

CHAPTER VII

TRANSESTERIFICATION OF PALM OIL USING KOH LOADING ON VARIOUS SUPPORTS IN A CONTINUOUS REACTOR

7.1 Abstract

In this study, a KOH loading on various supports such as Al_2O_3 , ZrO_2 , NaY, Na-mordenite zeolite, and bentonite clay, prepared by impregnation method for biodiesel production of refined palm oil with methanol using a continuous reactor, was studied. The KOH supported on NaY and mordenite displayed a reaction activity similar to as KOH supported on bentonite in batch and packed-bed reactors. About 76 % yield of biodiesel was obtained with 20 wt% K/bentonite in the packed-bed reactor, a methanol/oil molar ratio of 15:1; 60 g weight of catalyst; and flow rate of 0.3 ml/min at 60 °C (residence time 4.25 h). The reaction was carried out under laminar flow ($\text{Re} < 2300$) conditions; nevertheless, no external diffusion was found. Internal mass transfer was negligible when the catalyst size was lower than 10–20 mesh. It was found that the high basic property of each catalyst promoted transesterification activity. In addition, there was negligible loss in activity when the catalyst was operated at 60 °C for 7 days. Nevertheless, a level of potassium leaching on the 20 wt% K/bentonite was observed during the run.

7.2 Introduction

Palm oil can be used as a fuel for the combustion engine; however, viscosity of palm oil is much higher than conventional diesel fuel. To avoid damage to engines, palm oil is converted to biodiesel by transesterification. Biodiesel has a lot of advantages: for example; it contains negligible amounts of nitrogen and sulfur compounds, non-toxic, and biodegradable. In addition, properties of biodiesel such as cetane number, flash point, and lubricity are better than fossil fuel [1–3]. Biodiesel is produced by a chemical reaction of vegetable oils with alcohols and uses homogeneous base catalysts such as, NaOH or KOH, to accelerate the reaction. Base catalysts can promote faster transesterification than acid catalysts. Excess

homogeneous base catalysts have often caused environmental problems; large amounts of waste water result from the process, which is used to remove the base catalyst from the product.

To overcome these drawbacks, heterogeneous catalysts are considered as a substitute for homogeneous catalysts in industrial biodiesel production. A number of supports loaded with various alkaline solutions—KI/Al₂O₃, KF/Al₂O₃, K/KOH/Al₂O₃, and KOH/MgO—have been investigated [4–7]. Some research projects have also used alkaline earth—MgO, and SrO [8,9]—as catalysts because they are insoluble. A key factor of catalytic activity for biodiesel production, of prepared heterogeneous catalysts, depends on their basic properties. Generally, the basic properties of the solid catalyst are validated by using a Hammett indicator or CO₂ temperature-programmed desorption (CO₂-TPD). These methods use an acid molecule to measure the base strength and the amount of basicity. However, most activities of heterogeneous catalyst are less than that homogeneous catalyst due to mass transfer limitation between solid and liquid phase. Not only was catalytic activity observed, catalytic stability of the catalyst was also studied. The KNO₃/Al₂O₃ was reported that the activity of biodiesel over 90 wt% in the first run; but, the activity dramatically decreased after the first run due to loss of active species [10]. Moreover, the various types of alkaline or alkaline earth catalyst on the NaX [11], NaY [12], CaO [13], and Ca(OCH₃)₂ [14] also were tested. It was found that these catalysts gave a methyl ester yield > 90 wt% and exhibited extended stability under their optimum conditions. Durability of heterogeneous catalyst, therefore, should have been evaluated to increase its lifetime.

Normally, concept designed biodiesel production plants have been constructed with stirrer tanks or continuously stirred tank reactors (CSTR). The reactants are fed into each tank and have a rest time for reaction, separation, and purification process. The limitation of operation area and the CSTR process have prompted researchers and engineers to use other processes. The packed-bed reactor, in which the catalyst was packed, became an attractive alternative to stirrer tanks because the reactants, including oil and methanol, are fed into the packed-bed reactor and simultaneously produce biodiesel and glycerol. Of all the different reactor system packed-bed reactors have proven to be the most suitable reactors for biodiesel

production. Hama *et al.* [15] studied *Rhizopus oryzae* cells immobilized on polyurethane foam biomass in a circulated packed-bed reactor. With the stepwise addition of methanol to oil (4:1), a high ME content over 90 wt% was achieved in the first cycle of repeated-batch methanolysis at a flow rate of 25 L/h and a high value of 80 wt% was maintained, even after 10 batch reaction cycles. The Lipozyme TL IM enzyme under supercritical carbon dioxide for biodiesel production was implemented by Rodrigues *et al.* [16]. They found that fatty acid methyl esters yields (FAME) exceeded 98 wt%. Even though a high methyl ester yield was produced, high safety risks and high operation investment required. Moreover, Dossat *et al.* [17] also studied immobilized Lipozyme® in a continuous reactor. They noted that the remaining glycerol produced in the process adsorbed onto the enzymatic support, leading to a drastic loss of enzymatic activity with time. Nonetheless, many solid catalysts have been investigated in a packed-bed reactor. Shibasaki-Kitakawa *et al.* [18] reported that triolein with ethanol with a conversion of 98 wt% could be produced by using various ion-exchange resins as a heterogeneous catalyst. Hsieh *et al.* [19] achieved a high methyl ester yield of 15 wt% by using shell-core a CaO/CaCO₃ catalyst in a packed-bed reactor. They found that the yield of methyl ester increases with increased retention time. The use of heterogeneous catalysts in a packed-bed reactor has been developed to a state where they have reached an international standard of quality similar to that which has been achieved by processing homogeneous catalysts in a batch process.

In this present work, KOH has been used as active component and the prepared catalysts were introduced in a continuous reactor to achieve an optimum condition. The influence of the type of supports, catalyst weights, flow rates/retention times, and percentage of loading potassium were investigated. The reaction rate and stability was tested.

7.3 Experimental

7.3.1 Continuous Reactor

Palm oil and methanol, at 1:15 ratio, were pumped into a continuous packed-bed reactor made of stainless steel, with an internal diameter of 28 mm. The

bed depth of the column reactor was varied in terms of the height and weight of the packing catalyst. A peristaltic pump forced reactant mixtures into the column. A fine sieve (size 100–120 mesh) was used to hold the solid catalyst at the bottom of the column. The reactor had a controlled temperature of 60 °C. The reactants were introduced from the bottom of the column and the effluent was collected from the top. The reacted mixtures were collected periodically in glass vials placed at the reactor outlet. The excess methanol was removed by evaporated in water bath for 15 min at 70 °C. The biodiesel was separated from the glycerol by using a centrifuge, at 1000 rpm, for 5 min.

