Kinetic and thermodynamic studies of the esterification of acidified oil catalyzed by sulfonated cation exchange resin

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A B S T R A C T

This study describes the kinetics and thermodynamics of the esterification of acidified oil with methanol catalyzed by sulfonated cation exchange resins (SCER). The effects of the mass ratio of methanol to acidified oil, reaction temperature, and catalyst loading were studied to optimize the conditions for maximum conversion of free fatty acids (FFAs). The results showed that the optimal conversion rate of FFAs was 91.87% at the mass ratio of methanol to acidified oil of 2.5:1.0, reaction temperature of 65.0°C, catalyst loading of 5.0 g and reaction time of 8.0 h. The external and internal mass transfer resistances were negligible based on the experimental results and a pseudo-homogeneous kinetic model was proposed for the esterification. The activation energy and thermodynamic parameters including $\Delta G$, $\Delta S$ and $\Delta H$ were determined. The conversion rates of FFAs obtained from the established model were in good agreement with the experimental data.

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1. Introduction

As the global population grows, the consumption of petroleum products has been increasing fast, which results in rising concerns for the decreased fossil fuel reserves and increased oil prices. Therefore, in many countries researches on developing alternative energy are conducted in the hope of finding new energy resources that are both environmentally friendly and renewable [1]. Biodiesel, which consists of long carbon chain mono-alkyl esters (usually fatty acid methyl esters, FAME), was mainly produced from vegetable oils or animal fats by transesterification of triglycerides or esterification of free fatty acids (FFAs) with short-chain alcohols [2]. Biodiesel is one of the promising substitutes because of its biodegradability and nontoxicity [3–5]. In addition, its properties such as the viscosity and calorific value are similar to those of the petroleum diesel [6].

From the perspective of a chemical reaction, the refined vegetable oil is the desirable raw material for biodiesel production. However, as a major source of cooking oil in China, the output of vegetable oils falls far short of industrial demands. As a result, non-edible oil and waste grease such as the tung oil [7], acidified oil [8], waste cooking oil [9–11], microalgae [12,13] and Jatropha oil [14] become a main source of raw material for biodiesel syntheses. However, the acidified oil contains large amounts of FFAs and cannot be processed with the commonly practiced alkaline-catalysis technology. Therefore, the FFAs in acidified oil were firstly converted to mono-alkyl esters of fatty acid by acid-catalysts until the acid value was reduced to less than 2.0 mKOH/g. Then the converted FFAs were transesterified in the presence of base-catalysts. This scheme is usually referred to as the two-step acid/alkali-catalysis method [15].

The liquid acids such as methanesulfonic acid and sulfuric acid are usually used as the homogeneous acid catalysts [16]. However, the liquid acid-catalyzed esterification has many disadvantages such as the separation difficulty, side reactions, catalyst recovery and equipment corrosion [17]. Instead, many researchers chose to use solid acid catalysts like cation exchange resins [18,19], zeolite molecular sieves [20], and membrane catalysts [21–23]. Recently, cation exchange resins have attracted a considerable amount of attentions because of their multiple advantages such as easy separation of catalysts, mild reaction conditions, no equipment corrosion, high concentration of acid sites [24], and less wastewater. Furthermore, resins are available for long-time operations and commercial applications [25].

Although the research on the esterification of acidified oils has been carried out [8], data regarding to the kinetics and thermodynamic parameters such as $\Delta G$, $\Delta S$ and $\Delta H$ are scarce, especially when it comes to sulfonated cation exchange resins (SCER) as the catalyst. In the present work, the esterification of acidified oil with methanol in the presence of SCER was investigated. The effects of different reaction parameters such as the mass ratio of methanol to acidified oil, reaction temperature, and catalyst loading were studied to optimize the conditions for maximum conversion rate of FFAs. A
pseudo-homogeneous kinetic model was proposed on the basis of experimental data. The activation energy and thermodynamic parameters were determined.

