

# Determination of kinetic parameters for complex transesterification reaction by standard optimisation methods

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## Abstract

This paper represents a methodology for kinetic parameter estimation based on standard optimization methods. The parameter estimation procedure is applied to the example of modelling of non-catalytic transesterification reaction, based on laboratory experiments performed under elevated pressure. The kinetic model employed in this study consists of three consecutive and parallel reversible reactions of the second order, with six kinetic constants. The influence of the mass transfer effects was considered as well. The best results were obtained by Genetic Algorithm method. The application of this method resulted in kinetic parameters with improved accuracy in predicting concentrations of important reaction intermediates, *i.e.*, diglycerides and monoglycerides. Activation energies of kinetic parameters obtained by the Genetic Algorithm method are in line with theoretical values determined by molecular orbital calculations.

**Keywords:** optimisation technique, genetic algorithm, short-cut method, kinetic parameters, high pressure process.

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Research on chemical kinetics of complex reactions of industrial importance often requires the estimation of rate or equilibrium coefficients by nonlinear regression [1]. A variety of methods are applied to solve practical problems in parameter optimization, starting from traditional calculus methods and ranging to the so-called “evolutionary algorithms” [2]. These methodologies have been extensively applied during the past two decades to the modelling of various industrial processes [3].

The transesterification reaction represents challenge for many researchers, mainly due to its application for synthesis of renewable biofuels. This reaction can be performed without presence of homogeneous or heterogeneous catalyst, if reaction pressure and temperature are elevated above certain values. The subcritical transesterification is a promising method for a more environmentally friendly biodiesel production, as a result of its feedstock flexibility, production efficiency and environmentally friendly benefits. The investigation of subcritical and supercritical methanolysis of triglycerides and determination of kinetic parameters has been the objective of several papers published in the last ten years [4–9].

The methanolysis of triglycerides that forms fatty acid methyl esters (FAME), as end products, is the complex reaction which can be represented as parallel-

-consecutive kinetic model consisting of three second-order reversible reactions [4]. The composition of reaction mixture at the end of synthesis comprises mainly the products: methyl esters, the small amount of glycerol (up to 5 mass%), and the large excess of methanol. Monoglycerides and diglycerides are formed as intermediate products and could be present only in traces in a mixture upon reaction completion. However, those minute concentrations of reaction intermediates could impact on biodiesel quality and compliance with the current technical standards. Therefore, it is extremely important to be able to predict an optimum reaction time or a reactor space time, for this reaction [5,8].

This paper presents the determination of kinetic parameters of the non-catalytic biodiesel synthesis under elevated pressure and temperature. Three different numerical methods: Simulated annealing, the lsqcurvefit with Levenberg–Marquardt algorithm and Global optimization technique – Genetic Algorithm, have been used to calculate kinetic parameters. The influence of mass transfer was calculated, since it was found to influence strongly on the reaction rate in the initial phase of the reaction and consequently to the values of reaction kinetic parameters.

## EXPERIMENTAL PROCEDURE

The high pressure batch reactor, volume of 2 dm<sup>3</sup>, mechanically agitated (Ernst Haage, Germany), was used for the analysis of reaction rate of triglycerides methanolysis at 150 and 210 °C and 1.0 and 4.5 MPa.

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The specified amounts of methanol and sunflower oil corresponding to molar ratio 42 to 1 were used. Detailed description of the experimental procedure can be found in the literature [6,8]. The composition profile during reaction for both analysed conditions is shown in Table 1.

### Mathematical modelling and numerical optimisation

#### Kinetic model description

Transesterification or FAME synthesis under sub-critical conditions is a catalyst-free chemical reaction between triglycerides (the major component in vegetable oils, animal fats, and used vegetable oils) with a low molecular weight alcohol, usually methanol, at a temperature and pressure under the critical point of triglyceride-alcohol mixture. The overall reaction occurs as a sequence of three steps, parallel with respect to alcohol and consecutive with respect to triglyceride. Triglyceride (TG) reacts with an alcohol (ROH) in the first reaction and forms diglyceride (DG) and fatty acid

methyl ester (FAME). Monoglycerides (MG) and fatty acid methyl esters (FAME) are formed in the second reaction from diglyceride (DG) and methanol. The final products, appearing as products of the third reaction, are glycerol (GL) and again fatty acid methyl esters (FAME). The reaction scheme is shown below:



It is important to point out that the reversible reactions of DG, MG and GL with FAME control the maximum/equilibrium conversion of triglycerides. The reaction rate for each component in the system (constant volume batch system) can be represented by the following set of equations where each reaction step

Table 1. The reaction mixture composition profile during methanolysis of sunflower oil at 150 °C and 1.0 MPa, and at 210 °C and 4.5 MPa