7.4 Results and Discussion

7.4.1 Tranesterification Reaction in a Batch Reactor

7.4.1.1 *Influence of Potassium Loading on Various Supports in a Batch Reactor*

Figure 7.1 shows the catalytic activity of potassium loading on various types of support in a batch reactor under conditions as stated above. The results illustrate that the highest catalytic activity and biodiesel yield of over 90 wt% was achieved when loading of potassium was 10, 20, 20, 20, and 25 wt% of NaY, mordenite, bentonite, ZrO₂, and Al₂O₃, respectively. At these optimum potassium loadings, the methyl ester yield was found to be > 90 wt%. The different potassium loadings on each support gave different methyl ester yields due to their basic properties. The basic properties were investigated by CO₂-TPD, as summarized in Table 7.1; the peak temperature of CO₂ desorption was used to determine the basic strength of the catalyst after loading KOH. It was found that the CO₂ was desorbed from KOH supported on Al₂O₃ and ZrO₂ at temperature below 200 °C, suggesting the presence of weak base sites in both catalysts. The shift of the desorption peak to a slightly higher temperature in KOH supported on mordenite, NaY zeolite, and clay suggested a slight increase in basic sites in these catalysts. The temperature desorption peak for these catalysts can be attributed to basic properties, relating to the activity of these catalysts.

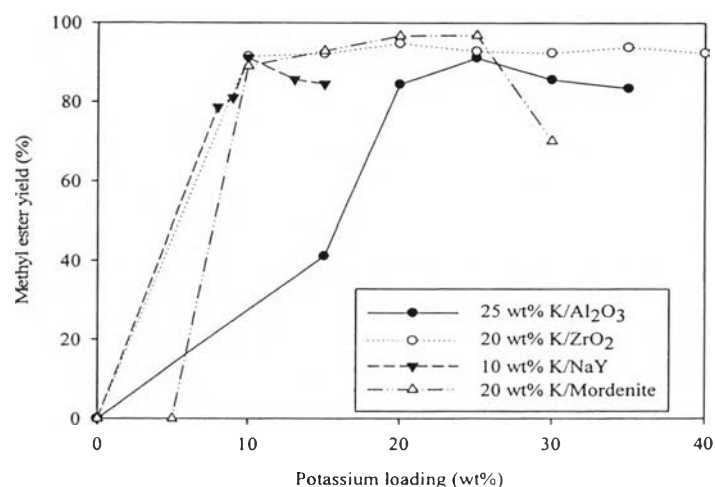


Figure 7.1 Effect of various types of support on the methyl ester yield of palm oil in the batch reactor (methanol/oil molar ratio 15:1, stirrer speed 300 rpm, catalyst mesh size 10–20 mesh, and reaction temperature at 60 °C).

Table 7.1 Basic strength, leaching potassium, and methyl ester yield of catalysts in a batch reactor

| Catalyst | CO ₂ Desorption Temperature Peak (°C) | Leaching Potassium (%) | Methyl Ester 1 st Run (%) |
|-----------------------------------------|--------------------------------------------------|------------------------|--------------------------------------|
| 25 wt% K/Al ₂ O ₃ | 200 | 51.26 | 95.48 |
| 20 wt% K/ZrO ₂ | 110 | 44.52 | 94.74 |
| 10 wt% K/NaY | 400 | 3.18 | 92.84 |
| 20 wt% K/mordenite | 300 | 10.63 | 96.67 |
| 20 wt% K/bentonite | 780 | 17.89 | 94.63 |

Moreover, we proposed that the catalyst could be retained for a recycle run. If minimal leaching of potassium occurs, the property of heterogeneous catalyst for the reaction was successfully to create biodiesel. Table 1,

thus, displays the leaching of potassium (measured by XRF). The amount of potassium leaching from Al_2O_3 and ZrO_2 was found to be 51.36 and 44.52%, respectively. As compared with zeolite and clay support, minimal leaching of the K on the catalyst could be obtained with lower than 20% on NaY, mordenite, and bentonite catalyst, resulting in higher probability to reuse.

7.4.2 Tranesterification Reaction in a Continuous Reactor

7.4.2.1 *Influence of Catalyst Type in a Continuous Reactor*

All of the 30 g catalyst samples were analyzed in a continuous reactor under the following conditions: a methanol-to-oil molar ratio of 15:1; reaction temperature of 60 °C; flow rate of 0.4 ml/min; retention time of 3.19 h; and catalyst size of 10–20 mesh. In Figure 7.2, the KOH on NaY and mordenite gave a biodiesel yield similar to the initial run of 48 wt% and was constant after 9 h (42 wt%); on the contrary, the methyl ester yield from the KOH on Al_2O_3 and ZrO_2 obtained an average of 52 wt% at 2 h and decline steadily to 26 wt% at 9 h. It could be suggested that the initial methyl ester yield of KOH on the Al_2O_3 and ZrO_2 catalysts was the result of a synergistic effect between both heterogeneous and homogeneous catalysts due to a high loss of potassium on the surface. Loss of potassium on Al_2O_3 and ZrO_2 catalysts gradually brought about a decline in of biodiesel yield.

The type of support played an important role for catalyst stability and durability in the transesterification process because of the difference of chemical bonding between the KOH and solid surface. The NaY and mordenite support showed trends, which lead to reduced loss of K on the catalyst surface during the reaction. To prolong the lifetime of the catalysts, the NaY and mordenite supports produce a high biodiesel yield even though the cost of these supports was higher than conventional homogeneous catalysts. Bentonite clay, however, was used in this reaction because the structure of the clay was comprised of hydrated aluminosilicate [20] which was similar to the zeolite extraframework. The biodiesel yield of 20 wt% K/bentonite was approximately 40 wt%, which was somewhat lower than K/NaY, after 9 h; however, K/bentonite showed good stability as K/NaY did. We found that

the economical preparation of the heterogeneous catalyst leads to a lower biodiesel cost, which could be competitive with biodiesel made from homogeneous catalysts.

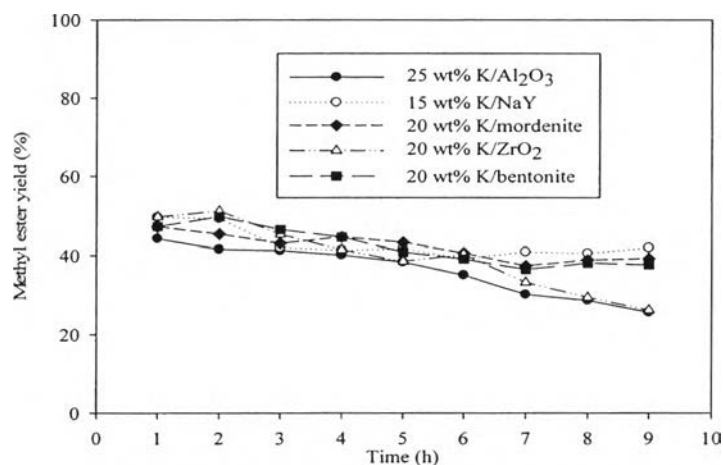


Figure 7.2 Effect of various types of support on the methyl ester yield of palm oil in the continuous reactor (methanol/oil = 15:1, flow rate=0.4 ml/min, amount of catalyst 30 g, catalyst mesh size 10–20, and reaction temperature 60 °C).