2. Experimental

2.1. Materials

SCER, CH-A in the H\(^+\) form, supplied by Shandong Dongda Chemical Industry (Group) Company, Zibo, China, was used as the heterogeneous acid catalyst. Physicochemical properties of SCER are listed in Table 1. Fresh resins were washed with secondary deionized water to remove the free acids before being dried at 100.0 °C in a vacuum oven [18]. The acidified oil (138.61 mgKOH/g), kindly supplied by Zibo Jinxuan Resources and Environmental Technology Development Co., Ltd., Shandong, China, was firstly filtered to remove solid impurities and then was put in a rotary vacuum evaporator to remove the trace water. Methanol (purity > 99.7% w/w) and 95.0% (v/v) ethanol were purified from Yantai Shuangshuang Chemical Company, Yantai, China. Other chemical reagents were of analytical grade.

2.2. Esterification

Esterification was performed in a three-necked flask (250 mL) fitted with a reflux condenser to prevent the evaporation of methanol. The reactants were stirred in a magnetic whisk and heated in a water bath. The reaction temperature was monitored using a thermocouple which was inserted in the flask. The experiments were carried out at a stirring speed of 600 rpm which ensured the absence of the external mass transfer resistance [18,26]. A certain amount of acidified oil and methanol was preheated in the flask. A predetermined quantity of catalysts was added into the flask when desired temperature was achieved, and the reaction time was set to zero. The experiments were carried out under various conditions: methanol to acidified oil (20.0 g) mass ratio (0.5:1.0–3.5:1.0), catalyst loading (1.0–6.0 g), reaction temperature (30.0–65.0 °C) and reaction time (1.0–8.0 h). In each run, about 1.0 mL of sample was collected at 1.0 h interval and analyzed by decompression distillation to remove excess methanol and water. The acid value of the sample (0.25–0.30 g) was determined by a regular titration method following the China Standard-GB/T5530-2005 (Animal and Vegetable Fats and Oils-Determination of Acid Value and Acidity).

The reaction components were cooled down to room temperature when the reaction was completed. Then the solid phase (catalysts) and the liquid phase (methanol, the mixture of fatty acid methyl esters and unreacted acidified oil) were separated to recycle the catalysts which were impregnated and washed with anhydrous methanol to displace remnant acidified oil. Finally, the catalysts were filtered and dried in a vacuum oven overnight at 80.0 °C [18]. The sulfur content in the raw acidified oil and product oil was determined by a Microcoulometric Analyzer (WK-2D, Jiangsu Jiangfeng Electroanalytical Instrument Co., Ltd., Jiangsu, China). The morphology of the original and used catalysts was examined by a Scanning Electronic Microscope (SEM) (Quanta 200, FEI, USA). The pore volume was tested by nitrogen sorption at p/p\(_0\) = 0.99 (ASAP 2020, Micrometitics USA).

3. Results and discussion

3.1. Effect of mass ratio of methanol to acidified oil on the esterification

The esterification of acidified oil with methanol is limited by the equilibrium of chemical reactions. The conversion rate of FFAs could be improved by increasing the concentration of methanol because excessive amounts of methanol could promote the forward reaction. Fig. 1 shows the conversion rates of FFAs at different mass ratios of methanol to acidified oil of 0.5:1.0, 1.0:1.0, 1.5:1.0, 2.0:1.0, 2.5:1.0, 3.0:1.0 and 3.5:1.0, the temperature of 65.0 °C and catalyst loading of 5.0 g. It can be observed that the conversion rate of FFAs was increased by addition of methanol. When the mass ratio of methanol to acidified oil rose from 0.5:1.0 to 2.5:1.0, the conversion rate of FFAs increased by addition of methanol. When the mass ratio of methanol to acidified oil rose from 0.5:1.0 to 2.5:1.0, the conversion rate of FFAs increased from 88.68% to 91.87%. However, the conversion rate slightly decreased from 91.87% to 87.13% when mass ratio changed from 2.5:1.0 to 3.5:1.0 at 8.0 h of operation. Similar results could be found in some reported literatures [21,27]. It showed that the concentration of methanol played a major role, and the increase in the mass ratio of methanol to acidified oil could improve the solubility of acidified oil or FFAs in methanol which would promote the collision of FFAs with methanol molecules [6]. The maximum conversion rate of 91.87% was attained at the mass ratio of methanol to acidified oil of 2.5:1.0 after 8.0 h of operation. However, the concentration of the catalyst decreased with an increase in the mass ratio of methanol to acidified oil. Moreover, methanol molecules and sulfonic acid group (–SO\(_3\)H) could form hydrogen bonds easy because methanol is a polar molecule [21], and could be adsorbed onto the active sites of the catalyst in the esterification system. The esterification was inhibited due to the poor accessibility of active sites when the methanol reached a certain high concentration level. When the methanol concentration reached a certain high level, the conversion rate of FFAs decreased [18]. Therefore, the mass ratio of methanol...
Effects of different reaction temperatures on the esterification. Employed reaction temperatures: (■) 30.0 °C, (●) 40.0 °C, (▲) 50.0 °C, (▼) 60.0 °C and (◀) 65.0 °C.

