

Kinetic Monte Carlo Study of Biodiesel Production through Transesterification of Brassica Carinata Oil

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In the present study, the kinetics of biodiesel production through transesterification of Brassica carinata oil with methanol in the presence of potassium hydroxide is investigated by kinetic Monte Carlo simulation. The obtained results from simulation agree qualitatively with the existing experimental data. The kinetics data for each step of the suggested mechanism are confirmed by simulation. Using the mechanism and kinetics data, the system is simulated at different methanol/oil feed ratios and a comparison between kinetic data is provided. The influences of temperature and percentage of catalyst on the amount of produced biodiesel at different times of reaction are obtained.

Keywords: Biodiesel, Kinetic Monte Carlo Simulation, KOH, Transesterification, Brassica carinata oil

INTRODUCTION

Biodiesel has been studied with a remarkable attention as a renewable resource and environment-friendly fuel for diesel engines. Biodiesel is produced using renewable resources such as vegetable oils and animal fats. In comparison with petroleum diesel, it is non-toxic, with low emission profiles. Utilizing of biodiesel has many environmental benefits compared to fossil fuels. In comparison with fossil fuels, biodiesel makes less pollutants in air and water. It has less greenhouse effect, so it has less risk to human health [1,2].

Biodiesel is chemically a mixture of alkyl esters of fatty acids, synthesized by transesterification of oil with low molecular weight alcohols [3,4]. The products of this reaction are biodiesel and glycerol. Since methanol has a low cost and suitable physical and chemical properties, it is usually applied in biodiesel production. The methanolysis reaction occurs in the presence of a catalyst [5]. In recent years, the homogeneous base catalysts such as NaOH and KOH are applied for biodiesel production [6]. Basic

catalysts are commonly preferred to acid catalysts because they need low reaction temperature and atmospheric pressure to catalyze reaction. In a basic catalytic medium, high conversion of oil to biodiesel occurs in a minimal time. Basic catalysts are also economical and widely accessible [7].

There have been several research activities on the rate of transesterification reaction of oils in the presence of KOH catalyst [8,9]. Lu *et al.* studied biodiesel production from *Jatropha curcas* L. oil in presence of KOH [10]. They reported that transesterification reaction rate of *Jatropha curcas* L. oil follows a pseudo second order mechanism. In another attempt, Berchmans *et al.* [11] studied the rate of the methanolysis of *Jatropha curcas* waste food oil. The results reported indicated a second order kinetic reaction model with a molar ratio of 6:1 for methanol to oil, and a mass ratio of 1 wt% for KOH to oil at reaction temperature of 50 °C. Freedman and coworkers [12] studied both acid- and alkaline-catalyzed transesterification of Brassica carinata oil by butanol and methanol. They proposed pseudo first-order kinetics at larger molar excess of alcohol transesterification and second-order kinetics combined with a shunt reaction scheme at the lower alcohol excess level.

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Also, Vicente *et al.* [13] studied transesterification of Brassica carinata oil with methanol. In this study, a second-order reaction mechanism was used for modeling of reaction kinetic. They determined the reaction rate constants and the activation energies for all reactions.

Reaction kinetics is an important parameter in design, simulation and control of reactors. Kinetic Monte Carlo simulation is a strong method for simulation of chemical systems [14-16]. This method has been extremely used for simulation of chemical reactions [17,18]. Recently, we have utilized this method for studying the mechanism of free radical production by light-reflective agents in sunscreens [19] and also for studying the ozonation of some pollutants in the presence of ZnO nanocatalyst [20,21].

In the present study, this method is employed to study the rate of transesterification of Brassica carinata oil with methanol in the presence of KOH. The study in characterizing the rate of biodiesel production led us to undertake the present study with a view to examining the effect of operational variables on the transesterification rate of Brassica carinata oil using KOH as a catalyst. According to the obtained kinetic data by simulation, the effect of alcohol/oil feed ratio, reaction temperature and percentage of catalyst on the rate of reaction will be investigated. These tests can provide a simple screen for developing methanolysis of Brassica carinata oil in presence of KOH. These data give the optimum reaction temperature, alcohol to oil feed ratio and percentage of catalyst.

SIMULATION METHOD

Stochastic simulation of reaction is a powerful and accurate tool for development of quantitative, microscopic models from experimental data. It is particularly used when the kinetic of reaction is complex. The system was simulated with the help of Chemical Kinetic Simulator (CKS) software, version 1.01 (from IBM, Almaden Research Center, <http://www.almaden.ibm.com/st/msim/>) [22].

