CHAPTER IV

A COMPARATIVE STUDY OF KOH/Al₂O₃ AND KOH/NaY CATALYSTS FOR BIODIESEL PRODUCTION VIA TRANSESTERIFICATION FROM PALM OIL

4.1 Abstract

The transesterification of palm oil to methyl esters (biodiesel) was studied using KOH loaded on Al₂O₃ and NaY zeolite supports as heterogeneous catalysts. Reaction parameters such as reaction time, wt% KOH loading, molar ratio of oil to methanol, and amount of catalyst were optimized for the production of biodiesel. The 25 wt% KOH/Al₂O₃ and 10 wt% KOH/NaY catalysts are suggested here to be the best formula due to their biodiesel yield of 91.07% at temperatures below 70 °C within 2–3 h at a 1:15 molar ratio of palm oil to methanol and a catalyst amount of 3–6 wt%. The leaching of potassium species in both spent catalysts was observed. The amount of leached potassium species of the KOH/Al₂O₃ was somewhat higher compared to that of the KOH/NaY catalyst. The prepared catalysts were characterized by using several techniques such as XRD, BET, TPD, and XRF.

4.2 Introduction

Biodiesel, which is considered to be a possible substitute of conventional diesel, is biodegradable, non-toxic, renewable, and has reduced emissions of CO, SO₂, particulates, and hydrocarbons as compared to conventional diesel [1]. Biodiesel can be used as conventional diesel in diesel engines because its properties are very close to petroleum-based diesel. For example, biodiesel has the proper viscosity, a high flash point, a high cetane number, and no engine modifications are required when using biodiesel. Transesterification is a reaction whereby vegetable oil or fat reacts with alcohol by using a catalyst to form alkyl esters and glycerol. The type of alkyl ester produced depends on the type of alcohol used and the type of free fatty acid in the vegetable oils. Methanol is one type of alcohol that is favored for use

in this process because it may provide a proper viscosity and boiling point and a high cetane number [2].

Nowadays, most of the commercial biodiesel comes from the transesterification of vegetable oil using a basic catalyst, such as NaOH or KOH, because a basic catalyst can catalyze faster than an acid catalyst [3]. But homogeneous catalysts have many problems and lead to a reduced yield of biodiesel. For example, hydrolysis and saponification are side reactions of transesterification, resulting in the formation of soap [4] which is hard and high cost to separate the catalyst from the product. And a large amount of wastewater is produced in separating and cleaning the catalyst and the products [5]. A heterogeneous catalyst is a new choice and has been receiving the most attention for replacing the homogeneous catalyst in the transesterification process. Solid bases have been observed to be more active than metal compounds and require milder reaction conditions than acids [9,10]. More recently, there has been an increasing development of heterogeneous catalysts, such as NaOH and a series of potassium catalysts supported on alumina [6,7], alkali-doped metal oxide [8], and zeolite [9]. The activity of solid bases generally increased with base strength. Although the reaction is complete, there are some interests in the leaching of active species on the support. It was reported that the heterogeneous catalysts lose some activity after their use. The leaching of potassium on γ -Al₂O₃ to methanol during the reactionwas reported [15]; however, no leaching tests of potassium on zeolite were investigated.

Some researchers proposed that the reusability depends on the active species on the surface, which could be determined by using atomic absorption spectrometry (AAS) or inductively coupled plasma-atomic emission spectrometry (ICP-AES), such as alkaline doped on metal oxide [7], NaOH/alumina [6], and K/ γ -Al₂O₃ [11] to determine the active species on the fresh and spent catalysts. It was suggested that the leaching of active species to the reaction mixture will reduce the activity and reutilization of a solid catalyst. Therefore, the determination of the leached active species on a solid support is important because that leached active species also has a negative effect on the amount of washing water in industry.

This present work was focused on the production of biodiesel from refined palm oil by using heterogeneous catalysts. We have developed two types of heterogeneous catalysts, KOH/Al₂O₃ and KOH/NaY, prepared by impregnation and applied to determine the optimum conditions for biodiesel production. Several factors which may influence the quality of the produced biodiesel were investigated, including the reaction time, wt% loading of the catalyst on the support, molar ratio of methanol to oil, amount of catalyst, and stirrer speed. Moreover, reusability was investigated by XRF to determine the amount of active species on the prepared and spent catalysts.