3.2. Effect of reaction temperature on the esterification

As the temperature usually affects the chemical reactions, the effects of temperature on the conversion rate of FFAs were investigated at the temperatures of 30.0 °C, 40.0 °C, 50.0 °C, 60.0 °C and 65.0 °C, mass ratio of methanol to acidified oil of 2.5:1.0, reaction time 8.0 h and catalyst loading of 5.0 g. Fig. 2 shows that conversion rate of FFAs increased rapidly with the increase in reaction temperature. For example, when the reaction temperature rose from 30.0 °C to 65.0 °C, the conversion rate of FFAs increased from 36.70% to 91.87%. A possible reason was that the increase in temperature could reduce the viscosity of acidified oil, which would enhance the contact between acidified oil and methanol, leading to a higher conversion rate of FFAs [4]. Therefore, the temperature is an important factor affecting the esterification. The relationship between the conversion rate of FFAs and temperature is very useful in calculating the equilibrium constant, activation energy and other thermodynamic parameters [28]. In an endothermic reaction, the reaction equilibrium constant and the conversion rate of FFAs increased with the reaction temperature. In general, conversion rates were low at low temperatures, as shown in Fig. 2. However, high temperatures would cause the excessive loss of alcohol due to evaporation, especially when the reaction temperature exceeded the boiling point of methanol [29]. Thus, the optimal reaction temperature was observed to be 65.0 °C.

3.3. Effect of catalyst loading on the esterification

The conversion rates of FFAs at different catalyst amounts of 1.0 g, 2.0 g, 3.0 g, 4.0 g, 5.0 g and 6.0 g, the temperature of 65.0 °C, mass ratio of methanol to acidified oil of 2.5:1.0 and reaction time of 8.0 h, were summarized in Fig. 3. As the amount of the catalyst increased from 1.0 g to 6.0 g, the conversion rate of FFAs rose correspondingly. This could be explained by an increase of active catalytic sites available for the reaction as the catalyst loading increased. The same results were described by Castanheiro et al. [23]. The conversion rate of FFAs increased rapidly from 53.76% to 91.87% when the SCER loading rose from 1.0 g to 5.0 g. However, the increase was no longer significant when the catalyst loading exceeded 5.0 g. For example, the conversion rate of FFAs increased slightly from 91.87% to 92.31% when SCER loading was increased from 5.0 g to 6.0 g. The possible reason was that there were not sufficient active catalytic sites in the reactant molecules to catalyze the reaction [4]. Apart from the increase in the conversion rate of FFAs, the viscosity of the reaction system increased when catalyst loading was over 5.0 g. Hence, the optimal SCER loading was determined to be 5.0 g.

The interactions between catalyst and reactant were more obvious at the early stage of the reaction [30]. It can be found in Fig. 3 that the conversion rate of FFAs gradually increased with the SCER loading. The FFAs conversion rate increased from 14.56% to 51.91% as the SCER loading increased from 1.0 g to 5.0 g at 1.0 h of operation. Therefore, it is very significant to study the initial rate of the reaction, which was described by Eq. (1) [31].

\[-r_{A0} = \left( \frac{C_{A0}X_A}{t} \right) \]

where, \( r_{A0} \) is the initial rate of reaction (mol/(L·h)), \( X_A \) is the conversion rate of FFAs, \( C_{A0} \) is the initial concentration of FFAs (mol/L) and \( t \) is the reaction time (1.0 h).

