A Heterogeneous Acid-Catalyzed Process for Biodiesel Production from Enzyme Hydrolyzed Fatty Acids

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In this work, biodiesel synthesis via fatty acids esterification with methanol is conducted by using a heterogeneous catalyst made from cation-exchange resin. The kinetics of esterification is studied at the different levels of catalyst loading (3.65–53.6%, w/w), reaction temperature (333–353 K) and molar ratio of methanol to fatty acids (1:1 to 20:1). The reaction rate and fatty acids conversion increased with increases in catalyst loading, reaction temperature and molar ratio of feeding reactants. A pseudo-homogeneous kinetic model coupling the effect of catalyst loading, reaction temperature and methanol/fatty acids molar ratio used for describing the process gave a correlation coefficient of 0.95 between experimental and predicted data. The proposed model was further used to predict the optimal operating condition for obtaining equilibrium conversion of 0.99. A reaction temperature of 372.15 K, molar ratio of feeding reactants of 14.9:1 and reaction time of 9.5 h was numerically calculated as the optimal operating condition. Under this optimal operating condition, an experimental verification was carried out and a satisfactory match was observed between experimental data and model prediction. © 2007 American Institute of Chemical Engineers *AIChE J,* 54: 327–336, 2008
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Introduction

Biodiesel is commonly produced by the transesterification of plant oil or animal fat with short chain alcohols.[1] This biomass fuel has received much attention, since it is a kind of alternative, biodegradable, nontoxic, and renewable energy.[2] In addition, use of biodiesel does not contribute to the accumulation of carbon dioxide in the atmosphere, because it is an integral part of the carbon cycle. The feedstock for biodiesel is synthesized by CO_2 sequestration through photosynthesis and it either decays or is utilized to produce CO_2 that reenters the cycle.[3,4]

For industrial biodiesel production, homogeneous basic catalysts such as sodium or potassium methoxide and hydroxide, are commonly used for transesterification of oil and methanol to produce fatty acid methyl esters and glycerol.[5,6] Since unrefined and waste oil normally used as a cheap feedstock contains more than 0.5% free fatty acids (FFAs), the amount of catalyst loss because of neutralization contributes to an added process cost.[7–9] To improve the economic competitiveness of producing biodiesel using low cost materials, homogeneous acidic catalysts, such as hydrochloric acid or sulfuric acid, are used to pre-esterify the FFAs prior to transesterification of oil by homogeneous basic catalysts.[4] However, irrespective of whether homogeneous acidic or basic catalysts are used for biodiesel production, the purification is adversely affected by the presence of residual catalysts and leads to serious pollution problems because a large amount of water is required to remove spent catalyst.[10]

Enzyme based processes can circumvent the above problems and are attractive alternatives. For example, lipases can transesterify triglyceride and esterify FFAs with methanol to fatty acid methyl esters. Although the biochemical processes are expected to be highly selective and eco-friendly, process economic issues arising from high cost of enzyme and deactivation of enzyme by methanol need to be addressed.[11–14]

Recently, ion-exchange resins have been introduced as heterogeneous catalysts for biodiesel synthesis because they possess distinct advantages over homogeneous catalysts. Heterogeneous catalysts are easily recycled by filtration or decantation; these catalysts can be used in continuous operation, can eliminate equipment corrosion, and can diminish waste water effluent and reduce process cost incurred in product separation.[9,15,16] Anion-exchange resin was used as heterogeneous basic catalyst in the transesterification reaction of triolein with ethanol by optimal batch and continuous modes.[2] Acidic cation-exchange resin has also shown positive results in the esterification of oil containing a high level FFAs with methanol.[1,17] A route for biodiesel synthesis using ion-exchange resins as heterogeneous catalysts therefore appears certainly attractive. In this work, FFAs obtained from enzymatic hydrolysis of soybean oil by lipase are used as a feedstock to produce biodiesel by heterogeneous catalytic process. The effect of catalyst loading, reaction temperature and molar ratio of methanol to FFAs on methanolysis of FFAs is investigated. A kinetic model is proposed to determine corresponding kinetic parameters and is employed to predict the optimal conditions for biodiesel synthesis. Finally, experiments are performed at the optimal conditions to verify the prediction of the model.

Table 1. Physical Characteristics of the Catalyst

Product Name and Provider	Dowex Monosphere 88 by Dow Chemical Company
Matrix	Styrene-divinylbenzene
Structure	Macroporous
Functional group	Sulfonate
Particle density (g L^{-1})	1.2
Particle size (mm)	0.5–0.6
Acidity (mmol g^{-1})	4.48

Materials and Methods

Materials

Soybean oil was obtained from Uni-president. located in Tainan County, Taiwan. Potassium hydroxide, lipase from *Candida rugosa*, and HPLC grade methanol and ethanol, were purchased from Sigma Chemicals Company (St Louis, MO). A strong acidic cation-exchange resin, Dowex Monosphere 88, used as the solid catalyst, was purchased from Dow Chemical Company (Midland, MI). The physical properties of this catalyst are shown in Table 1.

FFAs by enzymatic hydrolysis of soybean oil

Soybean oil was mixed with aliquots water at room temperature under constant agitation by magnetic stirrer to obtain an oil–water emulsion. The initial molar ratio of water to oil was 6:1. The hydrolysis reaction of oil was initiated by addition of enzyme solution (50 mg free lipase per milliliter of DI water) and the reaction was carried out overnight. In this way, FFAs were derived from enzymatic hydrolysis of soybean oil. The supernatant containing high level of FFAs was harvested by centrifugation at 10,000 rpm for 10 min at room temperature. The concentration of FFAs in this supernatant was determined and the enzyme hydrolyzed FFAs were used as the feedstock for the investigation of biodiesel production by the solid catalyzed esterification process.

Activation of cation-exchange resin

Commercially available acidic resin used as the solid catalyst for esterification reaction was prepared by the following steps. First, the acidic resin was washed thrice by DI water to remove impurities adsorbed on the resin. Because the catalytic performance of the resin is based on the acidification level of sulfonated groups (i.e., Brönsted acid sites), the resin was then activated by immersing in 1 M hydrochloric acid solution and agitated continuously for 1 h followed by washing with DI water until neutral pH. The activated resin was recovered and dried overnight at 60°C in an oven.

