

Kinetic modeling of simultaneous esterification and transesterification from rapeseed oil for the biodiesel production

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ABSTRACT

Biodiesel production is the process which produces biofuel, through the chemical reactions such as esterification and transesterification. Biodiesel (also known as FAME; fatty acid methyl ester) comprises of mono alkyl esters of long chain fatty acids, which is obtained from vegetable oils and animal fats by transesterification with methanol in the presence of suitable catalyst. The present work reports the kinetics of simultaneous esterification of myristic acid and transesterification of rapeseed oil with methanol at different temperatures (120°C, 150°C, 170°C) and oil to methanol ratio (1:20) with 3 wt% of sulphated zirconia catalyst. The estimation of forward and backward kinetic constants is done by using real coded genetic algorithm (RCGA) from the experimental data available in open literature. The calculated kinetic parameters were cross validated with the other experimental oil to methanol ratio (1:10), which are not included in the kinetic parameter estimation exercise. The result from the cross validated values also fitted well with the experimental data from the open literature.

Keywords: biodiesel, kinetic modeling, esterification, transesterification

1 INTRODUCTION

The crisis of international energy, which is coupled with fluctuating oil prices and incrementing cognizance of the environment, has intensified the research on renewable fuels [1, 2]. Biodiesel (also known as FAME: fatty acid methyl ester) comprises of mono alkyl esters of long chain fatty acids, which is obtained from vegetable oils and animal fats by transesterification with methanol in the presence of suitable catalyst [3]. Transesterification of oils by using homogeneous and heterogeneous catalysts have been reported in open literature [4, 5]. By utilizing the homogeneous catalysts, transesterification of vegetable oils speeds up the reaction, but it needs good quality of feedstock to avoid the formation of soap. But in heterogeneous catalysis, the side reaction like saponification can be removed; separation from the product is easy they can catalyse esterification and transesterification reactions simultaneously [6]. Rattanaphra et al. [6] utilized SO_4^{2-}/ZrO_4 (sulphated zirconia) catalyst for the simultaneous esterification and transesterification of myristic acid and rapeseed oil with methanol for the biodiesel production. They [6] engendered MAME (myristic acid methyl esters), total FAME at various temperatures, catalyst loading and oil to methanol molar ratio.

The objective of the present work is to evaluate the kinetic constants of the simultaneous esterification and transesterification of the myristic acid and rapeseed oil with methanol at 3 % SO_4^{2-}/ZrO_4 catalyst [6]. The resultant non- linear ordinary differential equations are solved by

using LIMEX DAE solver [7]. The kinetic parameters of esterification and transesterification reactions are estimated by minimizing the sum of the squares of the error between the experimental and simulated values of MAME and total FAME with 3 wt.% of catalyst at various temperatures and 1: 20 oil to methanol ratio. Real coded genetic algorithm (RCGA) [8] has been utilized for this purpose. The estimated kinetic parameters have been used for the cross validation (which are not included in the parameter estimation exercise) with oil to methanol ratio of 1:10.

2 MODEL

The Experiments for the production of FAME and MAME, starts with rapeseed oil, 10 % myristic acid, methanol and catalyst at various temperatures (120°C, 150°C, 170°C). The complete reaction scheme is given in Table 1 [6]. The corresponding rate of formation of components is provided in Table 2. In transesterification reaction, three moles of esters and one mole of glycerol can be produced from three moles of methanol and one mole of triglyceride, whereas one mole of FFA (free fatty acids) and one mole of alcohol requires to produce one mole of ester and one mole of water in esterification reaction [6]. More amount of methanol was used in experimental [6] to increase the rate of forward reaction though it requires 3 moles of methanol for each mole of triglyceride according to the stoichiometry [6]. Net formation rates of various compounds have been derived from kinetics. To estimate the kinetic parameters, the obtained ordinary differential equations from the model are solved by LIMEX DAE solver [7], is integrated with RCGA [8]. The solution may trap to a local minimum based on the initial guess provided in most of the classical optimization techniques. RCGA works with a number of solutions instead

of single solution, which are generated randomly based on the lower and upper limit provided for optimizing parameters. The kinetic parameters are estimated by minimizing the objective function (eq.1), which is based on the simulated and experimental concentrations of total FAME, OAME (oleic acid methyl ester), and MAME.

