CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

X-ray powder diffraction patterns of the prepared samples calcined at 500°C are shown in figure 4.1. It was revealed that phase transformation of zirconia occurred when NaOH was loaded onto zirconia support. The characteristic peaks of the monoclinic phase are at $2\theta = 28.5^\circ$ and 31.6° (Chuah and Jaenicke 1997), and the characteristic peak of the tetragonal phase is at $2\theta = 30.2^\circ$ (Ksapabutr *et al.*, 2004). The sample without loading NaOH contained both monoclinic and tetragonal phases while 1%NaOH in methanol loaded zirconia showed only the tetragonal phase. It is clearly suggested that NaOH solution does affect to the crystallization process of zirconia. These results are in agreement with the result reported by Parida et al. (1999). They explained that zirconium hydroxide gel prepared using ammonium hydroxide at $pH = 10.2$ on calcination at 500°C and doped with 0.5 mol% Na led to predominantly tetragonal phase. The presence of sodium in zirconia improved its catalytic activity of ketonisation. Moreover, the modified tetragonal zirconia was also used as catalyst for the transesterification reaction, and n-butane isomerization (Miao *et al.*, 1996).

In addition, the catalyst after being used for the transesterification reaction did not changed the phase, as can be seen in Figures 4.1 (c) and (d).

The calcination temperature effect for the 1%NaOH in methanol supported on zirconia catalyst was investigated by varying the temperature from 100° to 900°C. The XRD patterns given in Figure 4.2 illustrated that the monoclinic phase began to appear at 700°C. Furthermore, the complete transformation of tetragonal phase of zirconia to monoclinic phase occurred at 900°C. These results are agreed well with Liu and coworkers' (2007) study. They revealed that further calcination of $Na\text{-}ZrO_2$ at above 800°C led to the transformation of tetragonal to monoclinic phase.

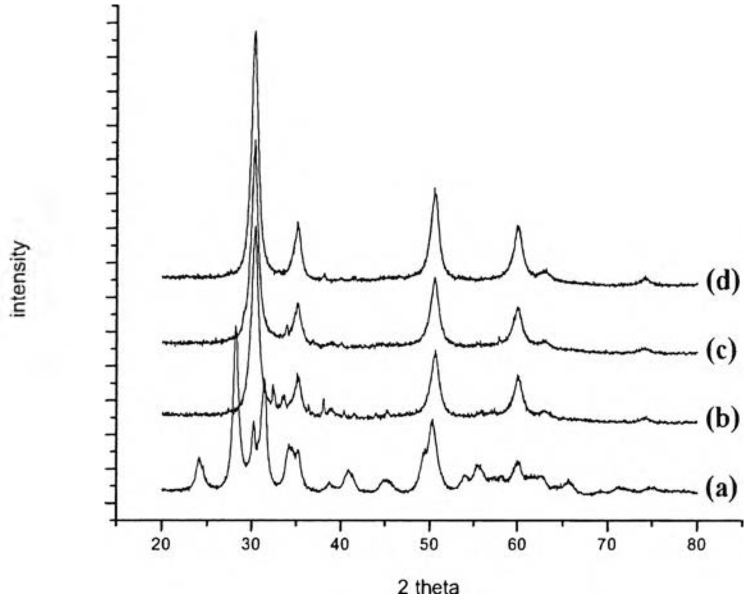


Figure 4.1 XRD patterns of zirconia calcined at 500°C for (a) pure zirconia, (b) 1%NaOH in methanol/zirconia, (c) used 1% NaOH in methanol/zirconia without calcination and (d) used 1% NaOH in methanol/zirconia with calcination.