The molecules of different chemical species are considered. Let consider that initial concentration of molecules of each species i is c_i . The species interact *via* chemical reactions. The n^{th} reaction can be written in the

following form:



where k_n is a reaction rate constant, R_i^n is a reactant molecule of a particular chemical species, and similarly for product molecules P_i^n . The number of reactants is r_n and the number of products is p_n . a_i^n and b_i^n are stoichiometric coefficients.

In the kinetic Monte Carlo simulation algorithm, the system evolves one reaction at a time, changing the number of reactant and product concentrations. In this algorithm, a transition rate (a_i) is computed for each reaction, which is proportional to its probability of occurrence relative to other reactions. The propensity for the first- and second-order reactions are $a_i = k_i C_i$ and $a_i = k_i C_i C_j$, respectively. Total transition rate is the sum of transition rate of reactions:

$$a = \sum_i^M a_i \quad (2)$$

The transition probabilities can be defined by the following equation:

$$p_i = a_i / a \quad \& \quad \sum (P_i = 1) \quad (3)$$

Two random numbers are used per iteration, they are sampled from a uniform distribution. The random numbers are between 0 to 1.

The first (r) is used to compute the time of each step (τ):

$$\tau = 1/a \cdot \ln(1/r) \quad (4)$$

The second random number (r') is applied to pick a reaction by taking n :

$$\sum_{i=1}^{n-1} a_i < r'a \leq \sum_{i=1}^n a_i \quad (5)$$

This procedure represents a single step in a simulation. This procedure is repeated and time of reaction increases until final time (t_f) is obtained. The algorithm of kinetic Monte

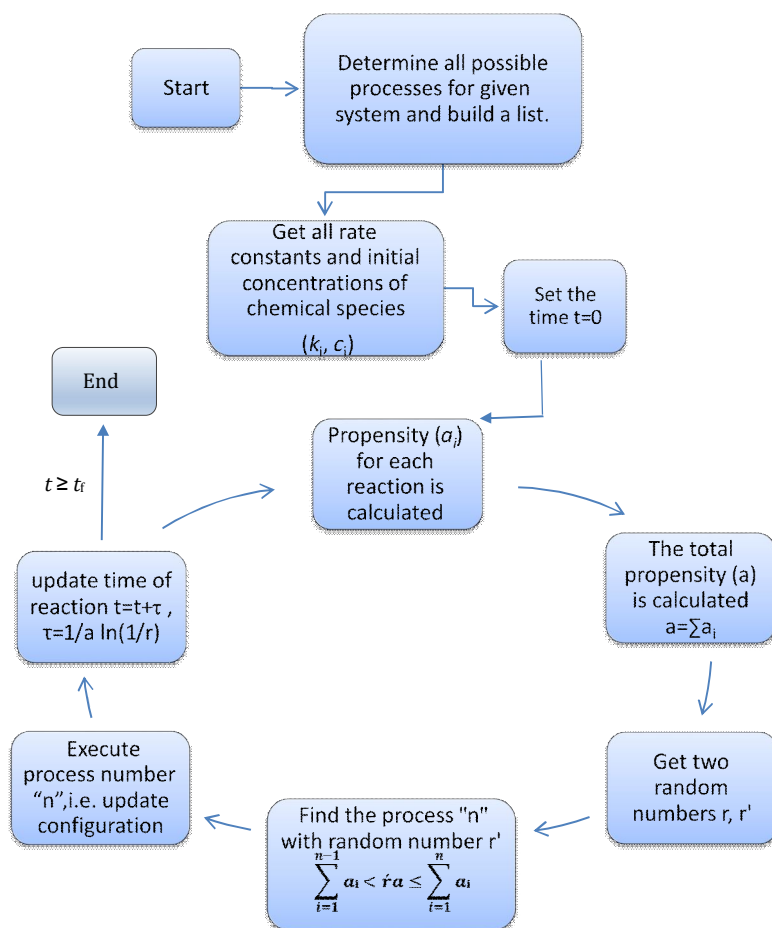

Fig. 1. Flow chart for the process-type list algorithm.