For evaluating the catalytic performance of the resin used, the total amount of Brönsted acid sites was determined by acid–base titration methods.[18] An amount of 1 g of resin was mixed with 200 ml of 0.1 M NaOH prepared in 5% NaCl, and allowed to stand overnight at room temperature. Fifty milliliter of the supernatant liquid was subsequently titrated with 0.1 M HCl using phenolphthalein as an indicator to determine residual amount of base (i.e., acidity of the resin).

Esterification

FFAs derived from enzymatic hydrolysis of soybean oil were used as the feedstock to produce biodiesel by esterification with methanol using the solid catalyst. In this experiment, the reactants (FFAs and methanol) were mixed with resin in a round stopper bottle with stirring. Catalyst loading, reaction temperature and molar ratio of methanol to FFAs were investigated in the ranges of 0–53.6% (w/w) of FFAs, 333–353 K, and 1:1 to 20:1, respectively. FFAs conversion was determined from sample withdrawn at regular intervals. Equilibrium conversion of FFAs was established when the conversion difference between successive samples became negligible.

Analysis

Acid–base titration was used to determine the FFAs conversion during esterification reaction. A sample of known weight was withdrawn from the reactor and dissolved in 20 ml diethlyether-ethanol solution (1:1 volume ratio). The sample was then titrated against 0.1 M KOH using phenolphthalein as an indicator. The acid value (AV) of the sample was defined as follows:

$$\mathrm{AV} = \frac{M_{\mathrm{W}} \times C \times V}{m \times f_0} \tag{1}$$

where M_{W} is the molecular weight of KOH, C is the molar concentration of KOH, V is the volume of KOH used in the titration procedure, m is the sample weight, and f_0 is weight fraction of FFAs in the beginning of the reaction. After the acid value was determined, the conversion of FFAs to fatty acid methyl esters (biodiesel) can be calculated by Eq. 2:

$$X = \left(1 - \frac{\mathrm{AV}}{\mathrm{AV}_0}\right) \times 100 \tag{2}$$

where X is given as the conversion and AV_0 is the initial acid value before the esterification reaction.

The mean molecular weight of FFAs in soybean oil and the acid value of FFAs completely converted from soybean oil were estimated, yielding value of 278.23 g mol^{-1} and 201 mg KOH used per gram of oil, respectively.

The predictive capability of model was evaluated by the squared correlation coefficient (γ^2) defined as the following equation:

$$\gamma^2 = 1 - \frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{\sum_{i=1}^{n} (y_i - \overline{y})^2} \tag{3}$$

where, n is the number of samples, y_i is the actual experiment data of ith sample, $\hat{y}_i$ is the model predicted data of ith sample, and $\overline{y}$ is the average of all experimental data. The coefficient γ^2 is normalized between 0 and 1. In this evaluation, high γ^2 demonstrated the reasonable agreement between reference value and predicted value of the model.

Mathematical models

The pseudo-homogeneous model gives a satisfactory representation of the heterogeneous catalytic reaction for esterification systems.[1,17,19,20] In this study, a pseudo-homogeneous model was therefore used to depict the kinetics of esterification of FFAs with methanol in the presence of cation-exchange resin based on the following assumptions: (1) no internal and external mass resistance exist,[19] (2) sorption effect of involved species is neglected, and (3) whole system is taken into account as an ideal solution.

The esterification reaction of FFAs with alcohol for producing fatty acid esters and water in the presence of catalytic resin is given as:

$$\mathrm{RCOOH} + \mathrm{R'OH} \underset{k_2}{\overset{k_1}{\longleftrightarrow}} \mathrm{RCOOR'} + \mathrm{H_2O}$$

This reaction can be considered as an elementary second order reversible reaction and the reaction rate of esterification can be expressed as:

$$\frac{-dC_{\mathrm{RCOOH}}}{dt} = k_1 \cdot C_{\mathrm{RCOOH}} \cdot C_{\mathrm{R'OH}} - k_2 \cdot C_{\mathrm{RCOOR'}} \cdot C_{\mathrm{H_2O}} \tag{4}$$

where k_1 is the forward reaction rate constant, C_{RCOOH} is the molar concentration of FFAs, $C_{\mathrm{R'OH}}$ is the molar concentration of alcohol and the alcohol here is methanol, k_2 is the backward reaction rate constant, $C_{\mathrm{RCOOR'}}$ is the molar concentration of fatty acid methyl esters, and $C_{\mathrm{H_2O}}$ is the molar concentration of water. Since the reactants and products concentration correspond to FFAs conversion, Eq. 4 can be further rewritten into the form of Eq. 5 in which FFAs conversion is expressed as a dependent variable.

$$\frac{dx}{dt} = k_1 C_{\mathrm{RCOOH},0} \left[(1-x)(\theta - x) - \frac{x^2}{K_{\mathrm{e}}}\right] \tag{5}$$

where x is the FFAs conversion, $C_{\mathrm{RCOOH},0}$ is the initial concentration of FFAs, θ is the molar ratio of methanol to FFAs, and K_e is the equilibrium constant. At equilibrium state, $dx/dt = 0$ and hence K_e, defined as the ratio of the forward reaction rate constant to the backward reaction rate constant, is calculated from the following equation:

$$K_{\mathrm{e}} = \frac{k_1}{k_2} = \frac{x_{\mathrm{e}}^2}{(1 - x_{\mathrm{e}})(\theta - x_{\mathrm{e}})} \tag{6}$$

where x_{e} is the FFAs conversion at the equilibrium state.

After the value of K_{e} is determined, Eq. 5 can be further integrated and rearranged as Eq. 7 (derivation procedure shown in Appendix).

$$\ln\left[\frac{(-1 - \theta + a_2)x + 2\theta}{(-1 - \theta - a_2)x + 2\theta}\right] = a_2 \cdot k_1 \cdot C_{\mathrm{RCOOH},0} \cdot t \tag{7}$$

where

$$a_2 = [(\theta + 1)^2 - 4a_1\theta]^{1/2} \tag{7.1}$$

$$a_1 = 1 - \frac{1}{K_{\mathrm{e}}} \tag{7.2}$$

From the experimental data and determined K_{e}, the forward reaction rate constant k_1 can be determined numerically by Eq. 7.