7.4.2.2 Influence of the Weight of Catalyst in a Continuous Reactor

The residence time (τ) of substrate in each flow rate (V) related to the bed height (h) and porosity (ϵ_c) of the catalyst as shown in Eq.1 and 2 [18].

$$\epsilon_c = 1 - \frac{W_c/\rho_c}{\pi h (\frac{d}{2})^2} \quad (1)$$

$$\tau = \frac{\epsilon_c \pi h (\frac{d}{2})^2}{V} \quad (2)$$

Where the porosity of the catalyst in the packed-bed reactor is affected by the diameter of the reactor (d), catalyst weight (W_c), density of catalyst (ρ_c) and the bed porosity. The residence time was calculated. The residence time correlated with the height of the catalyst at a constant diameter where as increasing

the catalyst size did not have a great effect on the height when compared to the same weight of catalyst (Figure 7.3). It could be noted that the size of the catalyst had no momentous effect on the residence time of the reactant in the packed-bed reactor. Furthermore, increasing catalyst weight increased the height which resulted in an increase of residence time for the reactant. The liner plot of height of the catalyst with residence times was shown as $\tau = 0.3379h - 0.190$ with $R^2 = 0.998$. All of the different weights exhibited the same tendency regardless of the difference in the bed porosity.

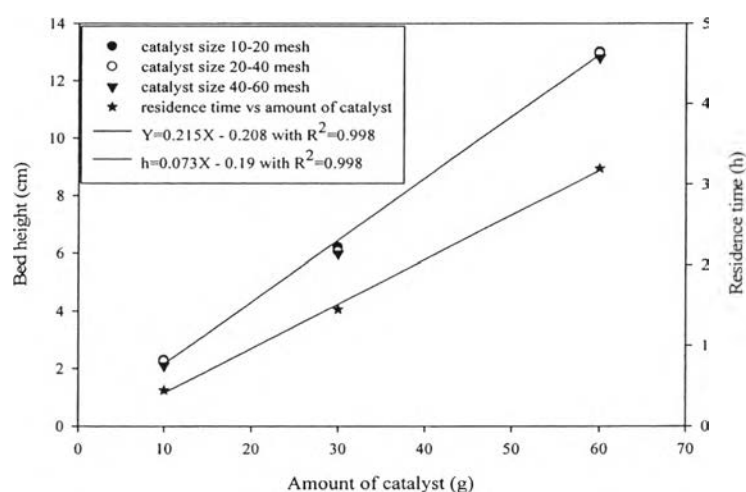


Figure 7.3 Relationship among amount of catalyst, bed height and residence time measured in the steady state of the continuous experimental system.

The effect of the weight of each catalyst on the methyl ester yield was investigated by increasing the amount of catalyst from 10 g to 60 g. The results (Figure 7.4) illustrate that the methyl ester yield initially increased with increasing packed-bed height due to an increase in contact time and active site. The bed height related to the residence time of the substrate in the reactor. The average methyl ester yield of 76 wt% was achieved with 60 g of catalyst.

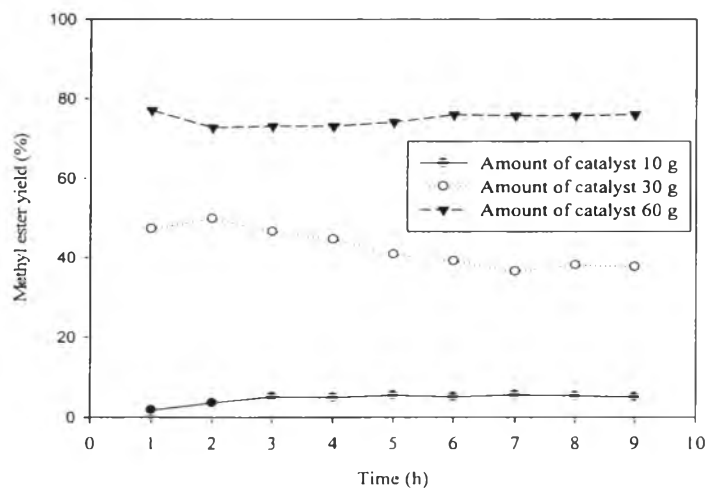


Figure 7.4 Effect of amount of catalyst on the methyl ester yield of palm oil in the continuous reactor (20 wt% K/bentonite clay, methanol/oil = 15:1, flow rate=0.4 ml/min, catalyst mesh size 10–20, and reaction temperature 60 °C).

7.4.2.3 Influence of Residence Time in a Continuous Reactor

The effect of the residence time on the methyl ester yield was investigated by varying the flow rate from 0.2 ml/min to 1 ml/min. The results (Figure 7.5) show that at a flow rate of 1 ml/min, the methyl ester yield had not reached a constant value yet and fluctuated around 60 wt%. The methyl ester yield decreased when increasing the flow rate due to the shorter residence time of reactants in the reactor. Our result was in agreement with Singh's explanation that increasing the flow rate of a substance attributes to a decrease in the contact time of the substance and the active site [21]. The methyl ester yield was increased at a flow rate lower than 1 ml/min because of the longer residence time of the reactants in the reactor; however, at the flow rates from 0.4 to 0.3 ml/min, the average maximum value of the methyl ester yield achieved was 76 wt%. When the flow rate decreased from 0.3 to 0.2 ml/min, the residence time increased from 4 h to 6 h; the methyl ester yield remained constant or only slightly decreased. Therefore, to achieve an optimum methyl ester yield, the reaction should be carried out at the flow rate of 0.3 ml/min to obtain a residence time of 4 h.

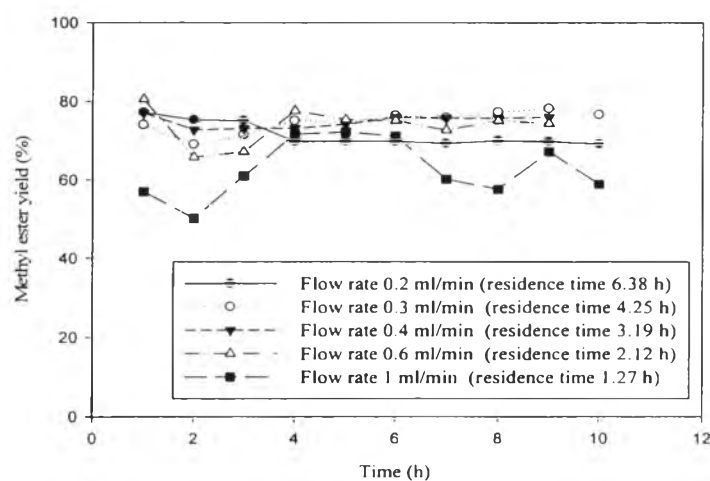


Figure 7.5 Effect of flow rate (or residence time) on the methyl ester yield of palm oil in the continuous reactor (20 wt% K/bentonite clay, methanol/oil = 15:1, amount of catalyst 60 g, catalyst mesh size 10–20 mesh, and reaction temperature 60 °C).

