Bioautomation, 2006, 5, 13 – 22 ISSN 1312 – 451X

Modelling Chemical Kinetics of Soybean Oil Transesterification Process for Biodiesel Production: An Analysis of Molar Ratio between Alcohol and Soybean Oil Temperature Changes on the Process Conversion Rate

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Received: August 1, 2006 **Accepted: October 30, 2006**

Published: December 8, 2006

Abstract: *A mathematical model describing chemical kinetics of transesterification of soybean oil for biodiesel production has been developed. The model is based on the reverse mechanism of transesterification reactions and describes dynamics concentration changes of triglycerides, diglycerides, monoglycerides, biodiesel, and glycerol production. Reaction rate constants were written in the Arrhenius form. An analysis of key process variables such as temperature and molar ratio soybean oil- alcohol using response surface analysis was performed to achieve the maximum soybean conversion rate to biodiesel. The predictive power of the developed model was checked for the very wide range of operational conditions and parameters values by fitting different experimental results for homogeneous catalytic and non-catalytic processes published in the literature. A very good correlation between model simulations and experimental data was observed.*

Keywords: *Biodiesel, Modelling, Transesterification kinetics, Soybean oils.*

Introduction

Biodiesel (free fatty acid alcohol esters) is alternative fuel for diesel engines produced from renewable source. Biodiesel (BD) is mainly produced from vegetable oil constituent and animal fats, constituided of triglycerides (TG), diglycerides (DG) and monoglycerides (MG), where free fatty acids (FFA) and water take place. Brazil is the second bigger producer of oils with capacity to increase and to diversify its production. Hence, exploring this renewable energy source is at a great interest. Because the carbon in the oil or fat originated mostly from carbon dioxide in the air the use of BD like substitution to conventional diesel is considered to contribute much less to global warming then fossil fuel [8]. Other BD advantages are that it is biodegradable and non-toxic fuel.

Conventionally, the oil transesterification (alcoholysis) reaction catalyzed by acids or bases in a homogeneous medium is performed. The kinetics reaction depends on the type of used

alcohol (methanol, ethanol, propanol or butanol), oil composition (including FFA and water), the type and amount of catalyst, temperature, alcohol-oil molar ratio.

The homogeneous reactions, in which a base is used as a catalyst, have shown that the esters production is faster than when an acid catalyst is used. The alkali hydroxide catalyst such as potassium or sodium is disadvantageous as during the process water is formed. The accumulation of water and the presence of KOH or NaOH accelerate irreversible reaction of oil hydrolysis and as a result soap is formed. The soaponification reaction decreases the conversion of triglycerides to biodiesel. In addition, the catalysts are removed with the glycerol layer, which makes the glycerol purification process difficult.

From economical point of view, BD production is limited to high price of oils and purification of secondary product (glycerol) [1, 9-11]. The search of a cheaper substrate leads to the use of not edible oils [10] such as used oils from restaurants and snack bars [8] and animal fats [9]. These oils are characterized with elevated amounts of FFA, but they are an alternative for the cost reduction of transesterification process. For oils with higher acidity (equivalent to the 2 mg KOH/g oil [8]) is recommended two stages process. The first step includes FFA esterification by acid catalyst and followed by the alcoholysis of TG by basic catalyst.

The objective of this work was to develop a flexible new kinetic model of transesterification process of soybean oil (SBO) including a reverse mechanism of three consecutive chemical reactions and check it on the different experimental data published in the literature.

Mathematical model

Using the well known mechanism of transesterification of branched TG with alcohol (ROH) into straight-chain molecules of methyl, ethyl or butyl esters BD one can write the three consecutive reactions with intermediate formation of DG and MG and GL as follows [7]:

$$TG + ROH \underset{K_{11}}{\overset{K_1}{\rightleftharpoons}} DG + BD \tag{1}$$

$$DG + ROH \underset{K_{22}}{\overset{K_2}{\rightleftharpoons}} MG + BD \tag{2}$$

$$MG + ROH \underset{K_{33}}{\overset{K_3}{\rightleftharpoons}} GL + BD \tag{3}$$

The overall reaction is

$$TG + 3ROH \rightarrow GL + 3BD \tag{4}$$

The proposed mechanism assumes homogeneous catalytic reactions that each reaction step is reversible and kinetics is first order with respect to the reacting components' concentration. Higher order forward and backward chemical reactions can also be assumed to take place, but for simplicity and clarity reasons the chosen first assumption is good enough. The mass–transfer and transport phenomena limitations are out of consideration. The kinetics constants can be written as a function of reaction temperature using the well-known Arrhenius model.