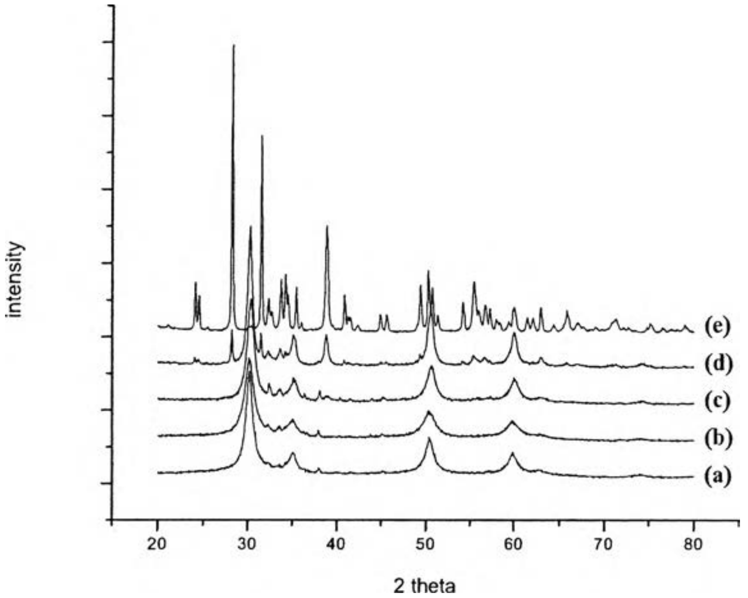


Figure 4.2 XRD patterns of 1%NaOH in methanol supported on zirconia after calcining for 5 h at various calcination temperatures of (a) 100°, (b) 300°, (c) 500°, (d) 700°, and (e) 900°C.

The SEM micrographs in Figures 4.3-4.4 show that morphologies of both unloaded and 1% NaOH in methanol loaded zirconia were quite different, especially, the surface of the NaOH loaded zirconia was much rougher. It is indicated that the loading of the NaOH affected to the surface of the zirconia by activating zirconia surface. The Na/Zr mass ratio from SEM-EDS (as shown in appendix B) indicated that the analyzed sodium element content on zirconia support was very closed to the sodium amount added for impregnation but leached after used for the reaction.

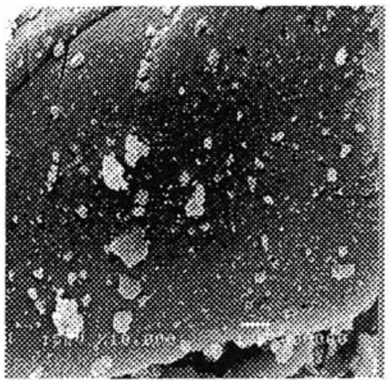
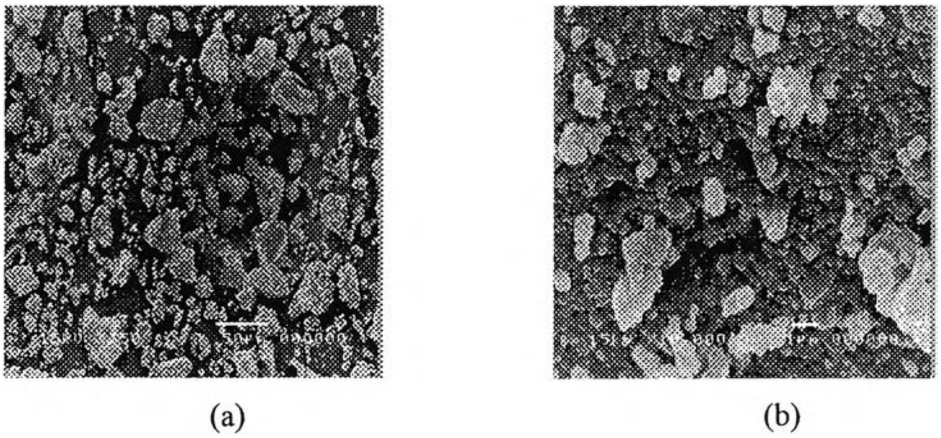


Figure 4.3 SEM micrograph of unloaded ZrO_2 calcined at 500°C.



(a) (b)

Figure 4.4 SEM micrographs of 1% NaOH in methanol/ZrO_2 calcined at 500°C with magnifications of (a) x350 and (b) x10000.

BET results (Table 4.1) revealed the lost of the surface area and the pore volume of the NaOH loaded zirconia, as compared to the pure zirconia. This could be resulted from blockage of sodium in the pores, as explained by Arzamendi and coworkers (2007). They investigated NaOH/alumina catalyst for biodiesel synthesis and also found the lost the specific surface area and the pore volume due to the blockage of sodium in the alumina pores. Even though the catalyst had low surface area, the presence of sodium in zirconia did enhance the basic sites and also improve its catalytic activity, as also discovered by Liu and coworkers (2007).