For determining the variation of FFAs conversion with time, Eq. 7 can be expanded and rearranged to obtain an explicit expression for x given by Eq. 8.

$$x = \frac{2\theta(e^{a_2 \cdot k_1 \cdot C_{\mathrm{RCOOH},0} \cdot t} - 1)}{[(-1 - \theta + a_2) - (-1 - \theta - a_2) \cdot e^{a_2 \cdot k_1 \cdot C_{\mathrm{RCOOH},0} \cdot t}]} \quad (8)$$

To consider the effect of reaction temperature and catalyst loading on the kinetic model, the modified Arrhenius model described by Seo and Hong[19] are listed as

$$k_1 = k_1' e^{-E_1/RT} \quad (9)$$

$$K_e = K_e' e^{-E_e/RT} \quad (10)$$

$$k_1' = (k_{10}' + k_{1w}' W) \quad (11)$$

$$K_e' = (K_{e0}' + K_{ew}' W) \quad (12)$$

where, k_1' and K_e' are pre-exponential factors respectively for forward reaction rate constant and equilibrium constant, E_1 and E_e represent the activation energy of forward and equilibrium reaction, R is the ideal gas constant, T is the reaction temperature, k_{10}' and k_{1w}' is the constant and coefficient number for describing the kinetic effect of catalyst loading for the forward reaction, K_{e0}' and K_{ew}' is the constant and coefficient number for describing the kinetic effect with respect to catalyst loading for the equilibrium reaction and W is weight fraction of catalyst to FFAs. Pre-exponential factors (k_1' and K_e') are expressed as a linear function with the operating catalyst loading. These equations are used to describe the rate constant of forward and equilibrium reaction with the effect of reaction temperature and catalyst loading.

Results and Discussion

The esterification reaction system is composed of FFAs, methanol and the resin as solid catalyst. For understanding the reaction kinetics of the esterification, three experimental parameters are considered. These are the fraction of resin weight to reactant, reaction temperature and the molar ratio of methanol to FFAs. The effect of parameters within different levels are expressed as operating conditions of a batch reactor and summarized in Table 2.

Table 2. Operating Conditions of the Batch Experimental Runs

Run	Catalyst Loading (Weight of Resin to FFAs, %)	Temperature (K)	Molar Ratio of Methanol to FFAs
1	3.65	333	10:1
2	7.31	333	10:1
3	13.4	333	10:1
4	26.8	333	10:1
5	53.6	333	10:1
6	26.8	343	10:1
7	26.8	353	10:1
8	26.8	343	1:1
9	26.8	343	20:1

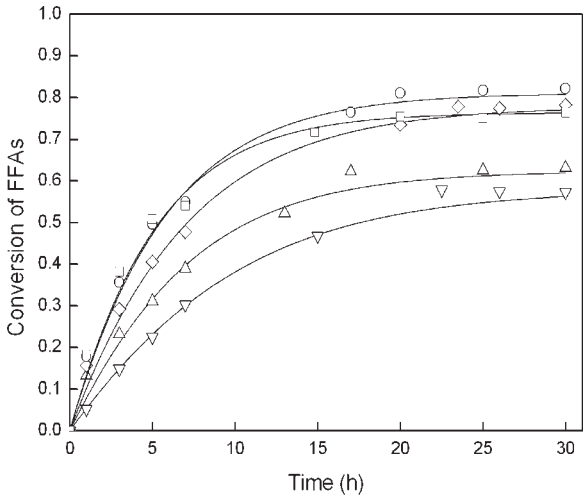

Figure 1. Conversion of FFAs vs. time for fatty acid methyl esters formation (T = 333 K, θ = 10:1) catalyzed by different amounts of Dowex Monosphere 88 expressed as mass fraction of FFAs (□, 53.6%; ○, 26.8%; ◇, 13.4 %; △, 7.31 %; ▽, 3.65%).

The solid line represents prediction results of the pseudo-homogeneous model.

Effect of catalyst loading

The catalyst loading was varied from 3.65 to 53.6% (w/w) of FFAs to evaluate its effect on the conversion of FFAs at the given temperature of 333 K and methanol:FFAs molar ratio of 10:1 (run 1–5 in Table 2). The time courses of FFAs conversion are shown in Figure 1. It is observed that with higher catalyst loading, a faster rate is obtained because the total number of active sites available for reaction increases.[16] As illustrated in Figure 1, the FFAs equilibrium conversion increased with an increase in catalyst loading from 3.65 to 26.8% (w/w). To further study the effect of catalyst loading on esterification reaction, the equilibrium conversion, the equilibrium constant K_e and the forward reaction rate constant k_1 were calculated from Eqs. 6 and 7, and from the data shown in Figure 1. The variation in these parameters with respect to catalyst loading has been plotted as Figure 2. The equilibrium conversion and equilibrium constant exhibits a first order response to catalyst loading (Figure 2). The forward rate constant has a similar initial response with changing catalyst loading but it passes through a maximum at W = 26.8% (w/w). In the region of catalyst loading from 26.8–53.6% (w/w), the reaction might be controlled by the mass transfer because the kinetics becomes independent of catalyst loading. At 26.8% (w/w) of catalyst loading, the equilibrium conversion saturates and forward reaction rate constant is maximal. Hence, it can be concluded that the optimal catalyst loading is 26.8% (w/w). Further experiments were conducted at this value of catalyst loading to study other operating conditions.

