final product remains constant and independent from catalyst. Moreover we can make a conclusion that traditional ideas of the processes of olefin epoxidation by organic hydroperoxides catalyzed by Mo-complexes do not work in this case.

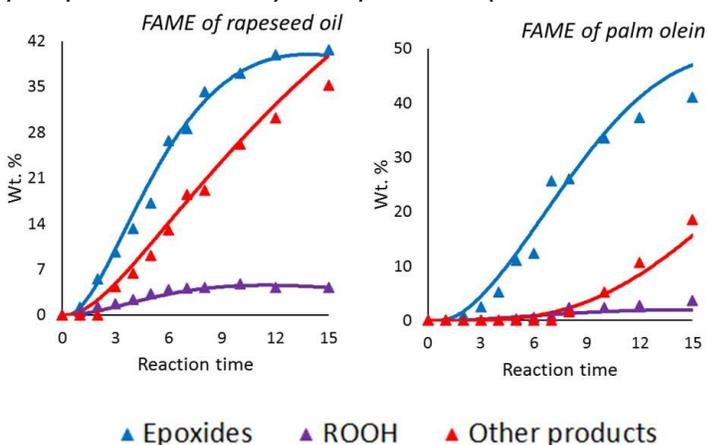


Figure 6. Math description of different FAME mixtures aerobic Mo-catalyzed oxidation at 110°C and 25 mL/s air supply speed

Mo-catalyzed oxidation of FAME of different vegetable oils by air oxygen also conforms the scheme of reactions (Figure 2) and math model described above, that is varying the content of mono- and di-unsaturated fatty acid esters doesn't change the set of reactions occurring in the system, but impacts on the ratio of rate constants (Table 5) and the final products quantities. In this way, it is taking place the growing of selectivity of epoxidation up to 85% with enhancing the share of mono-unsaturated compounds in the

raw material (Figure 7). It should be noted in case of the different share of mono- and di-unsaturated esters in initial mixture the constant  $k_4$  is nil again, in that way it proves only peroxy radicals are intermediates of epoxidation reaction at presence of Mo-complex.

Table 5. Rate constants for different FAME mixtures aerobic Mo-catalyzed oxidation at 110°C and 25 mL/s air supply speed

FAME of	$k_i, \text{hr}^{-1}$	$k_0, \text{hr}^{-1}$	$k_1, \text{hr}^{-1}$	$k_2, \text{hr}^{-1}$	$k_3, \text{hr}^{-1}$	$k_4, \text{hr}^{-1}$	$k_5, \text{hr}^{-1}$	$k_6, \text{hr}^{-1}$	$k_7, \frac{m_{mix}}{\text{hr} \cdot m_{comp}}$
Palm olein	0.07	0.21	1.05	19.25	0	0	0.080	0.180	0
Olive oil	0.5	0.15	1.20	19.20	0	0	0.045	0.030	0
Rapeseed oil	0.3	0.19	1.90	15.20	6.84	0	0.038	0.020	0.0015
Sunflower oil	-	0.325	5.20	19.50	29.25	0	0.098	0.033	0.0013

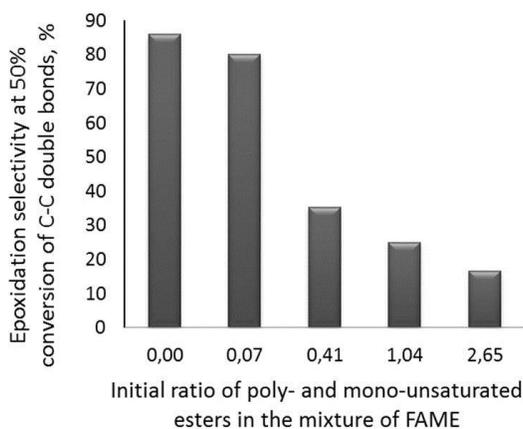


Figure 7. The growth of epoxidation selectivity with increasing of mono-unsaturated compounds in raw material