The three consecutive transesterification reactions can be either equilibrium reactions or forward reactions depending on working conditions and the chosen catalyst (if any is involved) and molar ratio Alcohol:Soybean Oil (ROH:SBO). Based on the above mechanism

and model assumptions, the kinetics of transesterification process can be described by using component mass balances as follows:

$$\frac{dC_{TG}}{dt} = -K_1.C_{TG}(t).C_{ROH}(t) + K_{11}.C_{DG}(t).C_{BD}(t) \tag{5}$$

$$\frac{dC_{DG}}{dt} = K_1.C_{TG}(t).C_{ROH}(t) - K_{11}.C_{DG}(t).C_{BD}(t) - K_2.C_{DG}(t).C_{ROH}(t) + \\ + K_{22}.C_{MG}(t).C_{BD}(t) \tag{6}$$

$$\frac{dC_{MG}}{dt} = K_2.C_{DG}(t).C_{ROH}(t) - K_{22}.C_{MG}(t).C_{BD}(t) - K_3.C_{MG}(t).C_{ROH}(t) + \\ + K_{33}.C_{GL}(t).C_{BD}(t) \tag{7}$$

$$\frac{dC_{GL}}{dt} = K_3.C_{MG}(t).C_{ROH}(t) - K_{33}.C_{GL}(t).C_{BD}(t) \tag{8}$$

$$\frac{dC_{BD}}{dt} = -3.\left(\frac{dC_{TG}}{dt}\right) - 2.\left(\frac{dC_{DG}}{dt}\right) - 1.\left(\frac{dC_{MG}}{dt}\right) \tag{9}$$

$$\frac{dC_{ROH}}{dt} = -\frac{dC_{BD}}{dt}, \tag{10}$$

where C_i stands for "ith" component concentration and K_i stands for "ith" forward reaction rate constant.

The system of ordinary differential equations (5 through 10) can be transformed in a such way where the each component concentration is presented as a mass ratio $X_{component}$ (kg component/kg ester) as shown in the work of [3, 4].

$$\frac{dX_{TG}}{dt} = -K_1.X_{TG}(t).C_{ROH}(t) + \frac{PM_{TG}}{PM_{DG}} K_{11}.X_{DG}(t).C_{BD}(t) \tag{11}$$

$$\frac{dX_{DG}}{dt} = \left(\frac{PM_{DG}}{PM_{TG}} K_1.X_{TG}(t) - K_2.X_{DG}(t)\right) C_{ROH}(t) + \\ + \left(\frac{PM_{DG}}{PM_{MG}} K_{22}.X_{MG}(t) - K_{11}.X_{DG}(t)\right) C_{BD}(t) \tag{12}$$

$$\frac{dX_{MG}}{dt} = \left(\frac{PM_{MG}}{PM_{DG}} K_2.X_{DG}(t) - K_3.X_{MG}(t)\right) C_{ROH}(t) + \\ + \left(\frac{PM_{MG}}{PM_{GL}} K_{33}.X_{GL}(t) - K_{22}.X_{MG}(t)\right) C_{BD}(t) \tag{13}$$

$$\frac{dX_{GL}}{dt} = \frac{PM_{GL}}{PM_{MG}} K_3.X_{MG}(t).C_{ROH}(t) - K_{33}.X_{GL}(t).C_{BD}(t) \tag{14}$$

$$X_{BD}(t) = 1 - X_{TG}(t) - X_{DG}(t) - X_{MG}(t), \tag{15}$$

where $C_{ROH}(t) = \dfrac{n_{ROH} - 3.n_{TG}\left(1 - X_{TG}(t) - X_{DG}(t) - X_{MG}(t)\right)}{\left(PM_{TG} n_{TG} + PM_{ROH} n_{ROH}\right)/1000}$

and $C_{BD}(t) = \dfrac{3.n_{TG}\left(1 - X_{TG}(t) - X_{DG}(t) - X_{MG}(t)\right)}{\left(PM_{TG}n_{TG} + PM_{ROH}n_{ROH}\right)/1000}$.