Time, min	Concentration, kmol/dm <sup>3</sup>					
	MeOH	TG	DG	MG	FAME	Glycerol
Experiment 1 (150 °C and 1.1 MPa)						
0	2.833	6.84E-02	0.00	0.00	0.00	0.00
256	2.807	4.75E-02	1.51E-02	3.71E-03	2.60E-02	8.18E-04
613	2.795	3.92E-02	1.98E-02	5.83E-03	3.83E-02	1.60E-03
1228	2.772	2.95E-02	2.83E-02	9.78E-03	6.07E-02	2.30E-03
1433	2.762	2.40E-02	3.13E-02	1.49E-02	7.08E-02	4.48E-03
1633	2.747	1.74E-02	2.02E-02	2.16E-02	8.57E-02	6.23E-03
1933	2.715	1.03E-02	9.10E-03	2.83E-02	1.18E-01	6.97E-03
2623	2.699	7.49E-03	7.87E-03	2.34E-02	1.34E-01	9.83E-03
3028	2.676	3.04E-03	6.56E-03	1.58E-02	1.57E-01	1.68E-02
9000	2.639	0.00	0.00	0.00	1.94E-01	6.06E-02
Experiment 2 (210 °C and 4.5 MPa)						
0	2.835	6.78E-02	0.00	0.00	0.00	0.00
130	2.806	3.56E-02	1.96E-02	1.92E-02	3.35E-02	0.00
160	2.755	3.42E-02	1.49E-02	2.54E-02	4.17E-02	0.00
190	2.735	2.92E-02	1.38E-02	2.83E-02	5.67E-02	0.00
220	2.715	2.20E-02	1.40E-02	2.80E-02	7.97E-02	4.37E-03
250	2.698	1.70E-02	7.89E-03	3.12E-02	1.05E-01	1.24E-02
280	2.675	1.29E-02	5.45E-03	2.78E-02	1.28E-01	2.23E-02
340	2.659	7.02E-03	5.90E-03	1.56E-02	1.58E-01	3.99E-02
400	2.648	3.65E-03	5.13E-03	7.92E-03	1.75E-01	5.17E-02
460	2.641	2.66E-03	5.04E-03	4.64E-03	1.79E-01	5.61E-02
520	2.637	1.49E-03	3.57E-03	2.48E-03	1.86E-01	6.09E-02
580	2.633	3.35E-04	4.96E-04	1.84E-03	1.95E-01	6.58E-02
640	2.632	2.49E-04	2.40E-04	1.44E-03	1.98E-01	6.65E-02
700	2.630	2.31E-04	2.90E-05	1.28E-03	2.00E-01	6.69E-02
760	2.630	0.00	0.00	7.61E-04	2.02E-01	6.77E-02

is assumed to be second order in both directions and therefore dependent on concentration of reacting components:

$$r_{TG} = \frac{dC_{TG}}{dt} = -k_{11}C_{TG}C_{ROH} + k_{12}C_{DG}C_{FAME} \quad (4)$$

$$r_{DG} = \frac{dC_{DG}}{dt} = k_{11}C_{TG}C_{ROH} - k_{12}C_{DG}C_{FAME} - k_{21}C_{DG}C_{ROH} + k_{22}C_{MG}C_{FAME} \quad (5)$$

$$r_{MG} = \frac{dC_{MG}}{dt} = k_{21}C_{DG}C_{ROH} - k_{22}C_{MG}C_{FAME} - k_{31}C_{MG}C_{ROH} + k_{32}C_{GL}C_{FAME} \quad (6)$$

$$r_{GL} = \frac{dC_{GL}}{dt} = k_{31}C_{MG}C_{ROH} - k_{32}C_{GL}C_{FAME} \quad (7)$$

$$r_{FAME} = \frac{dC_{FAME}}{dt} = -3\left(\frac{dC_{TG}}{dt}\right) - 2\left(\frac{dC_{DG}}{dt}\right) - \left(\frac{dC_{MG}}{dt}\right) \quad (8)$$

$$r_{ROH} = \frac{dC_{ROH}}{dt} = -\frac{dC_{FAME}}{dt} \quad (9)$$

If the reaction scheme is represented by the above equations the concentrations of reacting species are assumed to be numbers of moles divided by the overall reaction volume, regardless of the existence of multiple phases. Each reaction is characterized by its reaction rate constant (both forward and reverse reactions). The slowest forward reaction rate controls the overall reaction rate along with reaction equilibrium constant for each of the reversible reactions shown above [6].

Batch reaction system containing triglycerides and methanol, at investigated pressure and temperature, is characterised by the equilibrium between two liquid phases at the beginning of reaction. During methanolysis of triglycerides, the phase distribution is changing according to the actual composition of reaction mixture, temperature and pressure, for a given time of reaction. Distribution of methanol between the oil phase, the methyl esters phase and the glycerol rich phase strongly depends on operating conditions [8].

The rate of triglycerides methanolysis depends also on the phase equilibrium and on the methanol distribution in the oil-rich phase. Up to 150 °C and 1.1 MPa the oil is present only in one liquid phase together with a smaller amount of dissolved methanol [6,8]. The methanol to oil molar ratio is 1:1, three times less than required by stoichiometry, thereby causing very low reaction rate (complete conversion could be achieved after approximately 150 h). At 210 °C and 4.5 MPa the methanol to oil molar ratio in the oil phase is changing from 6:1 to 10:1 through the course of reaction, thus increasing the rate of reaction and resulting in complete conversion of triglycerides in approximately 10 h.

The methyl esters being produced form the third liquid phase which contains almost all diglycerides, monoglycerides and glycerol, together with certain amount of methanol. This is also the period when probability for reverse reaction between glycerol and FAME is much higher than probability of reaction between glycerides (present in low concentrations) and methanol. At the end of reaction (at 210 °C and 4.5 MPa) one liquid phase contains methanol, FAME and glycerol, as well as certain small amount of monoglycerides and diglycerides [6,8].

The sigmoid shape of the conversion curves, during FAME synthesis, points out to a complex reaction mechanism. Initially slow reaction rate increases with conversion and in its final stage the FAME yield curve reaches a plateau. At the beginning of reaction, the interfacial area between the phases containing reactants is dependent on the agitation intensity and mass transfer controls the overall reaction rate ( $k_{kinetic} \gg \gg k_{mass\ transfer}$ ). This is more pronounced at conditions corresponding to low methanol solubility in the oil phase, *e.g.*, under lower pressure and temperature. Therefore, the kinetic constant for the forward reaction of triglycerides conversion could be corrected with following equation, introducing the mass transfer effects [6]:

$$k_{11}' = k_{mt} + k_{11}(C_{DG} + C_{MG})/C_{TG0} \quad (10)$$

where the  $k_{mt}$  represents the mass transfer controlled kinetic constant in the initial phase of the reaction. Increasing conversion followed by changing phase distribution, increasing concentrations of intermediates (mono and diglycerides) and the enhancement of interfacial area will result in the increase of overall kinetic constant [6]. Based on the calculation of mass transfer coefficient in mechanically stirred system the numerical value of  $k_{mt}$  for the first and second experiment was determined as  $9.2 \times 10^{-7}$  and  $1.5 \times 10^{-6}$   $\text{dm}^3/(\text{kmol min})$  respectively [6]. Intense agitation provides sufficiently high values of mass transfer coefficient to accommodate for methanol consumed by the reaction in oil phase, while the extent of reaction in methanol rich phase can be neglected due to very low concentrations of glycerides in that phase [6,8]. Hence, the calculation of apparent values for kinetic parameters using the overall reaction volume can be applied with the incorporation of mass transfer effects at the beginning of reaction.