Effect of reaction temperature

The study of temperature effect is very important for determining activation energy and intrinsic rate. The reaction

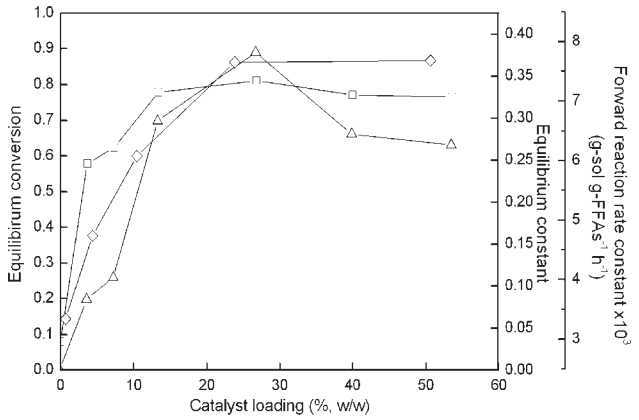

Figure 2. The effect of catalyst loading on reaction conversion and kinetic parameters (□, equilibrium conversion; △, equilibrium constant; ◇, forward reaction rate constant).

temperature was varied from 333–353 K to evaluate its effect on the esterification reaction at the given catalyst loading of 26.8% (w/w) and MeOH/FFAs molar ratio of 10:1 (run 4, 6, and 7 in Table 2). The boiling point of this mixture is about 348 K. The maximum practical temperature slightly over boiling point was therefore selected as 353 K. The time courses of FFAs conversion are displayed in Figure 3 which indicates that the reaction rates and final conversion increased with an increase in temperature at optimal catalyst loading of 26.8% (w/w). In many esterification reactions, the heat of reaction is small or equal to zero, that results in equilibrium conversion being independent of temperature.[21] However, the equilibrium conversion is observed to be dependent on temperature in this study. The equilibrium conversion increased from about 0.8–0.95 with an increase in temperature varied from 333–353 K.

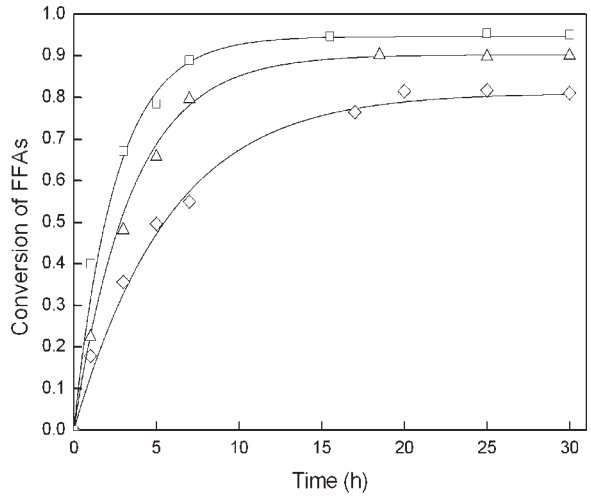

Figure 3. Conversion of FFAs vs. time for fatty acid methyl esters formation (catalyst loading = 26.8 % (w/w), θ = 10:1) at different reaction temperature (□, 353 K; △, 343 K; ◇, 333 K).

The solid line represents prediction results of the pseudo-homogeneous model.

Effect of reactant molar ratio

The initial molar ratio of methanol to FFAs was varied from 1:1 to 20:1 at a temperature of 343 K and 26.8% (w/w) catalyst loading (run 8, 6, and 9 in Table 2). Figure 4 shows the experimental results. As observed, not only the reaction rate but also equilibrium conversion increases with the initial reactants molar ratio. The equilibrium conversion of FFAs increased from about 0.45 at a feed molar ratio (methanol to FFAs) of 1:1 to 0.96 at a feed molar ratio (methanol to FFAs) of 20:1.

Theoretically, the esterification of FFAs requires 1 mole alcohol for yield of fatty acid methyl esters. According to LeChatelier's Principle, excess of alcohol used shifts the equilibrium of reversible reaction toward the direction of esters formation. In this work, increase in the methanol/FFAs molar ratio from 1:1 to 10:1 exhibited a significant effect on the fatty acid methyl esters formation. However, the esters formation increased less rapidly when the initial molar ratio was further increased from 10:1 to 20:1. Excess methanol is required to maintain the reaction rate and yield of biodiesel within acceptable limits. In actual process implementation, the excess methanol can be recycled to improve operation economics.[22,23]

Kinetic parameters estimation

Reaction Rate Constants. The equilibrium constant K_e can be determined from the final conversion of FFAs (Eq. 6). The conversion of FFAs is measured by titrating the residual FFAs in the mixture. The forward reaction rate constant k_1 must be determined by the experimental conversion of FFAs recorded with time as defined in Eq. 7. The values plotted in Figures 5a, b, and c are derived from the experimental data presented in Figures 1,3, and 4, respectively. The Figures 5a, b, and c show a linear relationship

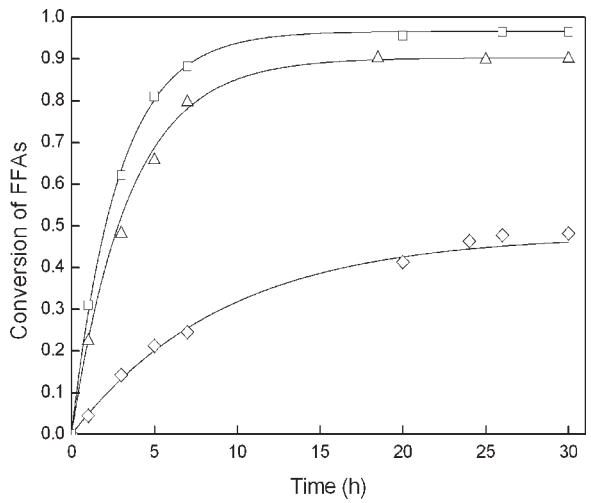

Figure 4. Conversion of FFAs vs. time for fatty acid methyl esters formation [T = 343 K, catalyst loading = 26.8 % (w/w)] at different initial reactant molar ratio, θ (□, 20:1; △, 10:1; ◇, 1:1).

The solid line represents prediction results of the pseudo-homogeneous model.