The comparison of non-catalytic oxidation and the Mo-catalyzed process in systems with the significant share of methyl oleate, for example, olive biodiesel, gives a perceptible inversion of the curves of epoxides and hydroperoxides accumulation, at the same time the by-products curve almost not changes (Figure 8). There is quite essential difference in behavior of mono- and poly-unsaturated systems in aerobic oxidation process, because of another character of concentration curves for sunflower FAME non-catalytic and Mo-catalyzed oxidation process (Figure 3). This is may be caused by several types of peroxy-radicals (and hydroperoxides) with different chemical properties existing in the system.

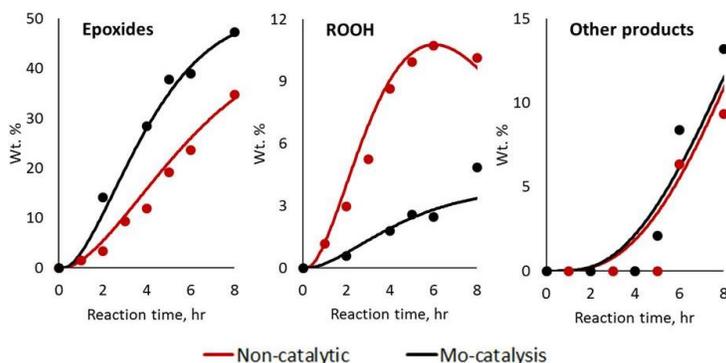


Figure 8. Concentration curves of non-catalytic and Mo-catalyzed aerobic oxidation of olive biodiesel at 110°C and 25 mL/s air supply speed

According to Figure 8 if the mono-unsaturated system undergoes aerobic oxidation by-products (“other products”) are starting to form several hours later than epoxides and hydroperoxides. Consequently, some types of peroxy-radicals that could be obtained only from mono-unsaturated fatty acid derivatives are able to epoxidize themselves.

It can be also concluded that Mo-catalyst in case of different content of biodiesel accelerates the reactions by means of interaction with  $RO_2\bullet$  radicals, which leads to the formation of final products including epoxy-compounds passing hydroperoxide formation stage likewise it was shown above for sunflower biodiesel. Thus, it goes without saying that FAME with different number of C-C-double bonds is reacting independently from each other in case of aerobic oxidation without catalyst as well as at the presence of Mo-catalyst. I.e. their reactivity could be characterized by different types of reactions where FAME have ability to interact.

#### 4. Conclusions

Simplified scheme of reactions and related math description that we derived provided of understanding the general kinetic regularities of FAME oxidation by air oxygen. It has become clearly that changing of temperature and air supply speed leads only to the acceleration of whole oxidation process. The Mo-catalyst addition is changing the nature of transformations in the system of aerobic oxidizing FAME, and all the reactions become to proceed via the interactions of  $RO_2\bullet$  radicals with molybdenum complex. Enhancing the catalyst concentration leads to sharp dropping down of hydroperoxides share, due to the growing of peroxy radicals consumption rate on epoxides or other final products. Consequently, the main intermediates of non-catalytic aerobic oxidation of biodiesel are hydroperoxides, but concerning Mo-catalyzed process in general intermediates are reoxy radicals. That means epoxidation of olefin bonds at present the molybdenum catalyst by generating *in-situ* hydroperoxides do not take place in this case as it was supposed previously.

The high selectivity of epoxy-compounds formation is possible to reach if the share of mono-unsaturated FAME in the raw material is predominant. It has been proved methyl esters of mono- and di-unsaturated fatty acids are showing different behavior in the process of oxidation by air oxygen that is explained by their various chemical properties as well as various types of particles (radicals) generating from each of them.

**Abbreviations**

*FAME* fatty acid methyl esters; *FA* fatty acids; *HP* hydroperoxides.

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