#### Parameter determination by different optimization techniques

The proposed kinetic model for biodiesel synthesis is nonlinear implying that finding the best set of values for kinetic parameters requires the use of optimization techniques and/or their combinations. In general, the techniques used for parameters estimation can be

divided into two groups: the short cut methods and the global optimization techniques that do not require initial guesses [10–15].

Due to the fact that most of the methods for parameters estimation require good initial guess to find the optimal set of results, finding the initial values of unknown parameters are essential for successful parameters estimation. In this study model parameters, or reaction constants, were determined using Simulated Annealing (SA), Isqcurvefit (LM) and Genetic Algorithm (GA) methods (as defined functions in MATLAB). In order to make a comparison among these optimization methods the following objective function was defined for all of them:

$$\text{Objective function} = \sum_{i=1}^6 \sum_{j=1}^n \left( \frac{C_{i,j}^{\text{Exp}} - C_{i,j}^{\text{Model}}}{C_{i,\max}^{\text{Exp}}} \right)^2 \quad (11)$$

where  $i$  refers to the component (TG, DG, MG, GL, FAME and ROH), and  $j$  refers to the experimental data for each component.  $C_{i,\max}^{\text{Exp}}$  is the maximum concentration of component  $i$  within the experimental data set.

The default parameters were defined as the parameters predetermined by MATLAB. The only deviation from this was the applied algorithm for solving optimization by Isqcurvefit which was changed from trust-region-reflective (default) to Levenberg-Marquardt.

#### Simulated annealing (SA)

Simulated annealing is a probabilistic global search method [16,17]. SA is stochastic search techniques and it is used when the structure of a space is not well understood or is not smooth. In particular, these techniques are frequently used to solve combinatorial optimization problems, such as the travelling salesman problem. The goal is to find a point in the space at which a real valued energy function (or cost function) is minimized. Simulated annealing is a minimization technique which has given good results in avoiding local minima; it is based on the idea of taking a random walk through the space at successively lower temperatures, where the probability of taking a step is given by a Boltzmann distribution [16,17].

#### The Isqcurvefit with Levenberg–Marquardt algorithm (LM)

The Isqcurvefit solves nonlinear data-fitting problems. The Isqcurvefit requires a user-defined function to compute the vector-valued function  $F(x, xdata)$ . The size of the vector returned by the user-defined function must be the same as the size of  $ydata$  [18,19].

The Levenberg–Marquardt algorithm (LMA), also known as the damped least-squares (DLS) method, is an iterative technique which provides a numerical solution to the problem of minimizing a function, generally nonlinear, over a space of parameters of the func-

tion. These minimization problems arise especially in least squares curve fitting and nonlinear programming. It has become a standard technique for non-linear least-squares problems, widely adopted in a broad spectrum of disciplines [18,19].

The LMA interpolates between the Gauss–Newton algorithm (GNA) and the method of gradient descent. When the current solution is far from the correct one, the algorithm behaves like a steepest descent method (slow but certain convergence). When the current solution is close to the correct solution, it becomes a Gauss–Newton method [17,18]. The LMA is a very popular curve-fitting algorithm used in many software applications for solving generic curve-fitting problems. However, the LMA finds only a local minimum, not a global minimum [18,19].

The first initial guess required for these two techniques (LM and SA) was found by applying combination of two short cut methods. This approach combines differential method of analysis [20] and method for kinetics parameters estimation proposed by Glowinski and Stocki [21]. In order to reveal the dependency of the optimum solution to the initial guess, three guesses were considered for each experiment. The first guess is  $0.1 \times \mathbf{x}_0$ , the second guess is  $\mathbf{x}_0$ , and the last one is  $10 \times \mathbf{x}_0$ , where  $\mathbf{x}_0$  is the vector containing the obtained values of reaction constants by linear technique.

#### Global optimization technique - Genetic Algorithm

Nowadays this technique is widely used. Commonly, genetic algorithm optimization technique is used to estimate initial values of parameters, because this approach does not require any initial assumption of parameters' value. The method compares experimental data of species' concentration with values predicted by the model. Due to the fact that concentration of species' values differ from each other by several orders of magnitude and sum of squares of deviation between experimental and modelled values are summarized in one objective function, the values should be brought to the same numeric interval. There are several techniques to achieve this: *i*) minimize square of relative error between experimental and model predicted values of concentration and *ii*) involve variances of experimental measurements. The drawback of using square of relative error is that error of each experimental measurement has significant impact on objective function. On the other side, using variance of experimental measurements are more convenient, since error of measurements is averaged which results in lower impact of individual measurement error on objective function. If values of variances of experimental values are not available, they can be optimized together with unknown rate reaction parameters. The drawback of this technique is that it increases number of parameters to be optimized [22–27].

The genetic algorithm technique makes use of the Darwinian survival of the fittest procedure. These are search procedures based on mechanics of natural genetics and natural selection [22]. Five GA operators are used in the DNA-GA to enhance the searching ability of the GA [23]. In particular, the “mutation step” helps in avoiding getting trapped in local minima during the search procedure [23]. The parameters were searched within non-negative numbers.

