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Experimentally Calculated Study of the Effectiveness on the Process of Non-Catalytic Synthesis of Biodiesel in Reactors of Various Type

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Abstract: It was experimentally established that the dependence of the partial pressure of methanol on the molar fraction of methanol in oil shows a pronounced negative deviation from Raoul's law, which significantly changes the idea of the influence of a large excess of methanol during non-catalytic synthesis of biodiesel. The efficiency of use of a molar excess of methanol is reduced as it grows, and with a more than 10-fold molar excess of the amount of reacted methanol, is practically constant. The comparison of biodiesel production processes in the range 220–235 °C showed that a slight change in the process temperature more effectively affects the biodiesel yield than an increase in the molar excess of methanol. A mathematical model of the process of transesterification of rapeseed oil in reactors of various types (batch and tubular reactors) is developed. A satisfactory correlation between the experimental and calculated data was observed. The calculation showed that the rate constants of the reverse reactions at 230 °C were not significant.

Keywords: transesterification; biodiesel; green chemistry; renewable raw materials; modeling; rapeseed oil; subcritical methanol

1. Introduction

Among the various methods for producing biodiesel by the transesterification of vegetable oils and animal fats with methanol, the most promising from an environmental point of view are methods for carrying out the process without a catalyst [1,2]. The main problems for their technical implementation are associated mainly with two difficulties, one of which is related to the reaction temperature; the second is due to the fact that the components of the reaction mixture form a two-phase reaction mass when mixed.

Non-catalytic transesterification practically does not occur at temperatures below 200 °C [3]. At temperatures of 250–350 °C, a few minutes are enough for the reaction [4].

For the homogenization of the reaction solution, a molar excess of methanol is used. The increased temperature and a large excess of methanol leads to the necessity of carrying out the process in methanol, since the system is homogenized due to the lower dielectric constant of methanol in the supercritical state [2,5,6].

However, the implementation of the process in such severe conditions, a large excess of methanol and the resulting pressure (increase up to 35–60 MPa [7]) reduces all the economic parameters of the process. In addition, we must not forget about the quality of fuel, since at high temperatures the isomerization of natural cis-isomers of biodiesel into trans-

esters occurs (up to 16–30% by weight) [8]. This greatly degrades the use of such biodiesel in cold climates.

It is clear that in order to resolve the issue of the industrial implementation of the non-catalytic process for producing biodiesel, it is necessary to reduce the severity of the conditions associated with high heat consumption. For example, Japanese researchers have achieved a slight reduction in heat costs by the non-catalytic process. They proposed to carry out the process in two stages, which include the non-catalytic hydrolysis of triglycerides to produce carboxylic acids and their subsequent esterification with methanol [6].

Of interest is also the proposal of the BIOX company ("cosolvent") to use a co-solvent, which allows homogenizing the reaction mass [9,10]. This idea led researchers to replace the co-solvent with the final product itself—biodiesel. It was found that with increasing the mass fraction of methanol, solubility is increased, and at mass fractions ≈ 70%, the mixture becomes homogeneous already at room temperature for any oil–methanol ratios [11].

An increase in temperature reduces the amount of additional co-solvent down to zero. For example, the complete homogenization of the reaction mixture at 270 °C and 20.0 MPa is visually observed [12]. From the beginning to the end of the reaction, there is only one phase.

Thus, all published work to date on the non-catalytic process share the opinion that the success of the methanolysis of triglycerides is associated primarily with the use of a large excess of methanol and high temperatures. Obviously, such a combination of conditions leads to high pressure in the reaction zone.

Obviously, the solution to the problem of finding milder conditions for the process is to search for conditions for the homogenization of the reaction mixture at low stoichiometric ratios of the components and at temperatures below critical, the so-called subcritical methanol [12,13]. Nevertheless, despite some softening of the conditions of the process, the question of reducing the large molar excess of methanol is still relevant.

In this work, we analyzed the data available in the literature on the non-catalytic biodiesel production process and conducted a series of experiments to find the conditions and carry out this process under milder conditions and with small excesses of methanol and, thereby, reduce the costs of methanol recovery and metal production and finally obtain a better product.

2. Materials and Methods

Refined edible rapeseed oil and methanol (99.9%), supplied by Dorwil and Sigma—Aldrich for this study, were used. The calculations were performed under the assumption that the molar mass of triglycerides was MW = 926 kg/kmol [14].