In these equations, n_{TG} stands for the number of SBO mols; n_{ROH} stands for the number of alcohol mols; $PM_{component}$ stands for molecular weight of component.

The rate constants in the forward (K_i) and reverse reactions (K_{ii}) are written as follows:

$$K_i = K_{i,0}.e^{-\frac{Ea_i}{R.T}} \tag{16}$$

$$K_{ii} = K_{ii,0}.e^{-\frac{Ea_{ii}}{R.T}} \tag{17}$$

In the equations (16, 17) Ea_i stands for energy of activation for the ith forward reaction and Ea_{ii} stands for energy of activation for reverse reaction, R is a gas constant and T stands for reaction temperature. $K_{i,0}$ and $K_{ii,0}$ stand for initial rate constants of forward and reverse reactions.

The normalized model (see equations (11) through (15)) was completed and was used for fitting experimental data of transesterification catalytic and non-catalytic processes under various operational conditions.

Results and discussion

To check the predictive power of the new developed model a set of experimental data taken from the literature were fitted [4]. All computer simulations were performed using Maple software. The ordinary differential equations of the system were solved using Rosenbrock numerical method from the Detools package with accuracy of 16 digits. The results were compared with the ones obtained by using RKF45, Gear, and lsode (adamsfull and backfull) numerical methods and no differences were observed. Nonlinear parameter identification procedure was based on the least squares with weights statistical criterion and computer program was written and executed in FORTRAN using as a local optimizer Simplex Optimization Method (SOM).The constants values estimated by SOM were further used as initial guesses for the global optimizer such as particle swarm optimization (PSO) [5].The PSO parameters values which have been used during the search procedure were as follows – number of individuals = 30, number of iterations = 30, maximum velocity = 0.9, minimum velocity = 0 and constants $C_1 = C_2 = 2$. The final results of the kinetics parameters values search are shown in Table 1 and Table 2.

Table 1. Estimated values of kinetic rate constants

Kinetic constants	**Estimated values**			
	Fig. 1	**Fig. 2**	**Ea**	**$K_{i,0}$**
K_1, [(kg Total)·(mol ROH)$^{-1}$·(h)$^{-1}$]	0.033	0.0745	113108.8	3.15×10^{10}
K_{11}, [(kg Total)·(mol BD)$^{-1}$·(h)$^{-1}$]	0.019	0.0045	-200072.7	1.22×10^{-21}
K_2, [(kg Total)·(mol ROH)$^{-1}$·(h)$^{-1}$]	0.028	0.0674	122019.4	2.35×10^{11}
K_{22}, [(kg Total)·(mol BD)$^{-1}$·(h)$^{-1}$]	0.018	0.0335	86283.8	2.47×10^{7}
K_3, [(kg Total)·(mol ROH)$^{-1}$·(h)$^{-1}$]	0.010	0.0109	11970.5	1.85×10^{-1}
K_{33}, [(kg Total)·(mol BD)$^{-1}$·(h)$^{-1}$]	0.009	0.0002	-528762.6	8.89×10^{-59}