## RESULTS AND DISCUSSION

The kinetic model, as defined by Eqs. (4)–(9), including modification of  $k_{11}$  rate constant as shown by Eq. (10), was applied to the experimental data of transesterification reaction performed under subcritical conditions (150 °C and 1.1 MPa and 210 °C and 4.5 MPa). Six kinetic parameters for forward and reverse reactions were obtained by different approaches using numerical methods.

The results obtained by SA method are presented in Table 2. The initial guess was obtained using linear technique. In order to reveal the dependency of the optimum solution on the initial guess, three guesses were considered for each experiment. The first guess is  $0.1 \times x_0$ , the second guess is  $x_0$ , and the last one is  $10 \times x_0$ . The optimum values of the kinetic constants depended significantly on the initial guess, and the second initial

guess was found to result in the minimum error (Eq. (11)).

The results obtained by LM method are shown in Table 3. The same initial guesses as in the case of SA were used. The results have indicated that the optimum value is practically insensitive and independent on the initial guess, and therefore only one set of results is shown in Table 3. Also, error values are considerably lower than in the case of SA method. In order to check whether the results obtained by LM are a local optimum or the global one, the LM program was performed with various initial guesses. For generating logical and different initial guess values and to avoid trapping into a local minimum, the initial guesses were determined using GA with sufficient population size (the default population size was changed from 20 to 500). In this way the time required for running the GA program increased significantly, but it has been confirmed that correct initial guess values have been obtained. The results showed that the data presented in Table 3 are really the global optimum.

The kinetic parameters obtained by GA method are shown in Table 4. The error values are slightly higher than in the case of LM method. By comparing results shown in Tables 2–4, it can be observed that LM method results in lower minimum error than SA method and even lower than GA method.

Table 2. Kinetic constants ( $\text{kmol}/(\text{dm}^3 \text{ s})$ ) obtained by SA method

Constant	Exp. 1		Exp. 1 with modified $k_{11}$		Exp. 2		Exp. 2 with modified $k_{11}$	
	Initial guess	Optimum	Initial guess	Optimum	Initial guess	Optimum	Initial guess	Optimum
$k_{11}$	7.58E-07	5.83E-06	7.58E-07	1.95E-05	3.70E-06	5.73E-05	3.70E-06	2.32E-04
$k_{12}$	0.00E+00	7.40E-06	0.00E+00	3.75E-05	0.00E+00	3.12E-03	0.00E+00	8.58E-06
$k_{21}$	2.20E-07	6.38E-06	2.20E-07	8.45E-06	7.83E-06	6.32E-05	7.83E-06	1.13E-04
$k_{22}$	0.00E+00	0.00E+00	0.00E+00	4.60E-06	0.00E+00	1.17E-04	0.00E+00	8.15E-04
$k_{31}$	2.15E-07	3.20E-05	2.15E-07	8.37E-05	6.18E-06	2.37E-03	6.18E-06	7.98E-04
$k_{32}$	0.00E+00	2.98E-05	0.00E+00	1.28E-04	0.00E+00	2.85E-03	0.00E+00	6.32E-05
Error		3.286		3.741		6.129		5.359
$k_{11}$	7.58E-06	1.67E-05	7.58E-06	2.80E-05	3.70E-05	3.70E-05	3.70E-05	2.63E-04
$k_{12}$	0.00E+00	4.45E-06	0.00E+00	1.58E-05	0.00E+00	0.00E+00	0.00E+00	3.62E-04
$k_{21}$	2.20E-06	5.03E-06	2.20E-06	1.25E-05	7.83E-05	7.83E-05	7.83E-05	1.30E-04
$k_{22}$	0.00E+00	0.00E+00	0.00E+00	2.13E-05	0.00E+00	0.00E+00	0.00E+00	7.35E-04
$k_{31}$	2.15E-06	4.82E-06	2.15E-06	5.20E-06	6.18E-05	6.18E-05	6.18E-05	9.30E-04
$k_{32}$	0.00E+00	0.00E+00	0.00E+00	1.78E-05	0.00E+00	0.00E+00	0.00E+00	1.20E-03
Error		2.678		2.656		1.552		4.999
$k_{11}$	7.58E-05	1.83E-05	7.58E-05	4.45E-05	3.70E-04	4.78E-05	3.70E-04	3.30E-04
$k_{12}$	0.00E+00	5.80E-04	0.00E+00	1.73E-04	0.00E+00	9.85E-04	0.00E+00	5.50E-04
$k_{21}$	2.20E-05	1.08E-05	2.20E-05	1.47E-05	7.83E-04	6.17E-04	7.83E-04	2.05E-04
$k_{22}$	0.00E+00	2.15E-04	0.00E+00	3.88E-04	0.00E+00	5.40E-03	0.00E+00	2.53E-03
$k_{31}$	2.15E-05	4.23E-05	2.15E-05	6.73E-05	6.18E-04	1.92E-03	6.18E-04	1.27E-03
$k_{32}$	0.00E+00	1.16E-03	0.00E+00	3.72E-04	0.00E+00	1.10E-02	0.00E+00	2.75E-03
Error		2.996		3.642		7.237		5.738

Table 3. Kinetic constants (kmol/(dm<sup>3</sup> s)) obtained by LM method

Constant	Exp. 1	Exp. 1 with modified $k_{11}$	Exp. 2	Exp. 2 with modified $k_{11}$
$k_{11}$	5.92E-06	2.77E-05	4.25E-05	2.30E-04
$k_{12}$	7.15E-05	3.92E-04	3.72E-19	1.57E-03
$k_{21}$	5.42E-06	5.80E-06	8.38E-05	1.43E-04
$k_{22}$	3.70E-20	3.70E-20	3.72E-19	2.12E-04
$k_{31}$	3.42E-06	3.52E-06	4.28E-05	4.68E-05
$k_{32}$	3.70E-20	3.70E-20	3.72E-19	3.70E-19
Error	0.582	0.683	1.167	0.892