Table 4.1 The surface area and the pore volume of pure zirconia and 1% NaOH in methanol loaded on zirconia

Sample	**S_{BET} (m^2/g)**	**V_P (cm^3/g)**
ZrO_2	53	0.084
1%NaOH in methanol /ZrO_2	24	0.077

4.2 Transesterification of palm oil

The yields of the transesterification reaction obtained from the variation of reaction conditions were determined by ^{1}H-NMR, following Gelbard and coworkers' work (1995), as detailed in Chapter II, by using the protons of the methylene groups adjacent to the ester moiety in triglycerols and the protons in the alcohol moiety of the methyl ester product to monitor the yield. Moreover, the fatty acid methyl ester (FAME) content was also confirmed using gas chromatography (GC), based on EN 14103 and calculated using the formula described in Chapter III.

4.2.1 Effect of NaOH Concentration

In this study, NaOH loading on zirconia was varied within a range of 0.1-1.5 wt% in methanol. The biodiesel yield was improved with increasing the amount of NaOH. From the results illustrated in Figure 4.5, biodiesel yield could be reached up to more than 90% with 1% NaOH in methanol/ZrO_2. As compared to the unloaded zirconia, the results were indicated that the addition of NaOH onto zirconia improved the catalytic activity of zirconia for the transesterification reaction. As discussed previously for the XRD and SEM results (Figures 4.1, 4.3, and 4.4), the phase transformation to the tetragonal phase occurred, and the surface of zirconia was changed to much rougher after loading NaOH, indicating much higher activated surface of zirconia, as a result, increasing the catalyst activity for transesterification. Liu and coworkers (2007) also found that mesoporous structure and strong basic metal oxides, viz. Na-ZrO_2, CaO/ZrO_2 and NaY, Na-ZrO_2, exhibited the best performance in the transesterification of methanol and propylene carbonate.

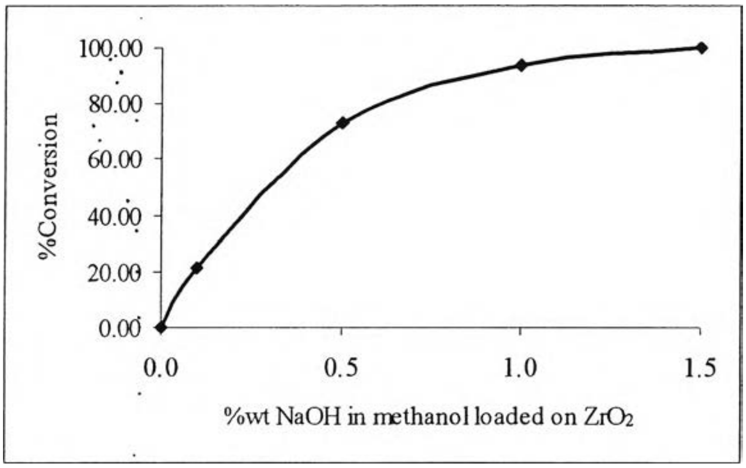


Figure 4.5 Effect of NaOH concentration loaded on zirconia support on biodiesel yield using 5%wt catalyst/oil ratio and 18:1 methanol/oil molar ratio, at 70°C reaction temperature for 120 min reaction time.

4.2.2 Effect of Catalyst Amount

The catalyst amount was varied within a range of 1-10 wt% of 1%NaOH in methanol/ZrO_2 (based on the weight of oil). From Figure 4.6, the results showed that when the amount of catalyst was not sufficed, the yields of biodiesel were relatively low. Moreover, the biodiesel yields were increased rapidly from ~6%

to 93% as the amount of 1%NaOH in methanol/ZrO_2 catalyst increased from 1 to 3 wt%. After the 3%wt catalyst, the conversion approached its equilibrium, meaning that the optimum condition is to use 3 wt% catalyst to obtain more than 90% yield of biodiesel. According to Xie and coworkers' work, they described the decrease of the biodiesel product before approaching its equilibrium owing to the increase of mixing problem between reactants, products and solid catalyst [Xie *et al.*, 2007].