Table 1. The Kinetics Parameters of Methanolysis of Brassica Carinata Oil in the Presence of KOH

Steps	A ($M^{-1} \text{ min}^{-1}$)	E_a (kJ mol^{-1})
$\text{TG} + \text{CH}_3\text{OH} \longrightarrow \text{DG} + \text{ME}$	2.44×10^{17}	1.05×10^2
$\text{DG} + \text{ME} \longrightarrow \text{TG} + \text{CH}_3\text{OH}$	1.50×10^{12}	7.10×10^1
$\text{DG} + \text{CH}_3\text{OH} \longrightarrow \text{MG} + \text{ME}$	7.01×10^{15}	9.24×10^1
$\text{MG} + \text{ME} \longrightarrow \text{DG} + \text{CH}_3\text{OH}$	8.38×10^{11}	7.07×10^1
$\text{MG} + \text{CH}_3\text{OH} \longrightarrow \text{GL} + \text{ME}$	5.49×10^1	1.20×10^1
$\text{GL} + \text{ME} \longrightarrow \text{MG} + \text{CH}_3\text{OH}$	3.40×10^{10}	7.01×10^1

Carlo simulation is summarized in a schematic flow chart that is shown in Fig. 1.

RESULTS AND DISCUSSION

In this section, we are going to simulate the methanolysis of *Brassica carinata* oil in the presence of KOH to understand its kinetics and mechanism. *Vicente et al.*¹³ studied transesterification of *Brassica carinata* oil with methanol. We used their empirical kinetics data of changes reaction species to check the simulation results.

Transesterification of triglyceride (TG) with methanol (CH₃OH), in the presence of KOH catalyst, yields esters of fatty acids and glycerol (GL). The forward and reverse reactions corresponding to the following mechanistic pathway were applied in simulation. The mechanism, which has a good fitting with experimental data, is:



Three consecutive and reversible reactions occur. ME represents methyl esters (biodiesel). Mono (MG) and diglycerides (DG) are the intermediates formed in these reactions. Reactions take place in the presence of catalyst and their rate is governed by the amount of the catalyst. It is assumed that the amount of the catalyst is constant during the reaction and therefore, the rate coefficient of reaction can be considered as:

$$k = k[\text{catalyst}] \quad (9)$$

The rate constant of each reaction is calculated by the Arrhenius expression:

$$k = A \exp\left(\frac{-E_a}{k_B T}\right) \quad (10)$$

where k_B and T are Boltzmann's constant and temperature, respectively. E_a and A are free activation energy and pre-exponential factor, respectively. The pre-exponential factor, A , is a constant that can be derived experimentally or

numerically.

The activation energy and pre-exponential factor of each step of mechanism have been obtained by *Vicente et al.* through computational modeling.¹³ The activation energies and pre-exponential factors of reaction steps used are shown in Table 1. We obtained the pre-exponential factor of last step by fitting the simulated data with empirical ones as adjustable parameters.

B. carinata oil and the methanol are not miscible, so the reaction system consists of two layers at the beginning. In this sense, the mass transfer controls the kinetics at the initial stage. As soon as the methyl esters appear in the reaction system, one layer is involved because they are soluble in the vegetable oil and in the methanol. At this stage, therefore, the chemical reaction controls the kinetics. However, the initial stage of mass-transfer control is negligible when the impeller speed is at least 600 rpm, and therefore, the chemical reaction stage controls the reaction rate.¹³

The input data for the simulations were temperature (298.15 K), initial concentration of oil ($[\text{TG}]_0 = 8.22 \times 10^{-1}$ M), initial concentration of methanol ($[\text{CH}_3\text{OH}]_0 = 4.934$ M), the amount of catalyst (0.10 wt%),¹³ the steps of mechanism and their rate constants. The kinetic modeling employed in the current study was performed at 120 min in accordance with the experimental conditions of *Vicente et al.*¹³

The concentrations of triglyceride, methyl ester, methanol and glycerol versus time have been obtained by simulation and the results are shown in Fig. 2. As seen in this Figure, there is a good agreement between simulated and experimental data. In statistics, the coefficient of determination, denoted R^2 and pronounced "R squared", is a number indicating the proportion of the variance in two series data. We used Excel to calculate R^2 formula to find the correlation between empirical and simulated data. Perfect correlation was obtained ($R^2 = 0.997$). This agreement demonstrates that the proposed mechanism can be suitable to study kinetics of biodiesel synthesis by methanolysis of *Brassica carinata* oil.