Table 4. Kinetic constants (kmol/(dm<sup>3</sup> s)) obtained by GA method

Constant	Exp. 1	Exp. 1 with modified $k_{11}$	Exp. 2	Exp. 2 with modified $k_{11}$
$k_{11}$	5.03E-06	1.60E-05	4.25E-05	2.10E-04
$k_{12}$	3.82E-06	1.19E-05	1.40E-05	1.37E-04
$k_{21}$	5.93E-06	8.03E-06	8.53E-05	1.54E-04
$k_{22}$	1.04E-07	5.17E-06	1.39E-05	1.41E-04
$k_{31}$	3.60E-06	4.62E-06	4.35E-05	5.12E-05
$k_{32}$	5.43E-09	6.62E-07	1.78E-06	1.19E-06
Error	0.629	0.999	1.182	1.040

Model equations (4)–(9) were solved using kinetic parameters obtained by LM and GA methods. The resulting composition profiles for each component, at

analysed temperatures and pressures, are shown in Figure 1 for LM method and Figure 2 for GA method.

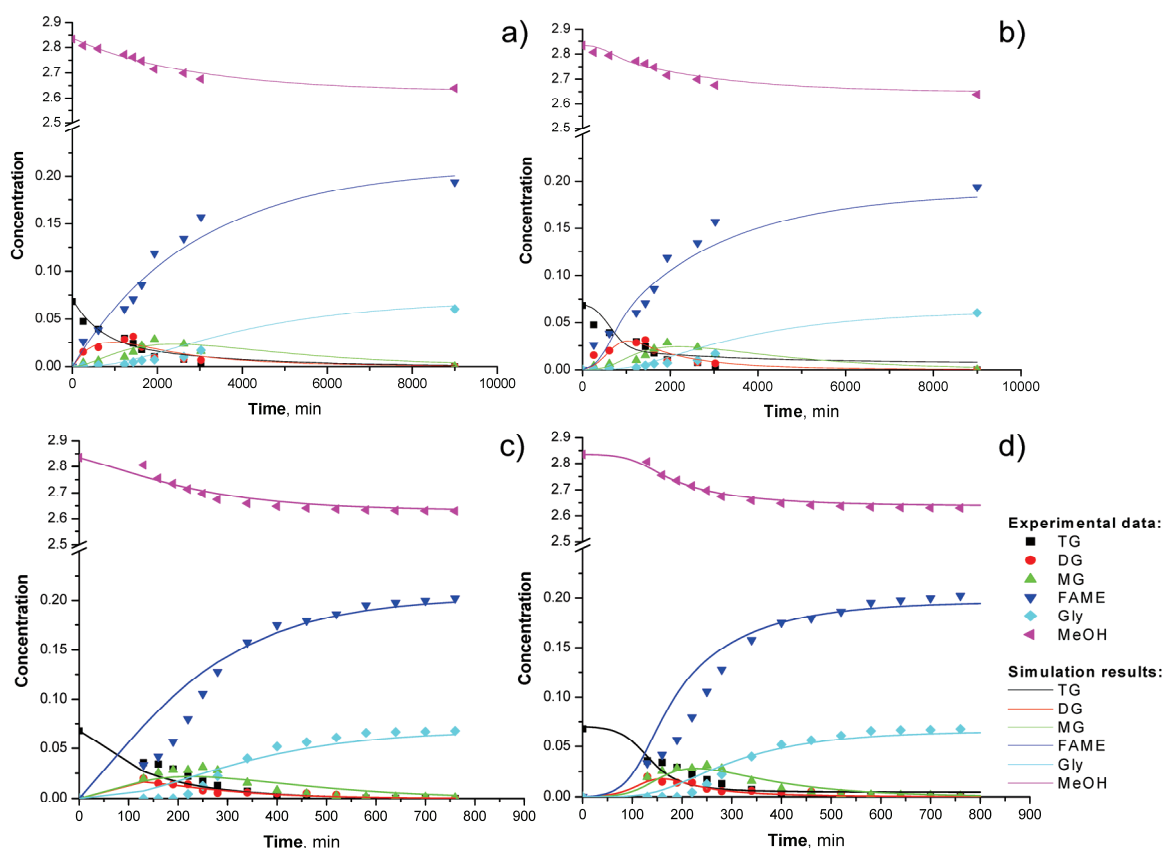


Figure 1. The comparison of model simulation results (kinetic constants obtained by LM method) and experimental results: a) Exp. 1; b) Exp. 1 with modified  $k_{11}$ ; c) Exp. 2; d) Exp. 2 with modified  $k_{11}$ .

