Effect of Water Content in Waste Cooking Oil on Biodiesel Production via Ester-transesterification in a Single Reactive Distillation

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Abstract. A single-column reactive distillation is employed to convert waste cooking oil to biodiesel via simultaneous esterification and transesterification reactions. The waste cooking oil contained 10 wt% of free fatty acid (FFA) and the contaminated water (2-8 wt%) was used as feedstocks for biodiesel production. Esterification was occurred in the upper of column to reduce FFA content to less than 1 wt% and to prevent the simultaneous saponification by base catalyst. Moreover, the contaminated water and by-product water (from esterification) together was removed in-situ as the distillate product. The reactive distillation has been optimally designed to have 16 stages consisting of 5 esterification, 9 transesterification stages and each stage for reboiler and condenser. The feed locations of oil and methanol were at the top of the column and at stage 6, respectively. The optimum methanol to oil ratio was 6:1 with reflux ratio 0.1 while the reboiler duty was in the range of 100-150 kW depended on the water content. This condition successfully converts 97 wt% of waste cooking oil to biodiesel with 96.5% purity.

1. Introduction
Nowadays, the energy requirement is continuously increasing; while, fossil fuel is decreasing and global warming is becoming an important issue. Therefore, the development of the clean and renewable energy to replace petroleum-based fuel is necessary. Biodiesel is one of the alternatives to replace petroleum-based diesel fuel because the similarity of their properties. The major feedstock used in the production of biodiesel are vegetable oils, animal fats and waste cooking oils (WCO). Typically, more than 70% of the production costs of biodiesel are dependent on the price feedstocks [1]. Low-cost raw material such as waste cooking oil (WCO) can reduce around 50% of the biodiesel cost comparing to the use of fresh palm oil, especially in Thailand. However, major drawback of using WCO as a feedstock is due to its typically high free fatty acid
(FFA) and water content. FFA content in WCO can react with base catalyst via saponification as displayed in figure 1, which consumes the catalyst resulting in lower yield of biodiesel.

To address this problem, several researchers have proposed a two-step process in which the WCO is first undergone esterification using acid catalyst (Figure 2) to lower the FFA content below 1wt% following by base-catalysed transesterification [1-3]. In this work, the heterogeneous catalyst, Amberlyst-15 resin and CaO/Al2O3 are applied.

The heterogeneous catalysis can overcome homogeneous catalysis by elimination of the washing section and the reduction of huge amounts of waste water [5]. Biodiesel production process can be separated into two main parts: the reaction and the separation parts. The combination of reaction and separation within single unit operation is called reactive distillation (RD). This unit is specially designed for the equilibrium limited reactions and consecutive reactions. The RD has been utilized for reactions such as esterification, ester-hydrolysis reaction, transesterification, and etherification [6]. Recently, Petchsoongsakul et al. [7] developed the hybridization of ester-transesterification for biodiesel production in a single RD column. This process used heterogeneous catalyst including of Amberlyst-15 and CaO/Al2O3. The pseudo-homogeneous kinetic model was used to simulate the combined ester-transesterifications which could not take into account the effect of water. When the esterification takes place, a by-product water is also produced. Moreover, the raw WCO has around 2-5 wt% water contaminated. It was found that the presence of water could influence on the catalyst activity. [6, 8, 9]. Therefore, the water content should be accounted into kinetic rate model. Therefore, the kinetic model needs to consider the water content to investigate the effect of water on the performance of the single hybridized reactive distillation. Steinigeweg and Gmehling [6] reported that the swelling and poisoning of Amberlyst-15 (a strong acidic ion-exchange resin catalyst) were observed in the presence of water and proposed the kinetic rate model of esterification of the fatty acid decanoic acid and methanol using Amberlyst-15 as a catalyst. The sorption of water was accounted into this kinetic model using a Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach. The kinetic model proposed by Steinigeweg and Gmehling [6] has been used to simulate for transesterification at the bottom of column. Therefore, this work aims to simulate the effect of water on the catalytic activity via esterification and transesterification using WCO on the number of stages, reflux ratio, methanol to oil molar ratio and feed location of the single reactive distillation. The mixture of oleic acid and triolein was used as a model compound for WCO as presented in table 1. The proposed kinetic rate model of esterification of the fatty acid as decanoic acid and methanol [6] was verified and validated prior to employ for esterification of oleic acid and methanol.
Table 1. Composition of WCO.