Methods of Transesterification in subcritical methanol

To obtain a mathematical description of the transesterification reaction, which would allow us to simulate the process in reactors of various type, we conducted a series of comparative experiments on the methanolysis of rapeseed oil at different temperatures, pressures and ratios of the reactants. We used the data obtained in a tubular reactor and a batch reactor.

Transesterification in a tubular flow reactor. The process carried out in a steel tubular flow reactor with an inner diameter of 31 mm, a length of 16 m and filled with Rashig rings. The reactor volume was 12 L. The reactor in the form of connected two-meter segments in a closed casing with a diameter of 400 mm is placed, which is filled with coolant with external heating. The temperature in the reactor was controlled with an accuracy of ± 1 °C. Establishment of the isothermal regime occurs already several minutes after the feeding the reaction mass. This circumstance allows us to consider the process as isothermal and to reveal its kinetic laws.

A mixer was placed in front of the reactor to which a predetermined amount of oil and methanol was supplied at room temperature, and the reaction mixture in the form of an emulsion was supplied to the reactor by a high-pressure membrane pump.

The reaction mass flow rate was measured at the reactor outlet. The residence time was calculated by dividing the volume of the reactor (12 L) by the volumetric feed rate of reagents Q (h-1). Hydrodynamic flow reaction regime was varied by combining different rate of reactant feed and recycling the reaction mass in the reactor. The reaction mixture was cooled to room temperature, the pressure was reduced to atmospheric pressure with a pressure reducer, and the resulting reaction mixture was analyzed.

Transesterification in a batch reactor. The transesterification process was carried out in a steel autoclave with a working volume of 0.7 L, with an electrically heated bottom, equipped with a mechanical stirrer with a rotational control. The calculated amount of oil and methanol was loaded into the reactor, hermetically closed, followed by turning on the stirring and heating. Monitoring the temperature of the reaction mass showed that its predetermined value (220–230 °C) is reached only after ≈ 1.5 h. Therefore, at short reaction times, it must be assumed that the reactor is polytropic. In the developed process and when the temperature was set in the reactor, the temperature and pressure in the reactor were controlled with an accuracy of ± 2 K and ± 0.06 MPa. As the reactor heated, pressure increased. When the set temperature was reached, the pressure growth stopped and its slow drop began. After passing the specified reaction time, the reaction was stopped by immersing the reactor in cold water and the contents of the reaction mixture were analyzed.

Analysis.

Analysis of the reaction mixture was carried out after removal of the remaining methanol on a rotary evaporator at 80 °C. After cooling, the reaction mass was divided into two phases. The upper layer (oil phase) contained unreacted oil, biodiesel (FAME, fatty acid methyl esters), and acylglycerides, the lower layer was almost pure glycerin (Table 1).

Table 1. The composition of the glycerol phase (in % by weight) obtained after removal of methanol from the reaction mixture at different degrees of conversion of the reagents (the reaction temperature—230 °C and a molar ratio of methanol to oil—6:1).

Oil Phase Outlet, %w	The Composition of the Glycerol Phase, %w				
	Glycerol	FAME	MG *	DG **	TG ***
75.1	92.3	2.1	0.9	3.0	1.2
80.9	95.7	0.2	2.6	< 0.5	1.5
70.1	86.6	0.5	6.9	< 0.5	3.3
80.7	89.9	1.2	1.1	< 0.5	7.8
82.3	88.9	0.1	6.3	< 0.5	4.7

(*) TG—triglycerides (oil); (**) DG—diglycerides; (***) MG—monoglycerides.

Component composition of the upper ("oil") phases are presented below in Tables 2 and 3. To study the kinetic patterns, the obtained mass percent of the reagents was converted to molar percent, taking the triglycerides (oil) as 100%mol. The amount of initial triglycerides $[TG]_0$ in the sample corresponded to one third of the sum of the current molar concentrations of biodiesel (ester), monoglycerides, diglycerides and triglycerides with the corresponding stoichiometric coefficients:

$$[TG]_0 = \frac{\left([FAME]_i + [MG]_i + 2 \cdot [DG]_i + 3 \cdot [TG]_i\right)}{3}, \tag{1}$$

The reaction products were analyzed on a chromatograph according to the procedure described in the European standard EN 14103 [15] and EN 14105 [16].