7.4.2.4 Influence of Mass Transfer on Solid Catalyst in a Continuous Reactor

The effect of external mass transfer was investigated by varying the flow rate (or residence time). At a residence time of 1.23 h, the methyl ester yield was still rather unstable about 60 wt%. It could be suggested that the insufficient residence time did not permit biodiesel to reach steady state in the continuous reactor. Moreover, the longer residence time from 1 to 4 h, showed an increase in the methyl ester yield from 60 to 76 wt%; however, the methyl ester yield did not change when the residence time was longer than 4 h. The tendency of the methyl ester yield was not affected by a flow rate above 0.3 ml/min, which can be defined as no limitation of liquid-solid mass transfer diffusion or external mass transfer resistance. The external mass transfer process involves the transfer of a reactant to a solid surface by convection force. At the feed ratio of MeOH/oil 15:1, the methanol-rich phase in the continuous reactor was selected in order to accelerate intermediates, or methoxide ion, on the solid surface. In general, oil is not soluble in methanol and causes a low initial reaction rate; however, when oil is converted to an

intermediate, di- or mono-glyceride is formed in the mixtures. It results in more oil can dissolve in the methanol-rich phase. The limit of diffused oil to methanol could be neglected. At a flow rate of 0.2 ml/min, the methyl ester yield slightly decreased to 71 wt% because the external mass transfer resistance retarded absorption of the reactant. This result was also found by Halim *et al.*, [22] that increasing the flow rate of substrate caused a reduction in mass transfer limitation. The methyl ester yield increased when there was increase in the flow rate. However, if the flow rate was increased to 1 ml/min, the reactants would pass through the catalyst without a reaction due to the limited contact time. Therefore, optimization of the flow rate should be considered to achieve the highest methyl ester yield. We found that with a flow rate under 0.3 ml/min, the external mass transfer limitations in the boundary layer surrounding the catalyst had no significant effect on the methyl ester yield and were not found intense macroscopic phase between oil and methanol when the reaction finished in a continuous reactor.

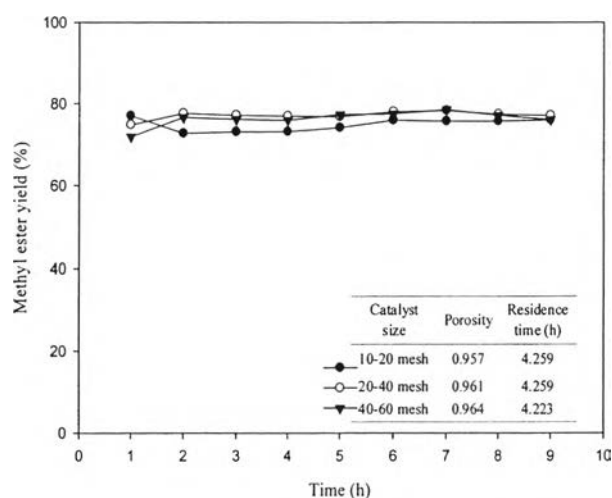


Figure 7.6 Effect of catalyst size on the methyl ester yield of palm oil in the continuous reactor (20 wt% K/bentonite clay, methanol/oil = 15:1, amount of catalyst 60 g, flow rate=0.3 ml/min, and reaction temperature 60 °C).

Although, employing a low flow rate had a relatively effect on the methyl ester yield, it was clear that the steady state of the methyl ester yield

was not affected by the size of the catalysts in this experiment. The various sizes of the catalyst of (10–20, 20–40, and 40–60) mesh were studied for their effect on the methyl ester yield at the flow rate 0.3 ml/min or a residence time longer than 4 h. The results in Figure 7.6 show that the smaller the size of the catalyst, the higher the porosities of the catalyst were, which resulted in a longer residence time; however, the sizes of the catalyst had no noteworthy affect on the methyl ester yield. Therefore, the liquid-solid internal mass transfer limitation was negligible.

7.4.2.5 Influence of Potassium Loading on Bentonite in a Continuous Reactor

Catalyst Characterization

Hammett indicators were used to measure the basic strength of the solid catalyst (Table 7.2.) The pure bentonite clay changed color of the bromothymol blue, but, there was no change in the color of the phenolphthalein, which was in range of $7.2 < H_- < 9.8$; that is typically as a weak basic site. After increasing the K from 5 wt% to 10 wt%, these modified catalysts changed color. The indicator in the range of $9.8 < H_- < 11$ revealed higher basic strength than the pure support. With the further loading of potassium > 15 wt%, the basic strength of the modified catalyst was in the range of $11 < H_- < 15$, and the indicator had no color change. Thus, the highest basic strength was obtained with an amount of potassium of more than 15 wt%.

The basic site had an influence on the catalytic activity for transesterification. Estimated titration was used to measure the basicity of these catalysts. The results (Table 7.2) indicate that the pure bentonite clay had a small basic site of 0.47 mmol/g of catalyst. When increasing the potassium loading to 20 wt% on the bentonite clay, the basic site increased almost tenfold over the pure support. Above 20 wt% of K, the basic site seldom increased. Therefore, the optimum basic properties was achieved at 20 wt% of K on the bentonite clay which gave a basic strength in the range of $11 < H_- < 15$, and a basicity of 3.95 mmol/g of catalyst.

Transesterification Reaction

The effect of potassium loading on the bentonite clay was investigated by varying the amount of K from 5 to 25 wt%. The pure bentonite clay showed no activity (Figure 7.7). At 5 wt% K loading on the bentonite clay, the initial methyl ester yield increased from 1 to 6 h and was constant at 42 wt% after 6 h. It could be suggested that the reactants contacted and reacted consequently with basic site on the catalyst to increase methyl ester yield at the beginning of the reaction. No oil reaction occurred on the active site but the methanol was absorbed and reacted to form methoxide. The rate of methoxide generation depended on both the methanol/oil ratio and an amount of the active site on the catalyst. With a methanol/oil ratio of 15:1, there was excess methanol, which could be attributed to the high dispersion of the reactants. Another limiting factor was the amount of reactive sites, indicated by the Hammett indicators and titration results, and that the low basic strength and basic site were found to be 5 wt%K/bentonite. At the minimally active site, the conversion of methanol to methoxide was fairly slow and corresponded with a gradual increase of the methyl ester yield. After adequate methoxide was created, the methyl ester yield reached the steady state at 6 h. At 10 wt% K/bentonite, the methyl ester yield increased and reached the steady state of 57 wt% in 4 h, which was faster than that of 5 wt% K/bentonite. When loading K from 10 wt% to 20 wt%, the methyl ester yield reached a steady state. The first hour and increased methyl ester yield to 76 wt% in 9 h. However, the methyl ester yield did not reach a steady state when loading K to 25 wt%. It could be explained that the basic strength and the basic site were not risen which resulted in constant of methyl ester yield. Thus, the highest K loading on the bentonite clay was 20 wt% which gave an average methyl ester yield of 76 wt% for transesterification in a continuous reactor.

