

Kinetic study of used vegetable oil for esterification and transesterification process of biodiesel production

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Abstract

A mathematical model describing chemical kinetics of transesterification of model 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. An analysis of process variables such as temperature and molar ratio model oil- methanol using response surface analysis was performed to achieve the maximum oil conversion rate to biodiesel. The reaction rate constants and activation energies were determined for all the forward and reverse reactions. The experimental results were found to fit a first-order kinetic law for the forward reaction and a second-order one for the reverse reaction. The results indicated that the rate-control step could be attributed to the surface reaction and the esterification processes can be well-depicted by the as-calculated kinetic formula in the range of the experimental conditions. A very good correlation between model simulations and experimental data was observed.

Key words: Biodiesel, waste cooking oil, kinetics, esterification, transesterification

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1. Introduction

The worldwide interest toward biofuels has recently significantly grown as a direct result of the renewed need of facing the global warming effect by reducing the greenhouse gases emissions that are related to the wide use of fossil fuels. In this respect, biodiesel represents a valuable alternative to petroleum-derived fuels due to both its renewable nature and its substantially reduced net carbon dioxide emission [1].

The production of biodiesel from vegetable oils has been widely researched; however, it is not an economical process because of using valuable vegetable oils. Therefore, waste vegetable oil or animal fat are recommended as raw materials to produce biodiesel. However, the presence of moisture and free fatty acids (FFAs) in these materials may influence the performance and efficiency of such a process. Both water and FFAs can react with the catalyst rapidly and form long chain soaps, which may bring on serious separation problems; a pretreatment step is generally required to decrease the FFAs amount to below 1 wt% [2-6].

In the two-stage process (esterification and transesterification reaction), the oil acidity is reduced below the acceptable limit by an esterification pre-treatment with methanol (acid catalyzed) producing methylesters (biodiesel) and water while, in the subsequent step, the traditional transesterification (base catalyzed) can be performed producing biodiesel and glycerol. The esterification reaction of acid oils or animal fats can then be used both as biodiesel direct production (in the case of substrates at very high content of FFAs) and as pre-treatment step in the framework of a conventional transesterification process (for feedstock with moderate free acidity [7,8]). The economic and environmental interest in using oils and fats involved in the production of biodiesel, the unavoidable need to remove FFA and the interest in characterizing the kinetics of the reaction with a view to optimizing the reactor dimensions led us to undertake the present study with a view to examining the influence of operational variables on the kinetics of esterification of FFA in sunflower oil using sulphuric acid as catalyst.

There are a number of kinetic studies in the literature on the transesterification of esters with alcohol. However, only a few of these studies deal with vegetable oils and fatty esters. The studies of transesterification kinetics for non-fatty acids esters include: the determination of the reaction rate constants, the equilibrium constant, and the activation energy for the acid-catalyzed reaction of butanol with ethyl acetate [9] and ethanol with butyl acetate and a review by Sridharan and Mathai on the transesterification reactions involving alcohol [10, 11].

The objective of this work was to propose a flexible new kinetic model for esterification and transesterification process of model acid oil and the kinetic parameters were determined by fitting the model with the experimental results.

2. Materials and methods

2.1. Materials

Model acid oil (simulated to waste cooking oil) is a mixture of pure oleic acid and the oil (refined oil "50% sunflower oil+ 50% soybean oil") with composition of (5 g of oleic acid and 95 g of refined oil) to give 8.5% FFA as oleic. Anhydrous methanol (Fluka Co., Assay : > 99.8%) was used, which is most commonly used because of its low cost (compared to other alcohols). Sulphuric acid was used as catalyst in esterification reaction (ADWIC, El Nasr Pharmaceutical product Co., Assay: 97-99%) and Potassium hydroxide: Alkaline catalyst (ADWIC, El Nasr Pharmaceutical product Co., Assay: min 85%).

2.2. Procedure

By studying the different factors affecting the yield of production (as alcohol to oil molar ratio, catalyst amount, temperature, reaction time) for either esterification and transesterification reaction to produce biodiesel from waste cooking oil (model oil in this study) with specifications comparable with the diesel and biodiesel standard values, figure (1) shows the proposed flow chart for biodiesel production process.