4.3 Experimental

4.3.1 Materials and Methods

4.3.1.1 Characterization of Vegetable Oil

The palm oil used in the present research was obtained from the Naval Engineering Command (Thailand) and was analyzed based on density at 27°C, kinematics viscosity (ASTM D-445), free fatty acid content (AOCS Cd 3a– 63), moisture content (AOCS Aa 3–38), and fatty acid composition (AOCS Ce 1– 62).

4.3.2 Catalyst Preparation

4.3.2.1 KOH/Al₂O₃ Catalyst

A series of KOH/Al₂O₃ catalysts with varying KOH loadings (10, 15, 20, 25, 30, and 35 wt%) were prepared by the impregnation of an Al₂O₃ support (COA World Chemicals) with an aqueous solution of KOH (Carlo Erba). The prepared catalysts were dried in an oven at 110 °C for 24 h and were calcined at 500 °C for 3 h.

4.3.2.2 KOH/NaY Catalyst

The NaY zeolite is the most widely used in industry because of its large pore openings and high surface area. The stability of a zeolite support depends on the structure and the Si/Al ratio [16]. The stability of the crystal lattice structure increases with increasing Si/Al ratio, which reveals that NaY (Si/Al = 2–4) has a higher crystal stability than NaX (Si/Al = 1–1.5) zeolite. A KOH/NaY was prepared by the method reported by Xie *et al.* (2007). NaY/zeolite was dried in an oven at 110 °C for 2 h to remove the absorbed water on the surface. The NaY zeolite (TOSOH Corporation) was impregnated with an aqueous solution of KOH with various loadings (8, 9, 10, 13, and 15 wt%) for 24 h. Finally, it was dried in air at 110°C for 24 h.

4.3.3 Catalyst Characterization

Temperature-programmed desorption (Micromeristics 2900) was used for observing desorbed molecules from the surface when the surface temperature is increased. The basic properties of the samples were determined using the temperature-programmed desorption of CO₂ (CO₂-TPD), which was used as the probe molecule. A 50 mg sample was degassed by heating in a flow of helium gas at a rate of 8 °C/min from room temperature to 600 °C, and was kept at 600 °C for 2 h. And then, adsorption of CO₂ gas occurred at 100 °C. After that, the physically adsorbed CO₂ gas was purged by a He flow at 25 °C for 2 h. CO₂-TPD was performed at the rate of 10 °C/min up to 600 °C. Energy dispersive X-ray fluorescence (XRF) spectrometry (Oxford model ED2000) was used to determine the bulk composition of a catalyst. The potassium content was measured by XRF in the fresh and spent catalysts. Leached potassium referred to the total amount of potassium in the fresh catalyst withdrawn from the amount of potassium in the spent catalyst.

Energy dispersive X-ray fluorescence (XRF) spectrometry (Oxford model ED2000) was used to determine the bulk composition of a catalyst. The potassium content was measured by XRF in the fresh and spent catalysts. Leached potassium referred to the total amount of potassium in the fresh catalyst withdrawn from the amount of potassium in the spent catalyst.

4.3.4 Transesterification

One hundred grams of vegetable oil was weighed and placed in a 500 ml three-necked flask. The vegetable oil was heated to 60 °C by heater. The desired amount of methanol and catalyst was weighed and added into the oil reactor. A magnetic stirrer was used for mixing the oil, methanol, and catalyst at the desired

speed. The reaction was carried out until it reached the desired reaction time. After that, the reaction had to be stopped by cooling the reactor to room temperature and the catalyst was immediately separated from the product mixture by using a suction flask. The mixture was placed in the separatory funnel and allowed to stand overnight to ensure that the separation of the methyl esters and the glycerol phase occurred completely. The glycerol phase (bottom phase) was removed and left in a separate container. Finally, the methyl esters (biodiesel) were dried by adding 25 wt% Na₂SO₄ (Fisher Scientific) base on weight of oil.

4.4 Results and Discussion

4.4.1 Characterization of Vegetable Oil

Some properties of the palm oil (such as density, kinematic viscosity, free fatty acid content, and moisture content) were determined, and are shown in Table 4.1.

