Kinetic Study and Simulation of Oleic Acid Esterification in Different Type of Reactors

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Abstract
Esterification reaction is most important reaction in biodiesel production. In this study, oleic acid was used as a suggested feedstock to study and simulate production of biodiesel. Batch esterification of oleic acid was carried out at operating conditions; temperature from 40 to 70 °C, ethanol to oleic acid molar ratio from 1/1 to 6/1, H2SO4 as the catalyst 1 and 5% wt of oleic acid, reaction time up to 180 min. The optimum conditions for the esterification reaction were molar ratio of ethanol/oleic acid 6/1, 5%wt H2SO4 relative to oleic acid, 70 °C, 90 min and conversion of oleic 0.92. The activation energy for the suggested model was 26625 J/mole for forward reaction and 42189 J/mole for equilibrium constant. The obtained results simulated to other types of reactors with different operating conditions using reactop cascade package. The conversion of oleic acid of simulation results at optimum operating conditions was 0.97 for isothermal batch and plug flow reactors, 0.67 for isothermal CSTR, while the conversions of oleic acid in the adiabatic mode were 0.82, 0.40, 0.74 for batch, CSTR, PFR reactors respectively.

Key word: Oleic acid, Esterification, Kinetic study, Simulation.

Introduction
Energy sources can be classified into three groups fossil, fissile, and renewable. The term fossil refers to an earlier geological age. Fossil fuels were formed many years ago and are not renewable. The fossil energy sources are petroleum, coal, bitumen, natural gas, oil shale, and tar sands. The main fissile energy sources are uranium and thorium [1].

One of the main and most important non-renewable energy sources is oil, the production rate of oil is expected to peak in the next few years therefore, the world needs an alternative and renewable energy source that are able to meet world energy needing [2].

The renewable energy sources such as biomass, hydro, wind, solar (thermal and photovoltaic), geothermal, marine, and hydrogen will play an important role in the future. It is predicted that in 2025, approximately half of the global energy supply will come from renewable energy, and electricity generation from renewable will be more than 80% of the total global electricity supply [3, 4].

Biomass can be converted into liquid and gaseous fuels through thermo-chemical and biological methods. Biofuel is a non-polluting, locally available, accessible, sustainable, and reliable fuel obtained from renewable sources [5]. Liquid biofuels fall into
the following categories: (a) vegetable oils and biodiesels, (b) alcohols, and (c) bio-crude and synthetic oils [1].

Esterification is one of the most important reactions in chemical industry; and the relative reaction is usually conducted by using, in general, homogeneous acid catalysts [6].

Esterification reaction carried out between carboxylic acids (free fatty acids) and alcohols with the presence of an acid catalyst (such as sulfuric acid, organic sulfonic acid, and hydrochloric acid) to form ester and water (see equatin 1) [7].

$$RCOOH + R’OH \rightarrow RCOOR’ + H_{2}O \quad \ldots(1)$$

The present work, intend to produce ethyl ester (biodiesel) from the oleic acid by esterification process. The effects of reaction temperature, amount of catalyst, and the molar ratio alcohol/oil were considered. Also, the kinetic of oleic acid esterification were studied and the results were simulated to different type of reactors and operating conditions.

**Experimental Work**

**Materials**

1. Oleic acid, obtained from local markets. The specific gravity of the oleic acid is 0.895, BDH Chemicals Ltd.
2. Ethyl alcohol obtained from local markets with specific gravity is 0.7692 (88 to 90 wt. %).
3. Sulfuric acid as an acid catalyst obtained from local markets, the purity of this acid is 98% (Sp.Gr. is 1.84) Aldrich.
5. Phenolphthalein (as indicator), Fluka.

**Apparatus**

The apparatus used in this study for esterification reaction is shown in Figure 1. The batch scale system consists of the followings:

1. Heat flat magnetic stirrer (Stuart (CB302)/USA.
2. Reflux Condenser (Germany).
3. Centrifuge (Griffin & George Loughborough/Britain)
4. Mercury thermometer from zero to 250 °C.
5. 3 Necks flask (500 ml).

**Esterification of Oleic Acid**

The esterification reaction carried out between acid and free fatty acid (FFA) to produce ester (biodiesel) and water. The system was maintained at atmospheric pressure and experiments were carried out at constant temperature. The agitation was kept constant at 300rpm. This process was studied at different percent of ethanol/oil mole ratio of 1/1, 3/1, 6/1 sulfuric acid as a catalyst of 1 and 5 wt% relative to oleic acid, reaction time up to 180 minutes and at different temperatures 40 to 70 °C.