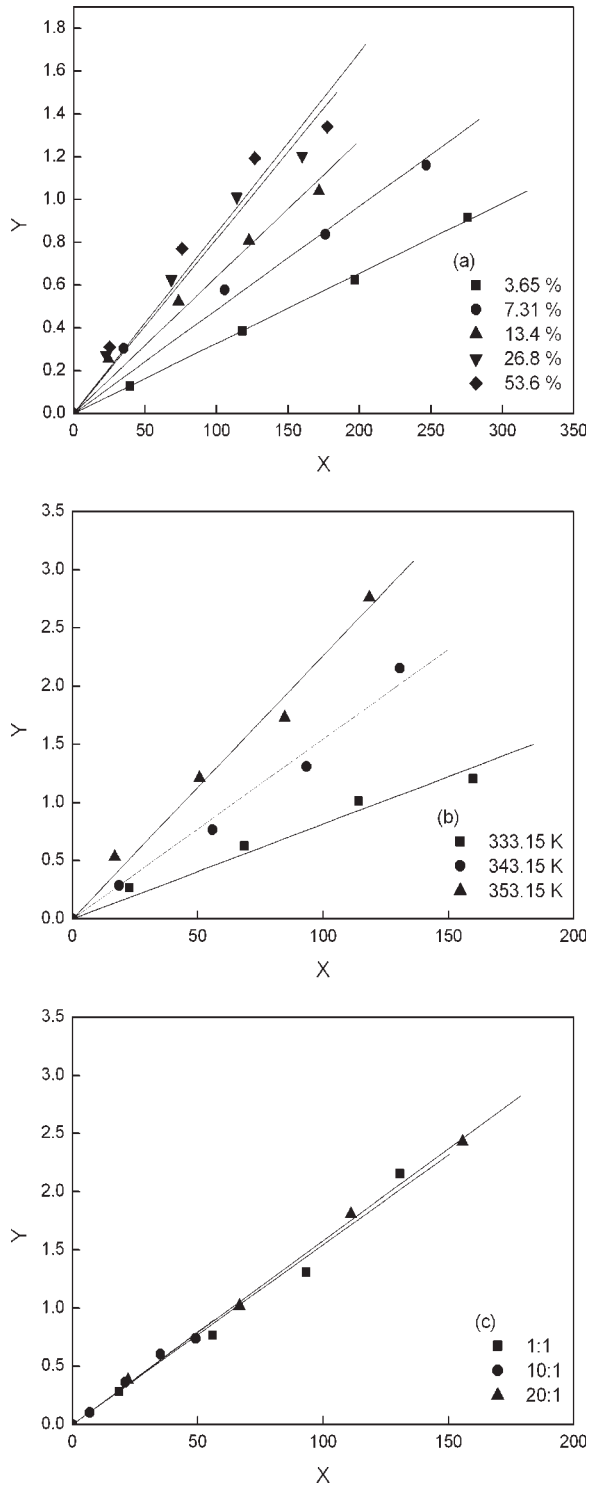

Figure 5. Second order model for calculation of forward reaction rate constant at the different (a) catalyst loading, (b) reaction temperature and (c) molar ratio of methanol to FFAs.

In these figures, the values of the abscissa and ordinate were computed from the relations $a_2 \cdot C_{RCOOH,0} \cdot t$ and $\ln[((-1-\theta+a_2)x+2\theta)/((-1-\theta-a_2)x+2\theta)]$, respectively.

between $\ln[((-1-\theta+a_2)x+2\theta)/((-1-\theta-a_2)x+2\theta)]$ and $a_2 \cdot C_{RCOOH,0} \cdot t$. Hence the forward reaction rate constant k_1 is obtained as the slope of each straight line. In addition, the excellent straight line fit observed in Figures 5a, b, and c, is a clear indication that the proposed kinetic model is valid. Calculated equilibrium constant K_e and forward reaction rate constant k_1 in the different levels of catalyst loading, reaction temperature and initial molar fraction of feeding reactants are summarized in Tables 3, respectively. It is evident that the equilibrium constant value increases as the catalyst loading, reaction temperature and molar ratio of methanol to FFAs increases. Higher forward reaction rate constant was also obtained at higher catalyst loading and higher reaction temperature. However, a slight difference in forward reaction rate constant was observed at different level of initial molar ratio of methanol to FFAs. Higher initial molar ratio of methanol/FFAs does not increase the forward reaction rate but suppresses the backward reaction rate.

This study shows that the esterification of FFAs with methanol is an endothermic reaction because equilibrium constant increases with an increase in reaction temperature.[15] This result is consistent with the literature reported.[15,17,24,25]

Activation Energy. As aforementioned, the forward reaction rate and equilibrium constants depending on temperature are represented by the Arrhenius model (Eqs. 9 and 10). Figure 6 shows the Arrhenius-Van't Hoff plot for the esterification reaction at different temperature. Higher linear correlation coefficients indicate the linearity as shown by the γ^2 indexes for forward reaction rate and equilibrium constants with 0.985 and 0.998, respectively. The activation energies can be further determined from the slopes of the straight lines in Figure 6. The activation energies of forward reaction and equilibrium reaction are 59.44 and 77.73 kJ mol^{-1}, respectively. Such high value of activation energies indicate that the temperature influence strongly on system kinetics and it implies that reactions are kinetically controlled not diffusion control. Hence, the assumption of absence of external and internal mass-transfer resistances in model development is confirmed because this reaction is established as kinetically controlled.[26–28]

Pasias et al.[17] used the same reaction model for the esterification of FFAs in vegetable oil with methanol using cation-exchange resin as catalyst. They reported activation energies of forward and backward reactions of 70.34 and 37.93 kJ mol^{-1}, respectively. These values are higher than the values obtained in this work. In the present study, the backward reaction is mass transfer resistance controlled because the activation energy of backward reaction is -18.52 kJ mol^{-1}. Different catalyst and system used in the respective studies might be the major reason for producing such differences.