$$F = \sum_{i=1}^N \left(\frac{C_{FAME,i}^{\text{exp}} - C_{FAME,i}^{\text{mod el}}}{C_{FAME,i}^{\text{exp}}} \right) + \sum_{i=1}^N \left(\frac{C_{OAME,i}^{\text{exp}} - C_{OAME,i}^{\text{mod el}}}{C_{OAME,i}^{\text{exp}}} \right) + \sum_{i=1}^N \left(\frac{C_{MAME,i}^{\text{exp}} - C_{MAME,i}^{\text{mod el}}}{C_{MAME,i}^{\text{exp}}} \right) \quad (1)$$

Table 1 Reaction mechanism [6]

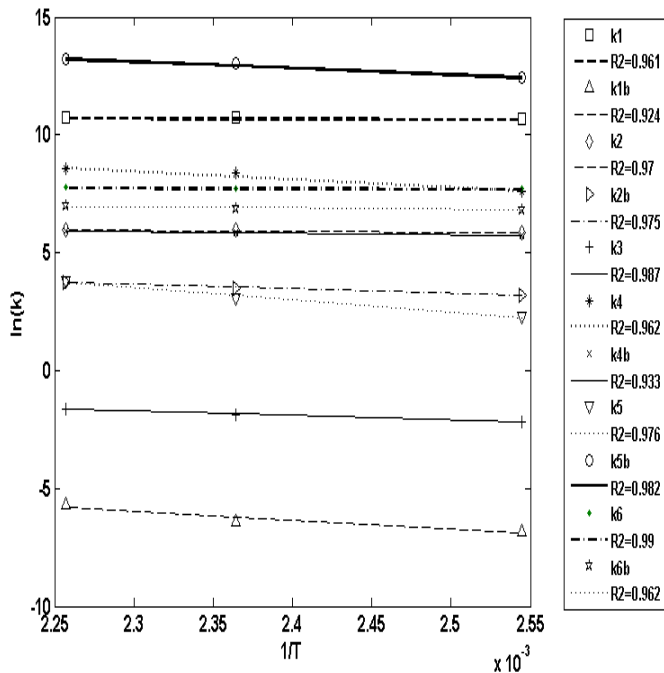
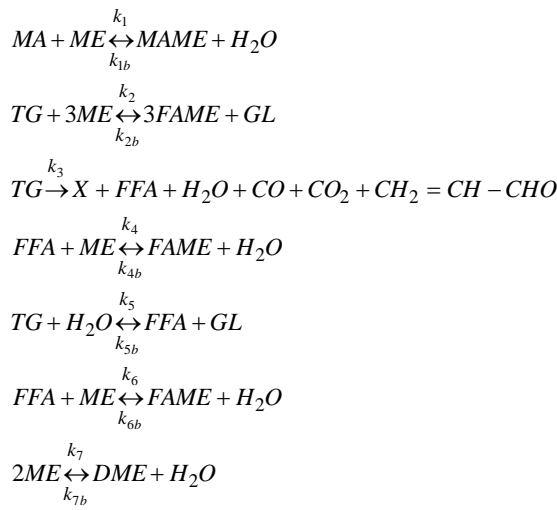


Figure 1: The Arrhenius plot (1/T vs. ln (rate constant))

Table 2 Rate of formation of different compounds from the above reaction mechanism

$$\begin{aligned} \frac{d[MA]}{dt} &= -k_1[MA][ME] + k_{1b}[MAME][H_2O] \\ \frac{d[ME]}{dt} &= -k_1[MA][ME] + k_{1b}[MAME][H_2O] - k_2[ME]^3[TG] \\ &\quad + k_{2b}[FAME]^3[GL] - k_4[FFA][ME] + k_{4b}[FAME][H_2O] \\ &\quad - k_6[FFA][ME] + k_{6b}[FAME][H_2O] - k_7[ME]^2 + k_{7b}[DME][H_2O] \\ \frac{d[MAME]}{dt} &= k_1[MA][ME] - k_{1b}[MAME][H_2O] \\ \frac{d[H_2O]}{dt} &= k_1[MA][ME] - k_{1b}[MAME][H_2O] + k_3[TG] + k_4[FFA][ME] \\ &\quad - k_{4b}[FAME][H_2O] - k_5[H_2O][TG] + k_{5b}[FFA][GL] \\ &\quad + k_6[FFA][ME] - k_{6b}[FAME][H_2O] + k_7[ME]^2 - k_{7b}[DME][H_2O] \\ \frac{d[TG]}{dt} &= -k_2[ME]^3[TG] + k_{2b}[FAME]^3[GL] - k_3[TG] \\ &\quad - k_5[H_2O][TG] + k_{5b}[FFA][GL] \\ \frac{d[FAME]}{dt} &= k_2[ME]^3[TG] - k_{2b}[FAME]^3[GL] + k_4[FFA][ME] \\ &\quad - k_{4b}[FAME][H_2O] + k_6[FFA][ME] - k_{6b}[FAME][H_2O] \\ \frac{d[GL]}{dt} &= k_2[ME]^3[TG] - k_{2b}[FAME]^3[GL] + k_5[H_2O][TG] \\ &\quad - k_{5b}[FFA][GL] \\ \frac{d[FFA]}{dt} &= k_3[TG] + k_5[H_2O][TG] - k_{5b}[FFA][GL] \\ &\quad - k_4[FFA][ME] + k_{4b}[FAME][H_2O] \\ \frac{d[DME]}{dt} &= k_7[ME]^2 - k_{7b}[DME][H_2O] \end{aligned}$$