To achieve the best understanding and development of this reaction, it is important to investigate it at different conditions. The obtained mechanism can be used to predict the rate of biodiesel synthesis by methanolysis of *Brassica*

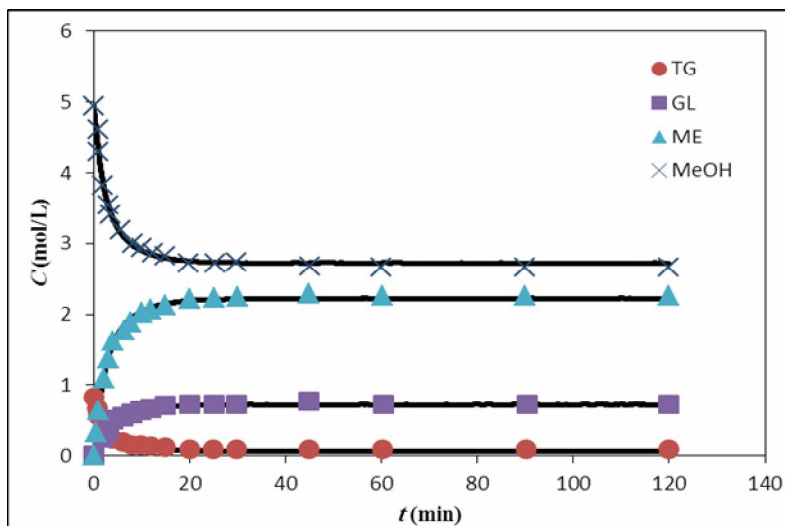


Fig. 2. The simulated (solid line) and experimental¹³ data of triglyceride (TG: ●), glycerol (GL: ■), methyl ester (ME: ▲) and methanol (MeOH: ×) concentrations during reaction.

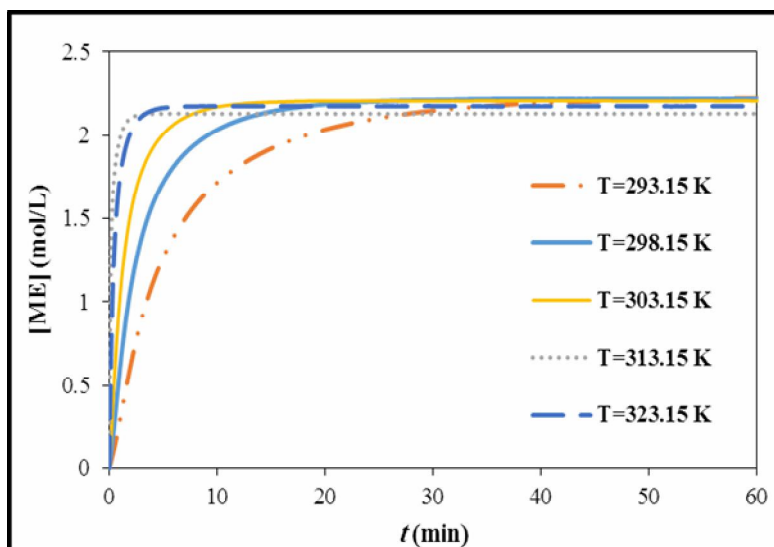


Fig. 3. Effect of reaction temperature on the rate of biodiesel production by transesterification of Brassica carinata oil in the presence of KOH.

carinata oil at different conditions. In the following, the mechanism and kinetic parameters are used to obtain the effect of temperature, percentage of catalyst and oil to methanol feed ratio on the rate of reaction.

Effect of Temperature on the Rate of Reaction

Temperature is an effective parameter on the rate of

reactions. To study the effect of temperature on the rate of methanolysis of Brassica carinata oil in presence of KOH, different temperatures were selected. Simulations were performed at temperatures including 293.15, 298.15, 303.15, 313.15 and 323.15 K. The other input data for the simulations are in accordance with the experimental conditions of Vicente *et al.*¹³ (Table 1).

Table 2. The Simulation Results of Transesterification of Brassica Carinata Oil in the Presence of KOH at Different Temperatures

Temperature (K)	Yield of reaction					
	20 (min)	40 (min)	60 (min)	80 (min)	100 (min)	120 (min)
293.15	84.84	90.69	91.71	91.91	91.95	91.95
298.15	90.97	92.08	92.10	92.15	92.15	92.15
303.15	92.34	92.39	92.39	92.40	92.40	92.40
313.15	93.04	93.04	93.07	93.09	93.09	93.09
323.15	94.11	94.11	94.12	94.13	94.13	94.13

Table 3. The Simulation Results of Transesterification of Brassica Carinata Oil in the Presence of KOH at Different Percentages of Catalyst

