The evaluation of various kinetic models for base-catalyzed ethanolysis of palm oil
Sanaz Shahla, Gek Cheng Ngoh *, Rozita Yusoff

Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

A R T I C L E   I N F O
Article history:
Received 25 July 2011
Received in revised form 2 November 2011
Accepted 3 November 2011
Available online 11 November 2011

Keywords:
Transesterification
Palm oil
Ethanolysis
Kinetic models
Activation energy

A B S T R A C T
In this paper, the kinetics of palm oil ethanolysis with various models have been investigated in a temperature range of 25–55 °C. The highest yield was achieved when the conversion to ethyl ester was 97.5 ± 0.5% in the stated temperature range, using ethanol:oil molar ratio of 12:1, and 1.0 wt.% sodium ethoxide. The level of conformity of the reaction with reversible second order, irreversible second order and first order kinetic models were evaluated by means of the $R^2$ values of the linear curves. The ethanolysis showed the best conformity with irreversible second order kinetic model with 92–98% level of confidence. The reaction rate constants were within 0.018–0.088 dm$^3$/mol min and the activation energy of the reaction was 42.36 kJ/mol.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Partially degrading chemical products have been proven to be harmful to the environment and living creatures. Thus, biodegradability and renewability of the products are important features for study (Graziani and Fornasiero, 2007). Application of vegetable oil alkyl esters is extended to include the production of biodegradable materials particularly bio-fuels, bio-surfactants and bio-lubricants (Dossat et al., 2002). Conversion of the vegetable oils to alkyl esters through transesterification using mono-alcohols qualifies their required specifications of the fuel such as viscosity, boiling point and flash point (Tiwari and Ghosal, 2007). Methanol is widely used in the formulation of bio-fuels due to its low cost and availability (Fukuda et al., 2001; Shahla et al., 2010). However, it has been documented that ethanol can replace methanol to improve the renewability of the produced bio-fuel. Moreover, ethanol offers enhanced solubility for vegetable oils and by applying minimum agitation speed of 600 rpm the mass controlled regime in ethanolysis reactions can be eliminated (Encinar et al., 2002; Marjanovic et al., 2010).

Previous studies on kinetics of vegetable oils alcoholysis are summarized in Table 1. It can be seen from this table that ethanolysis processes of vegetable oils are described with models considering different kinetic orders. In the findings reported so far, there is lack of information on the kinetics of ethanolysis of palm oil. In this work, three different kinetic models for palm oil ethanolysis were evaluated to determine the best conforming kinetic model for the reaction involved.

2. Kinetic model development

Transesterification of vegetable oils with mono-alcohols such as methanol and ethanol to produce alkyl esters are as shown in Eq. (1):

\[
\text{Triglyceride} + 3\text{Mono-alcohol} \rightarrow \text{Diglyceride} + \text{Alkyl ester}
\]

\[
\text{Diglyceride} + \text{Mono-alcohol} \rightarrow \text{Monoglyceride} + \text{Alkyl ester}
\]

\[
\text{Monoglyceride} + \text{Mono-alcohol} \rightarrow \text{Glycerol} + \text{Alkyl ester}
\]

The three stepwise reactions can be simplified into an overall reaction as shown in Eq. (2):

\[
\text{Triglyceride} + 3\text{Mono-alcohol} \rightarrow 3\text{Alkyl ester} + \text{Glycerol}
\]

In general, a molar ratio of alcohol to oil higher than the stoichiometric amount is required for the initiation and acceleration of the transesterification. Due to the presence of excessive alcohol...
in the reaction media, researchers often assumed that transformation of intermediates i.e. diglyceride and monoglyceride to alkyl ester occurs rapidly. Therefore, most of the kinetic studies on the methanolysis and ethanolation of vegetable oils were based on the overall reaction (Georgogianni et al., 2008; Li et al., 2009; Marjanovic et al., 2010; Om Tapanes et al., 2008; Richard et al., 2011; Silva et al., 2009). The overall equation of transesterification of palm oil with ethanol is rewritten in the form of Eq. (3).

\[ A + 3B \rightarrow 3C + D \]  

(3)

where A, B, C and D represent palm oil, ethanol, ethyl ester, glycerol and \( k_1 \) and \( k_2 \) refer to the rate constants for the forward reaction and the reverse reaction, respectively.

The reversible second order kinetic model is comprehensive and can be used for the investigation of chemical transesterification. A few assumptions have been made by researchers to simplify the kinetic model of vegetable oil ethanolysis such as irreversible second order model to first order kinetic model. In this work the conformity of alkaline ethanolation of palm oil was tested via different kinetic models including the reversible second order, irreversible second order and first order kinetic models.