First, the data from non-catalytic transesterification process of soybean oil [4] in two different working conditions (Fig. 1 – reaction temperature 220ºC and molar ratio Methanol:Soybean Oil (MEOH:SBO) 27:1; Fig. 2 – reaction temperature 235ºC and molar ratio Methanol:Soybean Oil (MEOH:SBO) 21:1) were used to evaluate the model parameters values of forward and reverse reactions. One can observe in Fig. 1 concentration dynamic changes of TG, DG, MG and BD versus time for the given reaction conditions. The solid curves are model concentration profiles and points represent experimental data. There are no available experimental data only for glycerol concentration profile and for this reason simulation results are not shown. An analysis of Fig. 1 can prove that the TG concentration continuously decreases, and at the end of the process is approaches value close to zero. The DG concentration increases rapidly during the first reaction hour reaching a maximum and after that slowly decreases, but it does not reach zero at the end of the transesterification process. MG concentration slowly increases during the process and its utilization is not completed at end of the reaction time. This residual concentration of MG (about 20%) has shown that the third forward trasnesterification reaction is very slow and can be considered as a limiting step of the overall transesterification process. The rate constants` values for the reaction temperature 220ºC (see Table 1 in column Fig. 1) have shown that the forward reactions dominate and the third reverse reaction (see K_{33}) can be considered for these operational conditions (non–catalyst reaction, molar ratio, reaction temperature, and pressure), because its values is similar to the value of (K_3). The K_1 and K_2 values are similar, but K_3 value is lower. As one can see the model simulation profiles of TG, MG have almost perfect match. There is some deviation between model prediction and experimental data for the BD profile. The deviation between model and experimental data of DG profiles is more significant, but this fact does not change the overall very good prediction of the model for these operational conditions.

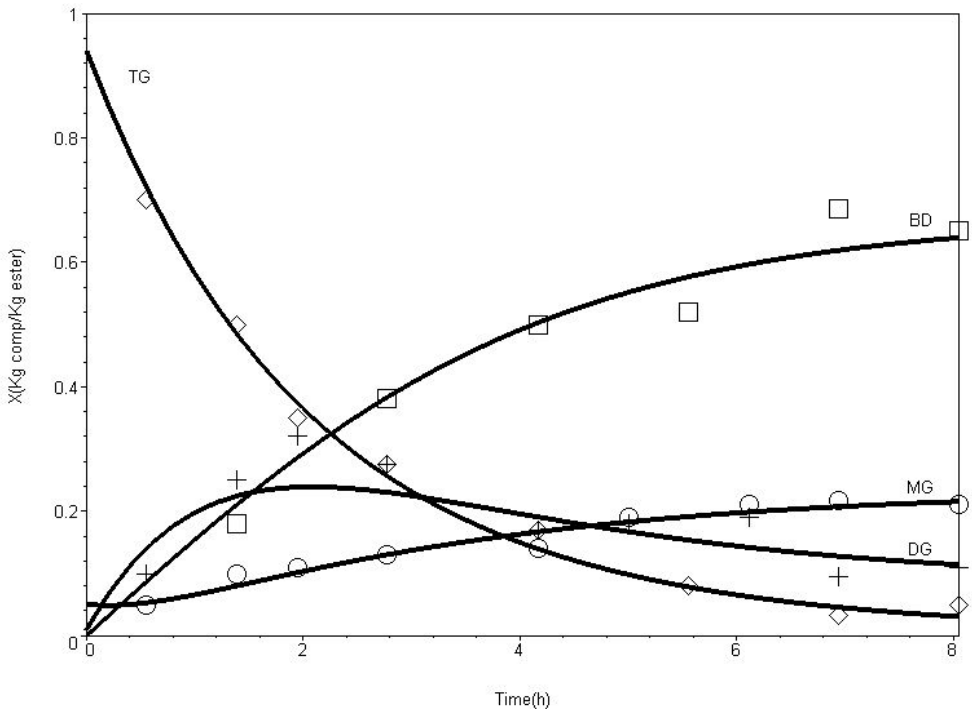


Fig. 1 Simulation results for transesterification of soybean oil and experimental results from work [4]. Reaction conditions: temperature 220°C, molar ratio ROH/TG 27/1, alcohol methanol, non-catalytic reaction.