Table 2. The composition of the upper layer of the reaction mass after phase separation and partial removal of methanol, depending on the process conditions in a tubular reactor (the reaction temperature—230 °C and a molar ratio of methanol to oil—6:1).

№	Q, L h⁻¹	n	Residence Time, h	The Composition of the Oil Phase, (%w)			
				FAME	MG	DG	TG
1	12	1	1	11.1	1.9	19.1	71.9
2	8	1	1.5	16.9	3.1	19.9	42
3	12	2	2	31.9	8.3	31.1	41.3
4	12	3	3	39.9	11.1	31.5	27
5	8	2	3	30.4	8	22.2	31.1
6	8	2	3	32.8	8.6	22.7	24.3
7	4	1	3	31.3	7.7	32.3	30.3
8	4	1	3	40.4	7.8	29.6	33.7
9	8	3	4.5	46	11.1	17.2	17.2
10	8	3	4.5	40.2	9.7	17.4	14.8
11	4	2	6	56.8	16.8	28.9	12.9
12	4	2 *	6	51.7	15	24.9	9.2
13	4	3 *	9	61.6	14.1	16.9	3.4
14	4	3	9	62.9	18.2	25.7	7.6
15	1	1	12	68.5	13.4	6.4	2.1
16	4	4 *	12	66.3	11.4	11.9	1.3

Q—reaction feed rate to the reactor; *n*—the number of cycles of the reaction solution; *—before recycle, methanol and glycerol were removed and fresh methanol was added while maintaining the initial molar ratio of methanol to oil.

Table 3. The composition of the upper layer of the reaction mass after phase separation and partial removal of methanol, depending on the process conditions in the batch reactor.

№	Residence Time, h*	T, °C	N	The Composition of the Oil Phase, %w			
				FAME	MG	DG	TG
1	4	220	9	52.1	15.3	23.3	9.3
2	8	220	9	81.6	11.8	6.1	0.6
3	12	220	9	78.0	14.3	7.2	0.5
4	16	220	9	82.9	10.8	5.8	0.5
5	8 + 8 **	220	9	90.9	5.2	3.5	0.5
6	8 + 8 + 8 **	220	9	96.2	0.5	2.8	0.5
7	0.5	230	6	45.5	11.3	22.5	20.8
8	0.5	230	9	58.1	14.7	16.3	10.9
9	0.5	230	15	29.4	7.7	30.2	32.2
10	8	230	6	79.9	10.4	6.9	2.8
11	8 + 8	230	6	87.2	9.1	3.2	0.5
12	8 + 8 + 8 **	230	6	93.2	4.1	2.3	0.4

(*) time after reaching the set temperature; (**) after every 8 h of reaction, methanol and glycerol were removed and fresh methanol was added, while maintaining the initial molar ratio of methanol to oil; N—molar excess of methanol in relation to oil.

3. Results and Discussion

3.1. Preliminary Studies

3.1.1. Mutual Solubility of the Initial Components

A preliminary study of the mutual solubility of the initial components of the reaction mixture and biodiesel showed that the homogenization of the reaction system quite easily takes place even with small additions of the reaction product at temperatures up to 50 °C.

The stoichiometric mixture of methanol to oil (3:1) is fully homogenized at 20% by weight, adding biodiesel at 20 °C. An increase in the temperature of mixing in a row up to 30 °C or up to 40 °C allows reducing the amount of biodiesel to 10% or 5% by weight, respectively. Heating in glass ampoules (8 mm in diameter) of binary mixtures of methanol with rapeseed oil at their low molar ratio ((3 ÷ 6):1), we visually observed the formation of one homogeneous phase even when the temperature reached 140–150 °C.

Summarizing the results obtained, it becomes obvious that the use of a large (up to 10-fold or more) stoichiometric molar excess of methanol is not only aimed at homogenizing the reaction solution, but using the "law of acting masses" to increase the reaction rate. However, against the background of the use of high pressures of supercritical methanol and, accordingly, the high metal consumption during the production process, reducing the reaction time to several minutes seems to be ineffective.

3.1.2. Effect of Molar Ratio

To assess the effect of the components ratio on the course of the biodiesel production reaction at 220 °C, we traced the pressure change in the autoclave during the 8 h of the reaction for different molar ratios of methanol to rapeseed oil, which changed from 1:1 to 18:1. Data on the initial and final methanol vapor pressure at a given temperature above the reaction solution are shown in Figure 1.