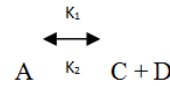
3. Results and Discussion

3.1. Kinetic model of esterification reaction

The kinetic model used in this work was based on the following assumptions:

- The esterification reaction was a reversible homogeneous process controlled by the chemical reaction.
- The rate of the non-catalyzed reaction was negligible relative to the catalyzed reaction.
- The chemical reaction occurred in the oil phase.
- The methanol/oleic acid mole ratio used was high enough for the methanol concentration to remain constant throughout the process.

Under these conditions, the reaction was assumed to be pseudo-homogeneous, first-order in the forward direction and second-order in the reverse direction, and hence to conform to the following kinetic law:



$$-\frac{d[A]}{dt} = K_1 \cdot [A] - K_2 \cdot [C] \cdot [D] \quad (1)$$

Where:

[A] denotes the concentration of FFA in mg KOH/g oil (i.e. the acid value)

[C] and [D] are the concentrations of FAME and water, respectively, formed during the reaction both also referred to 1 g of oil

K_1 and K_2 are the kinetic constants for the forward and reverse reaction, respectively.

If [D] and [C] are assumed to be zero at the start ($t = 0$), and $A = A_0 - E$ (E being the acidity removed), then, according to Carberry,[12]

$$\frac{dE}{dt} = K_1 \cdot (A_0 - E) - K_2 \cdot E^2 \quad (2)$$

Where A_0 is the initial concentration of FFA. Integration of Eq. (2) yields

$$2 \cdot K_2 \cdot \alpha \cdot t = \ln \frac{[A_0 + E \cdot (\beta - \frac{1}{2})]}{[A_0 - E \cdot (\beta + \frac{1}{2})]} \quad (3)$$

Where

$$\alpha = \sqrt{\frac{K^2}{4} + K A_0}$$

and

$$\beta = \frac{\alpha}{K} \quad K = \frac{K_1}{K_2}$$

K_1 and K_2 were determined by trial and error, using variable K & β values until a plot of the right-hand side of Eq. (3) consisting of a straight line with a negligible intercept was obtained. This was produced figure (2) as the fitting of the experimental data obtained by changing methanol/oil mole ratio of 3, 4, 5, 6 and 9 by changing the β values to reach the highest linearity coefficient (R^2) value for suitable fit. From figure (3 to 6), the best fit for β which gives highest values for R^2 was obtained, then by back calculation of K_1 & K_2 & α according to this value and then equal the two sides of equation (3) it gives an equal value as shown in table (1). The produced values for K_1 & K_2 at different molar ratios were drawn as shown in figure (7) From this figure it can be concluded that the K_2 value is negligible compared to K_1 values as expected which indicates that the hydrolysis reaction hardly took place. Based on the small value of K_2 , also it can be noted that by

Table 1: The values for the rate constant (K) at best fit for different β values with highest R^2 (comparing the calculated and theoretical values)

| Molar ratio | β | K_1 | K_2 | m (figure) | m (calculated) | R^2 |
|-------------|---------|-------|---------|-------------|----------------|--------|
| 3 | 0.8 | 0.015 | 0.0001 | 0.0168 | 0.017 | 0.9458 |
| 4 | 0.7 | 0.022 | 0.00013 | 0.0252 | 0.02516 | 0.9358 |
| 5 | 0.67 | 0.022 | 0.00014 | 0.0253 | 0.0253 | 0.9548 |
| 6 | 0.61 | 0.023 | 0.00015 | 0.0266 | 0.02662 | 0.9464 |
| 9 | 0.55 | 0.025 | 0.00016 | 0.0289 | 0.02888 | 0.9791 |