Table 7.2 Basic properties of bentonite and modified bentonite catalysts

| Catalyst | Basic Strength (H_-) | Basicity (mmol/g of catalyst) |
|------------------------------|-----------------------------|----------------------------------|
| Fresh bentonite | $7.2 < H_- < 9.8$ | 0.475 |
| Fresh 5 wt%K/bentonite | $9.8 < H_- < 11.0$ | 1.192 |
| Fresh 10 wt%K/bentonite | $9.8 < H_- < 11.0$ | 2.028 |
| Fresh 15 wt%K/bentonite | $11.0 < H_- < 15.0$ | 2.908 |
| Fresh 20 wt%K/bentonite | $11.0 < H_- < 15.0$ | 3.956 |
| Fresh 25 wt%K/bentonite | $11.0 < H_- < 15.0$ | 4.023 |
| Use 1 day 20 wt%K/bentonite | $11.0 < H_- < 15.0$ | 3.436 |
| Use 3 day 20 wt%K/bentonite | $11.0 < H_- < 15.0$ | 3.076 |
| Use 5 day 20 wt%K/bentonite | $11.0 < H_- < 15.0$ | 2.831 |
| Use 7 day 20 wt%K/bentonite | $11.0 < H_- < 15.0$ | 2.664 |
| Use 10 day 20 wt%K/bentonite | $9.8 < H_- < 11.0$ | 2.478 |

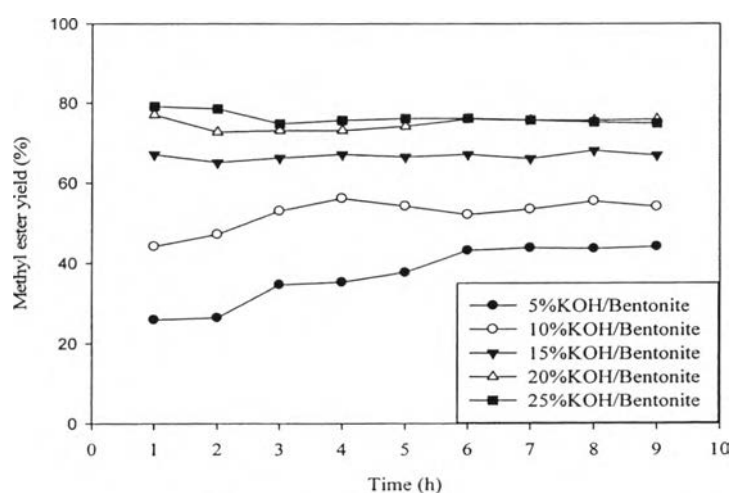


Figure 7.7 Effect of percentage of potassium loading on the methyl ester yield of palm oil in the continuous reactor (amount of catalyst 60 g, methanol/oil = 15, flow rate=0.3 ml/min, catalyst mesh size 10–20 mesh, and reaction temperature 60 °C).

7.4.2.6 Dimensionless Number which Characterize Flow and Intrinsic Kinetic Model

To clarify the characteristic of the flow rate in the experiment, the classical dimensionless has brought to investigate the type of flow in the packed-bed/tubular reactors, the Reynolds Number (Re) was used to classify the type of flow. The kinematic viscosity (ν , m^2/s) of the palm oil; the length of bed height (L , m); the volumetric flow rate (Q , m^3/s); and the pipe cross-sectional area (A , m^2) are used to calculate the Reynolds Number for the pipe (Eq. 3). The Reynolds Number is less than 2300 ($Re < 2300$) in laminar flow. Transient flow is obtained when the Reynolds Number is between 2300 and 4000 ($2300 < Re < 4000$) [23,24].

$$Re = \frac{QL}{\nu A} \quad (3)$$

In this work, the Reynolds Numbers (Table 7.3) are lower than 2300 which mean all flow rates in this experiment were conducted under laminar flow. Moreover, all we carried out under the smallest flow rate of $Re < 1$ and high porous catalyst. Originally, this concept is conducted to use in water which stay in the groundwater reservoir. In this instance, Darcy's law is applicable to explain the saturated of catalyst by methanol and palm oil. The geometry of flow must be accounted for the flow that is measured relative to a different direction. The integrated of Darcy's law flow is in Eq. 4.

$$Q = -Ak \frac{\Delta h}{L} \quad (4)$$

$$Q = -Ak \frac{d}{dz} \left(\frac{p}{\rho g} \right) \quad (5)$$

Where, k is hydraulic conductivity (m/s or ft/s), L is flow path length (m or ft), and h is hydraulic head (m or ft). Darcy's Law is not an application for the flow direction in a homogeneous fluid. Therefore, the geometry of flow must be accounted for the flow that is measured relative to a different direction. In the horizontal flow (x plane), the gravitation (g) is an important role for hydraulic

head as shown in Eq. 5. In vertical downward flow, $dp/dx = 0$, equation reduces to the unit gradient form. Thus, the volumetric flow rate depends only on the permeability of catalyst. On the other hand, the vertical upward flow, dp/dx term relates with the pressure drop. If bed height of catalyst slightly increased the pressure drop should be small. The flows of reactant occur from high pressure to low pressure, so total head pressure at bottom must include velocity head, elevation head, and pressure head to reach the condition that can be negligible the effect of pressure drop[25].

The reaction rate of transesterification of the solid catalysts was studied in a packed-bed reactor. The selectivity of the reaction was considered to be a unit the methyl ester yield which was an equal conversion [26]. To express the mole balance equation for palm oil were classically shown in the Eq. 6 [24], the conversion (x) of palm oil was calculated by using the molar flow rate of palm oil at the outlet (F_{palm} , mol/min), and the molar flow rate of palm oil at the inlet ($F_{palm,i}$, mol/min).

$$-r_{palm} = \frac{-dF_{palm}}{dWc} = \frac{-dF_{palm,i}(1-x)}{dWc} = \frac{dx}{d\left(\frac{Wc}{F_{palm,i}}\right)} \quad (6)$$

When the biodiesel conversion reached equilibrium, the intrinsic kinetic was conducted in the absence of mass-transfer limitation. Table 7.3 showed the results of the reaction rate by calculating and creating curve of data from Polymath. The fifth polynomial degree [$Y_{conversion} = 3.661E10^{-13} + (X \times 2.02E10^{-5}) - (X^2 \times 2.159E^{-10}) + (X^3 \times 1.138E^{-15}) - (X^4 \times 2.916E^{-21}) + (X^5 \times 2.869E^{-27})$] was used to incorporate all data and resulted in $R^2 = 1$. These model data show that the rate of reaction gradually decreased with a decrease in the Reynolds number, or flow rate. The final rate of reaction slowed and reached equilibrium. After the flow rate decreased to 0.2 ml/min, reaction rate was negative. The low flow rate of the reactant did not support the higher reaction rate due to reverse reaction at equilibrium. In the reaction step, methanol was absorbed on the surface and isolated to methoxide. Next triglyceride reacted with the methoxide and produced di-and mono-glycerides, methyl ester, and glycerol. Finally, the biodiesel and glycerol desorbed from the

surface into the media at equilibrium conditions. At a slow flow rate, the rich-glycerol in the media retarded desorption of glycerol on the surface. Thus, equilibrium was shifted from the right side to the left side of the equation due to reversible reaction. To eliminate this problem, the optimum flow rate should be set at 0.3 ml/min.