Table 4.1 Properties of the palm oil

Properties	Value
Density at 27 °C (g/ml)	0.901
Kinematic viscosity (cSt)	40.51
Free fatty acid (%)	0.357
Moisture content (ppm)	452.8

4.4.2 Characterization of Catalyst

4.4.2.1 X-ray Diffraction (XRD)

The XRD patterns of Al_2O_3 and KOH/Al_2O_3 with various wt% loadings of KOH are shown in Figure 4.1. The XRD patterns of fresh Al_2O_3 show the typical diffraction peaks at $2\theta = 20$, 32, 37, 46, and 67°. When the loading amount of KOH was increased to 5 and 10 wt%, the XRD patterns were almost the same as the typical pattern of Al_2O_3 because KOH can be well dispersed on the

Al₂O₃ support in the form of a monolayer at a low loading of KOH. And when the loading amount of KOH was further increased to 15 wt%, the new phase of K₂O can be observed at $2\theta = 31$, 39, 51, 55, and 62° [7]. A new phase of K₂O can also be observed in 20 and 25 wt% KOH/Al₂O₃ at the same position. But when the loading amount of KOH is further increased to over 30 wt%, a new phase of a compound containing potassium and alumina elements could be observed at $2\theta = 17$, 23, 25, 29, 30, 31, 34, 36, 38, 40, 44, 46, 47, 48, 51, and 52° (JCPDS 00-019-0927). These results agree well with the result of KNO₃/Al₂O₃ reported by Xie *et al.* [11]. They explained that at low KOH loading, the XRD patterns are identical to that of Al₂O₃ because of the good dispersion of KOH on Al₂O₃. And when the KOH loading was increased to 15–25 wt%, the new phase of K₂O was observed. And if there is a further increase in the KOH loading to over 25 wt%, the new phase of Al–O–K compound could be observed.



Figure 4.1 XRD patterns of the Al_2O_3 and KOH/Al_2O_3 catalysts: (a) Al_2O_3 , (b) 5% KOH/Al_2O_3 , (c) 10% KOH/Al_2O_3 , (d) 15% KOH/Al_2O_3 , (e) 20% KOH/Al_2O_3 , (f) 25% KOH/Al_2O_3 , (g) 30% KOH/Al_2O_3 , and (h) 35% KOH/Al_2O_3 .

The XRD patterns of KOH/NaY with various wt% loadings of KOH are shown in Figure 4.2. The result shows that XRD patterns of all the KOH/NaY catalysts had the same XRD patterns as that of the NaY zeolite, and the intensity of the XRD patterns decreased when the loading amount of KOH was increased, showing diffraction peaks at $2\theta = 6$, 10, 12, 13, 14, 16, 17, 18, 20, 21, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 38, 40, 41, 42, 43, 44, 45, and 46° (JCPDS 00-039-1380). It was suggested that the catalysts containing 7–15 wt% KOH had no significant effect on the crystalline structure. Xie *et al.* [12] explained that the KOH modification could maintain the pore structure of zeolite that is necessary for catalysis.



Figure 4.2 XRD patterns of the NaY and KOH/NaY catalysts: (a) NaY, (b) 7% KOH/NaY, (c) 8% KOH/NaY, (d) 9% KOH/NaY, (e) 10% KOH/NaY, (f) 13% KOH/NaY, and (g) 15% KOH/NaY.

4.4.2.2 BET Surface Area Measurement

The surface areas were determined by BET measurements of KOH/Al₂O₃ and KOH/NaY as shown in Table 4.2. The results show that the surface area of fresh KOH/Al₂O₃ and KOH/NaY catalysts decreased when the loading amount of KOH increased. The spent 25 wt% KOH/Al₂O₃ catalyst had a higher surface area than the fresh catalyst due to leaching of the active species. On the other hand, the spent 10 wt% KOH/NaY catalyst had a lower surface area than the fresh catalyst. However, the loss of surface area in the catalyst has lesser impact than the loss of active species on the catalyst.