Computer simulation results and experimental data analysis of TG, DG and MG profiles (Fig. 2) have shown that the TG concentration decreases with the same trend as shown in Fig. 1 reaching zero at the 6th hour. The DG concentration profile approaches zero at the 8th reaction hour. The MG concentration did show a clear trend to be stable after the 5th hour and reaches its plateau maximum value at end of the process (8th hour). The reaction temperature of this process is higher with 15°C than the one presented in Fig. 1, but molar ratio Methanol/TG is lower (21/1). For this kind of processes, where the final product BD is not removing from the reaction mixture during the process time, molar ratio and temperature appear to be the crucial parameters for maximum BD production. Hence, biodiesel productivity depends on the value of these two key control variables. Compare the results presented in Fig. 1 and Fig. 2 one can observe that the BD productivity is higher for the process shown in Fig. 2.

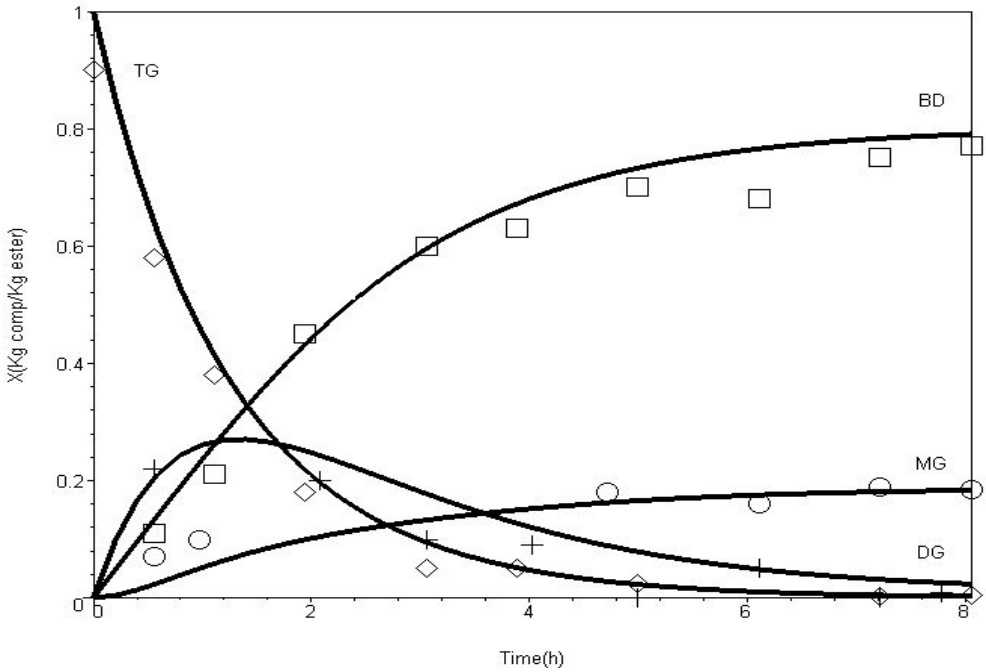


Fig. 2 Simulation results for transesterification of soybean oil and experimental results from work [4]. Reaction conditions: temperature 235°C, molar ratio ROH/TG 21/1, alcohol methanol, non-catalytic reaction.

Analyzing transesterification process when base catalyst is applied (see Table 2 and Fig. 3) one can conclude that the forward reactions dominate and the process can be completed in approximately 10 hours. The other transesterfication processes using base catalysts ca be performed from 1 to 30 hours depending on working conditions, catalyst and component concentrations. An analysis of the catalytic process represented in Fig. 3 has shown that the usage of a catalyst (in this case base catalyst) is crucial for overall process time and BD productivity. The rate constants values of forward reactions (K_1, K_2, and K_3) are very high compared to the ones of the reverse reactions (K_{11}, K_{22} and K_{33}, see Table 2). It means, that the forward reaction dominate and reverse reactions can be neglected for these operational conditions. The third forward reaction can be considered as a limiting step of the overall transesterification process. The residual MG mass fraction is higher than 20% based on the initial TG mass fraction. To achieve a higher conversion of SBO to BD the reaction time has to be extended minimizing the residual MG mass fraction. An analysis of the various experimental data from the different literature sources have shown that the third forward reaction is responsible for the overall BD production.