Catalyst Loading Coefficients and Constants. The pre-exponential factors, k'_1 and K'_e, can be obtained from the intercept of *y*-axis in Figure 6. These values may be used in Eqs. 11 and 12 to calculate the catalyst loading coefficients and constants. The linear domain of the equations (Eqs. 11 and 12) is between 3.65 and 26.8% (w/w) of catalyst loading. The coefficients can be obtained from the linear regression of experimental data as demonstrated in Figures 7a and b. Linear correlation coefficients of above 0.93 indicate reliable linearity. For forward reaction, the value of k'_{10} and k'_{1w} were obtained as $k'_{10} = 6.71 \times 10^6$ (g-sol g-FFAs^{-1} h^{-1}) and

Table 3. The Calculated Equilibrium Constant and Estimated Forward Reaction Rate Constant with the Different Levels of the Catalyst Loading, Reaction Temperature, and Molar Ratio of Methanol to FFAs

Run*	Catalyst Loading (%)	Equilibrium Constant (K_e)	Forward Reaction Rate Constant† (k_1)
1	3.65	8.44×10^{-2}	3.27×10^{-3}
2	7.31	1.10×10^{-1}	4.84×10^{-3}
3	13.4	2.97×10^{-1}	6.37×10^{-3}
4	26.8	3.78×10^{-1}	8.15×10^{-3}
5	53.6	2.68×10^{-1}	8.44×10^{-3}
Run*	Temperature (K)	Equilibrium Constant (K_e)	Forward Reaction Rate Constant† (k_1)
4	333	3.78×10^{-1}	8.15×10^{-3}
6	343	9.14×10^{-1}	1.54×10^{-2}
7	353	1.85	2.26×10^{-2}
Run*	Methanol/FFAs Molar Ratio	Equilibrium Constant (K_e)	Forward Reaction Rate Constant† (k_1)
8	1:1	8.39×10^{-1}	1.59×10^{-2}
6	10:1	9.14×10^{-1}	1.54×10^{-2}
9	20:1	1.44	1.58×10^{-2}

* The experimental conditions refer to Table 2.
† Unit of forward reaction rate constant is g-sol g-FFAs^{-1} h^{-1}.

$k'_{1w} = 3.66 \times 10^7$ (g-sol g-FFAs^{-1} h^{-1}). For equilibrium reaction, the value of K'_{e0} and K'_{ew} were obtained as $K'_{e0} = 4.2 \times 10^{10}$ and $K'_{ew} = 2.21 \times 10^{12}$.

Simulated experiments

Since all of the kinetic parameters in Eq. 5 were determined, the model was used in simulation experiments. The initial conditions for model simulation were the same as the experiments (Table 2). The conversion x as it evolves in time was computed using Eq. 5 and is shown as a solid line in Figures 1,3, and 4. The agreement between the experimental and simulated values of conversion was observed and linear correlation coefficient of 0.95 was obtained (Figure 8). Although some deviations between calculated value and reference value were observed during initial stage of experiments, a good overall correlation was obtained ($\gamma^2 = 0.95$).

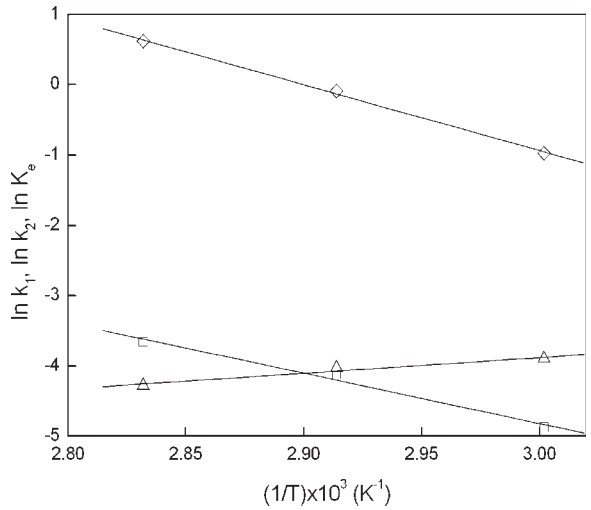

Figure 6. Arrhenius-Van't Hoff plot for forward reaction (□), backward reaction (△) and equilibrium reaction (◇) in the temperature within a range of 333–353 K.

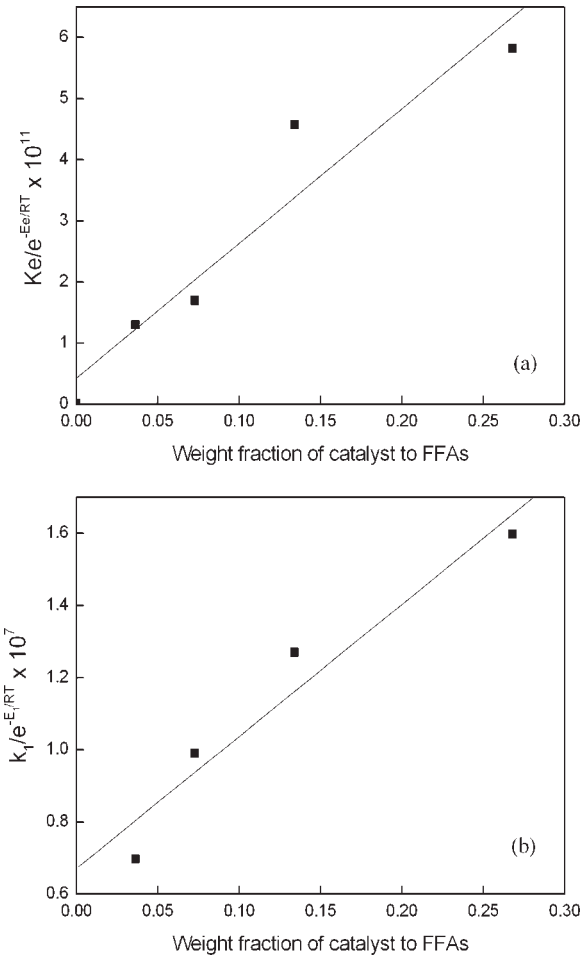

Figure 7. The linear regression of the experiment data for the determination of catalyst loading coefficients and constants for (a) equilibrium reaction and (b) forward reaction.

The pre-exponential factors of equilibrium reaction and forward reaction were plotted as a straight line against weight fraction of catalyst to FFAs. The catalyst loading coefficients and constants were respectively determined from the slope and intercept of the straight line.

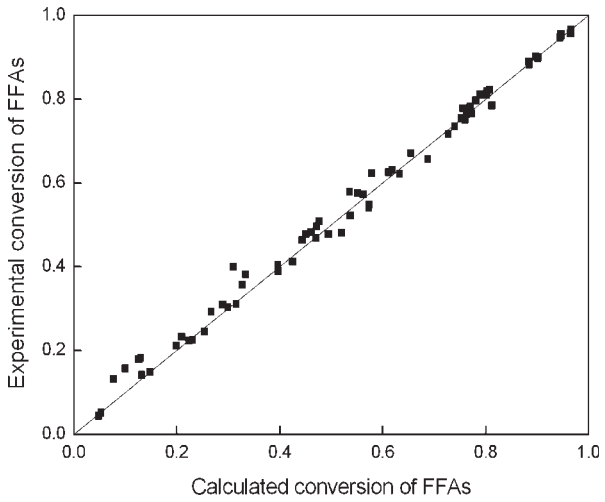

Figure 8. Correlation between experimental and simulated conversion.