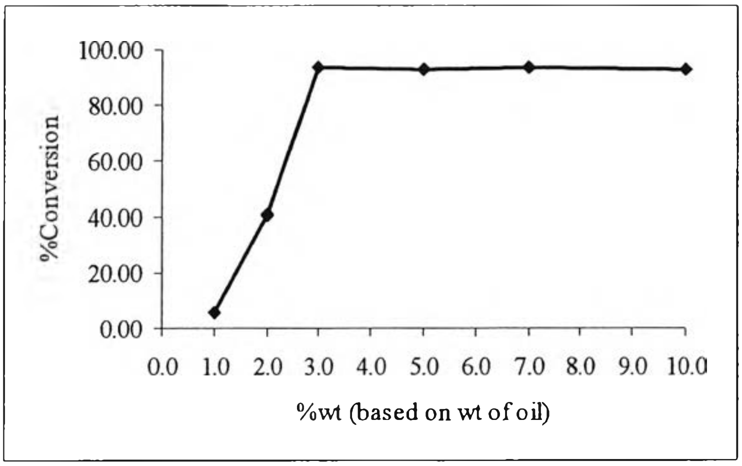


Figure 4.6 Effect of the amount of 1%NaOH in methanol loaded on zirconia support on the biodiesel yield using 18:1 methanol/oil molar ratio, at 70°C reaction temperature for 120 min reaction time.

4.2.3 Effect of Reaction Time

The reaction time effect was investigated by collecting the sample from the reactor every a period of time. Figure 4.7 shows that the ester yield gradually increased when the reaction took longer time. However, the yield of the ester no longer increased after 90 min and the ester yield at this point was 94%. Boocock and coworkers (1998) described that the rate constants for the conversion of diglycerides to monoglycerides, and monoglycerides to glycerol were very low when comparing to the rate constant of the conversion of triglycerides to diglycerides. Because the transesterification reaction is typically reversible, therefore, at a point where the conversion to diglycerides was predominant while the presences of methyl ester and glycerol were still low, some of diglycerides was converted back to triglyceride, resulting in equilibrium conversion. Consequently, the optimum of the reaction time for further study was set at 90 min.

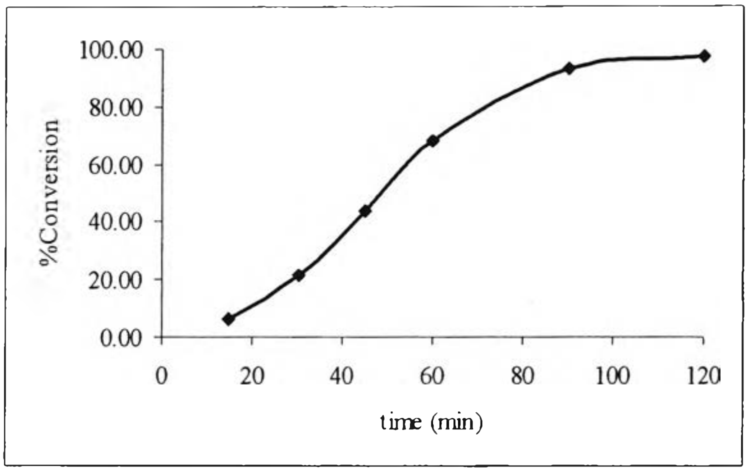


Figure 4.7 Effect of the reaction time on biodiesel yield using 3%wt of 1%NaOH in methanol/ZrO_2 catalyst to oil mass ratio, 18:1 methanol/oil molar ratio at 70°C reaction temperature.

4.2.4 Effect of molar ratio of methanol to oil

According to the reaction stoichiometry, the transesterification of vegetable oil including palm oil with methanol requires that the molar ratio of methanol to oil is 3:1. Since the transesterification process is reversible reaction, the excess of the methanol is required in order to shift the equilibrium forward. Moreover, when mass transfer was limitied due to a problem of mixing, the mass transfer rate seemed to be much slower than the reaction rate, thus the production yield could be elevated by introducing excess amount of the reactant to methanol [Kim *et al.*, 2004]. Figure 4.8 reveals that an increase of the methanol to oil ratio resulted in an increase of ester yield. After 12:1 methanol to oil ratio, the ester yield was slightly increased, and the ester yield of the 15:1 methanol to oil ratio was very close to the ester yield of 18:1 methanol to oil ratio. Therefore, the optimum molar ratio of methanol to oil chosen is 15:1 to give higher than 90% ester yield. These results are in agreement with Xie and Li' study (2006). They mentioned that when the reaction was carried out at reflux of methanol, with a molar ratio of methanol to oil of 15:1 for 8 h reaction time using 2.5 wt% catalyst amount, the highest conversion of soybean oil reached 96%. Furthermore, Arzamendi and coworkers (2007) found that performance of supported NaOH catalysts was very dependent on the methanol/oil molar ratio. This behavior could be interpreted in terms of a more favored methoxide formation as the the methanol/oil ratio increased due to an increased driving-force for methanol adsorption.