3 RESULTS AND DISCUSSION

The total FAME, OAME and MAME concentrations are validated with the experimental data which was conducted by Rattanaphra et al. [6] at different temperatures, reaction pressure of 22 bar with a stirring speed of 600 rpm. The optimized forward and backward kinetic parameters at 1:20 oil to methanol ratio and 3 wt% catalyst concentrations at three different temperatures are determined by RCGA. The Arrhenius plot (i.e. 1/T vs. ln (kinetic constants)) was prepared by using the estimated kinetic constants at three different temperatures (120°C, 150°C, 170°C) by using linear regression technique and is shown in figure 1. The pre exponential factor and activation energy can be obtained from the intercept and slope of the plot (Arrhenius plot). Comparison of experimental and model predicted FAME, OAME and MAME at different temperatures is shown from figure 2, 3 and 4. The figures at different temperatures show very good agreement with the experimental data. From these figures it is clear that as the reaction temperature increases, final FAME content and OAME also increases. This total FAME and OAME increase in content is more significant from 120°C to 150°C as compared to the 150°C to 170°C (Figs. 2 to 4). Myristic acid is almost completely converted MAME in the complete temperature range (120°C, 150°C, 170°C) within the reaction time. MAME production rate at 150°C and 170°C was almost similar and little higher than at

120°C. At higher temperature, the transesterification reaction is higher.

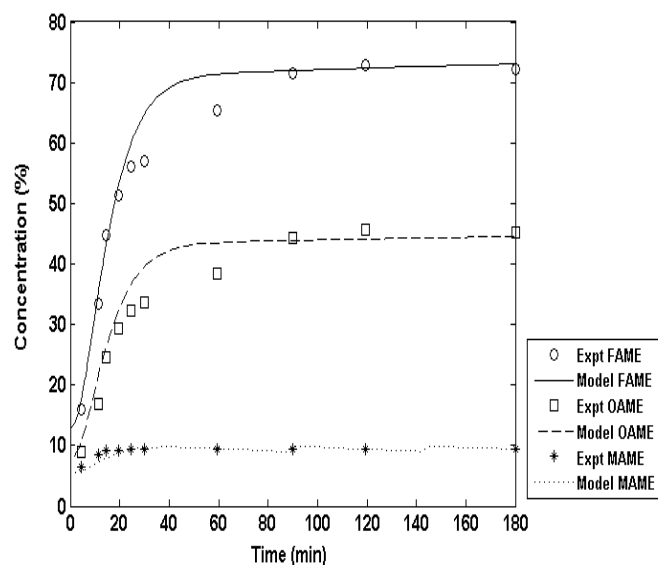


Figure 2: Model vs. experimental data of total FAME, OAME and MAME at 120°C

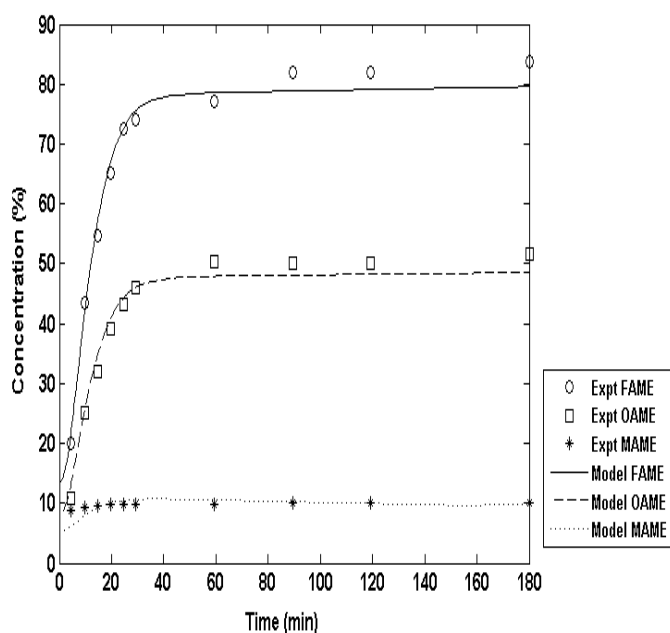


Figure 3: Model vs. experimental data of total FAME, OAME and MAME at 150°C

Figure 5 depicts the cross validation results of total FAME and OAME content at 170°C and 1:10 oil to methanol ratio, which is not included in the parameter estimation process. This cross validation results also exhibit good agreement with the experimental data from the open literature [6]. From these data, it is clear that the decrease in oil to methanol ratio from 1:20 to 1:10, there is no significant difference in the final FAME content.