Table 7.3 Calculation reaction rate (Catalyst weight = 60g)

| Renolds number | 0 | 0.0936 | 0.0560 | 0.0373 | 0.0280 | 0.0186 |
|--------------------------------------------|---|---------------------|---------------------|---------------------|---------------------|---------------------|
| Flow rate (V , ml/min) | 0 | 1 | 0.6 | 0.4 | 0.3 | 0.2 |
| $F_{palm,i}$ ($\times 10^{-3}$, mol/min) | 0 | 0.2122 | 0.3183 | 0.4244 | 0.6366 | 1.061 |
| x = conversion (60 °C) | 0 | 62.72 ± 7.47 | 73.75 ± 4.66 | 74.82 ± 1.58 | 75.05 ± 2.78 | 72.73 ± 3.03 |
| $-r_{palm}$ ($\times 10^{-6}$) | 0 | 4.74 | 1.21 | 0.0182 | 0.0122 | -0.0915 |
| x = conversion (50 °C) | 0 | 44.42 ± 4.85 | 56.16 ± 3.38 | 59.09 ± 1.03 | 60.58 ± 2.58 | 59.81 ± 3.65 |
| $-r_{palm}$ ($\times 10^{-6}$) | 0 | 4.363 | 1.671 | 0.313 | 0.158 | -0.949 |

The simplified kinetic model was analyzed using the transesterification reaction (Eq. 7). The transesterification is generally assumed to be a pseudo first-order reaction in the excess of methanol [27]. The reaction rate at equilibrium for transesterification (Eq. 8) is ascribed to be basis on the production rate per minute in a continuous reactor.



$$r_{palm} = k_1 C_a C_b - k_{-1} C_c C_d = k (C_a C_b - K' C_c C_d) \quad (8)$$

Where a = palm oil, b = methanol, c = methyl ester, d = glycerol, and $K' = k_{-1}/k_1$.

The Arrhenius equation was used to determine the activation energy (E_a) at an absolute temperature (T), in terms of Kelvins or Rankine. The rate

constant (k) was calculated with Eq. 9. The A was the pre-exponential factor and R is the Universal gas constant.

$$k = Ae^{\frac{-Ea}{RT}} \quad (9)$$

The value of T_1 , T_2 was substituted for the reaction temperature. The rate constant (k_1 and k_2) was obtained from Eq. 10 and the results are shown in Table 7.4.

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (10)$$

The activation energy of KOH on bentonite was calculate with Eq. 8 and obtained the value of 46.4 kJ/mol. The activation energy of the homogeneous catalysts, such as NaOH [28] and KOH [29], was in the range of 14–27 kJ/mol (Table 7.5). However, when using a pure solid as a catalyst for tranesterification, the activation energy of the Y-zeolite was 1170 kJ/mol [30]. In theory, the activation energy is classified as the minimum energy which is required for starting a chemical reaction. It could be implied that a minimum Ea , is the fastest reaction rate that would be observed in a catalyst. Some of the pure solids required a long reaction time. Adding an alkaline on the solid support prompted a decrease in Ea of the catalyst, which resulted in increasing rates of the reaction as shown in the Table 5. The Ea value of KF/Ca-Mg-Al [26] and KNO₃/Al₂O₃ [31] was less than that of the pure support because the catalyst, loaded with the alkaline, had high basic strength. When using CaO [32] as a base catalyst was found that the activation energy was 31 kJ/mol, this same as the classic values reported for the activation energies of impregnated base-catalyzed solids. The Ea values could be of relevance to the basic strength of the catalyst. The basic strength, shown by the Hammett indicators of less than 9.8 or a CO₂-desorption temperature lower than 300 °C could be attributed to a high Ea value of 1000 kJ/mol. After impregnation of the base species on the proper supports, the CO₂-desorption temperature was higher than 300 °C that it could be an attribute to the Ea value < 100 kJ/mol. Therefore, well-

prepared catalysts will enhance the basic strength, which means that this is the minimum E_a value in transesterification.

Table 7.4 Reaction of kinetic constants at various reaction temperatures

| Temperature (°C) | Rate constant (k) | K' |
|---------------------|----------------------|--------|
| 60 | 0.9106 | 10.406 |
| 50 | 0.5439 | 19.017 |

Table 7.5 Comparison of the E_a value in this study with standard homogeneous and heterogeneous catalysts used in biodiesel production

| Catalyst | Reactants | E_a value (kJ/mol) | References |
|--------------------------------------------------|----------------------------|-------------------------|------------|
| NaOH | Soybean oil and MeOH | 27.2 | [28] |
| KOH | Palm oil and MeOH | 14.7 | [29] |
| Y-type zeolites | Waste cooking oil and MeOH | 1170 | [30] |
| KF/Ca-Mg-Al | Palm oil and MeOH | 111.6 | [26] |
| KNO ₃ /Al ₂ O ₃ | Jatropha oil and MeOH | 26.96 | [31] |
| CaO | Sunflower oil and MeOH | 31.9 | [32] |
| KOH/bentonite | Palm oil and MeOH | 45.24 | Our work |

7.4.3 Stability Test

According to the petrochemical process, the operational stability of a catalyst is an important consideration in industrial due to operating and maintenance costs. Figure 7.8 shows the stability of 20 wt% K/bentonite in the packed-bed reactor, that transesterification reached equilibrium, and the methyl ester yield was 76 wt%. The stability of 20 wt% K/bentonite lasted longer than 148 h, and maintained a methyl ester value of 70–76 wt% through all out experiments. The efficiency of the process or mass productivity was calculated throughout the week

using the weight of the biodiesel in theory. Productivity of 96.1%, was achieved in this process. The rest of mass might result from efficiency in the separation step.

To elucidate this problem of deactivation during the run, this has been already proposed in our previous work to explain the activity decrease in a reactor [33]. The loss of active species was observed on used catalyst of 1, 3, 7, and 10 days by using XRF. Figure 7.8 shows that the potassium on the solid catalyst leached slightly with increased operating times for 10 days. On the first day, the potassium content in the catalyst rapidly decreased from 22 to 19 wt%, which could be attributed as a weak absorption of K species. The leached potassium was only 13.63% or 9.63×10^{-3} ppm of K/g of oil. The leaching of potassium rarely decreased or remained constant around 19–16 wt% from 3 to 10 days. The strong absorption of the active site on the surface of the catalyst played an important role in biodiesel conversion which this catalyst completely performed heterogeneous catalyst. Although the remaining potassium at 10 days was 16 wt%K on the bentonite, no prolonged activity on the catalyst was observed after 7 days. It could be suggested that the deactivation of 20 wt% K/bentonite catalyst correlated with the active sites that were blocked by adsorbing intermediates or product species. This idea that intermediates, such as di- and tri-glyceride or glycerol, are polar molecules that adsorbed and block the active sites on their catalysts is supported by another researcher [34,35]. The active site, normally, must be a polar molecule on the surface that it quickly absorbed and reacted with intermediate substance or other polar molecules.