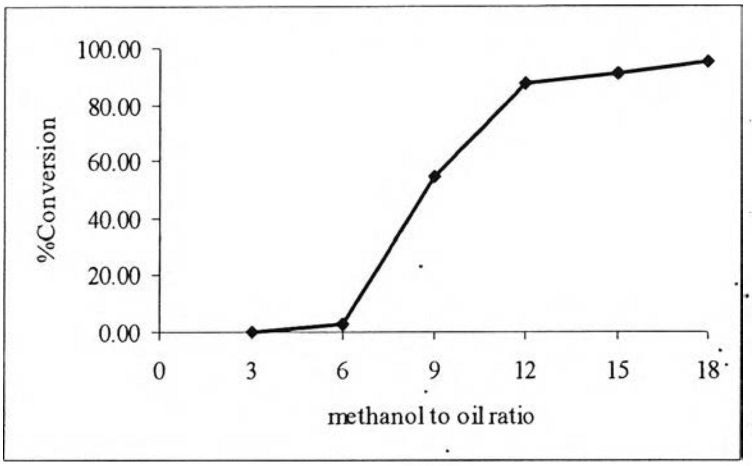


Figure 4.8 Effect of methanol to oil ratio on biodiesel yield using 3 wt% of 1% NaOH in methanol/ZrO_2 to oil mass ratio, at 70°C reaction temperature for 90 min reaction time.

4.2.5 Effect of reaction temperature

In this work, the reaction temperature was varied, starting from room temperature to 80°C. The experimental results in Figure 4.9 indicate that the biodiesel yield was very low, only 28%, at 40°C, but the yield increased with increasing the reaction temperature up to more than 90% at 70°C while 50°C reaction temperature gave less than 90% yield and 80°C reaction temperature was too high to cause methanol vaporization. The optimum reaction temperature for the transesterification of palm oil to biodiesel is thus considered to be around 70°C. Moreover, Liu and coworkers (2007) explained that if the reaction temperature was higher than boiling point, a large number of bubbles were formed, inhibiting the reaction on the three-phase interface of oil, methanol, and catalyst. These results were also found in Srivastava and Prasad's work (2000), when performing the reaction close to the boiling point of methanol (60° to 70°C) at atmospheric pressure.

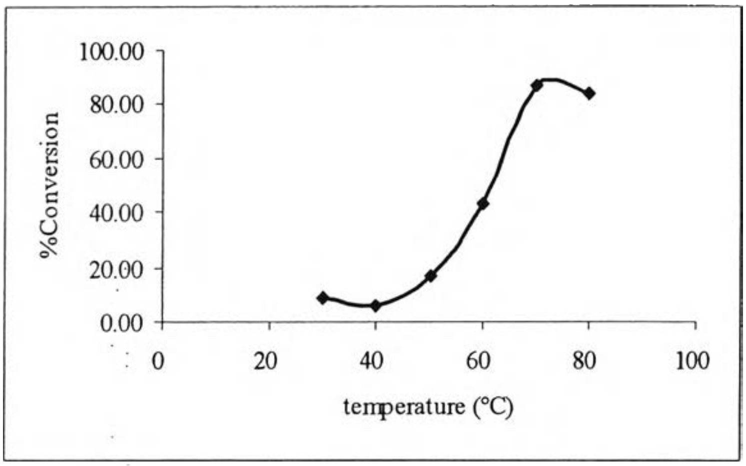


Figure 4.9 Effect of the reaction temperature on biodiesel yield using 3wt% of 1%NaOH in methanol/ZrO_2 to oil mass ratio, 90 min reaction time,and 15:1 methanol/oil molar ratio.