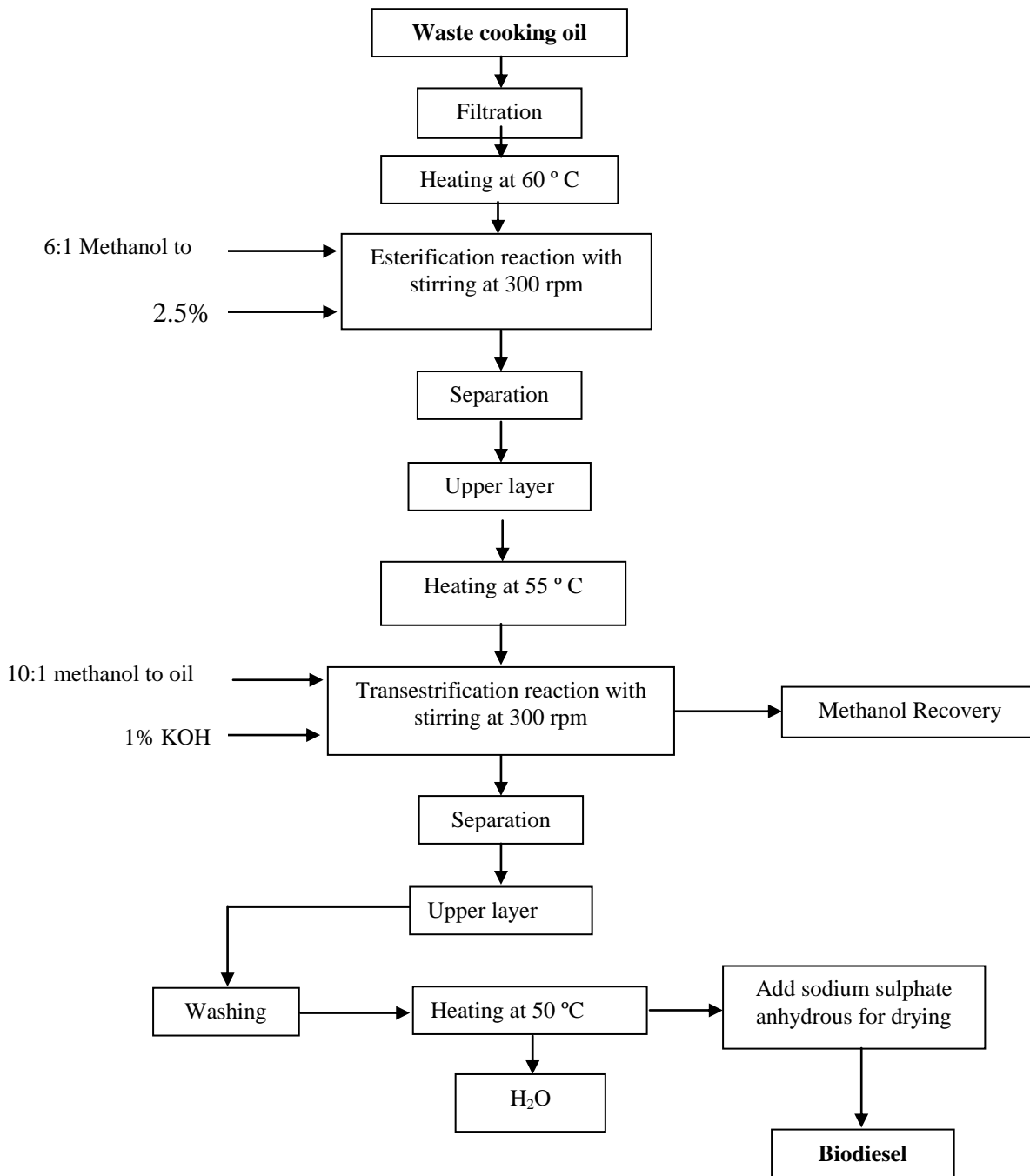


Fig. 1. Proposed Flow chart of biodiesel production

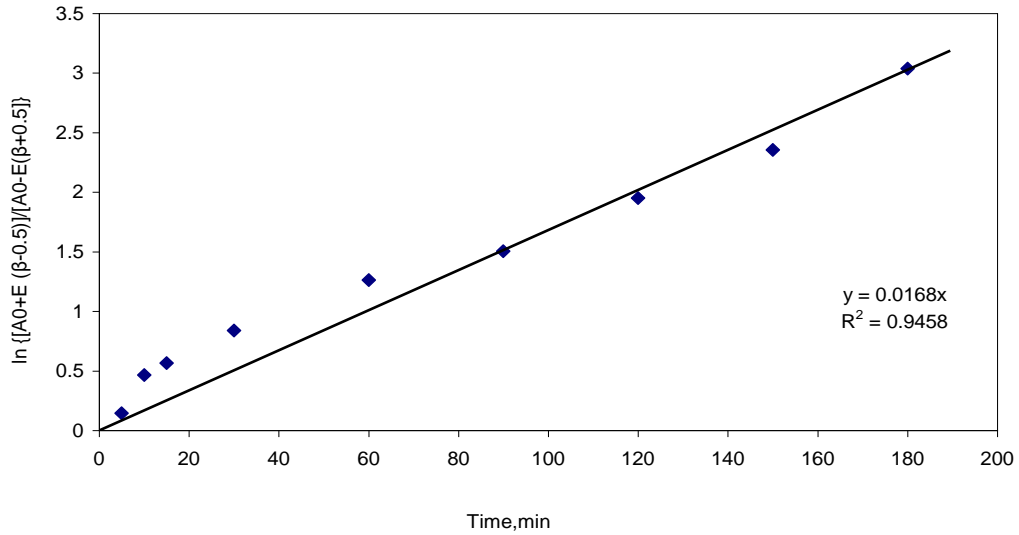


Fig. 2. Determination of the kinetic constants by using Eq. (3) at a methanol/oil molar ratio of 3:1