Since the pressure in the reactor could be determined practically only by methanol vapor, the diagram in Figure 1 is an illustration of Raoul's law with a pronounced negative deviation. A similar deviation from the law for the methanol–oil system cannot be considered an artifact, since it was noted by researchers earlier [17,18].
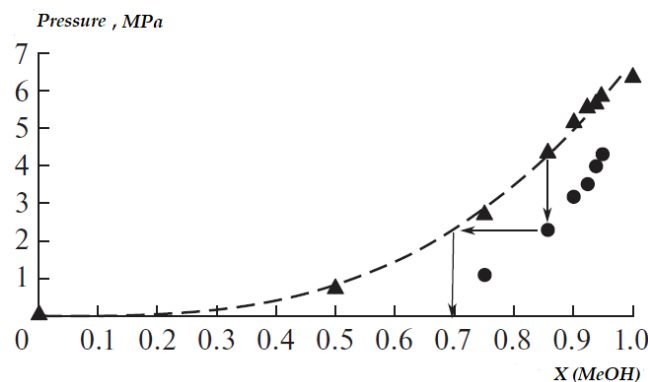

Figure 1. The pressure changes in the autoclave during the rapeseed oil methanolysis at 220 °C at the beginning of the reaction (symbols are triangles) and after 8 h (symbols are circles).

As seen in Figure 1, a low partial pressure of methanol (~0.5 MPa) up to the stoichiometric ratio of the components shows a good solubilization of methanol with vegetable oils. Apparently, the residual concentration of methanol in the oil due to a negative deviation from Raoul's law made it possible for Japanese researchers to obtain acceptable results of a non-catalytic process in a bubbler reactor at atmospheric pressure and temperatures of 250–290 °C [19].

Assuming that the conditions for the existence of a negative deviation from Raoul's law are not violated, we determined the change in the molar fraction of methanol over 8 h of the reaction. For this purpose, the partial pressure changes over the system were compared before and after the reaction (for 8 h). For example, selecting a point (Figure 1) corresponding to a pressure of 4.4 MPa (molar fraction of methanol 0.86, molar ratio of reactants 6:1), it was determined that after 8 h of reaction the pressure dropped to 2.3 MPa, which corresponds to a molar fraction of methanol 0.7 on the trend line of the original curve. From these data, given that the sum of the moles of all components of the reaction mixture is constant (according to the stoichiometry of the reaction), the amount of reacted

methanol was calculated. Having performed a similar calculation for all the data in Figure 1, we found that at initial molar ratios of methanol–oil of more than 12:1, the consumption of methanol does not increase. The calculation results are presented in Figure 2.
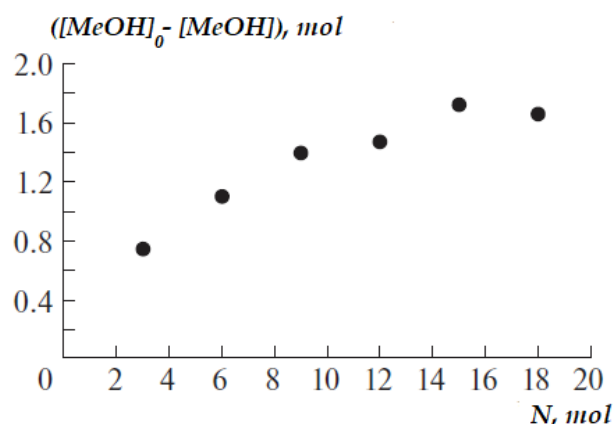

Figure 2. The calculated dependence of the specific change in the amount of moles of methanol on the initial ratio "methanol:oil" (N:1) in 8 h at 220 °C (a non-catalytic reaction in an autoclave).

Thus, we obtained convincing evidence that increasing the molar excess of methanol to a factor of 20 or more does not practically increase the output of biodiesel, but only leads to an increase in pressure in the reactor and, consequently, to unproductive technological costs associated with high-pressure equipment and methanol excess recovery costs.

3.2. Effect of Reactor Design

The idea to carry out the transesterification process with a small stoichiometric excess of methanol leads to an unexpected problem associated with the transition of the reagent to the gas phase and a corresponding decrease in its concentration in the reaction zone. Depending on the type of reactor used and the process implementation method (batch or continuous), a significant proportion of methanol can go into the gas phase. First of all, the transition of methanol to the gas phase should be expected in the case of using reactors with a stirrer, where the degree of filling of the reactor (α is usually $\alpha = 0.6$–0.8. This problem is partially solved by carrying out a continuous process in a tubular flow reactor.