 Table 4.2 Surface areas of the studied fresh and spent KOH on alumina and NaY

 zeolite catalysts

Catalyst	Surface Area (m ² /g)
Fresh Al ₂ O ₃	208.48
Fresh 10 % KOH/Al ₂ O ₃	142.8
Fresh 20 % KOH/Al ₂ O ₃	16.5
Fresh 25 % KOH/Al ₂ O ₃	7.68
Fresh 30 % KOH/Al ₂ O ₃	7.00
Spent 25 % KOH/Al2O3	47.00
Fresh NaY	738.01
Fresh 9 % KOH/NaY	161.46
Fresh 10 % KOH/NaY	35.59
Fresh 13 % KOH/NaY	19.68
Fresh 15 % KOH/NaY	13.81
Spent 10 % KOH/NaY	14.08

4.4.2.3 Temperature-programmed Desorption (TPD)

The TPD profiles of desorbed CO₂ on Al₂O₃, KOH/Al₂O₃, NaY, and KOH/NaY catalysts are shown in Figure 4.3. The results show desorption peaks of Al₂O₃ and 25 wt% KOH/Al₂O₃ at 155 and 195 °C, respectively. The peak at a temperature of ~ 155 °C can be attributed to the interaction of CO₂ with sites of weak basic strength [13]. It has been proposed that these sites correspond to the OH groups on the surface. A desorption peak for 25 wt% KOH/Al₂O₃ can be attributed to basic sites of medium strength, related to the activity of that catalyst [11]. It is clearly observed that the basic strength increases as the KOH loading increases. Similarly, the results show desorption peaks of NaY and 10 wt% KOH/NaY at 200 and 285 °C, respectively. The peak at a temperature of 200 °C can be attributed to the interaction of CO₂ with sites of weak basic strength [13]. It has been proposed that these sites correspond to the OH⁻ groups on the surface. A desorption peak for 10 wt% KOH/NaY can be attributed to basic sites of medium strength, related to the activity of that catalyst [11,14]. It is clearly observed that the basic strength increases as the KOH loading increases.



Figure 4.3 TPD profiles of CO₂ on Al₂O₃, NaY, 25 wt% KOH/Al₂O₃ catalysts, and 10 wt% KOH/NaY catalysts.

4.4.2.4 X-ray Fluorescence (XRF)

XRF was used to determine the potassium content before and after the reaction of 25 wt% KOH/Al₂O₃ and 10 wt% KOH/NaY for checking the capacity of the active species for reuse in the reaction (see Table 4.3). The results show that 51.26 % of the potassium of 25 wt% KOH/Al₂O₃ was leached from the surface, corresponding to the BET result of the spent 25 wt% KOH/Al₂O₃ catalyst, having a higher surface area than that of the fresh catalyst, because the part of the K initially deposited on the catalyst surface is leached from the solid, which reveals a lack of chemical stability of the catalysts under reaction conditions [6]. Therefore, the leached potassium of 25 wt% KOH/Al₂O₃ could catalyze the transesterification as a homogeneous catalyst. For the KOH/NaY catalyst, it was found that 3.18 % of the K was leached. The concentration of the K species related to the active sites did not change significantly; therefore, the overall performance shows that the 10 wt% KOH/NaY catalyst is expected to be a more appropriate catalyst compound than the 25 wt% KOH/Al₂O₃. In the heterogeneous catalyst, it is important to ensure that the active species are not leached from the solid support of the catalyst. If the leaching of the active species on the catalyst is high, the active species could act as a homogeneous part, and the process advantages of the heterogeneous catalysts are lost

[8,15]. The result of this present study implies that the support type strongly affects the activity of the heterogeneous catalyst for the transesterification of palm oil. It suggests that K in the NaY zeolite is more bound to the zeolite matrix.

Catalyst	K (wt%)
Fresh 25 %KOH/Al ₂ O ₃	25.75
Spent 25 %KOH/Al ₂ O ₃	12.55
Fresh 10 %KOH/NaY	12.07
Spent 10 %KOH/NaY	11.68

Table 4.3 Potassium content of the prepared catalysts from XRF analysis

4.4.3 Transesterification

KOH/Al₂O₃ and KOH/NaY zeolite catalysts are classified as basic and studied as a heterogeneous catalyst for transesterification. To investigate the optimum conditions for these catalysts on the transesterification of palm oil, the starting conditions for the potassium hydroxide on the supports were set with 20 wt% KOH/Al₂O₃ and 10 wt% KOH/NaY at a methanol to oil molar ratio of 15:1, a reaction temperature of 60 °C, 3 and 6 wt% of the catalyst (based on the weight of the vegetable oil), respectively, and a stirrer speed of 300 rpm.