Fig. 4 shows the initial reaction rates as the catalyst loading increased from 1.0 g to 5.0 g at the reaction temperature of 65.0 °C,
mass ratio of methanol to acidified oil of 2.5:1.0, and reaction time of 8.0 h. A linear relationship between the initial rate of reaction and catalyst loading was observed. The uncatalyzed initial reaction rate was determined by the intersection of this line with the y-axis and calculated from the following mathematical equation.

\[ y = 0.04663x + 0.02897 \]  
\[ y \text{ is the SCER loading. Eq. (2) is valid only at the reaction temperature of } 65.0 \, ^\circ\text{C}, \text{mass ratio of methanol to acidified oil of } 2.5:1.0, \text{and reaction time of } 1.0 \text{h.} \]

3.4. Catalyst reusability

To test the activity and stability of the SCER, a series of reactions were carried out at the optimum operating conditions: catalyst loading 5.0 g, reaction temperature 65.0 °C, mass ratio of methanol to acidified oil 2.5:1.0 and reaction time 8.0 h. The variations of the conversion rate of FFAs from 91.87% to 76.58%. From the third to fifth run, the catalyst showed a good catalytic activity in the first run where the FFAs conversion rate was 91.87%. However, the catalyst activity greatly decreased in the second run, resulting in a significant drop of the conversion rate of FFAs from 91.87% to 76.58%. From the third to fifth run, the activity of SCER declined slightly, resulting in a slight drop from 74.86% to 69.52%. The activity of the SCER was measured by Ion Exchange Capacity (IEC). IEC was expressed as milliequivalents of exchangeable ion (H\(^+\)) per gram of dry polymer. The resin samples were soaked in 0.1 mol/L sodium chloride (NaCl) aqueous solution and stirred to promote the sodium cation-proton (Na\(^+\)-H\(^+\)) exchange for 24.0 h. Then the acid concentration in the solution was determined by titration with the potassium hydroxide solution (0.1 mol/L KOH) using the phenolphthalein as an endpoint indicator. The IEC values of the samples were calculated using Eq. (3) and the results are shown in Table 2.

\[ \text{IEC} = \frac{C_{\text{KOH}}V_{\text{KOH}}}{W_{\text{dry}}} \]  
\[ \text{where, } IEC \text{ is the ion exchange capacity (meq/g); } C_{\text{KOH}} \text{ is the concentration of KOH (mol/L); } V_{\text{KOH}} \text{ is the volume of KOH consumed (mL) and } W_{\text{dry}} \text{ is the weight of the dry resin (g).} \]

As shown in Table 2, the IEC values of the samples decreased with each run of recycling. The catalyst activity sharply decreased after the second use. In the subsequent experiments, the activity of SCER declined slightly. One possible reason for the decrease of activity might include the loss of catalyst and sulfur leaching in the course of breaking [32]. Sulfur leaching occurred due to the detachment of sulfonic acid group from the polymer matrix. It was also observed from the Micro-coulometric Analyzer that the contents of sulfur in the raw acidified oil and the first product were 78.5 ppm and 96.3 ppm, respectively. This indicated that sulfur leaching contributed to the decrease of catalyst activity. Another possible reason for the decrease of activity was the contamination of the surface of SCER that resulted from the pore blockage. Contamination included the presence of metal ions in the acidified oil [4]. The pore volumes of catalyst in the second run and first run were 1.188 mL/g and 0.977 mL/g, respectively. After the fifth run, the catalyst under the experimental conditions was easily broken and could not be used for subsequent experiments. A series of SEM images are presented in Fig. 6 for comparison of the original and used catalysts. The fresh macroporous SCER exhibited smooth surfaces (Fig. 6a), which became rough and bumpy after the second run (Fig. 6b).

