CHAPTER IV

RESULTS & DISCUSSION

This chapter present the results are presented for the tranesterification of purified palm oil and esterification of palm fatty acid in supercritical methanol with sulfated zirconia (SO_4^{2-}/ZrO_2) catalyst. Firstly, the SO_4^{2-}/ZrO_2 catalysts were synthesized at different conditions and were characterized. The results were compared with the commercial SO_4^{2-}/ZrO_2 catalysts. Then, these catalysts were tested for the production of biodiesel by transesterification and esterification of purified palm oil and palm fatty acids. The most suitable catalyst was then selected for the study to determine the suitable operating conditions such as mass ratio of SO_4^{2-}/ZrO_2 catalysts to reactants (0-1 wt %), reaction temperature (200-300 °C), reaction time (0-15 minutes), and molar ratio of methanol to reactant, (6:1-42:1) for purified palm oil and (3:1-12:1) for palm fatty acid, on FAMEs yield. Then the effect of catalyst recycling on the FAMEs yield were determined and presented.

4.1 SO_4^{2-}/ZrO_2 catalysts characterization

In this study, three different SO_4^{2-}/ZrO_2 catalysts (denoted SZ1, SZ2, and SZ3) were prepared by the impregnation of H_2SO_4 over commercial zirconium oxide (ZrO_2) precursor. Here, 40 g of ZrO_2 was immersed in a specified volume of 0.1 mol/liter of H_2SO_4 at 70 °C for 30 minutes, which was then dried at 110 °C for 24 hours, and calcined for 2 hours. In this work, SZ1 was prepared using 18 ml of H_2SO_4 solution, and was calcined at 500 °C, while SZ2 and SZ3 were prepared using 30 ml of H_2SO_4 solution, and the calcining temperatures were 500 and 900 °C, respectively. The physical properties of the SO_4^{2-}/ZrO_2 catalysts at different preparation conditions were summarized in Table 4.1 and 4.2. It can be seen that SZ1 and SZ2 have greater specific surface area and higher sulfur content over the surface of the support, which should thus provide considerably higher reactivity (for both esterification and transesterification) compared to SZ3 and commercial SZ. The low specific surface area of SZ3 is due to the sintering of zirconia during the calcination process. The high calcination temperature (900 °C) could collapse the pores in catalyst support therefore

a larger average pore diameter and lower pore volume were observed, and consequently lower surface area (Lo´pez et al., 2008). From Table 4.2, SZ1 and SZ2 have comparable sulfur content despite the amount of H_2SO_4 used, thus it can be concluded that adding excess sulfur (H_2SO_4) during impregnation process did not show significant impact on the wt % of sulfur on the surface of solid zirconia.

Table 4.1 Physical properties of SO_4^{2-}/ZrO_2 catalysts

Catalyst	Calcination temperature (°C)	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore diameter (nm)
SZ1	500	148	0.27	4.5
SZ2	500	143	0.24	4.9
SZ3	900	14	0.09	68.6
Commercial SZ	500	121	0.26	4.8

Table 4.2 Elemental analysis of SO_4^{2-}/ZrO_2 catalysts

Catalyst	Sulfur content in SZ (wt %)
SZ1	3.04
SZ2	3.01
SZ3	1.92
Commercial SZ	0.72

4.2 Effect of catalyst preparation conditions on FAMEs yield

The catalytic activities of SO_4^{2-}/ZrO_2 catalysts prepared at different conditions (SZ1, SZ2 and SZ3) were tested and compared with the commercial grade SO_4^{2-}/ZrO_2 catalysts on the catalytic transesterification of purified palm oil and catalytic esterification of palm fatty acid in supercritical methanol. The reaction conditions employed were at 290 °C, methanol:reactant molar ratio of 42:1 for purified palm oil and 6:1 for palm fatty acid, the SO_4^{2-}/ZrO_2 catalysts:reactants mass ratio of 0.5 %, and the reaction time of 10 min and 1 min for purified palm oil and palm fatty acid, respectively. Figure 4.1 shows the effect of SO_4^{2-}/ZrO_2 catalyst preparation conditions

on FAMEs yield which indicated that the FAMEs yields of biodiesel by both catalytic transesterification of purified palm oil and catalytic esterification of palm fatty acid in supercritical methanol for both SZ1 and SZ2 were comparable. This was very likely that the increments of loaded SO_4^{2-} up to a certain amount could cause a negative effect on the catalytic activity. It has been reported that the agglomeration of the active SO_4^{2-} phase and/or the cover of basic sites by the exceeded SO_4^{2-} could occur, and hence would lower the surface areas of active components, which would thus lower the catalytic activity (Xie et al., 2007).