Absorbed molecules decreased the availability on the active site leading to a decrease in catalytic activity. An FT-IR was used to test the glycerol absorbed on the surface of the catalyst. The FTIR spectrum on spent catalyst were found at (3500–3000, 2927, 2845, 1668 and 1422) cm^{-1} , which all these peaks involved with the substances and the reacted species. The peak at 3500-3000 is attributed to O–H stretching while the peak at 2927 and 2845 cm^{-1} revealed C–H (CH_3 or CH_2) stretching of alkane, which is found in both glycerol and biodiesel products. The peak at 1668 and 1450 cm^{-1} showed C–O and C=C (unsaturated hydrocarbon), respectively [36,37]. No characteristic peak of bentonite clay was found. The results indicate that the biodiesel and glycerol absorbed on the catalyst

surface. Biodiesel is generally non-toxic with the catalyst due to low polarity; however, glycerol is highly polarity that it might prefer to absorb on active site which led to the quite short operational life of the catalyst.

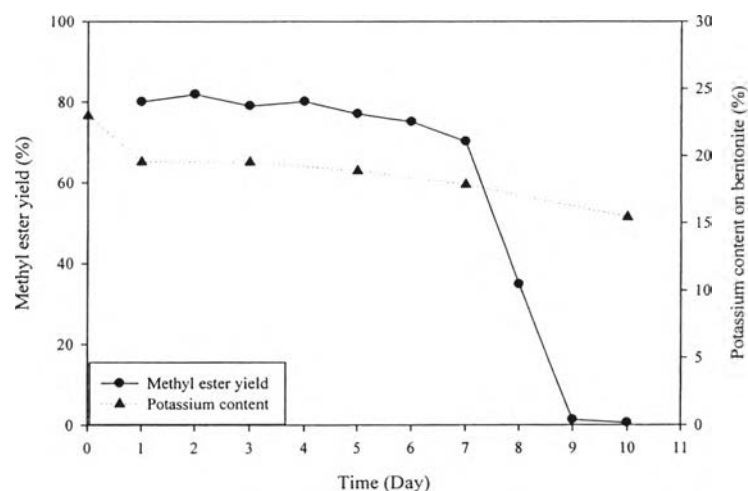


Figure 7.8 Catalyst stability of continuous reactor (20 wt% K/bentonite clay, methanol/oil = 15:1, amount of catalyst 60 g, flow rate=0.3 ml/min, catalyst mesh size 10–20 mesh, and reaction temperature 60 °C).

The basic properties of the spent catalyst were tested. The basic strength of the spent catalyst did not change for 7 days and decreased from $11.0 < H_- < 15.0$ to $9.8 < H_- < 11.0$ at 10 days of operation. Nevertheless, the basic sites of the spent catalyst were observed that the amount of basic site of the catalyst reduced to (13.14, 22.24, and 37.36) % on first, third, and ten days, respectively. On the ten day, the basic sites of the spent catalyst decreased due to both leaching and blocking on the active species. After ten day, the remaining potassium on the bentonite clay, after leaching, was found to be 16 wt%. It should have basic sites higher than 2.8 mmol/g of catalyst in comparison to the fresh catalyst; however, the basic sites of spent catalyst decreased to 2.4 mmol/g, caused by blocking of intermediates and glycerol species. The major decreasing the active site came from the absorbed glycerol, which results in low amount of the basic site was observed. In order to increase stability of the catalyst, the poisonous molecules, which were blocking to active site, should be

removed or separated out to minimize the methyl ester yield and increase the life time of the catalyst. Thus, deactivation of the 20 wt% K/bentonite catalyst was found after 7 days under an operational system due to reducing or blocking of the basic strength and the basic site of the catalyst.

From an economic point of view, prolonged stability and sustained activity are the most importance for the industry in order to decrease the cost of biodiesel. The deactivation of the catalyst cannot be avoided and naturally occurs in all of the solid catalysts. Therefore, 20 wt% K/bentonite support showed evidence of well-operated process for 7 days under the above optimized conditions.

7.5 Conclusions

A comparative study of different supports was demonstrated in a continuous reactor. The KOH sample loaded on NaY, mordenite zeolite, and bentonite clay did not drop an activity and reached a steady state under condition; in contrast, KOH on ZrO_2 and Al_2O_3 dramatically decreased activity due to a large amount of leaching on the active site during the run. Bentonite clay, which was less expensive than zeolite, was productively employed to use for biodiesel process.

In order to demonstrate optimum conditions, the flow rate, no distinct external diffusion limitation was observed. The internal transfer was negligible with catalysts less than 10–20 mesh. The results indicated that a decrease in the flow rate below 0.3 ml/min had no significant effect on the conversion of biodiesel. In addition, the 20 wt% of potassium loading on bentonite exhibited high basic properties which promoted transesterification reaction. The 20 wt% K/bentonite catalyst produced a methyl ester yield of 76 wt% with a reaction temperature of 60 °C, methanol-to-oil molar ratio of 15:1, residence time of 4.25 h, mesh size of catalyst of 10–20, and amount of catalyst of 60 g. The activation energy of this catalyst for the transesterification reaction of 45.24 kJ/mol was calculated. The stability test of 20 wt% K/bentonite took 7 days, and no significant decrease in potassium on the bentonite was observed after first day. The results indicated that deactivation of this catalyst was caused by an intermediate—glycerol molecule—which blocked the basic site on the catalyst surface.

7.6 Acknowledgments

This work was financially supported by the National Metal and Materials Technology Center, Thailand, and the National Excellence Center for Petroleum, Petrochemicals, and Advanced Materials, Thailand.

7.7 References

- [1] J.V. Gerpen, Biodiesel processing and production, *Fuel Process. Technol.* 86 (2005) 1097–1107.
- [2] Y.C. Chien, M. Lu, M. Chai, F.J. Boreo, Characterization of biodiesel and biodiesel particulate matter by TG, TG-MS, and FTIR, *Energy Fuels* 23 (2009) 202–206.
- [3] E. Torres-Jimenez, M. Svoljšak-Jerman, A. Gregorc, I. Lisec, M.P. Dorado, B. Kegl, Physical and chemical properties of ethanol-biodiesel blends for diesel engines, *Energy Fuels* 24 (2010) 2002–2009.
- [4] W. Xie, H. Li, Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil, *J. Mol. Catal. A.* 255 (2006) 1–9.
- [5] X. Bo, X. Guomin, C. Lingfeng, W. Ruiping, G. Lijing, Transesterification of palm oil with methanol to biodiesel over a $\text{KF}/\text{Al}_2\text{O}_3$ heterogeneous base catalyst, *Energy Fuels* 21 (2007) 3109–3112.
- [6] H. Ma, S. Li, B. Wang, R. Wang, S. Tian, Transesterification of rapeseed oil for synthesizing biodiesel by $\text{K}/\text{KOH}/\gamma\text{-Al}_2\text{O}_3$ as heterogeneous base catalyst, *J. Am. Oil. Chem. Soc.* 85 (2008) 263–270.
- [7] O. Ilgen, A. N. Akin, Transesterification of canola oil to biodiesel using MgO loaded with KOH as a heterogeneous catalyst, *Energy Fuels* 23 (2009) 1786–1789.
- [8] E. Li, V. Rudolph, Transesterification of vegetable oil to biodiesel over MgO -functionalized mesoporous catalysts, *Energy Fuels* 22 (2008) 145–149.
- [9] X. Liu, H. He, Y. Wang, S. Zhu, Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst, *Catal. Commun.* 8 (2007) 1107–1111.