A data point lying on the line with slope equal to unity represents exact correlation.

Consequently, the proposed kinetic model can reliably depict this reaction system and predict behavior of this reaction under other operating conditions.

Model prediction, optimization, and experimental verification

The parameters of the kinetic model were determined from the experimental data. This model with the determined parameters was then further employed to predict the operating conditions (reaction temperature, reaction time, and feeding molar ratio of reactants) required for given conversion of FFAs (Figure 9). On the basis of Eq. 8, the equilibrium conversion of FFAs (x_e) is a function of initial methanol/FFAs molar ratio (θ) and reaction temperature (T) which is formulated as Eq. 13.

$$x_e = \lim_{t\to\infty} \frac{2\theta(e^{a_2\cdot k_1\cdot C_{RCOOH,0}\cdot t} - 1)}{[(-1-\theta+a_2) - (-1-\theta-a_2)\, e^{a_2\cdot k_1\cdot C_{RCOOH,0}\cdot t}]} \cong \frac{2\theta}{1+\theta+a_2} \tag{13}$$

Combining Eqs. 7.1, 7.2, and 13, the relations between initial molar ratio of methanol to FFAs and reaction temperature on the given condition of final conversion x_e can be plotted as the left half part of Figure 9 ($T - \theta$ curve). At the given equilibrium conversion x_e, temperature T and molar ratio of reactants θ can be substituted into Eq. 8 for computing the reaction time t required for biodiesel production. The relations between molar ratio of reactants θ and reaction time t are subsequently plotted as the right half part of Figure 9. Therefore, for any given temperature and initial molar ratio of methanol to FFAs, it is possible to determine the time required for achieving a desired conversion directly by traversing from the left half to the right half of Figure 9.

The operating strategy for biodiesel production depends on the selection of reaction temperature and initial molar ratio of methanol to FFAs. As observed in Figure 9, tuning of temperature is a preferable strategy for obtaining higher conversion of FFAs. The magnitude of change in molar ratio per unit change in reaction temperature is defined as $d\theta/dT$ (i.e., the slope of $T - \theta$ curve) and indicates economical and engineering trade-off consideration. For obtaining high quality biodiesel, $x'_e = 0.99$ is taken into account as an example. Under this requirement, $d\theta/dT$ varies from about $-\infty$ to zero as the temperature increases from 350 to 400 K. As the value of $d\theta/dT$ approaches zero, the temperature required for the desired conversion crosses the practical operating temperature. Similarly, when the value approaches $-\infty$, the initial methanol/FFAs molar ratio becomes uneconomical. Clearly, $(d\theta/dT)_{x_e=0.99} = -1$, defines the optimal operating condition because a change in temperature results in a proportionately equal change in molar ratio only at this point. This optimal operating condition calculated numerically has been obtained as the point A, where the molar ratio of reactants is 14.9, reaction temperature is 372.15 K and reaction time of 9.5 h is obtained at the point B in Figure 9. We performed a wet-lab experiment at this operating condition to verify the prediction from Figure 9. A conversion of 0.985 was achieved. The agreement between the predicted and experimental result and the accuracy of prediction demonstrates that the proposed model is appropriate (relative error of 0.5%) for this reaction system.

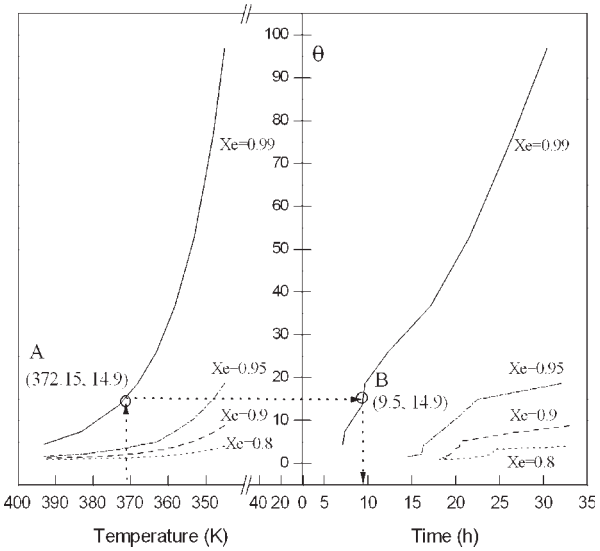

Figure 9. A family of curves showing the relation between the reactant molar ratio θ and the temperature T (left half) and the reactant molar ration θ and the time of reaction t (right half) for different values of conversion x_e as parameter are plotted.

Curves for x_e = 0.8, 0.9, 0.95 and 0.99 are shown. For any given operating temperature and conversion there exists a unique point in the left half of the figure. Traversing along a constant molar ratio line to the right half of the figure, the time required for the reaction can be obtained from the point of intersection with the corresponding x_e curve. The points A and B shown correspond to the optimal operating condition.

Conclusions

Biodiesel is a renewable energy resource and has received much attention because it is completely compatible with the petroleum diesel engine and possesses specific advantages over petroleum fuel. The problems associated with acidic/basic homogeneous catalyst may be addressed using heterogeneous catalytic resins. In this study, the cation-exchange resin used as acidic catalyst was employed to investigate the esterification kinetics under varying catalyst loading (3.65–53.6%, w/w), reaction temperature (333–353 K) and methanol/FFAs molar ratio (1:1 to 20:1). A pseudo-homogeneous kinetic model of coupling the effects of catalyst loading, reaction temperature and molar ratio of methanol to FFAs was developed. A good agreement between reference value and calculated value was observed and correlation coefficient of 0.95 was evaluated. The optimal operating condition for obtaining equilibrium FFAs conversion of 0.99 was further determined by the proposed model and calculated as reaction temperature of 372.15 K, molar ratio of feeding reactants of 14.9:1 and 9.5 h required for reaction. Experimental conversion of 0.985 was obtained and compared with the value predicted by the proposed model.