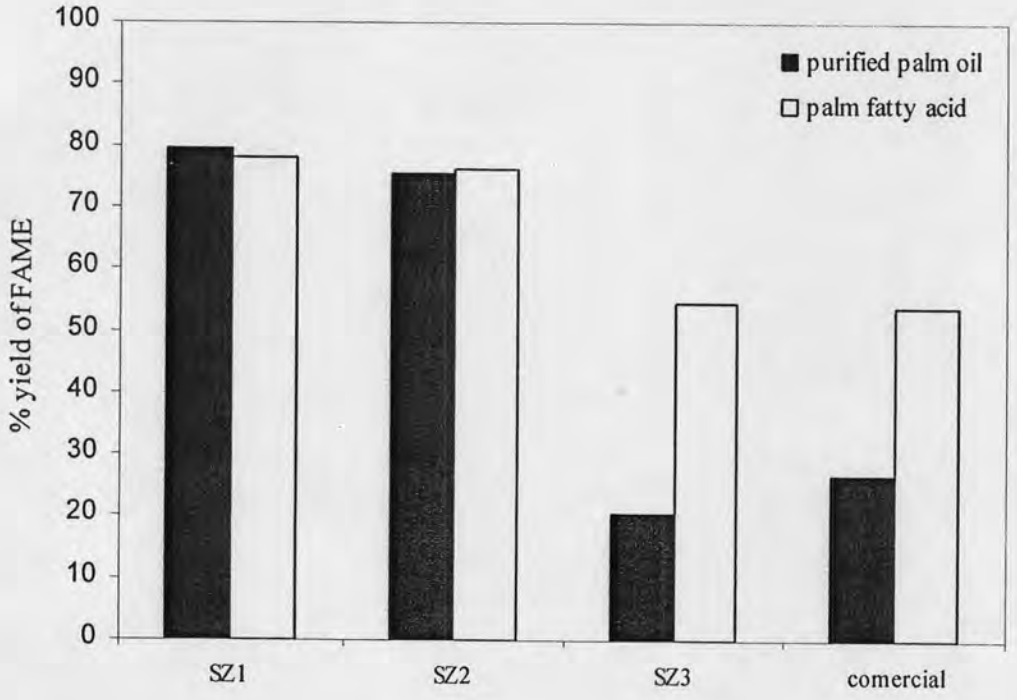

Figure 4.1 Effect of catalyst preparation conditions on FAMEs yield, molar ratio of methanol to purified palm oil was 42:1, molar ratio of methanol to palm fatty acid was 6:1, SO_4^{2-}/ZrO_2 catalysts:reactants mass ratio was 0.5 , reaction temperature 290 °C, and reaction time was 10 minutes for transesterfification and 1 minute for esterifiication.

When compare between the FAMEs yield of SZ2 and SZ3 for catalytic transesterifications of purified palm oil and catalytic esterifications of palm fatty acid in supercritical methanol, it was found that the FAMEs yields obtained with use of SZ2 (79 % and 78 for the transesterifications and esterifications, respectively) were higher than those obtained with SZ3 (21 % and 55 %, respectively). The lower catalytic activity of SZ3 was due to the fact that the catalyst was prepared at high

calcinations temperature (900 °C compared with 500 °C for SZ1 and SZ2). It has been purified palm oil reported that the higher the calcination temperature, the lower the resulting surface area (Lopez et al., 2008), and for transesterification and esterification reactions, SO_4^{2-}/ZrO_2 catalyst have been typically calcined at temperatures ranging between 500 and 600 °C (Ni and Meunier, 2007).

Comparing the synthesized SO_4^{2-}/ZrO_2 catalysts (SZ1 and SZ2) with the commercial SO_4^{2-}/ZrO_2 catalyst, the catalytic activities for the biodiesel production of both of the prepared catalysts were considerably higher for both the transesterification and esterification. That is, above 78 % of the FAMEs yields were obtained for transesterification and esterification catalyzed with SZ1 and SZ2, compared with 27 % and 54 % yield obtained for the transesterification and estrification with the commercial SO_4^{2-}/ZrO_2 catalyst at the same reaction conditions. This result could purified palm oil possibly be explained by the higher wt % of sulfur on the surfaces of the synthesized SO_4^{2-}/ZrO_2 catalysts (3.01 and 3.04 wt %, respectively) compared with 0.72 wt % of the commercial SO_4^{2-}/ZrO_2 catalyst. Based on the above results, the most suitable SO_4^{2-}/ZrO_2 catalyst that was selected for further investigation was SZ1.