Percentage of catalysis	Yield of reaction					
	20 (min)	40 (min)	60 (min)	80 (min)	100 (min)	120 (min)
0.5%	84.42	90.30	90.36	91.59	91.61	91.75
1%	90.97	92.08	92.10	92.15	92.15	92.15
1.5%	92.22	92.64	92.68	92.74	92.78	92.80
2%	92.54	92.65	92.69	92.75	92.78	92.81

Table 4. The Simulation Results of Transesterification of Brassica Carinata Oil in the Presence of KOH at Different oil to Methanol Feed Ratios

Oil to methanol ratio	Yield of reaction					
	20 (min)	40 (min)	60 (min)	80 (min)	100 (min)	120 (min)
1:3	62.77	64.73	64.96	64.96	64.96	65.08
1:5	84.67	86.33	86.49	86.49	86.49	86.49
1:6	90.97	92.08	92.10	92.15	92.15	92.15
1:8	96.64	96.88	96.88	96.93	97.12	97.12
1:9	97.90	98.11	98.12	98.28	98.28	98.28
1:12	99.42	99.44	99.44	99.44	99.44	99.44
1:18	99.87	99.87	99.87	99.87	99.87	99.87

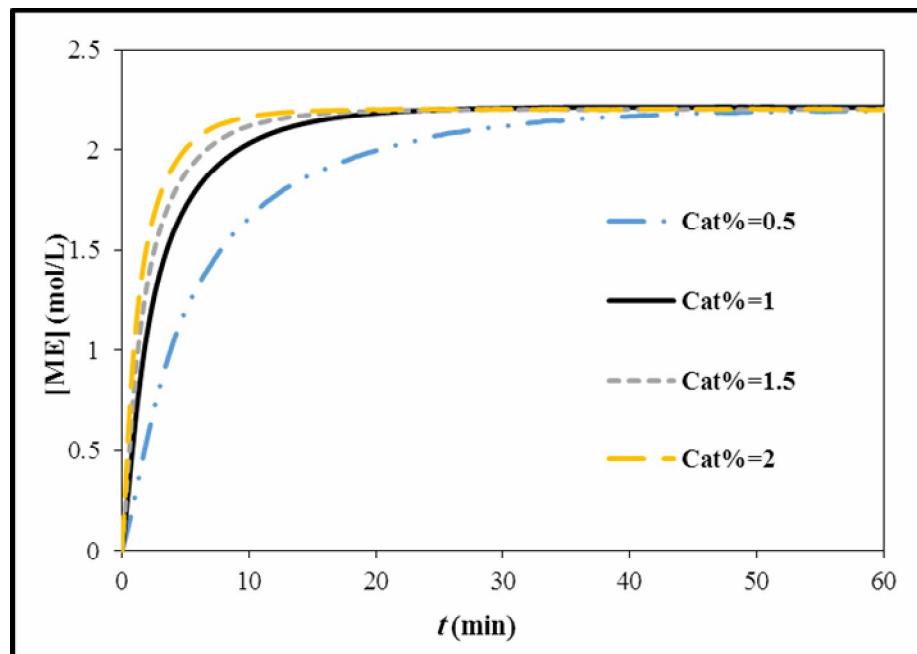


Fig. 4. The produced methyl ester concentrations at different percentages of catalyst.