- [10] D.M. Alonso, R. Mariscal, R. Moreno-Tost, M.D.Z. Poves, M.L. Granados, Potassium leaching during triglyceride transesterification using $K/\gamma\text{-Al}_2\text{O}_3$ catalysts, *Catal. Commun.* 8 (2007) 2080–2086.
- [11] G.J. Suppes, M.A. Dasari, E.J. Doskocil, P.J. Mankidy, M.J. Goff, Transesterification of soybean oil with zeolite and metal catalysts, *Appl. Catal. A Gen.*, 257 (2004) 213–223.
- [12] A. Brito, M.E. Borges, N. Otero, Zeolite Y as a heterogeneous catalyst in biodiesel fuel production from used vegetable oil, *Energy Fuels*, 21 (2007) 3280–3283.
- [13] A. D’Cruz, M.G. Kulkarni, L.C. Meher, A.K. Dalai, Synthesis of biodiesel from canola oil using heterogeneous base catalyst, *J. Am. Oil. Chem. Soc.* 84 (2007) 937–943.
- [14] X. Liu, X. Piao, Y. Wang, S. Zhu, H. He, Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol, *Fuel* 87 (2008) 1076–1082.
- [15] S. Hama, H. Yamaji, T. Fukumizu, T. Numata, S. Tamalampudi, A. Kondo, H. Noda, H. Fukuda, Biodiesel-fuel production in a packed-bed reactor using lipase-producing *Rhizopus oryzae* cells immobilized within biomass support particles, *Biochem. Eng. J.* 34 (2007) 273–278.
- [16] A.R. Rodrigues, A. Paiva, M.G. Silva, P. Simões, S. Barreiros, Continuous enzymatic production of biodiesel from virgin and waste sunflower oil in supercritical carbon dioxide, *J. Supercrit. Fluids.* 56 (2011) 259–264.
- [17] V. Dossat, D. Combes, A. Marty, Continuous enzymatic transesterification of high oleic sunflower oil in a packed bed reactor: Influence of the glycerol production, *Enzyme Microbial Technol.* 25 (1999) 194–200.
- [18] N.S. Kitakawa, H. Honda, H. Kuribayashi, T. Toda, T. Fukumura, T. Yonemoto, Biodiesel production using anionic ion-exchange resin as heterogeneous catalyst, *Bioresour. Technol.* 98 (2007) 416–421.
- [19] L.S. Hsieh, U. Kumar, J.C.S. Wu, Continuous production of biodiesel in a packed-bed reactor using shell–core structural $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$ catalyst, *Chem. Eng. J.* 158 (2010) 250–256.

- [20] F. Bergaya, B.K.G. Theng, G. Lagaly, Handbook of Clay Science, Developments in Clay Science, First ed., Elsevier Ltd., 2004.
- [21] R.S. Singha, G.K. Saini, J.F. Kennedy, Continuous hydrolysis of pullulan using covalently immobilized pullulanase in a packed bed reactor, Carbohydr. Polym. 83 (2010) 672–675.
- [22] S.F.A. Halim, A.H. Kamaruddin, W.J.N. Fernando, Continuous biosynthesis of biodiesel from waste cooking palm oil in a packed bed reactor: Optimization using response surface methodology (RSM) and mass transfer studies, Bioresour. Technol. 100 (2009) 710–716.
- [23] W.M. Deen, Analysis of Transport Phenomena, second ed., Published by Oxford University Press, Inc, New York, 1998.
- [24] H.S. Fogler, Elements of Chemical Reaction Engineering, fourth ed., Pearson Education International, 2006.
- [25] R.A. Freeze, J.A. Cherry, Groundwater, Prentice Hall, (1979).
- [26] Y. Xiao, L. Gao, G. Xiao, J. Lv, Kinetics of the transesterification reaction catalyzed by solid base in a fixed-bed reactor, Energy Fuels 24 (2011) 5829–5833.
- [27] S. Yan, M. Kim, S.O. Salley, K.Y.S. Ng, Oil transesterification over calcium oxides modified with lanthanum. Applied Catalysis A: General, 360 (2009) 163–170.
- [28] M. Morgenstern, J. Cline, S. Meyer, S. Cataldo, Determination of the kinetics of biodiesel production using proton nuclear magnetic resonance spectroscopy (^1H NMR), Energy Fuels 20 (2006) 1350–1353.
- [29] D. Darnoko, M. Cheryan, Kinetics of palm oil transesterification in a batch reactor, J. Am. Oil. Chem. Soc. 77 (2000) 1263–1267.
- [30] A. Brito, M.E. Borges, N. Otero, Zeolite Y as a heterogeneous catalyst in biodiesel fuel production from used vegetable oil, Energy Fuels 21 (2007) 3280–3283.
- [31] A.P. Vyas, N.S. Payal A. Patel, Production of biodiesel through transesterification of jatropha oil using $\text{KNO}_3/\text{Al}_2\text{O}_3$ solid catalyst, Fuel 88 (2009) 625–628.

- [32] Dj. Vujicic, D. Comic, A. Zarubica, R. Micic, G. Boskovic, Kinetics of biodiesel synthesis from sunflower oil over CaO heterogeneous catalyst, *Fuel* 89 (2010) 2054–2061.
- [33] P. Intarapong, A. Luengnaruemitchai, S. Jai-In, Biodiesel production from palm oil over KOH/NaY zeolite in a packed-bed reactor, *IJRER*, 1 (2011) 271–280.
- [34] S. Yan, H. Lu, B. Liang, Supported CaO Catalysts used in the transesterification of rapeseed oil for the purpose of biodiesel production, *Energy Fuels* 22 (2008) 646–651.
- [35] H. Gorzawski, W.F. Hoelderich, Transesterification of methyl benzoate and dimethyl terephthalate with ethylene glycol over superbases, *Appl. Catal. A: Gen.* 79 (1999) 131–137.
- [36] J.S. Oliveira, R. Montalvão, L. Daher, P.A.Z. Suarez, J.C. Rubim, Determination of methyl ester contents in biodiesel blends by FTIR-ATR and FTNIR spectroscopies, *Talanta*, 69 (2006) 1278–1284.
- [37] H. Imahara, E. Minami, S. Hari, S. Saka, Thermal Stability of Biodiesel Fuel as Prepared by Supercritical Methanol Process, The 2nd Joint International Conference on “Sustainable Energy and Environment (SEE 2006)” C-037 (P) 21-23 November 2006, Bangkok, Thailand.