2.1. Reversible second order kinetic model

The kinetic model of chemical transesterification of vegetable oils (Eq. (3)) is a reversible second order model as shown in Eq. (4). During the reaction, one mole of palm oil has been transesterified into three moles of ethyl ester and one mole of glycerol. Substitution of these equivalents into Eq. (4) results in Eq. (5). Furthermore, conversion of palm oil (\( \chi_A \)) can be obtained using Eq. (6). The integration of this equation yields Eq. (7) in which, \( M = \frac{C_{BO}}{C_{AO}} \) C_{BO} and C_{AO} are the initial molar concentrations of palm oil and ethanol, respectively. The equilibrium constant, \( K = \frac{k_1}{k_2} \) and \( A \) can be calculated from the integrated Eqs. (8) and (9). The equations are the modified forms of the equations developed by Stamenkovic et al. (2008).

\[ -r_A = -\frac{dC_A}{dt} = k_1C_AC_B - k_2C_CC_D \]  

(4)

\[ \frac{d\chi_A}{dt} = k_1C_{AO}[1 - \chi_A](M - 3\chi_A - 3k\chi_A^2) \]  

(5)

\[ \chi_A = \frac{C_{AO} - C_A}{C_{AO}} \]  

(6)

\[ \frac{1}{2C_{AO}\sqrt{A}} \ln \frac{6(1 - K)\chi_A - (M + 3)}{6(1 - K)\chi_A - (M + 3) + \sqrt{A}} = Kt + C \]  

(7)

\[ K = \frac{(1 - \chi_{AE})(M - 3\chi_{AE})}{3\chi_{AE}^2} \]  

(8)

\[ A = (M + 3)^2 - 12M(1 - K) \]  

(9)

The conformity of the reaction with reversible second order kinetic model was tested by plotting \( Y(t) \) versus \( t \). \( Y(t) \) was calculated based on the terms on the left side of Eq. (7), whereas the integration constant of \( C \) was equal to the intercept of the achieved trend line.

2.2. Irreversible second order kinetic model

By assuming the fast disappearance of the reaction intermediates being transformed into alkyl esters, the kinetic model of the reaction can be simplified to Eq. (10). This equation can be further expressed in the form of Eq. (11) which is integrated to Eq. (12). Conformity of the reaction kinetics with irreversible second order kinetic model is tested through plotting \( Y(t) = \frac{1}{(M - 3\chi_A)(1 - \chi_A)} \) versus \( t \).

\[ -r_A = -\frac{dC_A}{dt} = k_1C_AC_B \]  

(10)

\[ \frac{d\chi_A}{dt} = k_1C_{AO}(1 - \chi_A)(M - \chi_A) \]  

(11)

\[ \frac{1}{C_{AO}(M - 3)} \ln \frac{(M - 3\chi_A)}{(1 - \chi_A)} = k_1t + C \]  

(12)

2.3. First order kinetic model

Some researchers assumed that, by minimizing the alcohol loss during the reaction, the concentration of vegetable oil can be considered as the sole determining factor of the reaction kinetics (Joelaniingsih et al., 2008). Hence, the reaction kinetic model can be simplified into a pseudo first order kinetic model as shown in Eq. (13). This equation was rearranged in terms of palm oil conversion as shown in Eq. (14). Subsequent integration of this first order equation yields Eq. (15).

\[ -r_A = -\frac{dC_A}{dt} \]  

(13)

\[ \frac{d\chi_A}{dt} = k_1(1 - \chi_A) \]  

(14)

\[ -\ln(1 - \chi_A) = k_1t + C \]  

(15)

The conformity of the reaction with the first order kinetic model can be tested by plotting \( Y(t) = -\ln(1 - \chi_A) \) versus \( t \). Meanwhile, the activation energy of the reaction can be calculated using Arrhenius equation as shown in Eq. (16):

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

(16)
where \( E_a \) is the activation energy and \( A \) is the frequency factor.

By plotting \( \ln k \) versus \( 1/T \), the slope and intercept of the trend line gives the value of \(-E_a/R\) and \( A \), respectively.

## 3. Methods

HCl 0.1 N Titrisol and \( n \)-hexane analytical grade were purchased from Merck. Palm oil (refined, bleached and deodorized) was obtained from local market. Ethanol and sodium ethoxide were purchased from R&M Chemicals and Fluka, respectively.