| Model compound | wt%  |
|----------------|------|
| Triglyceride   | 82-88|
| FFA            | 10   |
| Water          | 2-8  |

2. Kinetic experimental

2.1. Kinetic Modeling
Steinigeweg and Gmehling [6] proposed the LHHW equation for a reversible esterification using an ion-exchange resin (Amberlyst-15) as a catalyst (eq. (1));

\[
r = \frac{1}{v_i} \frac{dn_i}{dt} = m_{\text{cat}} \left( k_{f,c,c} \cdot k_{M,OH} \cdot k_{MeOH} \cdot k_{MeOle} \cdot k_{H,O} \cdot a_{H,O} \right) \frac{c_{i,0} + k_{f,c,c} + k_{MeOH} + k_{MeOle} + k_{H,O} \cdot a_{H,O}}{1 + (k_{Oleic} \cdot a_{Oleic} + k_{MeOH} \cdot a_{MeOH} + k_{MeOle} \cdot a_{MeOle} + k_{H,O} \cdot a_{H,O})^2}
\]

(1)

where the activities were used instead of concentrations or mole fraction. Water is preferably adsorbate and therefore the sorption effects can be summarized with a singular sorption constant \( K_{\text{Sorb}} \). Then the eq. (1) can be simplified as following eq. (2).

\[
r = \frac{1}{v_i} \frac{dn_i}{dt} = m_{\text{cat}} \times \left( k_{i, Oleic} \cdot a_{MeOH} \cdot k_{MeOle} \cdot k_{H,O} \cdot a_{H,O} \right) \frac{k_{i, Oleic}}{K_{\text{Sorb}}^2 a_{H,O}}
\]

(2)

2.2. Materials oormatting
Oleic acid was obtained from Vicchi enterprise in Thailand. Analytical grade methanol (99.8% purity) from Ajax FineChem is used as reactant of esterification reaction. Amberlyst-15 ion-exchange resin from Sigma-Aldrich was dried at 110 °C overnight then kept in desiccator before used. Methyl valerate and 2-propanol used as internal standard and solvent, respectively for GC analysis were provided by Sigma-Aldrich.

2.3. Esterification experiment
The experiments were performed in a 3-neck-flask with condenser and thermometer into an oil bath to control temperature of reaction mixture at 60 °C using a stirring speed of 600 rpm. Prior to the experiment, both reactants were pre-heated to the desired temperature of 60 °C in a separate tank. Then, the reaction time was started when the catalyst was added to the reaction mixture at the desired temperature. A sample of 1 mL was taken every 30 min and centrifuged to separate the catalyst from methanol and oil to stop reaction.

2.4. Sample analysis
The resulting solution was then analysed by gas chromatography from Shimadzu GC-2010 Plus with DB-WAX capillary column and detected by flame ionization detector (FID). Methyl valerate was used as an internal standard. The column temperature was programmed as follows: starting at 40 °C with a holding time of 3 min, ramping to 235 °C at a rate of 15 °C/min, holding for 2 min, ramping to 260 °C at a rate 10 °C/min, and holding for 20 min. The weight fraction is calculated by the following eq. (3);

\[
\text{Weight fraction} = \frac{C_{i,j} \times MW \times V_{i,0}}{Mass_{i,0}}
\]

(3)

where \( C_{i,j} \) is concentration of oleic acid at a different time, MW is molecular weight of oleic acid, \( V_{i,0} \) is initial reaction volume of resulting sample and \( Mass_{i,0} \) is initial total mass of reaction mixture.
3. Simulation

Simulations were carried out under the steady state condition using the AspenPlus® software version 8.0. The RADFRAC model has been used in the design of RD columns [7]. RADFRAC relies on an equilibrium stage model. Besides, pure component properties and Dortmund-UNIFAC interaction parameters, the column heat loss and the reaction kinetics data were incorporated into the simulator. The number of stages was counted from the top to the bottom, with the first stage is the condenser and the stage N is the reboiler. Oleic acid and triolein were used as a model compound for FFA and triglyceride, respectively.