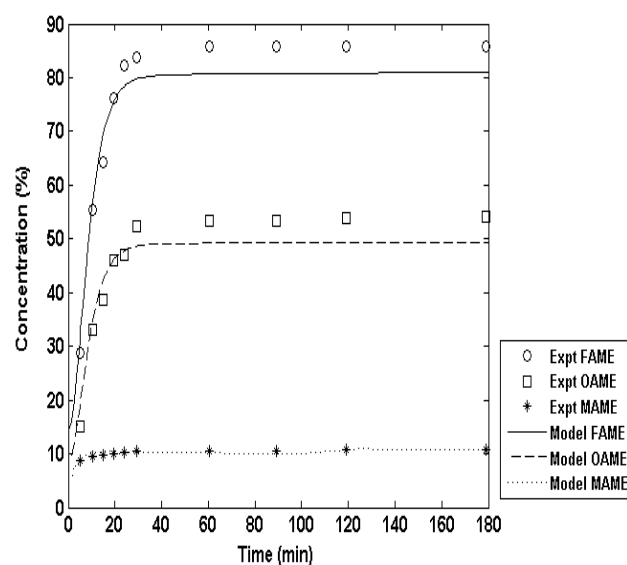


Figure 4: Model vs. experimental data of total FAME, OAME and MAME at 170°C

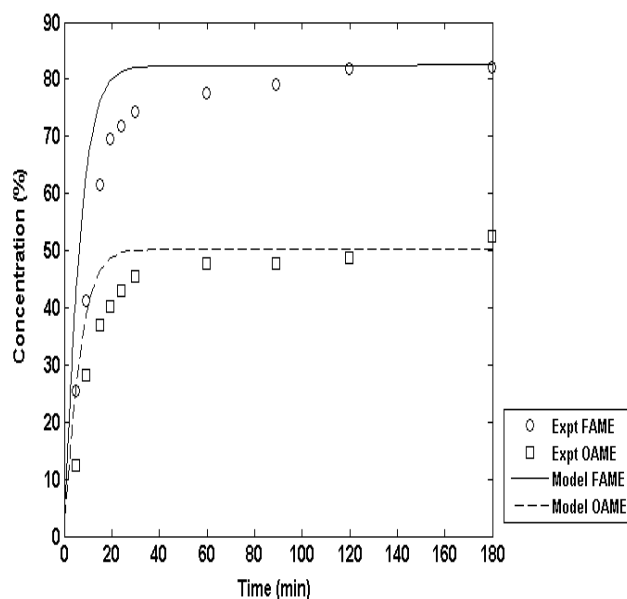


Figure 5: Cross validation results of Model vs. experimental data of total FAME, OAME at 170°C (1:10 oil to methanol ratio)

4 CONCLUSIONS

Kinetic parameters at different temperatures have been estimated by utilizing the real coded genetic algorithm for the simultaneous esterification of myristic acid and transesterification of rapeseed oil with methanol (1:20 oil to methanol ratio) in the presence of 3 wt% sulphated zirconia catalyst. Based on the estimated kinetic parameters, the total FAME, OAME and MAME concentrations were compared with the experimental data from the open literature and found to be good agreement. Further, the kinetic model has

been used for the cross validation of 1:10 oil to methanol ratio, which is also fitted well with the experimental data from the open literature. Total FAME and OAME production increases with increase of reaction temperature and is more significant from 120°C to 150°C as compared to the 150°C to 170°C.

NOMENCLATURE

DME: Dimethylether

FAME: Fatty acid methyl ester

FFA: Free Fatty acid

GL: Glycerol

MA: Myristic acid

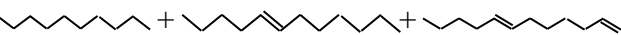
ME: Methanol

MAME: Myristic acid methyl esters

OAME: Oleic acid methyl ester

RCGA: Real coded genetic algorithm

TG: Triglyceride

X: 

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