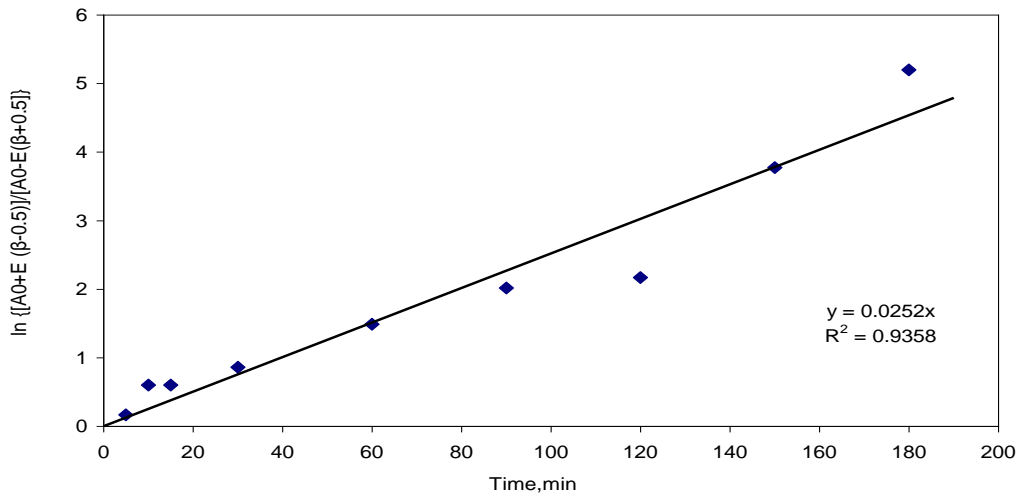


Fig. 3. Determination of the kinetic constants by using Eq. (3) at a methanol/oil molar ratio of 4:1

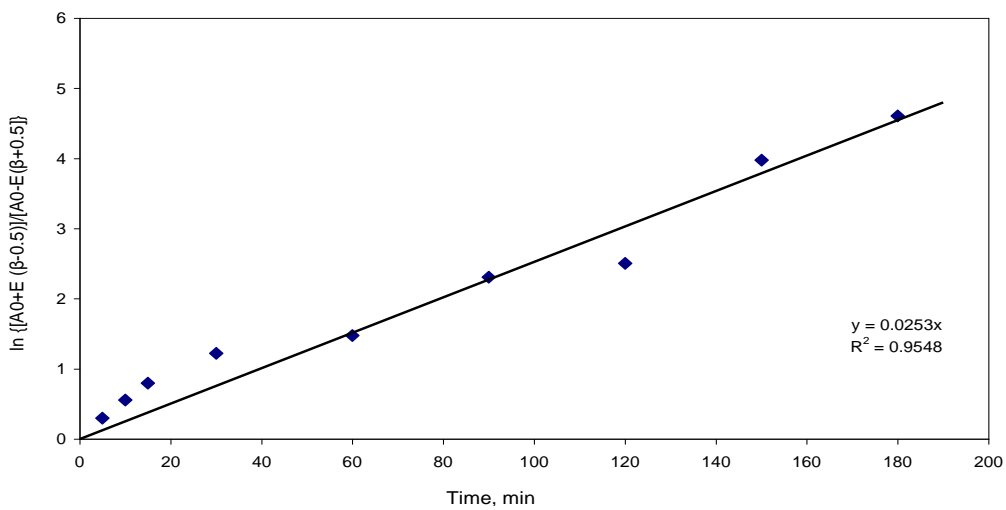


Fig. 4. Determination of the kinetic constants by using Eq. (3) at a methanol/oil molar ratio of 5:1