To clarify the issue of the effectiveness of milder conditions for the implementation of methanolysis of vegetable oils, we performed a comparative analysis of the kinetic laws of the non-catalytic transesterification of rapeseed oil with methanol in a tubular reactor (continuous process) and in a batch reactor (autoclave).

3.2.1. Transesterification in a Tubular Flow Reactor

The process of transesterification of rapeseed oil with methanol in a tubular flow reactor was carried out at 230 °C; the molar ratio of MeOH:oil was 6:1. The pre-mixed reaction solution was fed into the reactor at different space velocities ($Q = 1.0$~12 L/h), providing different residence times of the reaction mixture in the reactor. In addition, the reaction time was changed due to recycle of the reaction mixture («n» is the number of recycles). The results of the analysis of samples of the reaction solutions obtained under different reaction conditions are presented in Table 2 (experimental data taken from our early work [20]).

The data presented in Table 2 reflect not only the general picture of the reactions occurring in the reaction zone, but also indicate some features of the process. The most obvious general reaction scheme is presented in Figure 3.
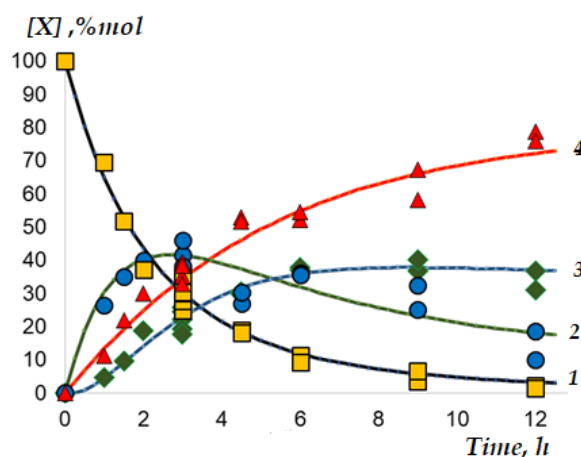
Figure 3. Changes in the relative concentrations of TG (1), DG (2), MG (3) and FAME (4) depending on the residence time in a tubular flow reactor in the reaction in subcritical methanol with rapeseed oil at 230 °C; MeOH:oil = 6:1. *Experimental points and calculated curves are given in Section 3.2.3. In the figure, for convenience, biodiesel concentrations are reduced by three times.*

Consumption of starting triglyceride successive formation of di- and monoglycerides, and finally the formation of the final product—biodiesel—is a typical picture of consecutive reaction products changing concentrations. Polynomial trend lines for each series of points of triglycerides, diglycerides, monoglycerides and fatty acid methyl esters show a high approximation accuracy (R^2 = 0.98; 0.85; 0.86 and 0.98, respectively).

The approximation functions do not depend on the hydrodynamics of the flow of the reaction mixture, which was changed by combining different feed rates of the reactants and recirculation of the reaction solution into the reactor.

This behavior of the reaction system is characteristic of the course of the reaction in only one liquid phase. On the other hand, this fact can be considered as confirmation of the reaction in the kinetic region, and the residence time of the reaction solution in the reactor can be considered as "true" reaction time.

In order to obtain information on reverse reactions, we investigated the composition of the reaction solution at high conversions of triglycerides with and without intermediate removal of glycerol. Comparing the compositions of the reaction masses obtained at the same reaction time and different hydrodynamic conditions, or with intermediate removal of glycerol and without its removal (Table 2, series of experiments 4–8 and pairs of experiments 11–12; 13–14 and 15–16, respectively); we did not find the effect of reverse reactions. In all these cases, the experimental data within the experimental error coincided with each other and were located around the trend line. However, more accurate equilibrium data can be obtained by mathematical analysis of the entire set of kinetic curves.