4.4.3.1 Influence of Reaction Time on the Biodiesel Yield

The effect of reaction time on the yield of biodiesel was studied using the 20 wt% KOH/Al₂O₃ and 10 wt% KOH/NaY catalysts. The reaction time was varied within a range from 1 to 6 h. As can be seen from Figure 4.4, for the KOH/Al₂O₃ catalyst, the yield increased in the initial 2 h and afterwards remained nearly constant as a result of near-equilibrium conversion. A maximum yield of 87.5% was obtained after 6 h. The optimum reaction time was obtained at 2 h, where the yield of biodiesel was about 81.96%. Similarly, for the KOH/NaY catalyst, the yield increased in 2–3 h and afterwards remained nearly constant. The optimum reaction time was obtained at 3 h and the yield of biodiesel was about 91.07%.



Figure 4.4 Yield of biodiesel as a function of reaction time.

4.4.3.2 Influence of wt% of KOH Loading on the Biodiesel Yield

The effect of wt% KOH loading on the yield of biodiesel was studied. The KOH/Al₂O₃ catalysts were prepared by varying the loading amount of KOH from 15 to 35 wt% and were used to catalyze the transesterification reaction. Reaction conditions for the KOH/Al₂O₃ was 2 h reaction time, 15:1 methanol to oil molar ratio, 3 g of the catalyst, 300 rpm stirrer speed, and 60 °C. The results shown in Figure 4.5 reveal that as the loading amount of KOH was increased from 15 to 25 wt%, the biodiesel yield was increased, and the highest yield (91.07%) was obtained at a KOH loading of 25 wt% on Al₂O₃. However, when the amount of loaded KOH was over 25 wt%, the biodiesel yield decreased. It is believed that the agglomeration of the active KOH phase or the covering of the basic sites by the excess KOH occurred, and hence a lowering of the surface area of the catalyst and less activity. Even though it is unclear how the KOH impregnated on the surface of the support, it is likely that when the amount of loaded K was raised to 15 wt%, new characteristic XRD peaks (Figure 4.1) were observed. These results agree well with the result of KNO_3/Al_2O_3 [11]. It was found that the new phase of K_2O was the cause of the high catalytic activity and basicity of the catalyst since, when increasing the KOH loading to 15-25 wt%, the new phase of K₂O was observed and the biodiesel yield was increased. And when further increasing the KOH loading to over 25 wt%, a new

phase of Al–O–K compound was observed and the biodiesel yield decreased. This is because the new phase (Al–O–K) compound has lower catalytic activity and basicity than the K₂O phase. Correspondingly, the KOH/NaY catalysts were prepared by varying the loading amount of KOH from 8 to 15 wt% and were used to catalyze the transesterification reaction. The reaction conditions for KOH/NaY were 3 h reaction time, 15:1 methanol to oil molar ratio, 6 g of the catalyst, 300 rpm stirrer speed, and 60 °C. The results showed that as the loading amount of KOH was increased from 8 to 10 wt%, the biodiesel yield was increased, and the highest yield (91.07%) was obtained at a KOH loading of 10 wt% on NaY. When the amount of loaded KOH was over 10 wt%, the biodiesel yield was decreased.



Figure 4.5 Yield of biodiesel as a function of wt% KOH.

In addition, the product distribution in the esteric phase for the run performed at 60 °C in the presence of KOH/Al₂O₃ and KOH/NaY was determined by GC analysis. The methyl ester content and mono-, di-, tri-glycerides of biodiesel with various wt% loadings of KOH on Al₂O₃ and NaY are shown in Figures 4.6 and 4.7, respectively. For KOH/Al₂O₃, methyl ester content was increased when the loading amount of KOH was increased from 15 to 25 wt% and the highest methyl ester content of 95.48% w/w was obtained at a KOH loading of 25 wt% on Al₂O₃. But mono-, di- and tri-glycerides content decreased when increasing the KOH loading since transesterification consists of a sequence of three consecutive and reversible reactions. In the first step, tri-glyceride is converted to diglyceride. In the second, diglyceride is converted to monoglyceride, and then monoglyceride is converted to glycerol. For each step, one molecule of methyl ester is liberated, so when the methyl ester increased, the mono-, di- and tri-glycerides were decreased because these three types of glyceride are converted to methyl ester.

In the same way, for the KOH/NaY catalyst, it was found that the methyl ester content was increased when the loading amount of KOH was increased from 8 to 13 wt%, and the highest methyl ester content of 92.84% was obtained at a KOH loading of 13 wt% on NaY.