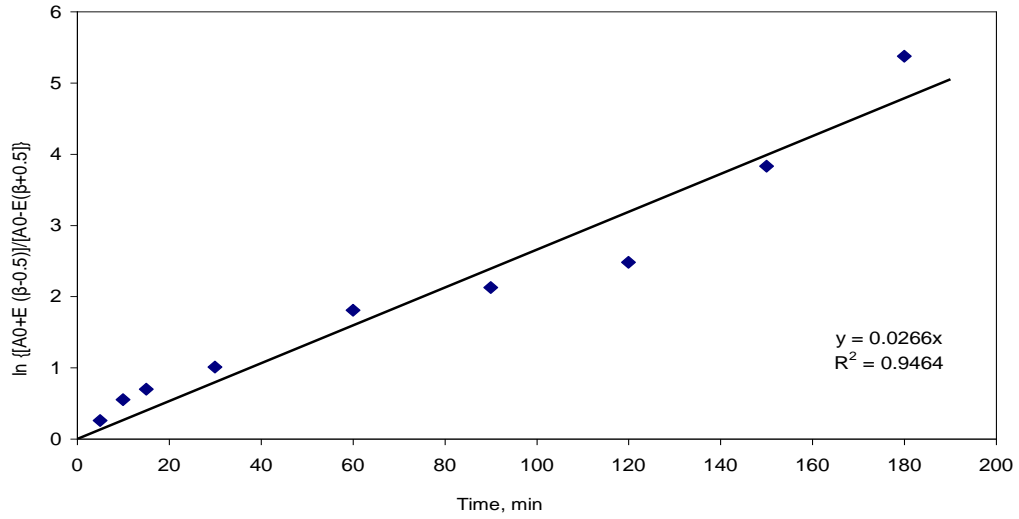


Fig. 5. Determination of the kinetic constants by using Eq. (3) at a methanol/oil molar ratio of 6:1

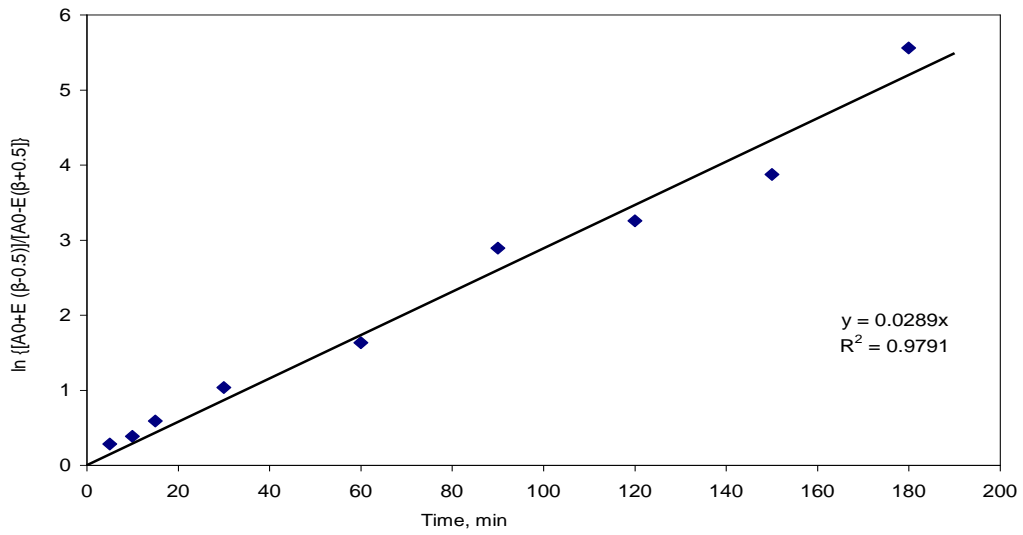


Fig. 6. Determination of the kinetic constants by using Eq. (3) at a methanol/oil molar ratio of 9:1