3.2.2. Transesterification in a Batch Reactor

Non-catalytic transesterification of rapeseed oil in a batch reactor was carried out at 220 °C and 230 °C and a different molar ratio of reagents (MeOH:oil = 6:1~15:1). To clarify the effect of the glycerol formed on the conversion depth of the initial and formed glycerides, parts of the experiments were carried out with an intermediate separation of glycerol from the reaction solution. The experimental data are shown in Table 3 (experimental data were taken from our early work [21]).
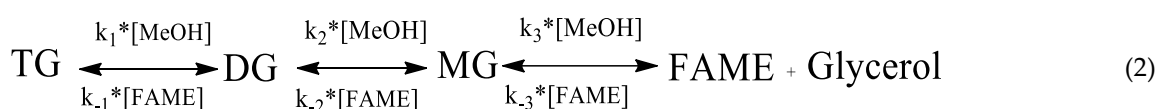
The process in a batch reactor has a significant difference from the process in a tubular flow reactor. The transesterification reaction begins by heating the reaction mixture from ambient to a predetermined operating temperature. During this time (~1.5 h), even at low molar ratios of the reagents, a significant amount of methyl esters of fatty acids is formed (experiments 7 and 8, Table 3). However, with an increase in the molar excess of methanol relative to the oil from 9:1 to 15:1, we observed a sharp decrease in the reaction

rate. The formation of fatty acid methyl esters decreased in this case by half (experiment 9, Table 3). Apparently, at a reagent ratio of 15:1, the reaction mixture remained heterogeneous, which removed some of the methanol from the reaction zone.

Our experimental data (see Table 3) confirm the negative effect on the reaction rate of the formed glycerol mainly at the last stage (experiments 4 and 5, Table 3). With its intermediate removal from the reaction mixture, the amount of formed fatty acid methyl esters increases, but practically does not affect the consumption of the initial oil. After about 16 h of reaction and without removing glycerol, the content of triglycerides is less than 0.5% by weight.

3.2.3. Reaction Kinetics in Tubular Flow and Batch Reactors

It is known that the process of transesterification of triglycerides with methanol is a sequence of three reversible reactions:

$$TG \underset{k_{-1}*[FAME]}{\overset{k_1*[MeOH]}{\rightleftharpoons}} DG \underset{k_{-2}*[FAME]}{\overset{k_2*[MeOH]}{\rightleftharpoons}} MG \underset{k_{-3}*[FAME]}{\overset{k_3*[MeOH]}{\rightleftharpoons}} FAME + Glycerol \tag{2}$$

We found that binary mixtures of methanol with rapeseed oil at their low molar ratio $((3 \div 6):1)$ form one homogeneous phase even when the temperature reaches 140–150 °C, which greatly simplifies the task of obtaining a mathematical model of the process. Mass transfer phenomena and the associated limitations in the system under consideration are absent; reactions proceed in the kinetic region.

Experiments with the intermediate separation of glycerol from the reaction solutions (Table 2, pairs of experiments of the table: 7 and 14; 8 and 15; 12 and 16, and in Table 3, experiments 4 and 5), showed only a weak effect of feedback on the whole process under these experimental conditions. The formation of glycerol does not affect the first and second reactions, but has a slightly negative effect on the last reaction—the interaction of monoglyceride with methanol. This conclusion is suitable for reactions occurring both in a flow reactor and in a batch reactor.

Based on the reaction scheme, the kinetics of the process of transesterification of rapeseed oil with methanol can be described by the standard system of differential Equations (3)–(7):

$$d[TG]/dt = -k_1[TG][MeOH] + k_{-1}[DG][ester] \tag{3}$$

$$d[DG]/dt = k_1[TG][MeOH] + k_{-2}[MG][ester] - (k_{-1}[ester] + k_2[MeOH])[DG] \tag{4}$$

$$d[MG]/dt = k_2[DG][MeOH] + k_{-3}[GL][ester] - (k_{-2}[ester] + k_3[MeOH])[MG] \tag{5}$$

$$d[GL]/dt = k_3[MG][MeOH] - k_{-3}[GL][ester] \tag{6}$$

$$d[ester]/dt = d[DG]/dt + 2\,d[MG]/dt + 3\,d[GL]/dt \tag{7}$$

Assuming that the volume of the reaction mass during the reaction does not change, for the mathematical processing of experimental data and subsequent modeling of the process, we replaced the concentrations of the reactants with their dimensionless analogues—the relative concentrations of the reactants ($[X]_i$). For this purpose, we obtained the ratio of the molar concentrations of each reagent to the initial number of moles of triglycerides (oil) in the reaction medium, taking for 100% of the initial value of the relative concentration of triglycerides, i.e., $[X_{TG}]_0 = 100\%$. The initial conditional concentration of methanol corresponded to the expression $[X_{MeOH}]_0 = M*100\%$, where M is the molar excess of methanol with respect to oil.