The esterification reactor was loaded with 15 ml (13.43 g) of oleic acid, and the desired amount of ethanol. The mixer was agitated and preheated to
the desired temperature and then H₂SO₄ was added. At each period of time (15 or 30 minutes), 5 ml from the mixture reaction was taken and 2 drops of phenolphthalein was added as indicator and titrated with 1 molarity of NaOH in order to obtain oleic acid conversion[8].

Results and Discussion
Effect of Operating Temperature and Time on the Oleic Acid Conversion

Figures 2 and 3 show the oleic acid conversion with reaction time at various temperatures and ethanol/oleic acid molar ratio 6/1 with 1 and 5 wt.% of H₂SO₄.

As shown in the fig 2 the conversion of oleic acid at 6/1 ethanol/oleic mol. ratio and 1% H₂SO₄ was 0.87 at 70°C after 150 minutes and was 0.92 at 70°C after 90 minutes with 5% H₂SO₄, which is the highest conversion achieved in this study (as shown in Fig.3).

The oleic acid conversion increased with increasing temperature. Increasing the temperature may cause increase of molecule activity, which means that more molecules have more energy, thus, the possibility of molecule to react increased.

These results are in a good agreement with the results of the production of fatty acid ethyl ester (FAEE) from oleic acid (FAA) with short-chain alcohols (ethanol, propanol and butanol) under ultrasonic irradiation reported by Hanh et al. [9] The higher conversion for the esterification process was 0.92 at the reaction temperature 60°C and 3/1 mol. ratio of ethanol to oleic acid with 5% H₂SO₄ after 2 hours irradiation.

Effect of Ethyl Alcohol/Oil Mol. Ratio on the Oleic Acid Conversion

Molar ratio of ethanol to oleic acid is one of the most important variables that affect the conversion of oleic acid. The experiments of esterification reaction of oleic acid with ethanol were carried out under various ethanol/oil mol. ratios (1/1 to 6/1).

Figures 4 and 5 show the conversion of oleic acid with reaction time at various ethanol/oleic acid molar ratios using 1 and 5 wt. % H₂SO₄ (as catalyst) at 70°C.

It can be observed that the oleic acid conversion increased from 0.61 at a molar ratio of 1/1 to 0.87 at a molar ratio of 6/1 after 180 min using 1 wt% of H₂SO₄ at 70°C (Fig. 4). By using 5 wt% H₂SO₄ at 70°C, the oleic acid conversion increased from 0.87 at 1/1 of ethanol/oil mol. ratio after 180 min.
to 0.92 at 6/1 ethanol/oil mol. ratio after 90 min, which is the highest conversion achieved in this study (in Fig.5).

**Effect of Catalyst Amount on the Oleic Acid Conversion**

The amount of catalyst affect on the oleic acid conversion is given in Fig.6. It shows the relationships between the oleic acid conversion and time at various catalyst concentrations with ethanol/oleic acid molar ratio 6/1 and 70°C. The oleic acid conversion increased with increasing the catalyst concentration.

Increasing in ethanol/oleic mol. ratio causes increasing in the conversion in oleic acid, because the esterification of oleic acid with ethanol is an equilibrium-limited chemical reaction and the position of equilibrium controls the amount of ester formed

![Fig. 4, effect of the ethyl alcohol/oleic mol. ratio on oleic acid conversion by esterification reaction, at the temperature 70°C and 1 wt% H₂SO₄](image)

![Fig. 5, effect of the ethyl alcohol/oleic mol. ratio on oleic acid conversion by esterification reaction, at the temperature 70°C and 5 wt% H₂SO₄](image)

Kinetic obtained from laboratory unit are usually play an important role in modeling and scale up designs for new biodiesel production units.

The reaction rate of esterification is directly proportional to the amount of a catalyst, so the catalyst is used to enhance the reaction rate and conversion. The amount of sulfuric acid employed as a catalyst is related to the formation of H⁺ that catalyzes the reaction.

**Kinetic of Oleic Acid Esterification**

Kinetic obtained from laboratory unit are usually play an important role in modeling and scale up designs for new biodiesel production units.

The data obtained by Differential method of analysis obtained data has
been used to find favorable kinetic model for oleic acid esterification.

The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative \(-r_A\), and testing the goodness of fit of the equation with experiment.