4. Kinetics of esterification

Using SCER as the catalyst, the esterification of methanol with acidified oil for producing mixed fatty acid methyl ester and water was described as follows:

\[ \text{R}_1\text{COOH(F)} + \text{CH}_3\text{OH(M)} \xrightarrow{\text{Catalyst}} \text{R}_1\text{COOCH}_3(\text{E}) + \text{H}_2\text{O(W)} \]  
\[ \text{(4)} \]

The kinetic model was established under the following hypotheses:

(1) The esterification was a reversible reaction process. The reaction rate was controlled by chemical reaction under the operating conditions;
(2) Compared with the catalyzed reaction the spontaneous reaction without catalyst could be neglected;
(3) All active catalytic sites at the catalyst surface were identical.

Generally, the esterification was controlled by chemical reaction and diffusion. In this study the reaction rate was controlled by the chemical reaction step. In order to verify this assumption, theoretical calculations were carried out with respect to external and internal mass transfer resistances.

4.1. External mass transfer resistance

All experiments were performed at a stirring speed of 600 rpm. On the basis of the dimensionless Mears parameter (\(C_M\)), theoretical calculation was used to examine the effect of the external mass transfer resistance on the conversion rate of FFAs [33].

\[ C_M = \frac{r_{A,\text{obs}}\rho_br_{in}}{k_cC_{Ab}} \]  
\[ \text{(5)} \]

\[ r_{A,\text{obs}} = \frac{r_{A0}}{W_c} \]  
\[ \text{(6)} \]
where, $\rho_b$ is the bulk density of catalyst (g/mL), $R_c$ is the catalyst radius (m), $n$ is the reaction order, $C_{ab}$ is the bulk concentration of limiting reactant (mol/L) and $k_c$ is the mass transfer coefficient (m/s) was expressed in the form of the Dwivedi-Upadhyay mass transfer correlation [28].

$$k_c = \frac{2D_{AB}}{d_p} + 0.31N_{Sc}^{2/3} \left( \frac{\Delta \rho \mu_c g}{\rho_c^2} \right)^{1/3} \tag{7}$$

where, $D_{AB}$ is the diffusivity of the solute A (limiting reactant) in the solution (m$^2$/s), $d_p$ is the diameter of the catalyst (m), $\mu_c$ is the viscosity of the solution (Pa·s), $g$ is the gravitational acceleration (m/s$^2$), $N_{Sc}$ is the Schmidt number (defined as $\mu_c/(\rho_c d_p)$) and $\Delta \rho$ is the absolute differential density of the catalyst and solution (g/mL).

The calculated value of the dimensionless Mears parameter was 0.15 which were in accordance with the experimental results.

The calculated value of the dimensionless Mears parameter was less than 1.0, implying that the external mass transfer diffusion can be negligible in the kinetic study [33]. As listed in Table 3, the calculated Mears parameters at different temperatures were less than 0.15 which were in accordance with the experimental results.

### 4.2. Internal mass transfer resistance

In order to consider the effect of the internal mass transfer resistance on the conversion rate of FFAs, the dimensionless Weisz-Prater parameter ($C_{WP}$) was introduced as follow:

$$C_{WP} = \frac{-T_{abs}}{D_{eff}C_A} \tag{8}$$

where, $\rho_c$ is the catalyst density (g/mL), $R_c$ is the effective radius of catalyst (the ratio of catalyst pellet volume to the external surface area) (m), $C_A$ is the concentration of limiting reactant in the mixture (mol/L) and $D_{eff}$ is the effective diffusivity (m$^2$/s).

$$D_{eff} = \xi_v^2 D_{lm} \tag{9}$$

where, $\xi_v$ is the void fraction and $D_{lm}$ is the diffusivity of limiting reactant in the mixture (m$^2$/s).

If the value of the Weisz-Prater parameter is less than 1, the internal mass transfer usually could be negligible. As shown in Table 3, the experimental values were found to be less than 1.0.

The experimental results confirmed that the external and internal mass transfer resistances were negligible in the kinetic study. Theoretical calculations were in accordance with assumptions. The intrinsic kinetics could be studied under the current experimental conditions.

Different kinetic models can be described for the esterification based on heterogeneous and homogeneous approaches. It was worth noting that the pseudo-homogeneous approach was successfully used in strong polar solvents [34]. Methanol, as a strong polar solvent, was used in this study. So the forward and reverse reactions were assumed to be pseudo-homogeneous second-order reaction [18,32].