4.3 Effect of mass ratio of SO_4^{2-}/ZrO_2 catalysts to reactants

The quantity of the catalysts has been shown to have an influence on the yield of biodiesel. Therefore in this work, the effect of the amount of catalysts on the transesterification of purified palm oil and esterification of palm fatty acid were studied. The mass ratio of SO_4^{2-}/ZrO_2 catalysts (SZ1) to purified palm oil and palm fatty acid were varied in the range of 0-1 %. The reaction was carried out for 10 min with methanol at the molar ratio of 42:1 for purified palm oil and at 6:1 for palm fatty acid, and at 290 °C. The results are shown in Figure 4.2, which indicates the FAMEs yield increased considerably when SO_4^{2-}/ZrO_2 catalyst was added to the reaction as the catalyst played a key role in the activation energy reduction for a reaction. For transesterification and esterification reaction of vegetable oils and fats with alcohols, Jitputti et al. (2007) have demonstrated that solid catalysts (such as ZrO_2, ZnO, SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2, KNO_3/KL zeolite and KNO_3/ZrO_2) could considerably increased the level of the biodiesel production. When mass ratio of SO_4^{2-}/ZrO_2 catalysts to reactants was increased (between 0-0.5 %), the FAMEs yield increased from about 30 % to 80 % and 60 % to 80 % for purified palm oil and palm fatty acid, respectively.

Catalyst addition, there is a faster rate at which reaction equilibrium was reached because of the increase in the total number of available active catalytic sites for the reaction (Wang et al., 2007). However, when mass ratio of SO_4^{2-}/ZrO_2 catalysts to reactants was increased above 0.5 %, the FAMEs yield decreased due to the quantity of catalysts that was increased has an influence on the reaction which occur the reversible reaction. Then, it was found that the total FAMEs yield decreased. Therefore, the optimum mass ratio of SO_4^{2-}/ZrO_2 catalysts to reactants for both catalytic transesterification of purified palm oil and catalytic esterification of palm fatty acid in supercritical methanol was 0.5 %.

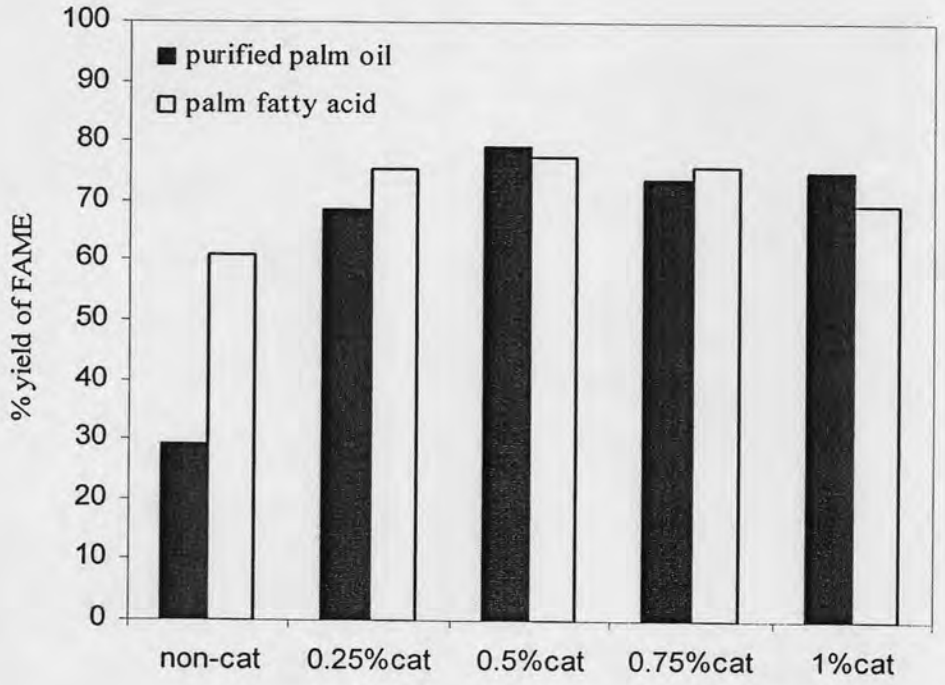

Figure 4.2 Effect of mass ratio of catalysts to reactants on FAMEs yield, molar ratio of methanol to purified palm oil was 42:1, molar ratio of methanol to palm fatty acid was 6:1, reaction temperature 290 °C and reaction time were 10 minutes for transesterification and esterification