4.2.6 Effect of calcination temperature

The calcination temperature of 1%NaOH in methanol supported on zirconia was varied from 100° to 900°C. The experimental results, as shown in Figure 4.10, illustrated that the biodiesel yields were slightly different when using the catalysts calcined at various calcination temperatures. It can be concluded that the biodiesel yield was slightly affected by the calcination temperature. Moreover, it can be implied that either tetragonal or monoclinic phase of modified zirconia can be used as catalyst for transesterification of palm oil with methanol.

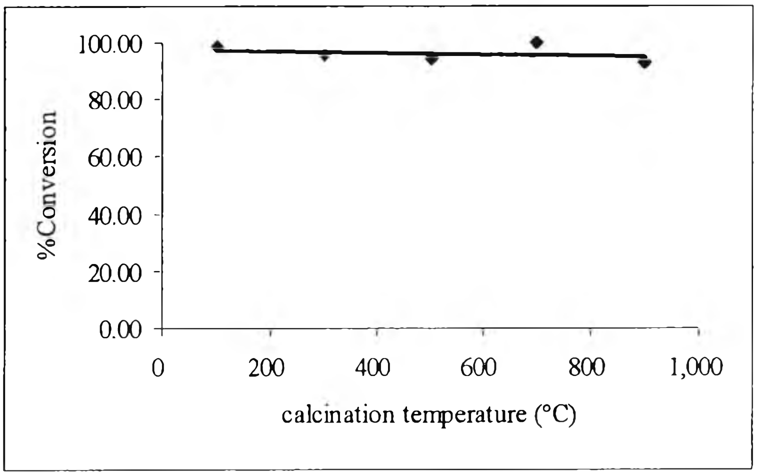


Figure 4.10 Effect of calcination temperature on biodiesel yield using 3% of 1% NaOH in methanol/ZrO_2 to oil mass ratio, 15:1 methanol/oil molar ratio at 70°C reaction temperature for 90 min reaction time.

4.2.7 Reused Catalyst

The reaction catalyzed by used catalyst gave only 33% conversion which was much lower than that catalyzed by fresh 1%NaOH in methanol/ZrO_2, indicating that the used catalyst was deactivated and could not be directly reused for transesterification reaction without further treatment. However, when the used NaOH/ZrO_2 catalyst was regenerated by impregnation with NaOH and dried at 110°C for 24 h, followed by calcination at 500°C for 5 h, the reaction resulted in high %conversion (~98%). This indicates that the used NaOH/ZrO_2 catalyst from transesterification can be easily regenerated and resulted in the same activity as the fresh catalyst if it is retreated. This result is also in agreement with Jitputti and coworkers' study (2006) who found that the spent SO_4^{2-}/ZrO_2 was fully deactivated and could not be directly reused for the reaction without further treatment. Moreover, the regenerated catalyst gave the same activity as in the fresh catalyst.

4.3 Properties of the Synthesized Biodiesel

A few properties of biodiesel, viz. fatty acid methyl ester content; linolenic acid methyl ester; kinematic viscosity; flash point and heating value, were studied. It was found that the fatty acid methyl ester content and linolenic acid methyl ester based on EN 14103 were around 92% (96.8% from department of Chemical technology, Chulalongkorn University) and 0.23%, respectively. The kinematic viscosity based on ASTM D445 was 4.54 cSt. The flash point according to ASTM D92 (open cup) and the heating value following ASTM D611 were 182±2°C and 40858±199.50 kJ/kg, respectively.

According to standard specification of biodiesel as shown in Table 4.2, the property values obtained were in the range of the biodiesel used in an automobile. The heating value was not mentioned in the regulation, however, the heating value of the biodiesel product as compared to the conventional diesel oil (46800 kJ/kg) was lower.

Table 4.2 Some standard specifications of biodiesel (Announcement of Department of Energy Business, Ministry of Energy [in 2005])

Test conducted	**Specification**	**Unit**	**Standard test**
Methyl ester	>96.5	%wt	EN14103
Linolenic acid methyl ester	<12	%wt	EN14103
kinematic viscosity at 40 °C	3.5-5.0	cSt	ASTM D445
Flash Point	>120	°C	ASTM D93