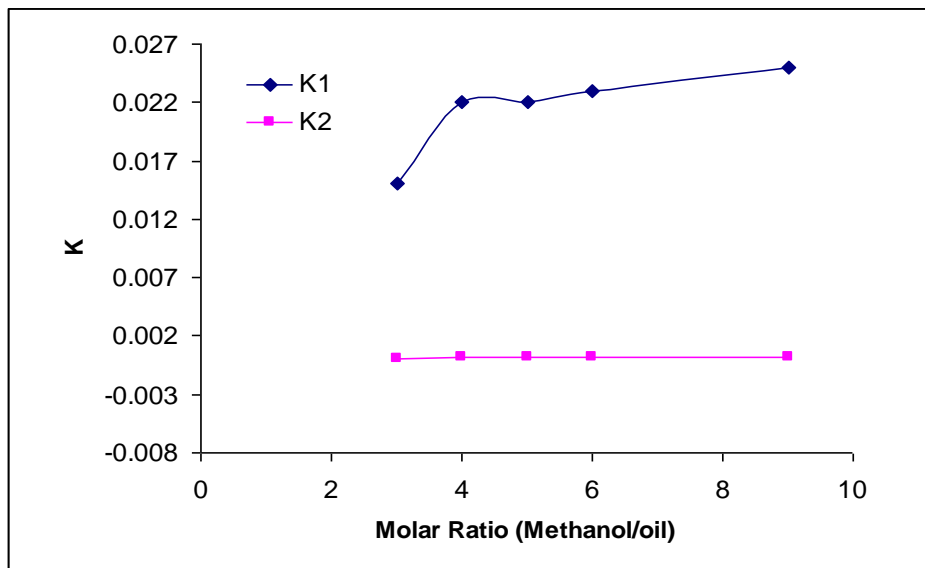


Fig. 7. Variation of the rate constants with the methanol/oil molar ratio

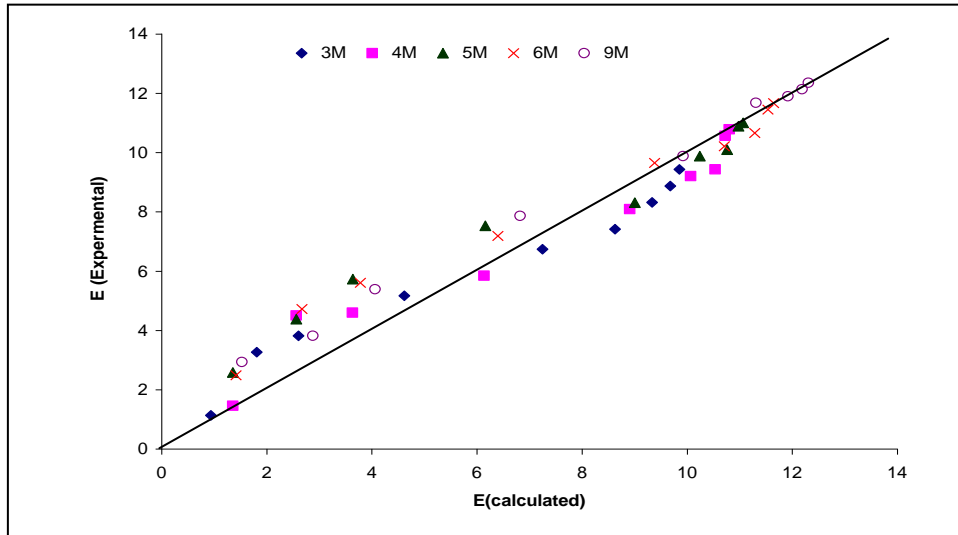


Fig. 8. Comparison of the experimental acid value and that predicted by Eq. (4)