The conversions of biodiesel with various wt% loadings of KOH on Al_2O_3 and NaY are shown in Figure 4.8. For the KOH/ Al_2O_3 catalyst, the highest conversion (86.93%) was obtained at a KOH loading of 25 wt% on Al_2O_3 . In the KOH/NaY catalyst, the highest conversion (84.55%) was obtained at a KOH loading of 13 wt% on NaY.



Figure 4.6 Methyl ester content and mono-, di-, tri-glycerides of biodiesel as a function of wt% KOH loading on alumina.



Figure 4.7 Methyl ester content and mono-, di-, tri-glycerides of biodiesel as a function of wt% KOH loading on NaY.



Figure 4.8 Conversion of biodiesel as a function of wt% KOH loading.

4.4.3.3 Influence of Molar Ratio of Methanol to Oil on the Biodiesel Yield

From the stoichiometry, transesterification requires a molar ratio of methanol to oil of 3:1. Since this reaction is a reversible reaction, the effect of this molar ratio on the yield of methyl ester was studied by varying the methanol from 6 to 21. In addition, for the transesterification catalyzed using a heterogeneous catalyst, mass transfer is limited, leading to low biodiesel yield, as shown in Figure 4.9. The reaction conditions for the KOH/Al₂O₃ were 2 h reaction time, 25 wt% KOH, 3 g of catalyst, 300 rpm stirrer speed, and 60 °C. The results showed that when the molar ratio of methanol to oil was increased, the biodiesel yield was increased and the highest yield (91.07%) was obtained at a methanol to oil molar ratio of 15:1. Beyond the molar ratio of 15:1, the excess amount of methanol had no effect on biodiesel yield. However, it has been reported that when the amount of methanol was over 15:1, glycerol separation becomes more difficult, resulting in a decrease of biodiesel yield [5]. For the KOH/NaY catalyst, reaction conditions were 3 h reaction time, 10 wt% KOH, 6 g of catalyst, 300 rpm stirrer speed, and 60 °C. The result showed that when the molar ratio of 15:1. When further increasing the molar ratio to oil over 15:1, the excess amount of methanol to oil was increased, and the highest yield (91.07%) was obtained at a methanol to oil was increased, the biodiesel yield increased, and the highest yield (91.07%) was obtained at a methanol to oil molar ratio of 15:1. When further increasing the molar ratio to oil over 15:1, the excess amount of methanol had no effect on biodiesel yield increased, and the highest yield (91.07%) was obtained at a methanol to oil molar ratio of 15:1. When further increasing the molar ratio to oil over 15:1, the excess amount of methanol had no effect on biodiesel yield.



Figure 4.9 Yield of biodiesel as a function of molar ratio of methanol to oil.

4.4.3.4 Influence of Amount of Catalyst on the Biodiesel Yield

To determine the influence of amount of catalyst on biodiesel yield, the catalyst amount was varied within the range of 1-5 wt%. The reaction was

carried out with 25 wt% KOH/Al₂O₃ at a methanol to oil molar ratio of 15:1, a stirrer speed of 300 rpm, and a temperature of 60 °C. The results showed that when the amount of catalyst was not sufficient, the yields of biodiesel are relatively low (w80%). Biodiesel yields were increased from 80.35 to 91.07% as the amount of KOH/Al₂O₃ was increased from 1 to 3 g. And with a further increase in the amount of catalyst to over 3 g, the mixture of reactants and catalyst became too viscous, leading to a problem of mixing. To avoid these problems, the optimum condition must be employed at 3 g, which gave a 91.07% yield of biodiesel. The reaction with the KOH/NaY catalyst was carried out with 10 wt% KOH/NaY at a methanol to oil molar ratio of 15:1, 300 rpm stirrer speed, and 60 °C. The results showed that at low amounts of catalyst, the yields of biodiesel are relatively low (~73%). With a further increase in the amount of catalyst, the biodiesel yields increased from 73.21 to 91.07%. The optimum amount of catalyst was 6 g, and a 91.07% yield of biodiesel was obtained as shown in Figure 10. Moreover, the optimum stirrer speed was at 300 rpm. The result is in agreement with the result of a heterogeneous base catalyst reported by Kim et al. [5].



Figure 4.10 Yield of biodiesel as a function of amount of catalyst.