When compare the results from catalytic and non-catalytic biodiesel production the one can observe that the conversion values are close, but the two main differences have to be taken into account. First, non-catalytic process has advantage in GL recuperation which is crucial second product. On the other hand, catalytic process offers very soft operational conditions (low reaction temperature and pressure which does not require special equipment to be used).

Once again, the process optimization is a compromise between costs and maximum conversion rates. The better results can be achieved using additive optimization criterion based on the process effectiveness and production costs for equal other conditions.

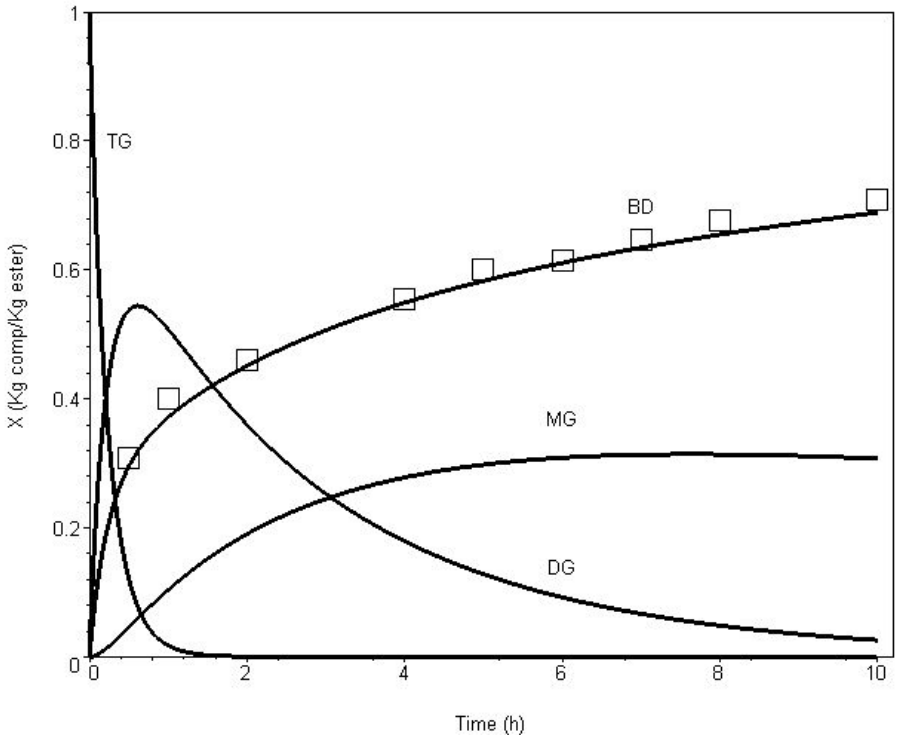


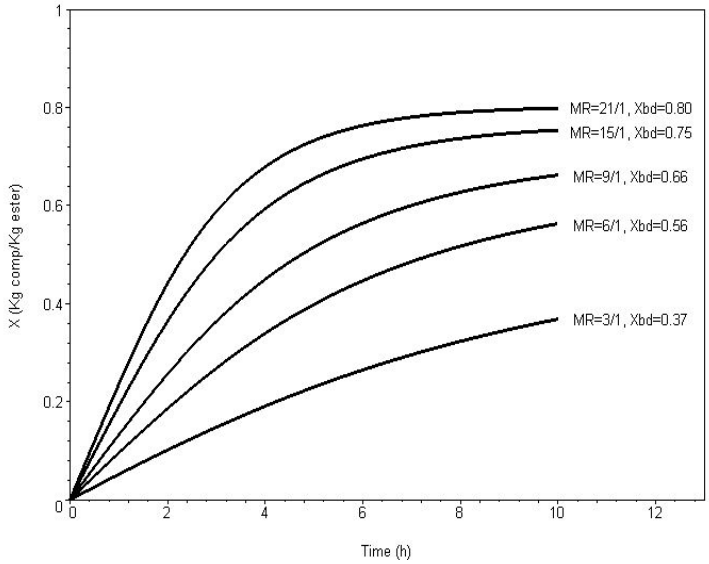
Fig. 3 Simulation results for transesterification of soybean oil and experimental results from work [2]. Reaction conditions: temperature 20°C, molar ratio ROH/TG 6/1, alcohol methanol, base-catalytic reaction – 0.5% $NaOCH_3$.