3.1 Validation

3.1.1 Kinetic model of esterification. Figure 3 shows the experimental results in the dot and simulation results in continuous lines obtained from the proposed kinetic rate model [6]. The results indicated that there was no significant difference in the experimental results (esterification of oleic acid and methanol) and simulation result of esterification of decanoic acid and methanol provided by Steinigeweg and Gmehling [6].

The kinetic constants and activation energies were reported by Steinigeweg and Gmehling [6], as presented in table 2, for the esterification of decanoic acid using Amberlyst-15. However, oleic acid is used as the feedstock in this work; therefore, the validation of FFA conversion as a function of reflux ratio was also performed as shown in figure 4. It is found that the obtained simulation calculations are close to experimental results at various reflux ratios with the maximum error of 16%.

Table 2. Kinetic parameters of LHHW model (K_{step}=2.766). [6]

| Reaction      | i     | k_0 (mol /g s) | E_{A,i} (kJ /mol) |
|---------------|-------|----------------|-------------------|
| Esterification| 1     | 3.1819×10^6    | 72.23             |
| Hydrolysis    | -1    | 3.5505×10^3    | 71.90             |

![Figure 3. Kinetic model fitted eq. 1. (continuous line) and experiment (*) condition are T=60 °C methanol to oil ratio 5:1. X_{water}^0=0.019.](image)

![Figure 4. Acid conversion as a function of reflux ratio. Experimental data [6] (*) and simulation results (continuous line).](image)
3.1.2 Transesterification. The kinetic constants were reported by Pasupulety et al [10], presented in table 3, for the transesterification of soybean oil catalysed by CaO/n-Al₂O₃ (neutral- Al₂O₃) and the value of activation energy was found to be 30.7 kJ/mol. However, triolein is used as feedstock in this work; therefore, the validation of FAME yield as a function of time was also performed as shown in figure 5. It was found that the obtained simulation calculations are close to the experimental results at different time with the maximum error of 27%. Although this seems to be excessive but the equilibrium are similar, whereby, the simulation relies only on the equilibrium.

| Temperature (°C) | Rate constant, k (1/min) | R²  |
|------------------|--------------------------|-----|
| 125              | 0.0029                   | 0.99|
| 150              | 0.0047                   | 0.997|
| 175              | 0.0072                   | 0.994|
| 200              | 0.013                    | 0.999|

Figure 5. FAME yield as function of time. Experimental data [10] (•) and simulation result (continuous line) T = 150 °C, methanol to oil = 9:1 at pressure = 1 bar.

Figure 6. Ester-transesterification in single reactive distillation for biodiesel production.
3.2 Ester-transesterification in a single reactive distillation

Petchsoongsakul et al [7] proposed the ester-transesterification in a single RD. The upper column was packed with Amberlyst-15 for esterification and the lower column was packed with CaO/Al₂O₃ for transesterification. Methanol and waste cooking oil were co-fed at the second stage.

In this work (Figure 6), the same concept has been adopted but the feedstock contains water and the kinetic model of the esterification has been changed to LHHW model in order to account the influence of water on the operating parameter of the reactive distillation.