Palm oil, ethanol and sodium ethoxide that was previously dissolved in ethanol were charged into a glass reactor. The desired reaction temperatures were monitored by a circulating water bath. Ethanol loss from the reactor was minimized using a Graham coil condenser. Ethanol to oil molar ratio of 12:1 and sodium ethoxide concentration of 1.0 wt.% were used for the kinetic studies of palm oil ethanolysis where the temperature was in the range of 25–55°C and the agitation speed was fixed at 600 rpm.

Samples of the reaction blend were taken at certain time intervals using a Pasteur pipette and added to the 1.5 ml centrifuge tubes which already contained 0.1 ml of 0.1 N HCl for neutralization of the catalyst and termination of the reaction. Samples were centrifuged for 15 min and then allowed to rest for a few hours to ensure the separation of the reaction phases. The ethyl ester phase was withdrawn by Pasteur pipette and purified by passing through a 0.2 µm PTFE syringe filter. Samples of the ethyl ester were analyzed by Agilent GC-MSD equipped with 30 m × 0.25 mm id × 0.25 µm DB-Wax column, using hydrogen as the carrier gas.

## 4. Results and discussion

Throughout the experiments, agitation was applied to initiate the reaction, causing the formation of white slurry which turned into a clear yellow blend within a few seconds. This induction period of the catalyst is assumed to be the time required for catalyst activation. It continued for 50 s, 20 s, 12 s and 7 s at increased reaction temperatures of 25°C, 35°C, 45°C and 55°C, respectively. The induction period is thought to be the mass transfer controlling stage of the reaction. It can be seen that this interval is shorter than 1 min at 25°C and it decreases significantly at higher reaction temperatures. Therefore, with respect to the short induction period and by applying agitation speed of 600 rpm, the mass transfer effect could be ignored in the transesterification with ethanol (Encinar et al., 2002; Marjanovic et al., 2010) and the kinetic models were developed solely based on the chemical reactions.

### 4.1. Conversion of palm oil to ethyl ester

Kinetic study on transesterification of palm oil with ethanol was conducted at a temperature range of 25–55°C using ethanol/oil molar ratio of 12:1 and 1.0 wt.% catalyst. Conversion results of the reaction blends to ethyl esters at different time intervals and temperatures are summarized in Table 2 and plotted in Fig. 1. It can be observed from these results that the ethyl ester yield from ethanolysis of palm oil reached a maximum of 97.5 ± 0.5% at the equilibrium point for all reaction temperatures. As the reaction temperature was increased, the same conversion was achieved but at shorter times. It was observed that ethanolysis at 25°C, 35°C, 45°C, and 55°C reached to the equilibrium point with reaction times of 30 min, 15 min, 10 min, and 6 min, respectively. This observation concurs with the results obtained for the ethanolysis of castor oil at 30°C, which resulted in 99% ethyl ester in 30 min (Silva et al., 2009) and also the ethanolysis of sunflower oil which completed within 20–30 min (Marjanovic et al., 2010).

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>25</th>
<th>35</th>
<th>45</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>6.59</td>
<td>13.04</td>
<td>63.23</td>
<td>68.52</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>12.40</td>
<td>58.80</td>
<td>74.55</td>
<td>83.71</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>63.92</td>
<td>68.55</td>
<td>85.58</td>
<td>87.36</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>66.72</td>
<td>70.93</td>
<td>87.41</td>
<td>91.51</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>70.82</td>
<td>79.00</td>
<td>93.76</td>
<td>96.30</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>77.88</td>
<td>80.96</td>
<td>95.99</td>
<td>97.34</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>89.87</td>
<td>91.61</td>
<td>97.95</td>
<td>97.52</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>92.54</td>
<td>97.06*</td>
<td>97.34</td>
<td>96.01</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>94.16</td>
<td>96.01</td>
<td>96.82</td>
<td>97.19</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td>96.58</td>
<td>96.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>97.30*</td>
<td>96.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>97.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>96.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>96.66</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Equilibrium conversion of palm oil = highest conversion at each reaction temperature.

### 4.2. Kinetic model

A number of models implementing different kinetic orders for ethanolysis of vegetable oils have been reported in the literature. However, there are no studies reporting whether using simplifying assumptions for the development of the kinetic model affects on the conformity of the model. This work evaluates the conformity of the alkaline catalyzed ethanolysis of palm oil with different kinetic models from the most detailed equations to the simplest version. Kinetics of the reaction was tested with reversible second order, irreversible second order and first order kinetic models according to Eqs. (7), (12), and (15), respectively. The results obtained are presented in Figs. 2–4. As can be seen in these figures, the slope and the intercept of the trend lines give the forward
reaction constant and the model integration constant, respectively. Furthermore, it is important to note that the values of $R^2$ of the trend lines presented in Table 3 give the confidence levels of the reaction conformity with the corresponding kinetic model. Here, the conformity of the experimental results with all the kinetic models from the simplest form to the most specified one is discussed. Table 3 shows that the alkaline catalyzed ethanolysis of palm oil gave 90.1–97.6% confidence level in conformity with pseudo first order kinetic model while the lowest confidence of 90.1% applies to the reaction at 25°C and the highest confidence of 97.6% corresponds to the reaction at 55°C.