The rate of reaction could be described as:

$$-\frac{dC_F}{dt} = k_1C_F C_M - k_2C_F C_W \tag{10}$$

where, $C$ is the concentration (mol/L), and the subscripts F, M, E and W represent acidified oil, methanol, mixed fatty acid methyl ester and water, respectively. $k_1$ is the rate constant for the forward reaction and $k_2$ is that for the reverse reaction.

When the mass ratio of methanol to oil is 2.5:1.0, the approximate calculated molar ratio of methanol to oil is 31.8:1.0. The equation of kinetics can be expressed as follows:

$$K = \frac{k_1}{k_2} \tag{11}$$

$$-\frac{d(C_{F0}(1-x))}{dt} = k_1(1-x)(31.8-x)C_{F0}^2 - k_2x^2C_{F0}^2 \tag{12}$$

According to $\int \frac{dx}{\sqrt{\alpha^2 - x^2}} = \frac{1}{2\alpha} \ln \left| \frac{\sqrt{\alpha^2 - x^2}}{\alpha} \right| + C$, the kinetic equation can be transformed into:

$$\ln \left( \frac{2(K-1)x - 32.8K - \alpha}{2(K-1)x - 32.8K + \alpha} \right) = k_2\alpha C_{F0} t \tag{13}$$

where, $\alpha = \sqrt{948.64K^2 + 127.2K}$, where, $C_{F0}$ is the initial concentration of FFAs, $x$ and $K$ refer to the conversion rate of FFAs and the reaction equilibrium constant, respectively.

The kinetic equation was valid if the left side of Eq. (13) was linearly related to time $t$. Experiments were carried out at different temperatures (30.0 °C, 40.0 °C, 50.0 °C, 60.0 °C and 65.0 °C). The other

Table 3

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>Catalyst loading (g)</th>
<th>$C_M$</th>
<th>$C_{WP}$</th>
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</thead>
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<td>5.0</td>
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<td>7.22E-5</td>
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<td>5.98E-4</td>
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<td>1.74E-3</td>
</tr>
<tr>
<td>333.15</td>
<td>5.0</td>
<td>1.61E-3</td>
<td>2.95E-3</td>
</tr>
<tr>
<td>338.15</td>
<td>5.0</td>
<td>1.87E-3</td>
<td>3.42E-3</td>
</tr>
</tbody>
</table>

Fig. 6. SEM images of the surfaces of the SCER in different states. (a) Fresh and (b) used.
operating conditions were kept at the mass ratio of methanol to oil of 2.5:1.0 and catalyst loading of 5.0 g. The Arrhenius equation was used to calculate the activation energy and pre-exponential factor and to predict the relationship between the reaction time and the conversion rate of FFAs.

\[
k = A \exp\left(\frac{-E_a}{RT}\right)
\]

(14)

The reaction rate constants at different temperatures can be calculated to achieve the activation energy \(E_a\) and pre-exponential factor \(A\) according to Eq. (15) converted from Eq. (14).

\[
\ln k = \frac{-E_a}{RT} + \ln A
\]

(15)

4.3. Reaction rate constants

The linear relationship between the left side of Eq. (13) and time \(t\) was established at the temperature of 60.0 °C as shown in Fig. 7. The rate constant for the reverse reaction \(k_2\) was determined from the slope of the line. The rate constant for the forward reaction \(k_1\) was calculated using \(k_2\) and equilibrium constant \(K\). It was found that the \(k_1\) and \(k_2\) values increased with the reaction temperature, indicating that the esterification of acidified oil with methanol catalyzed by SCER is an endothermic reaction. The kinetic of esterification can be described by Eq. (13).