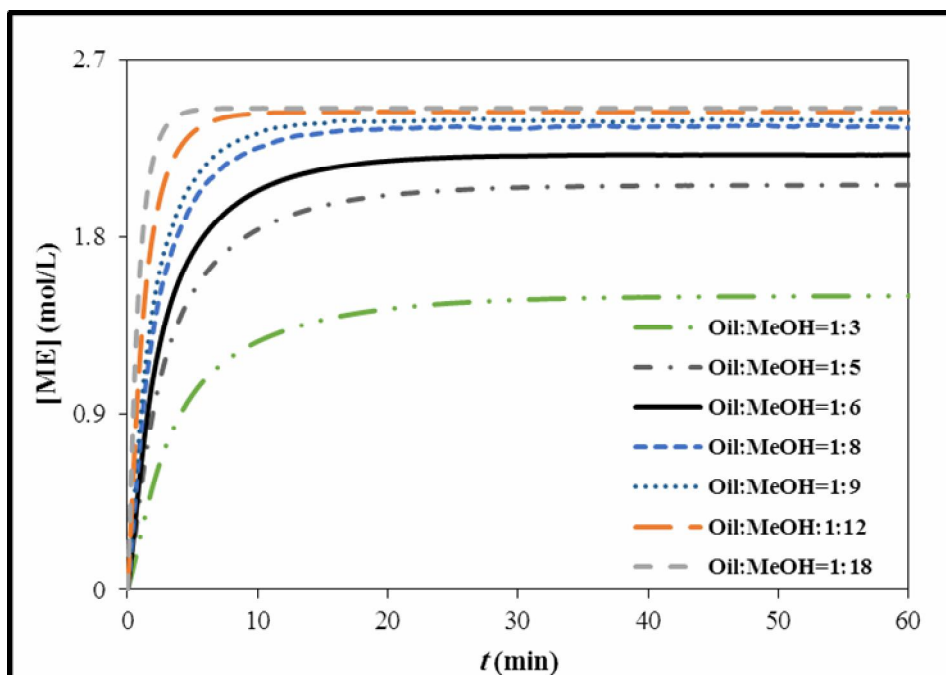


Fig. 5. Effect of Oil to Methanol Feed Ratio on the Rate of Biodiesel Synthesis.

Figure 3 represents the simulated values of the produced methyl ester as a function of time at different temperatures. As seen in Fig. 3, temperature is an effective parameter on the rate of biodiesel production by transesterification of Brassica carinata oil in the presence of KOH. At high temperature, hydrogen decomposition takes place fast, while by decreasing temperature more time is required to complete the reaction.

The obtained results of simulation after 120 min are presented in Table 2. In this table, the yields of reaction (ratio of the reduced concentration of oil to its initial concentration) at different temperatures are reported. The maximum yield of reaction is obtained during 20 min at room temperature.

Effect of the Percentage of Catalyst on the Rate of Reaction

Using the obtained mechanism and kinetic parameters, the simulation was carried out for different percentages of catalyst. To study it, different percentages of catalyst were chosen. Different percentages of catalyst used in input data of simulation, are presented in Table 3. Figure 4 represents the effect of percentage of catalyst on the rate of reaction. As seen in Fig. 4, as the catalyst concentration increases, the conversion of triglycerides and also the yield of biodiesel increase. However, the yield of biodiesel is reduced if the alkali catalysts are added above their optimum concentration, since this causes more soap formation [23].

Different percentages of catalyst were examined by simulation to obtain time of reaction. In the presence of 0.5% catalyst, the reaction does not complete up to 120 min. Time of reaction was increased up to 240 min and the maximum yield was obtained during 120 min. If the reaction occurs in the presence of 1% catalyst, the maximum yield will be obtained after 60 min. It is shown in Table 3 that maximum yields in the presence of 1.5% and 2% catalyst are obtained during 20 min.

Effect of Oil to Methanol Feed Ratio on the Rate of Reaction

Using the obtained mechanism and kinetic parameters, the system was simulated at different ratios of oil to methanol. Figure 5 represents the effect of different ratios of oil to methanol on the obtained concentration of methyl

ester. As seen in Fig. 5, by decreasing the oil to methanol feed ratio, the rate and the yield of reaction increase.

The yields of reaction during 120 min were calculated and are presented in Table 4. It is shown that time of reaction with high methanol to oil ratio is less than 20 min. Table 4 shows that oil to methanol ratio less than 1:8 does not produce the yield of reaction more than 92%. The suggested oil to methanol feed ratio by simulation is 1:8. The reversible nature of reaction needs for an excess methanol concentration in order to produce maximum methyl esters production. However, from a practical viewpoint, there are incentives to keep methanol levels low because of the increasing costs of downstream methanol separation.

CONCLUSIONS

The kinetic of methanolysis of Brassica carinata oil in the presence of KOH was investigated. The mechanism and rate constants of each step were studied by simulation. The obtained results are in a good agreement with experimental data. Using experimental data, it was shown that this mechanism is suitable for the study of transesterification of Brassica carinata oil in the presence of KOH.

The obtained kinetic parameters were used to study the effect of temperature; oil to methanol feed ratio and percentage of catalyst on the rate of transesterification of Brassica carinata oil. Temperature, percentage of catalyst and methanol to oil feed ratio strongly affect the rate of reaction. Simulation results show reaction time can be determined with respect to these parameters. By increasing these parameters, the required time to complete biodiesel syntheses decreases. Between these parameters, oil to methanol ratio is the most effective parameter on the rate and yield of reaction.

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