3.2.1 Number of stages. To reduce FFA below 1 wt%, 5 reactive stages were required for the esterification and 9 stages of transesterification to produce biodiesel according to EN standard. The obtained biodiesel yield was higher than 96.5% using the methanol to oil ratio of 6:1, the reflux ratio of 0.1 and the reboiler duty in the range of 100-150 kW as depended on the water content in WCO. WCO contaminated with water content of 2-8 wt% and FFA of 10 wt% as the oil feedstock. The results are shown in figure 7. It was found that the biodiesel purity was increased with the increase of water content from 2 to 8 wt% while biodiesel yield was no significant different when the water content in WCO was increased. However, the reaction rate of transesterification was decreased with increasing amount of water resulting in higher biodiesel purity when using higher amount of water in WCO. Figure 8 shows the effect of the water content in feedstock on the number of stage. It was found that the water content does not show significant effect on the number of stages because the water as well as methanol were removed to the top of the column resulting to a trace amount of the water was in biodiesel at the transesterification section in the bottom of column. The water content at this reaction section was less than 0.1 wt%.

3.2.2 Reflux ratio. Figure 9 shows the effect of the reflux ratio on the purity of produced biodiesel with different water contents in WCO. The reflux ratio of 0.1 was used to purify the biodiesel conforming to the standard. Moreover, the higher reflux ratio has a negative effect on the esterification as corresponding to the Steinigeweg and Gmehling work (Figure 4) [6].
3.2.3 Methanol feed location. Liquid mass fractions of the components are presented in figure. 10A and B. Where, in 10A, methanol is fed at the middle of column and high liquid fraction of product (FAME) is achieved. On the other hand, in figure 10B, methanol is fed at the bottom of the column and the product’s liquid fraction is lowered. In the current work, the bottom of the column has high temperature, resulting to sudden vaporization of methanol as found in the lower level of methanol in the liquid phase. This is leading to lower reaction rate which confirm by the biodiesel yield and purity as indicated in figure 11. The biodiesel yield and purity become lower when methanol was fed at the lower section of column. This was not corresponding to the conventional biodiesel production in RD. The oil feedstock is usually fed at the top of the column; while methanol is fed at the bottom [6, 7].
Figure 10. Liquid mass fraction in ester-transesterification in a single reactive distillation feed oil at stage 2 and (a) feed methanol at stage 6 (first stage for transesterification) and (b) feed methanol at the bottom of column using water content 4 wt%, reflux ratio of 0.1 and reboiler duty of 100 kW. (TG = triolein, FFA = oleic acid, MeOH = methanol and FAME = fatty acid methyl ester).

Figure 11. Function of biodiesel purity and yield methanol feed stage using water content of 4 wt% in WCO.

Figure 12. Biodiesel purity as function of methanol to oil ratio using different water content (2-8 wt%) of WCO.
3.2.4 Methanol to oil feed ratio. Figure 12 and 13 show the biodiesel purity and yield respectively, as function methanol to oil mole ratio using different water content (2-8 wt%) in WCO. The optimum ratio was 6:1 because the excess methanol excess was contaminated in biodiesel at the bottom product.

4. Conclusions
The kinetic model of the decanoic acid reaction can represent the oleic acid esterification using Amberlyst-15 as solid acid catalyst. Transesterification, on the other hand, was used Pseudo-homogeneous kinetic model because of the trace amount of water was in this reaction zone. Therefore, the LHHW has been adopted to demonstrate the effect of the contaminated water on the esterification of WCO. The simulation results of the single reactive distillation for simultaneous ester-transesterification to produce biodiesel from WCO has found the optimum design of the RD column with 16 stages, consisting of 5 esterification stages and 9 transesterification stages. The methanol to oil ratio was kept for 6:1, when WCO was fed at top of the column and methanol was fed at the first stage of transesterification using the reflux ratio of 0.1 and the reboiler duty in the range of 100-150 kW. Biodiesel yield and purity more than 96.5% were obtained using WCO with contaminated water content of 2-8 wt% and FFA 10 wt%. This design of a single reactive distillation has a capability to withhold the water contaminated in the range of 2 to 8 wt% for simultaneous ester-transesterification of WCO.

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