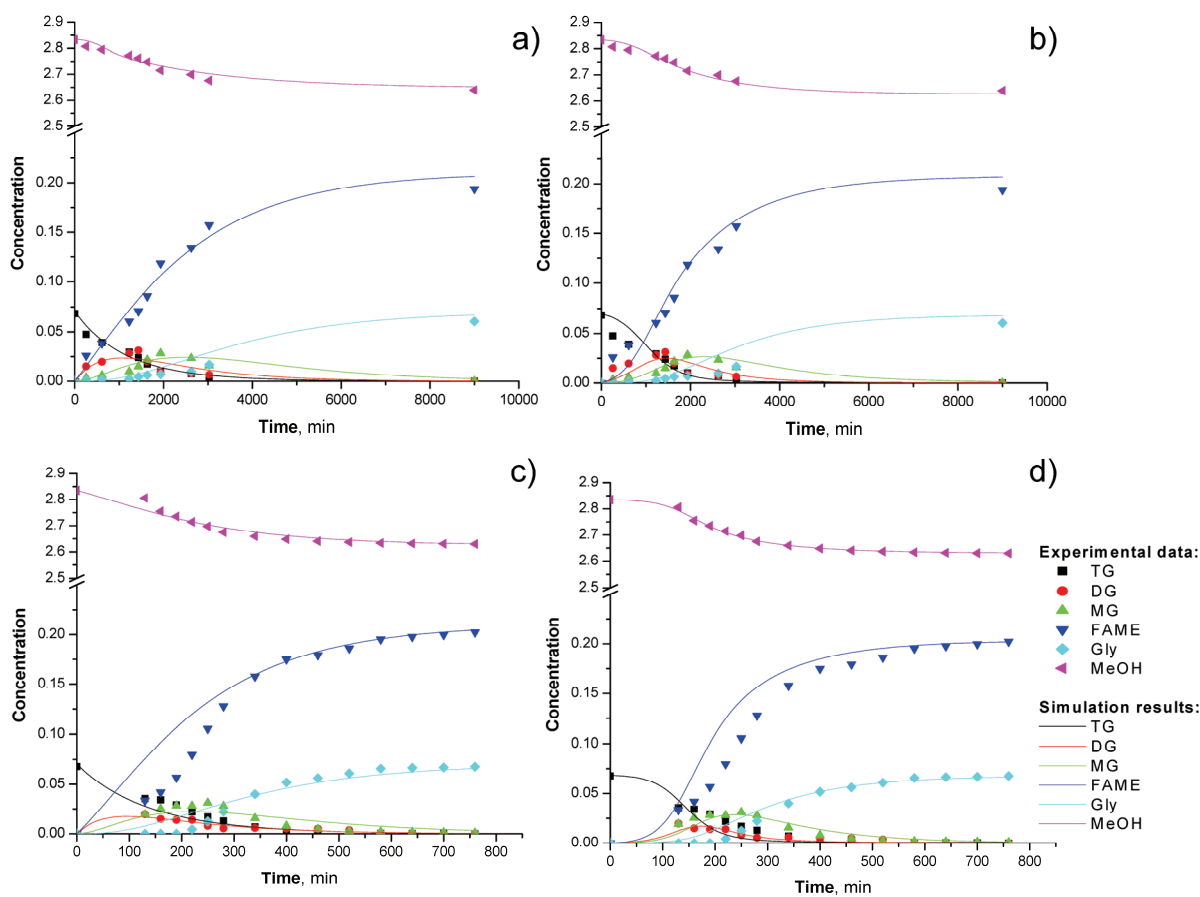


Figure 2. The comparison of model simulation results (kinetic constants obtained by GA method) and experimental results: a) Exp. 1; b) Exp. 1 with modified  $k_{11}$ ; c) Exp. 2; d) Exp. 2 with modified  $k_{11}$ .

The obtained results indicate that kinetic parameters determined by LM and GA are in line with experimental data obtained at 150 °C and 1.1 MPa (Exp. 1) with (Figure 1a and b) or without (Figure 2a and b) mass transfer limitations included in the expression for kinetic constant  $k_{11}$ . However, kinetic parameters deviate considerably from the experimental results at 210 °C and 4.5 MPa, if the mass transfer limitations are not included in the kinetic constant  $k_{11}$  (Figures 1c and 2c). Introducing the mass transfer modification of  $k_{11}$  kinetic constant improves accuracy, but still doesn't lead to the excellent correlation of experimental data. This is especially the case for concentration profile of FAME. Judging by FAME concentration profile, it would seem that kinetic parameters obtained by numerical optimisation methods correlate experimental data slightly worse than the parameters obtained by simplified kinetic procedure (Figure 6b in reference [6]).

Error values were thus calculated (using Eq. (11)) for the procedure based only on triglycerides conversion and these were found to be 3.899 and 3.459 for the Exp. 1 and Exp. 2, respectively. Obviously these values are considerably higher than for LM and GA methods. Concentration profiles of intermediate species (digly-

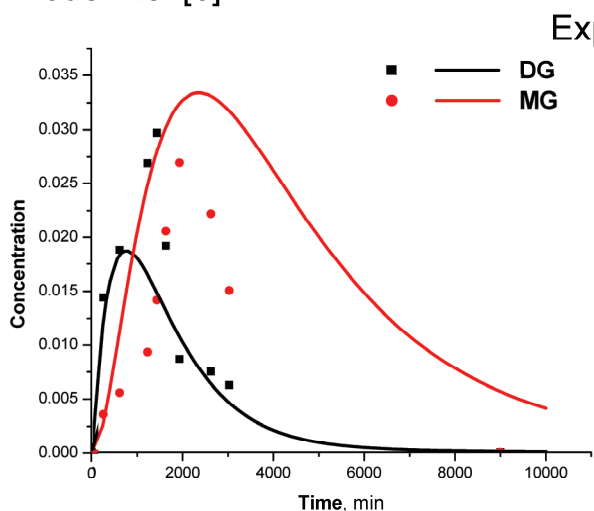
cerides and monoglycerides) for these three methods are shown in Figure 3.

It is clear that kinetic parameters obtained by optimisation methods are superior in predicting concentration profiles of diglycerides and monoglycerides, and this is especially the case for GA method. The ability to predict accurately concentrations of intermediates could be extremely important for proper design of reactor system for FAME synthesis. This is in fact critical parameter for FAME biodiesel quality due to limitations imposed by pertaining technical standards.