Table 2. Evaluated kinetic rate constants value for base catalyst used

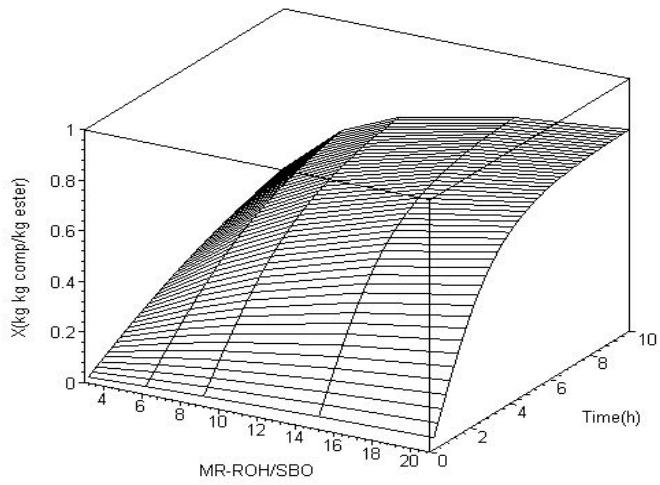
Constant	Evaluated Value
K_1, [(kg Total)·(mol ROH)$^{-1}$·(h)$^{-1}$]	1
K_{11}, [(kg Total)·(mol BD)$^{-1}$·(h)$^{-1}$]	0.1
K_2, [(kg Total)·(mol ROH)$^{-1}$·(h)$^{-1}$]	0.01
K_{22}, [(kg Total)·(mol BD)$^{-1}$·(h)$^{-1}$]	0.4×10^{-6}
K_3, [(kg Total)·(mol ROH)$^{-1}$·(h)$^{-1}$]	0.22×10^{-6}
K_{33}, [(kg Total)·(mol BD)$^{-1}$·(h)$^{-1}$]	0.11×10^{-6}

The further steps of model development were included application of response surface analysis (RSA) as methodology to check system behavior as a function of key process variables. In the biodiesel production, the RSA methodology was applied to evaluate sensitivity of the system response where molar ratio (MR) Alcohol-SBO was change from stoichiometric value to the one which is used in the biodiesel industry to maximize the

biodiesel production. We have concentrated our study efforts in the range of MR changes from 3/1 to 21/1 for the given operational conditions. The simulation results are shown in Fig. 4. As one can see the maximum BD production can be achieved for MR 21/1 (the value BD = 80%, for the 8 hours process time), but the problem appears in the downstream processes of alcohol recuperation. On the other hand, the conversion of SBO to biodiesel for the stoichiometric MR 3/1 decreases significantly for the same reaction conditions and reaches (the value of BD = 37%). It means that during optimization procedure of biodiesel production the compromise between maximum productivity and production cost should be made.



(a)

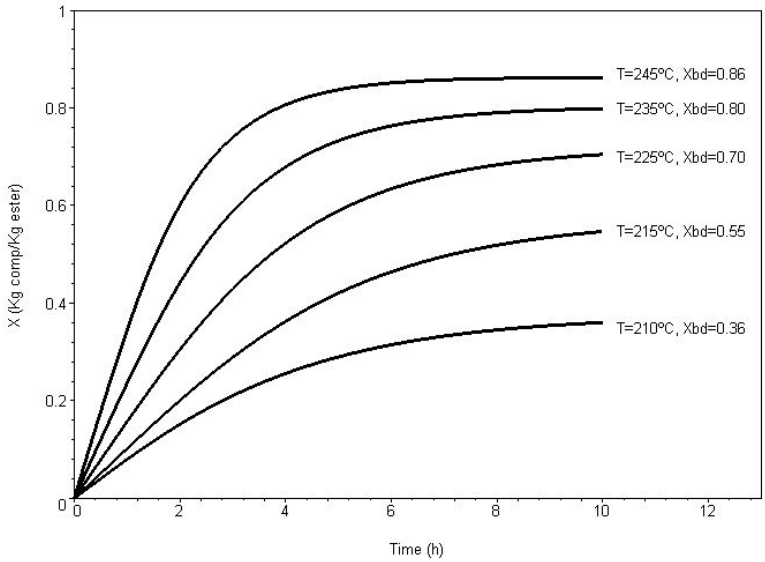


(b)