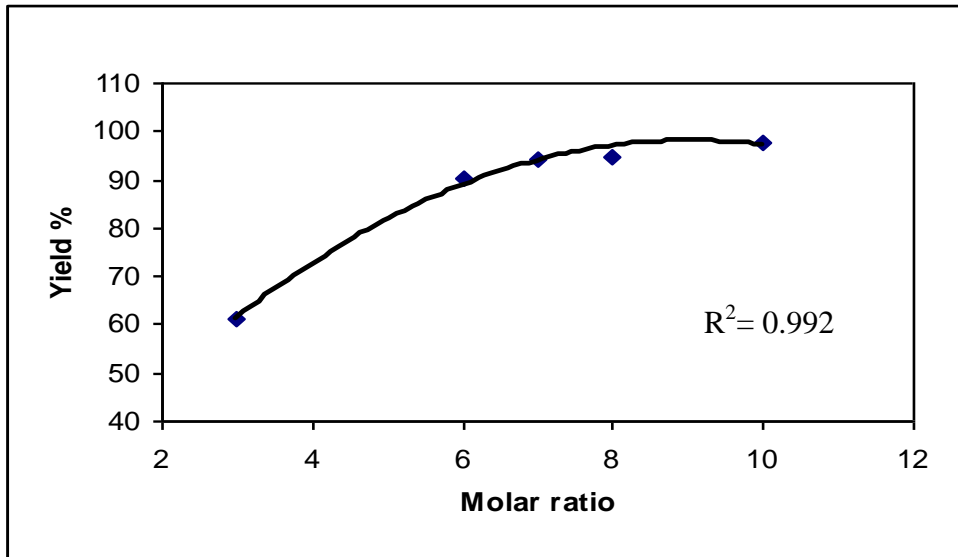


Fig. 9. Fitting curve for relation between %yield and molar ratio

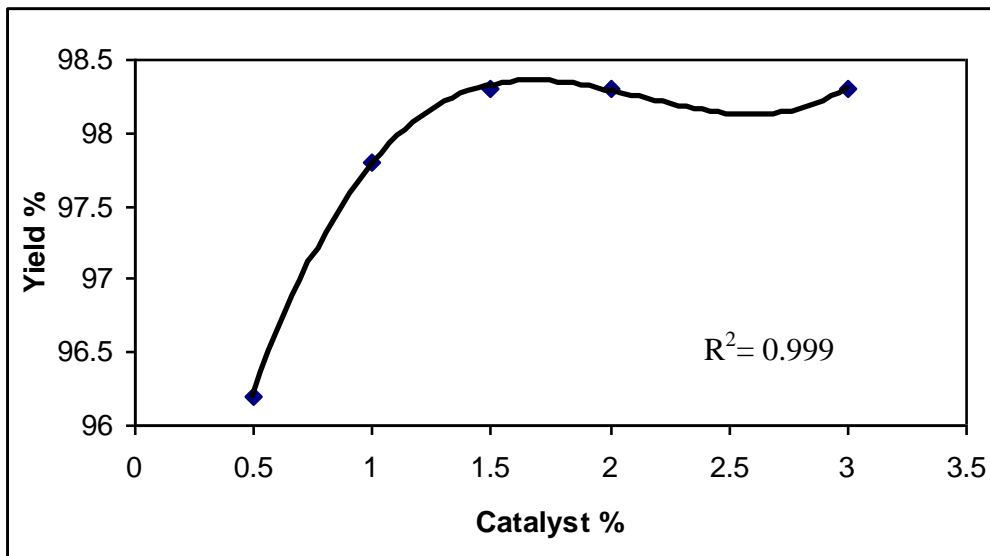


Fig. 10. Fitting curve for relation between %yield and catalyst amount

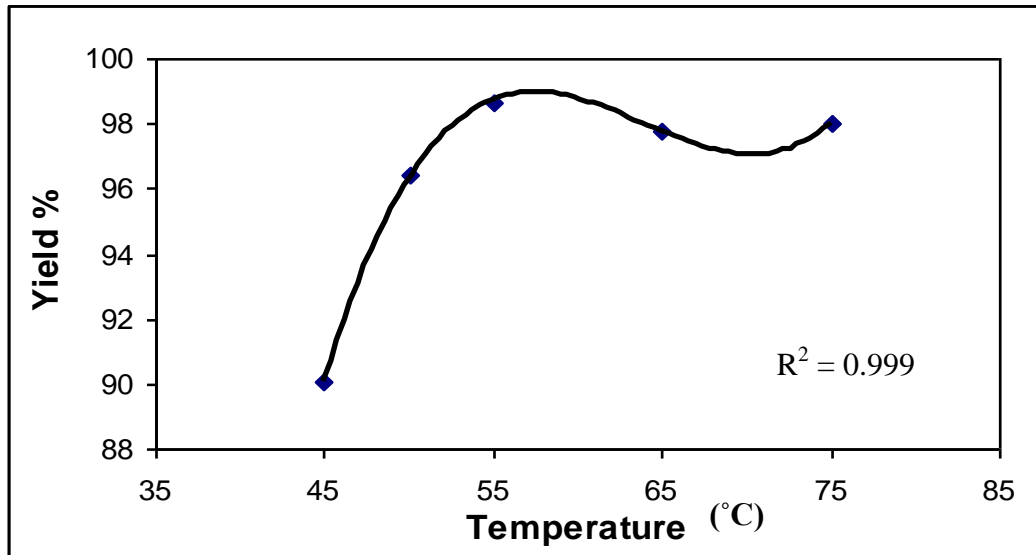


Fig. 11. Fitting curve for relation between %yield and reaction temperature

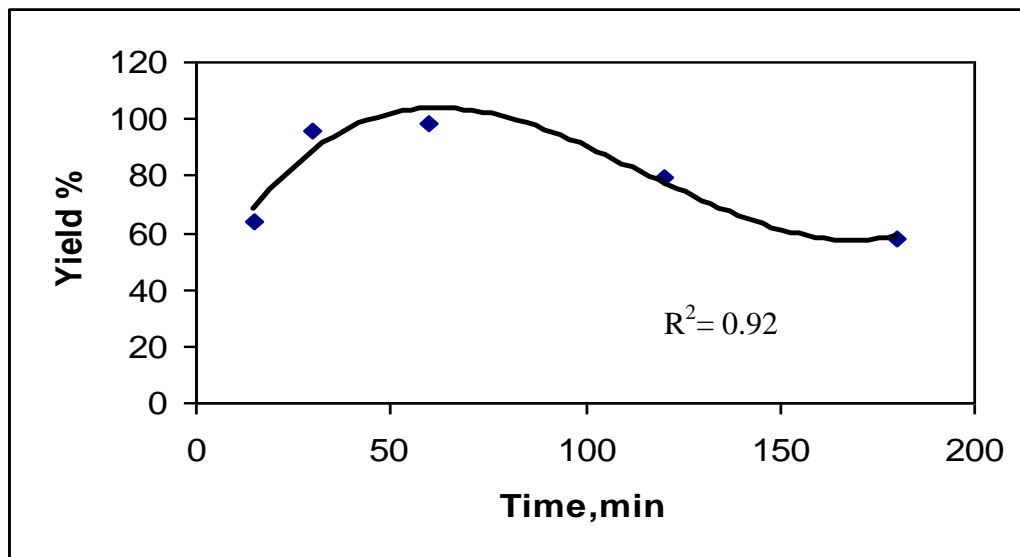


Fig. 12. Fitting curve for relation between % yield and reaction time

increasing the molar ratio of methanol to oil the K_1 value increased, some authors have proposed fitting experimental data to a first-order kinetic law [13,14].

Finally, the goodness-of-fit of the experimental data to the proposed model was assessed by comparing the experimental acid value removed with the theoretical prediction of Eq. (3) by substitution in Eq. (4) at different methanol/ oil molar ratio (Figure (7)). Also from figure (8) it is clear that E experimental was most of the time \approx E calculated.

$$E = \frac{A_0(e^{2K_2\alpha t} - 1)}{\beta(1 + e^{2K_2\alpha t}) + 0.5(e^{2K_2\alpha t} - 1)} \quad (4)$$

3.2. Kinetic model of transesterification reaction:

The transesterification reaction factors were fitted by using polynomial function with different degree according to the experimental points for each factor. The relation between percentage yield and molar ratio was fitted by using polynomial 2 as shown in figure (9), the model equation for this factor presented in equation (5) :

$$\% \text{ Yield} = -1.0133 (\text{MR})^2 + 18.285\text{MR} + 15.572 \quad (5)$$