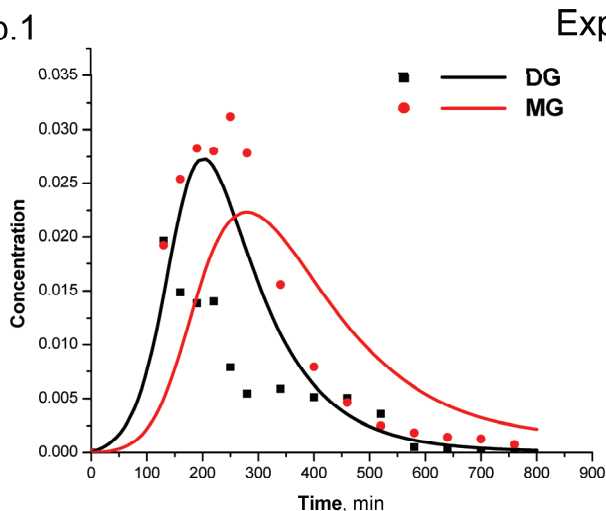
As stated previously the error values of LM method are slightly better than for GA method. However, careful inspection of values for kinetic parameters  $k_{11}$ – $k_{32}$  in Table 3 shows that kinetic constant for the first reverse reaction  $k_{12}$  is higher than forward reaction. However, this type of behaviour shouldn't be seen in this type of reactive system [28]. Also, values of  $k_{22}$  at 150 and 210 °C indicate that activation energy for  $k_{22}$  should be equal to 1026.2 kJ/mol which is hardly possible when compared to the values obtained in theoretical study using molecular orbital calculations [29,30].

Kinetic constants obtained by the GA method (Table 4) indicate that equilibrium constants are always above

Model Ref.[6]

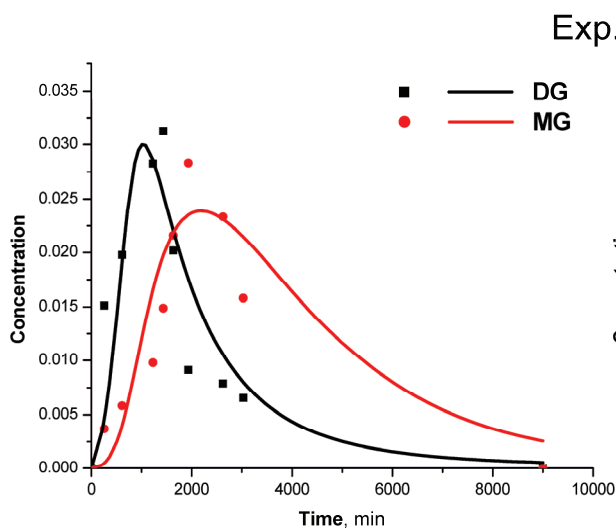


Exp. 1

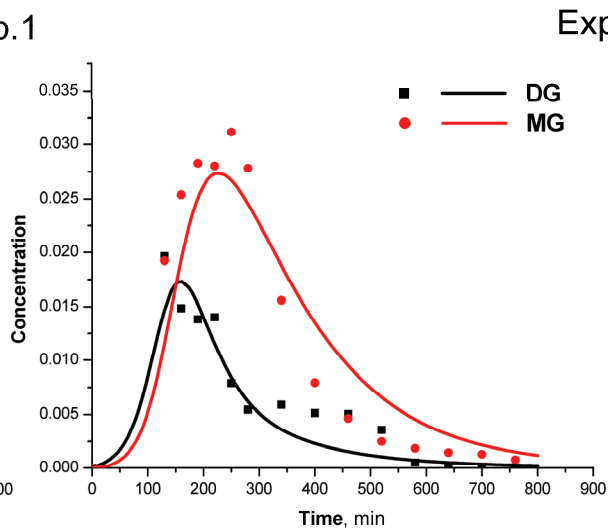


Exp. 2

LM

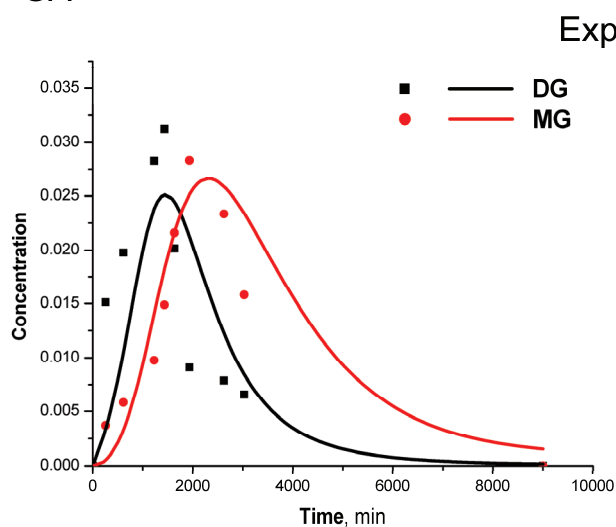


Exp. 1

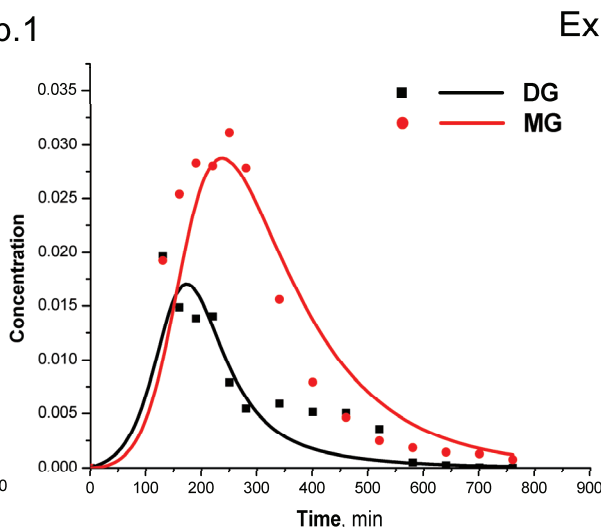


Exp. 2

GA



Exp. 1



Exp. 2

Figure 3. Comparison of the experimental and simulated data using kinetic constants obtained with the GA and LM optimisation methods and the simplified procedure [6].