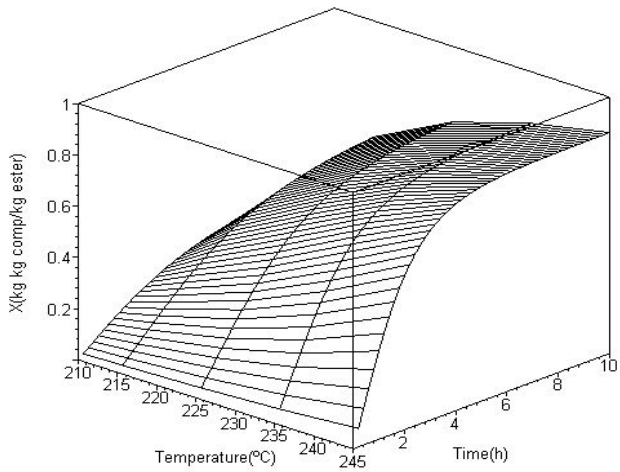
Fig. 4 RSA of the system changing MR as a control variable in the range - 3/1 to 21/1 – for the fixed T=235°C; (a) bi-dimensional representation of the MR influence on the system; (b) three-dimensional representation of the MR influence on the system

Analysis of the temperature influence on the system response has included an application of RSA where the BD production was a function of temperature changes for the same process time. We have studied the effect of the temperature changes in the range from 210°C to

245°C for the same operational conditions as shown in Fig. 4. The simulation results are shown in Fig. 5a, b. As one can see the maximum BD production can be achieved for T = 245°C (BD = 86%, for the 8 hours process time). The lower SBO conversion to biodiesel is observed for the T = 210°C (BD = 36%). It means that during an optimization procedure of biodiesel production the compromise between maximum productivity and production cost should be made.



(a)



(b)

Fig. 5 RSA of the system changing T as a control variable in the range - 210 to 245ºC – for fixed MR=21/1; (a) bi-dimensional representation of the T influence on the system; (b) three-dimensional representation of the T influence on the system

Finally, compare the results from Fig. 4a, b and Fig. 5a, b, the one can observe that the MR and T changes have a similar influence on the BD production and the model simulations have proved that these two variables can be considered as the key control variables during the transesterification process of SBO to BD conversion.

The RSA is very useful tool in model development steps giving an information about system sensitivity to key parameter changes. The comparison between two processes is important stage of the study minimizing the risk in the procedure of making of decisions. Non-catalytic transesterification process is very challenging because of the glycerol recovery. However, reaction conditions (high pressure and high temperatures) required special equipment to be used.

Conclusions

A new mathematical model describing kinetics of transesterification of soybean oil has been developed. The model is based on the assumption that three consecutive forward and reverse first-order transesterification reactions take place, and it describes the changes dynamics of triglycerides, diglycerides and monoglycerides as well as production of biodiesel (methyl, -ethyl and -butyl fatty acids esters) and glycerol. The reaction rates constants are written in the Arrhenius form**.** An analysis of the key process variables such as temperature and MR of Alcohol-SBO using RSA was performed to achieve the maximum soybean conversion rate to biodiesel. The model predictive power was checked for the very wide range of operational conditions and parameters values by fitting different experimental data for catalytic and non-catalytic transesterification processes. A very good correlation between model simulations and experimental data was observed. The developed new kinetics model behaves excellently and can be successfully used for experimental design, optimization of biodiesel production process, and for educational goals.

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