When comparing the $R^2$ values of the irreversible second order with the pseudo first order kinetic models, Table 3 illustrates that the reactions at temperature range of 25–45°C showed better conformity with the irreversible second order kinetic model than the pseudo first order kinetic model. Meanwhile, the reaction at 55°C follows both pseudo first order and irreversible second order kinetic models with a close level of conformity. On the other hand, when comparing the reversible second order with the irreversible first order kinetic models at 25°C, the former gave better conformity. However, reactions at other temperatures indicated less conformity with reversible second order kinetic model than both irreversible second order and first order kinetic models.

It is apparent that taking all the temperature range into consideration, chemical ethanolysis of palm oil in this study fitted well with an irreversible second order kinetic model. Since the reaction at 25°C showed minimum confidence level of conformity, the inclusion of the effect of mass transfer controlling regime in the kinetics study might gave a better conformity with all the kinetic models studied. This agrees with the findings reported on the ethanolysis of sunflower oil (Richard et al., 2011).

### 4.3. Rate constants and activation energy

The best conforming kinetic model for the transesterification of palm oil with ethanol was the irreversible second order. Table 4 presents the rate constants for this model, which were calculated from the slope of the trend lines in Fig. 3. The rate constant at 25°C was found to be 0.018 dm$^3$/mol min and it increased to 0.088 dm$^3$/mol min at 55°C which clearly indicates that elevated temperatures accelerate ethanolysis and reduce reaction duration to achieve maximum product. This observation is in agreement with the equilibrium times of the reaction at different temperatures as previously shown in Table 2. The rate constants of the forward and reverse reactions of alkaline ethanolysis of C12–C18 fatty acids based on a reversible second order kinetic model were in the range of $0.0021–0.0174$ dm$^3$/mol min and $0.0016–1.1673$ dm$^3$/mol min, respectively (Camara and Aranda, 2011). The rate constants obtained in this work were obviously within the range reported by other researchers (Pisarello et al., 2010).

Based on Eq. (16) and Fig. 5., the calculated activation energy of the ethanolysis of palm oil was 42.36 KJ/mol which also agreed

---

**Table 3**

<table>
<thead>
<tr>
<th>Reaction temperature (°C)</th>
<th>Pseudo first-order kinetic model (Eq. (15))</th>
<th>Irreversible second-order kinetic model (Eq. (12))</th>
<th>Reversible second-order kinetic model (Eq. (7))</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.901</td>
<td>0.918</td>
<td>0.906</td>
</tr>
<tr>
<td>35</td>
<td>0.968</td>
<td>0.978</td>
<td>0.901</td>
</tr>
<tr>
<td>45</td>
<td>0.942</td>
<td>0.946</td>
<td>0.934</td>
</tr>
<tr>
<td>55</td>
<td>0.976</td>
<td>0.975</td>
<td>0.797</td>
</tr>
</tbody>
</table>

**Table 4**

<table>
<thead>
<tr>
<th>Reaction temperature (°C)</th>
<th>Rate constant (dm$^3$/mol min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.018</td>
</tr>
<tr>
<td>35</td>
<td>0.037</td>
</tr>
<tr>
<td>45</td>
<td>0.055</td>
</tr>
<tr>
<td>55</td>
<td>0.088</td>
</tr>
</tbody>
</table>
well with the activation energies of alkaline transesterification of vegetable oils reported in Table 1.

5. Conclusions

Ethanolysis of palm oil yielded 97.5 ± 0.5% ethyl ester at a temperature range from 25 °C to 55 °C. The catalyst activation time and the reaction duration were inversely proportional to the temperature. Palm oil ethanolysis conformed well to an irreversible second order kinetic model at temperatures up to 45 °C whereas the reaction conformed to both pseudo first order and irreversible second order kinetic models at 55 °C. The rate constants and activation energy obtained were within the range of findings of other researches. The present investigation has verified that modification of the kinetic models into simpler forms affect its level of conformity.

Acknowledgements

Financial support by University Malaya PPP grant PS129/2009C and UMRG grant RG006/09AET is gratefully acknowledged.

References