Since the system of equations includes only second-order reaction rate equations, when converting molar concentrations of reagents to relative (dimensionless), each rate constant must be multiplied by the initial concentration of triglycerides. Thus, the system of differential Equations (3)–(7) transforms to the system of differential Equations (8)–(12):

$$d[X_{TG}]/dt = -[TG]_0(k_1[X_{TG}][X_{MeOH}] - k_{-1}[X_{DG}][X_{ester}]),$$ (8)

$$d[X_{DG}]/dt = [TG]_0(k_1[X_{TG}][X_{MeOH}] + k_{-2}[X_{MG}][X_{ester}] - (k_{-1}[X_{ester}] + k_2[X_{MeOH}])[X_{DG}]),$$ (9)

$$d[X_{MG}]/dt = [TG]_0(k_2[X_{DG}][X_{MeOH}] + k_{-3}[X_{MG}][X_{ester}] - (k_{-2}[X_{ester}] + k_3[X_{MeOH}])[X_{MG}]),$$ (10)

$$d[X_{GL}]/dt = [TG]_0(k_3[X_{MG}][X_{MeOH}] - k_{-3}[X_{GL}][X_{ester}]),$$ (11)

$$d[X_{ester}]/dt = d[X_{DG}]/dt + 2\,d[X_{MG}]/dt + 3\,d[X_{GL}]/dt,$$ (12)

where $[X_{TG}]$, $[X_{DG}]$, $[X_{MG}]$, $[X_{GL}]$, $[X_{MeOH}]$ and $[X_{ester}]$ are the molar ratios of each reagent (mol(i)) to the initial number of moles of oil in the reaction mixture.

Initially, to calculate the parameters of the system of differential Equations (8)–(12), we used the experimental data obtained for the tubular reactor (Table 2), since the reaction time in this case was determined quite accurately, in contrast to the data for the reaction in the batch reactor.

The initial concentration of triglycerides for a 6-fold molar excess of methanol can be determined as $0.8\ \text{mol L}^{-1}$ using the method of additivity of liquid volumes. However, due to the difficulty of determining the oil concentration in the reaction mixture at temperatures of 220–230 °C, and for technical calculations it is advisable to use the values of the given rate constants (k_i^*) in the form of products:

$$k_i^* = k_i[TG]_0$$ (13)

All calculations were carried out using the Maple program [22]. To solve the system of differential Equations (8)–(12), the modified Euler method was used.

Scheme refining and obtaining the numerical values of the parameters of differential equations was carried out by minimizing the sum of squared deviations between the calculated and experimental values of the relative concentrations of glycerides and reaction products—fatty acid methyl esters of rapeseed oil. In the best coincidence of calculated and experimental data, $[X_i]$ value pair constants of all three stages of the process were recorded: $(k_1^*\ и\ k_{-1}^*)$, $(k_2^*\ и\ k_{-2}^*)$ и $(k_3^*\ и\ k_{-3}^*)$, which are given in Table 4.

When modeling the process in a tubular reactor using Equations (8)–(12), we found that the constants of the reverse reactions are determined with a large error, and the constant (k_{-1}^*) turned out to be statistically insignificant. The reason for the low sensitivity of the constants of the reverse reactions is, apparently, in the insufficient depth of the conversion of di- and mono-glycerides and a low concentration of formed glycerol. To clarify the values of the rate constants, we used the kinetic data obtained in a series of experiments in a batch reactor. For this purpose, we used the system of differential Equations (8)–(12), but with the exception of the time parameter. We transformed the system of Equations (8)–(12) in the form of relations (14), thereby eliminating time:

$$d[X_{TG}]/d[X_{ester}], \qquad d[X_{DG}]/d[X_{ester}], \qquad d[X_{MG}]/d[X_{ester}],$$ (14)

To construct the dependences of the relative concentrations $[X_{TG}]$, $[X_{DG}]$, $[X_{MG}]$, $[X_{GL}]$ and $[X_{MeOH}]$ on $[X_{ester}]$, it is not necessary to integrate sufficiently complex expressions of

Equation (14), but you can use the calculated data obtained when writing the concentration dependencies reaction system in time. Figure 4 shows these dependencies.