The relation between percentage yield and catalyst amount was fitted by using polynomial 3, as shown in figure (10) as the model equation for this factor with $R^2 = 0.999$ equation (6):

$$\% \text{ Yield} = 0.6075 (\text{catalyst amount } \%)^3 - 3.8916 (\text{catalyst amount } \%)^2 + 7.9282 (\text{catalyst amount } \%) + 93.138 \quad (6)$$

Figure (11) shows the relation between percentage yield and temperature which fitted by using polynomial 3, as the model equation for this factor with $R^2 = 0.999$ shown in equation (7) :

$$\% \text{ Yield} = 0.0018 (\text{temperature})^3 - 0.3469 (\text{temperature})^2 + 21.434 (\text{temperature}) - 359.49 \quad (7)$$

While the relation between percentage yield and time of reaction was fitted by using polynomial 3, as shown in figure (12) with $R^2 = 0.92$ as follows:

$$\% \text{ Yield} = 8 \times 10^{-5} (\text{time})^3 - 0.266 (\text{time})^2 + 2.4201 (\text{time}) + 37.457 \quad (8)$$

A model equation which collect the different factors studied are joined in equation (9) with $R^2 = 0.98$

$$\% \text{ Yield} = 3.551 (\text{Molar Ratio}) + 2.2659 (\text{Catalyst amount } \%) + 0.9733 (\text{Temperature}) - 0.0956 (\text{Reaction time}) \quad (9)$$

From this equation, it can be concluded that the most effective factor is the molar ratio as it has the highest coefficient, followed by the catalyst amount and reaction temperature and finally the lowest effect for reaction time.

4. Conclusion

A mathematical model describing kinetics of transesterification of model 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 oil 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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