Notation

a = a constant of a quadratic equation
AV = acid value (mg KOH g^{-1} oil)
AV_0 = initial acid value before the esterification reaction (mg KOH g^{-1} oil)
b = a constant of a quadratic equation
c = a constant of a quadratic equation
C = molar concentration of KOH (M)
C_{H_2O} = molar concentration of water (M)
C_{RCOOH} = molar concentration of FFAs (M)
$C_{RCOOH,0}$ = initial molar concentration of FFAs (M)
$C_{RCOOR'}$ = molar concentration of fatty acid methyl esters (M)
$C_{R'OH}$ = molar concentration of methanol (M)
E_1 = activation energy of forward reaction (J mol^{-1})
E_e = activation energy of equilibrium reaction (J mol^{-1})
f_0 = weight fraction of FFAs in the beginning of the reaction
k_1 = forward reaction rate constant (g-sol g-$FFAs^{-1}$ h^{-1})
k'_1 = pre-exponential factors for forward reaction rate constant (g-sol g-$FFAs^{-1}$ h^{-1})
k'_{10} = constant for describing the kinetic effect of catalyst loading on the forward reaction (g-sol g-$FFAs^{-1}$ h^{-1})
k'_{1w} = coefficient for describing the kinetic effect of catalyst loading on the forward reaction (h^{-1})
k_2 = backward reaction rate constant (g-sol g-$FFAs^{-1}$ h^{-1})
K_e = equilibrium constant
K'_e = pre-exponential factors for equilibrium constant
K'_{e0} = constant for describing the kinetic effect respected to catalyst loading on equilibrium reaction
K'_{ew} = coefficient for describing the kinetic effect respected to catalyst loading on equilibrium reaction
m = sample weight (g)
M_W = molecular weight of KOH (g mol^{-1})
n = number of samples
R = gas constant (J mol^{-1} K^{-1})
t = reaction time of esterification reaction (h)
T = reaction temperature (K)
V = volume of KOH used in the titration procedure (ml)
W = weight fraction of catalyst to FFAs (g-sol g-$FFAs^{-1}$)
x = conversion of FFAs
x_e = equilibrium conversion of FFAs
$\bar{y}$ = average of all experimental data
y_i = actual experiment data of sample i
$\hat{y}_i$ = model predicted data of sample i

Greek letters

θ = molar ratio of methanol to FFAs
γ^2 = squared correlation coefficient

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Appendix: Derivation of Symbolic Solution for Pseudo-homogeneous Kinetic Model

It is possible to extend this integral procedure to obtain the symbolic solution of the proposed kinetic model. A linear equation will be derived for determining forward reaction rate constant, k_1, numerically. The kinetic model with FFAs conversion as dependent variable, Eq. 5, is thus extended as Eq. A1.

$$\frac{dx}{dt} = k_1 C_{\mathrm{RCOOH},0}\left[\left(1-\frac{1}{K_e}\right)x^2 - (1+\theta)x + \theta\right] \tag{A1}$$

Equation A1 is further written as an integral formulation, expressed as Eq. A2.

$$\int_0^x \frac{dx}{\left(1-\frac{1}{K_e}\right)x^2 - (1+\theta)x + \theta} = k_1 \cdot C_{\mathrm{RCOOH},0} \cdot t \tag{A2}$$

From integral formular table,[29] the integration of a quadratic equation corresponding equivalently to Eq. A2 is expressed as follows

$$\int \frac{dx}{ax^2+bx+c} = \frac{1}{\sqrt{b^2-4ac}} \ln\left[\frac{2ax+b-\sqrt{b^2-4ac}}{2ax+b+\sqrt{b^2-4ac}}\right] \tag{A3}$$

where a, b, and c are constants of a quadratic equation and correspond to $\left(1-\frac{1}{K_e}\right)$, $-(1+\theta)$, and θ of Eq. A2, respectively.

Thus, the integration of Eq. A2 yields

$$\frac{1}{\sqrt{(1+\theta)^2-4\left(1-\frac{1}{K_e}\right)\theta}} \times \ln\left[\frac{2\left(1-\frac{1}{K_e}\right)x-(1+\theta)-\sqrt{(1+\theta)^2-4\left(1-\frac{1}{K_e}\right)\theta}}{2\left(1-\frac{1}{K_e}\right)x-(1+\theta)+\sqrt{(1+\theta)^2-4\left(1-\frac{1}{K_e}\right)\theta}}\right]\Bigg|_0^x = k_1 \cdot C_{\mathrm{RCOOH},0} \cdot t \tag{A4}$$

With using notations from Eqs. 7.1 and 7.2, Eq. A4 can be derived as following equations (Eqs. A5, A6, and A7).

$$\ln\left[\frac{2a_1x-(1+\theta)-a_2}{2a_1x-(1+\theta)+a_2}\right]\Bigg|_0^x = a_2 \cdot k_1 \cdot C_{\mathrm{RCOOH},0} \cdot t \tag{A5}$$

$$\ln\left\{\left[\frac{2a_1x-(1+\theta)-a_2}{2a_1x-(1+\theta)+a_2}\right]\cdot\left[\frac{-(1+\theta)+a_2}{-(1+\theta)-a_2}\right]\right\} = a_2 \cdot k_1 \cdot C_{\mathrm{RCOOH},0} \cdot t \tag{A6}$$

$$\ln\left[\frac{2a_1x(-1-\theta+a_2)+4a_1\theta}{2a_1x(-1-\theta-a_2)+4a_1\theta}\right] = a_2 \cdot k_1 \cdot C_{\mathrm{RCOOH},0} \cdot t \tag{A7}$$

Finally, Eq. A7 is rearranged as Eq. A8 to obtain a symbolic solution of pseudo-homogeneous model for the present study.

$$\ln\left[\frac{(-1-\theta+a_2)x+2\theta}{(-1-\theta-a_2)x+2\theta}\right] = a_2 \cdot k_1 \cdot C_{\mathrm{RCOOH},0} \cdot t \tag{A8}$$

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