It should be noted that the calculated curves of the dependence of tri-, di-, and monoglycerides on the amount of ester formed (see figure curves 1, 2 and 3, respectively) fit the data obtained both for the reaction in a tubular flow reactor and those obtained in a batch reactor when reaction time is not determined exactly.
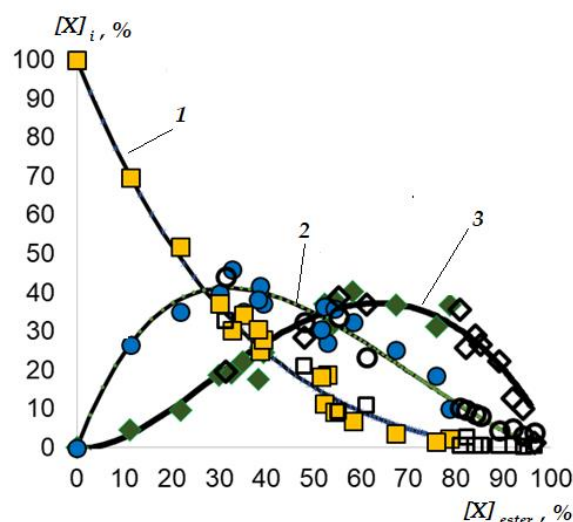

Figure 4. Correlation between current relative concentrations of $[X_{TG}]$ (1), $[X_{DG}]$ (2), $[X_{MG}]$ (3) depending on $[X_{Ester}]$ during transesterification of rapeseed oil in subcritical methanol according to Tables 2 and 3. *The curves are calculated according to the model, and the dots represent the experimental data obtained in the tubular (filled symbols) and in the batch (unfilled symbols) reactor.*

It should be noted that the experimental data obtained for both reactors complemented each other. The bulk of the data related to the flow reactor are located on the left side of the diagram when there is little glycerol in the reaction mixture. On the contrary, the dataset relating to the batch reactor is located on the right side when there is a lot of glycerin in the reaction mass. These data made it possible to refine the values of the rate constants of the reverse reactions. Nevertheless, the rate constant of the reverse reaction of the first stage of the process (k_{-1}^{*}) remained insignificant.

The best description of the experimental values of the reduced concentrations of all glycerides and biodiesel in both reactors at 230 °C and a 6-fold molar excess of methanol (which corresponded to 2:1 by stoichiometry) is obtained at the values of the rate constants which are given in Table 4. In this case, the reliability score for the linear regression of all the experimental and calculated values was $R^2 = 0.98$.

Table 4. The given rate constants of the process of transesterification of rapeseed oil at 230 °C and a molar ratio of methanol to oil 6:1.

$k_i^{*} \cdot 10^4$, mol L^{-1} h^{-1}	k_1^{*}	k_2^{*}	k_3^{*}	k_{-1}^{*}	k_{-2}^{*}	k_{-3}^{*}
	7.10 ± 0.04	6.10 ± 0.04	3.90 ± 0.02	< 0.01	0.41 ± 0.03	0.40 ± 0.03

The fact that the experimental data for the process obtained at 220 °C and a triple stoichiometric excess of methanol also fit the calculated curves can be explained by the fact that the decrease in the rate constants due to temperature was compensated by an increase in the concentration of methanol.

4. Conclusions

The fit between the correlations of the dimensionless concentrations of the reaction products Xi and Xef (Figure 4) for the transesterification of rapeseed oil in both the tubular and the batch reactors indicates the identity of the mathematical description of the processes occurring in both types of reactors. Additionally, in the case of using an autoclave, the hypothesis that significant part of the methanol would be in a gas–vapor phase was not confirmed, since at 220–230 °C (see Figure 1) the concentration of methanol in the liquid phase is disproportionately higher than would be expected if Raul's law were observed.

For practical implementation, the absence of a catalyst in the reaction products, the composition and good separation of the two phases formed, as well as the process with a slight excess of methanol are weighty arguments in favor of choosing the studied one [23,24].

Since the presence of reversible reactions (at any conversion of the initial oil) does not allow us to obtain a quantitative yield of the main product, an additional stage of removing glycerol from the reaction mass is necessary. Next, the methanolysis of unreacted mono- and diglycerides is repeated, yielding an almost quantitative yield of both the final products—biodiesel and pure glycerol.

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