1 and also that equilibrium constants decrease with increasing temperature, which is in accordance with theoretical calculations of phase and chemical equilibrium [28]. Furthermore, the values of activation energies for forward reactions (in  $k_{11}$ ,  $k_{21}$  and  $k_{31}$ ) are in line with the values obtained through theoretical calculations based on molecular orbital calculations for synthesis under acidic conditions [29–31]. Values for route (c) from [30] have been used to make comparison and this is shown in Table 5.

Table 5. The comparison of  $E_a$  (kJ/mol) for forward reactions based on molecular orbital calculations [30] and values obtained in this study by the GA method

Constant	$E_a$ taken from [30]	$E_a$ by GA method
$k_{11}$	79.4	72.8
$k_{21}$	71.1	83.5
$k_{31}$	83.6	68.0

## CONCLUSION

The parameter estimation procedures were applied to the determination of kinetic parameters of non-catalytic fatty acids methyl esters (FAME) synthesis under elevated pressure. Experimental data were obtained using mechanically agitated batch reactor of constant volume at 150 °C and 1.1 MPa and 210 °C and 4.5 MPa. The kinetic model used in this study consisted of three consecutive and parallel reversible reactions of second order. The kinetic constants for forward and reverse reaction steps were obtained by three different types of numerical methods: Simulated Annealing (SA), lsqcurvefit with Levenberg–Marquardt algorithm (LM) and Genetic Algorithm (GA). The proposed kinetic model and kinetic parameters determined by the GA method, with the inclusion of mass transfer limitations, fitted well the experimental data. Predictions of triglycerides conversion and FAME yield were very good, as well as the predicted concentrations of intermediates (mono- and diglycerides). The activation energies of forward reactions are in line with values obtained by molecular orbital calculations.

## Nomenclature

### Symbols

$C$	concentration (kmol dm <sup>-3</sup> )
$E_A$	activation energy (kJ kmol <sup>-1</sup> )
$K$	equilibrium constant
$k$	kinetic constant of reaction (kmol dm <sup>-3</sup> min <sup>-1</sup> )
$P$	pressure (MPa)
$T$	temperature (°C)
$t$	time (minute or second)
$V$	volume (dm <sup>3</sup> )

## Abbreviations

TG	triglycerides
DG	diglycerides
MG	monoglycerides
FAME	fatty acid methyl esters
MeOH	methanol

## Subscripts

$n1$	$n = 1,2,3$ , index for the forward reaction
$n2$	$n = 1,2,3$ , index for the reverse reaction

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## IZVOD

## ODREĐIVANJE KINETIČKIH PARAMETARA SLOŽENE REAKCIJE TRANSESTERIFIKACIJE PRIMENOM STANDARDNIH OPTIMIZACIONIH METODA

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(Naučni rad)

U ovom radu je predstavljena metodologija i rezultati određivanja kinetičkih parametara za složenu reakciju transesterifikacije korišćenjem standardnih optimizacionih metoda. Određivanje kinetičkih parametara različitim optimizacionim metodama izvedeno je za nekatalizovane reakcije transesterifikacije suncokretovog ulja sa metanolom. Reakcija je ispitivana eksperimentima u šaržnom reaktoru pod uslovima povišenog pritiska i temperature. Ova reakcija predstavlja jedan složen reakcioni sistem, kako sa aspekta kinetike hemijskih reakcija tako i sa aspekta ravnoteže faza i prenosa mase. Sistem je višekomponentni pri čemu se ukupni sastav znatno menja tokom reakcije, a u zavisnosti od temperature i pritiska, reakcioni sistem menja i broj i sastav faza u ravnoteži. Primenjeni kinetički model čini sistem od tri povratne uporedno-uzastopne reakcije drugog reda. Pod uslovima pritiska i temperature ispitanim u ovom radu (150 °C i 1,1 MPa; 210 °C i 4,5 MPa), ovaj reakcioni sistem u početnoj fazi čine dve tečne faze u termodinamičkoj ravnoteži. Zbog ove činjenice u početnoj fazi reakcije u obzir je uzet i uticaj prenosa mase na kinetičke parametre. Tokom reakcije koju karakteriše nastajanje međuproizvoda, mono i diglicerida, dolazi do stvaranja mikroemulzije što je potvrđeno prethodnim istraživanjima. Stoga se ovakav sistem u naknadnoj fazi može smatrati uniformnim po celoj zapremini. Optimizacione metode primenjene u ovom radu zasnivaju se na primeni Levenberg–Marquardt logaritma, *Simulated Annealing* i genetskog algoritma. Najbolji rezultati su dobijeni primenom genetskog algoritma, odnosno kinetički parametri dobijeni tim proračunom pokazuju najmanje odstupanje predviđanja koncentracija svih reaktanata i proizvoda u odnosu na eksperimentalne podatke. Primenom optimizacionih metoda na ovako složen sistem moguće je dobiti bolje predviđanje koncentracija intermedijera u odnosu na druge metode koje se mogu naći u literaturi. Takođe, postoje razlike u kvalitetu rešenja dobijenim različitim optimizacionim metodama. Kinetički parametri dobijeni primenom Levenberg–Marquardt algoritma dobro numerički opisuju realni sistem ali vrednosti kinetičkih parametara ne odgovaraju teoretskim vrednostima koje se očekuju na osnovu mehanizma reakcije. Sa druge strane, vrednosti energija aktivacije ove složene reakcije koje su dobijene primenom genetskog algoritma, u veoma su dobrom slaganju sa vrednostima energija aktivacije koje su dobijene proračunom molekularskih orbitala.

*Ključne reči:* Optimizacione metode • Genetski algoritam • Kinetički parametri složene reakcije transesterifikacije • Matematičko modelovanje nekatalizovane transesterifikacije triglicerida