The conversion of oleic acid (x) fitted by the power degree formula according to the time at certain temperature, and then finding the rate coefficients (k\textsubscript{1} and k\textsubscript{2}) as well as the orders of the reactants and products materials (n\textsubscript{1}, m\textsubscript{1}, n\textsubscript{2} and m\textsubscript{2}) using least squares method for the suggested reaction kinetics equation (eqs. 2 to 6).

\begin{equation}
C_{18}H_{34}O_2 + C_2H_4O \leftrightarrow C_{20}H_{38}O_2 + H_2O \ldots(2)
\end{equation}

\[-r_A = k_1C_A^{n_1}C_B^{m_1} - k_2C_C^{n_2}C_D^{m_2} \ldots(3)\]

\[K_{eq}=\frac{k_1}{k_2} \ldots(4)\]

\[K_{eq} = \frac{C_C^{n_2}C_D^{m_2}}{C_A^{n_1}C_B^{m_1}} \ldots(5)\]

\[-r_A = k_1C_A^{n_1}C_B^{m_1} - \left(\frac{k_1}{k_{eq}}\right)C_C^{n_2}C_D^{m_2} \ldots(6)\]

Where:
- k = rate coefficient of reaction.
- 1= forward reaction, 2= backward reaction, n and m are the reaction orders.
- \(K_{eq}\) = equilibrium constant.
- \(C_A, C_B, C_C, C_D\) = reactants and products moles at any time.
- \(C_{Ae}, C_{Be}, C_{Ce}, C_{De}\) = reactants and products moles at equilibrium time.

According to Arrhenius law [12] a plot of Ln k vs. 1/T gives a straight line, with slope for E/R to find activation energy for forward reaction and equilibrium reaction (figs.7 and 8).

The values of constants in the esterification reaction of oleic acid are summarized in Table 1.

**Table 1, Constant values of the esterification reaction kinetic model**

<table>
<thead>
<tr>
<th>Constant value</th>
<th>Esterification reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{eq})</td>
<td>2.1*10^7</td>
</tr>
<tr>
<td>(E_{eq} (J/mole))</td>
<td>42189</td>
</tr>
<tr>
<td>(k_{eq1})</td>
<td>196.3</td>
</tr>
<tr>
<td>(E_1 (J/mole))</td>
<td>26625</td>
</tr>
<tr>
<td>(n_1)</td>
<td>1.25</td>
</tr>
<tr>
<td>(m_1)</td>
<td>0.5</td>
</tr>
<tr>
<td>(n_2)</td>
<td>1</td>
</tr>
<tr>
<td>(m_2)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The obtained values of rate coefficients, equilibrium constant, orders of reactants and products materials, heat of reactions and activation energy were used to simulate the results. Predicted values calculated from empirical model and experimental data are shown in fig.9.
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Fig. 9, Experimental and predicted values of apparent rate constant by using suggested model of esterification of oleic acid with 6/1 ethanol/oleic molar ratio, 5% H₂SO₄ as catalyst and temperature range from 40 to 70 °C.

Statistical analysis of the experimental data shows that the solution of the model (eq. 6) is proportional with the experimental data. The distribution of the experimental data around the model solution of esterification (correlation coefficient (R)) is about 0.9061, standard deviation (S) is 6.9*10⁻³, and average relative error is 1.34% in 95 % confidence level, as summarized in Table 2.

Table 2, statistical analysis of the model

<table>
<thead>
<tr>
<th>statistical analysis</th>
<th>Esterification reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation coefficient (R)</td>
<td>0.9061</td>
</tr>
<tr>
<td>Standard deviation (S)</td>
<td>6.9 * 10⁻³</td>
</tr>
<tr>
<td>Average relative error</td>
<td>1.34%</td>
</tr>
<tr>
<td>Confidence level</td>
<td>95%</td>
</tr>
</tbody>
</table>

Simulation Results

Simulation for the behavior of batch, plug and mixed flow reactors in different operating modes (adiabatic and isothermal) was carried out at optimum conditions (70 °C, 6/1 ethanol/oleic mol ratio, 5% H₂SO₄ as catalyst) and the previously obtained results of kinetic models (Table 1) by using reactop cascade package to predict best reaction time.

Fig. 10 shows the reactants and products moles in experimental and simulation isothermal batch reactor with reaction time at best operating conditions.

Figs. 11 and 12 show the oleic acid conversion with reaction time in batch, PFR and CSTR operating in isothermal and adiabatic mode, respectively.

The oleic acid conversion in isothermal batch and plug flow reactors were 0.97 after 90 min from the reaction, whereas the conversion in mixed flow reactor reached highest conversion 0.63 after 33 min and then the conversion dropped (fig. 11).

Fig. 12 shows the oleic acid conversion with time in batch, PFR and CSTR in adiabatic mode. The beginning of reaction the system has only liquid phase of reactant (oleic acid and ethanol with 12% water content). As time proceeds, reactant consumed, while water and ester formed. At the simulated results, the reactants consumed and products formed faster than the experimental results (as shown in Table 3).