4.4. Activation energy and pre-exponential factor

Fig. 8 shows a linear relationship between \(\ln k\) and \(1/T\). The reaction activation energy \(E_a\) was confirmed by the slope of the line. It was very significant to determine the reaction activation energy and validate the correctness of the kinetics model. The kinetic parameters of esterification such as activation energy, the pre-exponential factor and rate constants were calculated from the Arrhenius equation using Origin 8.0. The results indicated that the pre-exponential factor \((A)\) and activation energy \((E_a)\) for the forward reaction between acidified oil and methanol were found to be 117.67 (mol·L·s)\(^{-1}\) and 46.76 kJ/mol, and those for the reverse reaction were 6.05 × 10\(^{-3}\) (mol·L·s)\(^{-1}\) and 15.56 kJ/mol, respectively. It showed that the esterification was kinetically controlled rather than diffusively controlled due to the high activation energy [35]. Therefore, the rate of reaction can be expressed as follows:

\[
r = 117.67 \exp\left(-\frac{46.76}{RT}\right)C_M - 6.05 \times 10^{-3} \exp\left(-\frac{15.56}{RT}\right)C_E
\]

(16)

4.5. Model prediction

In order to verify the accuracy of the kinetic model, a series of experiments were carried out under the conditions of the mass ratio of methanol to acidified oil of 2.5:1.0, catalyst amount of 5.0 g, reaction temperature of 60.0 °C, and reaction time of 8.0 h. The agreement of the experimental data with the predicted model was evaluated by comparing the experimental conversion rate of FFAs with the theoretical results. Fig. 9 shows that the reaction rate raised significantly as the reaction time increased. Root mean square (RMS) error was
used to evaluate the agreement of experimental data with theoretical prediction. RMS was described by Eq. (17)

$$ \text{RMS} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (X_{\text{exp}}^i - X_{\text{cal}}^i)^2} $$  \hspace{1cm} (17)

where, $X_{\text{exp}}$ and $X_{\text{cal}}$ are the experimental and theoretical predicted acid conversion rates, respectively. $N$ is the number of samples.

The result showed that the error between the experimental data and the predicted values was less than 3.0%, confirming that the predictive kinetic model was in good agreement with the experimental results.

5. Thermodynamics of esterification

The esterification was assumed to be a pseudo-homogeneous second-order reversible reaction. Thus, the equilibrium constant for the reaction can be defined by Eq. (18)

$$ K_{\text{eq}} = \frac{[F][W]}{[M][E]} $$  \hspace{1cm} (18)

where, $[F]$, $[M]$, $[E]$, $[W]$ represent the equilibrium concentrations of acidified oil, methanol, mixed fatty acid methyl ester and water, respectively.

According to Van't Hoff equation, the Gibbs free energy was expressed as follows:

$$ \Delta G = -RT \ln K $$  \hspace{1cm} (19)

The values of Gibbs free energy of the reactions at different temperatures were 6.16 (30.0 °C), 5.64 (40.0 °C), 4.76 (50.0 °C), 4.13 (60.0 °C) and 3.10 kJ/mol (65.0 °C), respectively. If the enthalpy change with the temperature was assumed to be constant, Eq. (20) was available.

$$ \ln K = \left( \frac{-\Delta H}{RT} \right) + \left( \frac{\Delta S}{R} \right) $$  \hspace{1cm} (20)

Eq. (20) could be transformed into Eq. (21)

$$ -R \ln K = \left( \frac{\Delta H}{T} \right) - \Delta S $$  \hspace{1cm} (21)

Fig. 10 shows that there was a linear relationship between $-\ln K$ and $1/T$. The reaction enthalpy ($\Delta H$) was calculated from the slope of the line and the reaction entropy ($\Delta S$) was determined using the intercept. The reaction enthalpy and entropy were found to be 31.21 kJ/mol and 82.10 J/(K·mol), respectively.

6. Conclusions

The kinetics of the pre-esterification of acidified oil with methanol in the presence of SCER was investigated, concluding that the esterification followed the second-order reaction. The highest conversion rate of 91.87% was obtained at the optimal conditions. A pseudo-homogeneous kinetic model was introduced to describe the esterification. The thermodynamic parameters including $\Delta S$ and $\Delta H$ were found to be 82.10 J/(K·mol) and 31.21 kJ/mol, respectively. The model to predict the conversion rate of FFAs was in good agreement with the experimental results. The use of acidified oil as low-cost feedstock and catalyzing by SCER displayed enormous application potentials for the industrial biodiesel production.

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