4.5 Conclusions

The heterogeneous catalysts, KOH/Al₂O₃ and KOH/NaY, can be used as solid base catalysts for biodiesel production via transesterification. The optimum conditions for KOH/Al₂O₃ was 2 h reaction time, 25 wt% KOH/Al₂O₃, 15:1 methanol to oil molar ratio, 3 g of catalyst, 300 rpm stirrer speed, and 60 °C. At the optimum conditions, a biodiesel yield of 91.07 % was obtained. On the other hand, the optimum conditions for KOH/NaY was 3 h reaction time, 10 wt% KOH/NaY, 15:1 methanol-to-oil molar ratio, 6 g of catalyst, 300 rpm stirrer speed, and 60 °C. At the optimum conditions, a biodiesel yield of 91.07 % was obtained. By using the optimum conditions, a biodiesel yield of 91.07 % was obtained. By using the optimum conditions, a biodiesel yield of 91.07 % was obtained. By using the optimum conditions, about 51.26 and 3.18 % of the K was leached from 25 wt% KOH/Al₂O₃ and 10 wt% KOH/NaY, respectively. The 10 wt% KOH/NaY should be proper for the transesterification reaction as a heterogeneous catalyst since the amount of K in the fresh catalyst is about the same as in the spent catalyst. It is reasonable to conclude that the type of support strongly affects the activity and leaching of the active species of the catalyst.

4.6 Acknowledgements

This work was partially supported by the Energy Policy and Planning Office, Ministry of Energy, Royal Thai Government, and by the National Excellence Center for Petroleum, Petrochemicals and Advanced Materials, Thailand.

4.7 References

- [1] Vicente G, Martinez M, Aracil J. Methyl esters of sunflower oils as fuels: alternative to petroleum-derived diesel fuel. Ing Quim 1999;31:153–159.
- [2] Fangrui M, Milford AH. Biodiesel production: a review. Bioresource Technol 1999;70:1–15.
- [3] Freedman B, Butterfield RO, Pryde EH. Transesterification kinetics of soybean oil. J Am Oil Chem Soc 1986;63:1375–1380.

- [4] Jitputti J, Kitiyanan B, Rangsunvigit P, Bunyakiat K, Attanatho L, Jenvanitpanjakul P. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. Chem Eng J 2006;116:61–66.
- [5] Kim HJ, Kang B-S, Kim M-J, Park YM, Kim D-K, Lee J-S. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. Catal Today 2004;93-95:315–320.
- [6] Arzamendi G, Campo I, Arguiñarena E, Sănchez M, Montes M, Gandía LM. Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts. Chem Eng J 2007;134:123–130.
- [7] Xie W, Li H. Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. J Mol Catal A Chem 2006;255:1–9.
- [8] Macleod CS, Harvey AP, Lee AF, Wilson K. Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. Chem Eng J 2008;135:63–70.
- [9] Suppes GJ, Dasari MA, Doskocil EJ, Mankidy PJ, Goff MJ. Transesterification of soybean oil with zeolite and metal catalysts. Appl Catal A Gen 2004;257:213–223.
- [10] Serio MD, Ledda M, Cozzolino M, Minutillo G, Tesser R, Santacesaria E. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. Ind Eng Chem Res 2006;45:3009–3014.
- [11] Xie W, Peng H, Chen L. Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. Appl Catal A Gen 2006;300:67-74.
- [12] Xie W, Huang X, Li H. Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst. Bioresource Technol 2007;98:936–9.
- [13] Yin S-F, Zhang Q-H, Xu B-Q, Zhu W-X, Ng C-F, Au C-T. Investigation on the catalysis of CO_x-free hydrogen generation from ammonia. J Catal 2004;224:384–396.
- [14] Sun LB, Chun Y, Gu FN, Yue MB, Yu Q, Wang Y. A new strategy to generate strong basic sites on neutral salt KNO₃ modified NaY. Mater Lett 2007;61:2130–2134.

- [15] Martín Alonso D, Mariscal R, Moreno-Tost R, Zafra Poves MD, López Granados M. Potassium leaching during triglyceride transesterification using K/γ-Al₂O₃ catalysts. Catal Commun 2007;8:2074–2080.
- [16] Xu B, Rotunno F, Bordiga S, Prins R, van Bokhoven JA. Reversibility of structural collapse in zeolite Y: alkane cracking and characterization. J Catal 2006;241:66–73.