From this Table 3, simulated results are always higher than the experimental results which could be attributed to the effect of side reactions, which cause consumption of oleic acid to form undesirable products, such as water that reduced the formation of ester [8].

Figs. 11 and 12 show the oleic acid conversion with reaction time in batch, PFR and CSTR operating in isothermal and adiabatic mode, respectively.
conversion of oleic acid were 0.84 and 0.75 after 90 min in a batch reactor and plug flow reactor, while the conversion in CSTR was 0.40 after 40 min and then dropped.

However, it is obvious that batch and PFR is substantially better than the CSTR for obtaining high conversions in both isothermal and adiabatic mode.

Fig. 11, shows oleic acid conversion with time in batch, PFR and CSTR reactors in isothermal mode at the best operating conditions.

Fig. 12, shows the oleic acid conversion with time in batch, PFR and CSTR reactors in adiabatic mode at the best operating conditions.

Table 4 shows numerically the highest and best conversion in simulation and experimental results at different types of reactors (from figures 10 to 12).

Table 3, higher results at the best conditions from experimental and simulated results

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Oleic</th>
<th>Ethanol</th>
<th>Ester</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>4.44</td>
<td>0</td>
<td>1.15</td>
</tr>
<tr>
<td>15</td>
<td>0.3</td>
<td>3.74</td>
<td>0.7</td>
<td>1.85</td>
</tr>
<tr>
<td>30</td>
<td>0.23</td>
<td>3.67</td>
<td>0.77</td>
<td>1.92</td>
</tr>
<tr>
<td>60</td>
<td>0.13</td>
<td>3.57</td>
<td>0.87</td>
<td>2.02</td>
</tr>
<tr>
<td>90</td>
<td>0.08</td>
<td>3.52</td>
<td>0.92</td>
<td>2.07</td>
</tr>
</tbody>
</table>

Table 4, highest conversion in simulation and experimental at operating conditions (T=70 °C, ethanol/oleic molar ratio=6/1, H2SO4 =5%wt)

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Operating mode</th>
<th>Time (min)</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>Isothermal</td>
<td>90</td>
<td>0.92</td>
</tr>
<tr>
<td>Batch</td>
<td>Isothermal</td>
<td>90</td>
<td>0.97</td>
</tr>
<tr>
<td>Batch</td>
<td>Adiabatic</td>
<td>90</td>
<td>0.82</td>
</tr>
<tr>
<td>CSTR</td>
<td>Isothermal</td>
<td>20</td>
<td>0.67</td>
</tr>
<tr>
<td>CSTR</td>
<td>Adiabatic</td>
<td>40</td>
<td>0.40</td>
</tr>
<tr>
<td>PFR</td>
<td>Isothermal</td>
<td>90</td>
<td>0.97</td>
</tr>
<tr>
<td>PFR</td>
<td>Adiabatic</td>
<td>90</td>
<td>0.74</td>
</tr>
</tbody>
</table>

**Conclusion**

1. The maximum conversion of oleic acid was 0.92 at 6/1 of ethanol/oleic acid mol. ratio after 90 minutes, 70° C and 5% H2SO4.

2. Increasing the ethanol/oleic acid molar ratio from 1 to 6 increases the conversion of oleic acid.

3. The activation energies for the suggested kinetic model were 26625
J/mole for the forward reaction and were 42189 J/mole for equilibrium constant.

4. The conversion of oleic acid in the simulated model in batch and plug flow reactors is higher than the conversion in CSTR reactor in each isothermal and adiabatic mode.

**Nomenclatures**

\[-r_A = \frac{dx}{dt}\] reaction rate of oleic acid

A = oleic acid, B = ethanol, C = ester, D = water

k = rate coefficient of reaction.

1 = forward reaction, 2 = backward reaction, n and m are the reaction orders.

n_1\text{ for oleic }, m_1\text{ for ethanol}, n_2\text{ for ester}, m_2\text{ for water}

K_{eq} = equilibrium constant.

C_A, C_B, C_C, C_D = reactants and products moles at any time.

C_{Ae}, C_{Be}, C_{Ce}, C_{De} = reactants and products moles at equilibrium time.

E_1 = activation energy for forward reaction (J/mole)

E_{eq} = activation energy for equilibrium reaction (J/mole)

k_o = frequency factor ((mol)^{-0.74}/minute) for forward reaction

k_{oe} = frequency factor for equilibrium reaction

**References**