4.4 Effect of reaction time on FAMEs yield

In this work, the effect of reaction time between 0-15 minutes was determined. The methanol:reactants molar ratio used were 42:1 for purified palm oil and 6:1 for palm fatty acid, the reaction temperature was 290 °C, and the amount of SO_4^{2-}/ZrO_2 catalysts (SZ1) was 0.5 wt %. As shown in Figure 4.3, the result indicated that the

FAMEs yield was increased when reaction time increased between 0-10 minutes for purified palm oil and 0-1 minutes for palm fatty acid, and after which the yields remained nearly constant or slightly decreased. This was due to thermal decomposition that occurred after transesterification and esterification reached nearly reaction equilibrium (Xie et al., 2006). Thus, the transesterification of purified palm oil and esterification of palm fatty acid were nearly completed at about 10 and 1 minute, respectively.

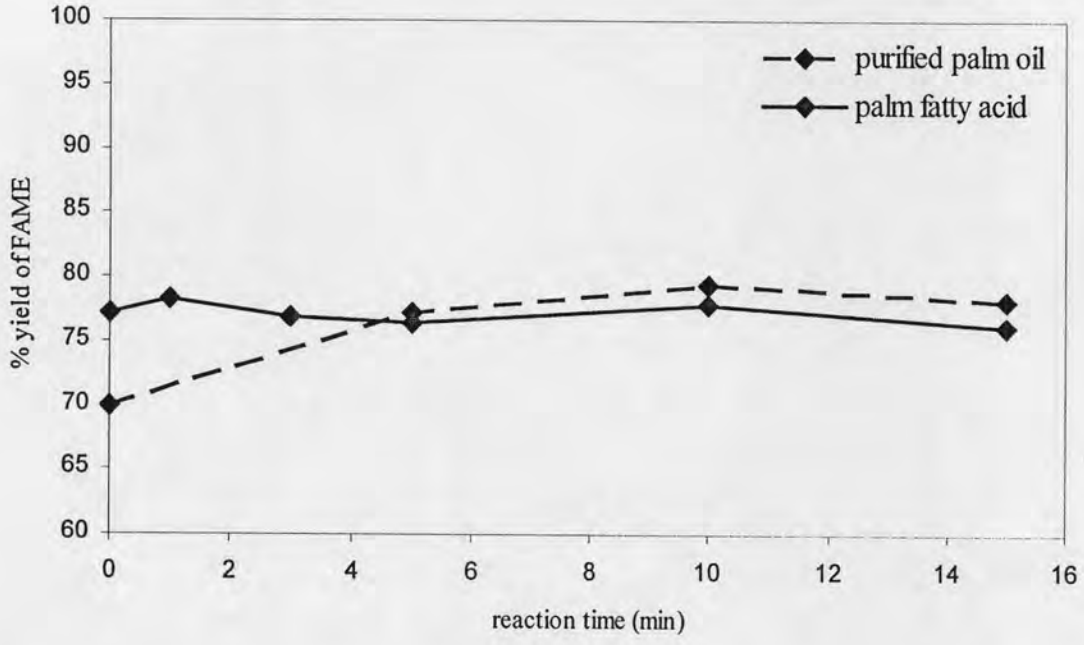

Figure 4.3 Effect of reaction time on FAMEs yield, molar ratio of methanol to purified palm oil was 42:1, molar ratio of methanol to palm fatty acid was 6:1, SO_4^{2-}/ZrO_2 catalysts:reactants mass ratio was 0.5 and reaction temperature 290 °C for transesterification and esterification

When compared with non-catalytic transesterification and esterification in supercritical methanol (Table 4.3), the reactions in supercritical methanol with catalyst required much shorter reaction time. To obtain an equal FAMEs yield of around 80 %, 90 minutes would be required for the non-catalytic transesterification of purified palm oil at 280 °C, and 50 minutes would be required at 300 °C. For esterification of palm fatty acid, around 45 and 15 minutes were required for the reaction at 250 and 300 °C, respectively. On the other hand, catalytic transesterification and esterification required only 10 minutes and 1 minute, respectively, at the reaction temperature of 290 °C.

Table 4.3 Reaction time of non-catalytic supercritical methanol to achieve 80 % yield of FAMEs (Jomtib, 2006; Yujaroen, 2006)

Reactant	MeOH:reactant	Reaction time (min)		
		250 °C	280 °C	300 °C
purified palm oil	45:1	-	~90	~50
Palm fatty acid	6:1	~45	-	~15

4.5 Effect of molar ratio of methanol to reactants

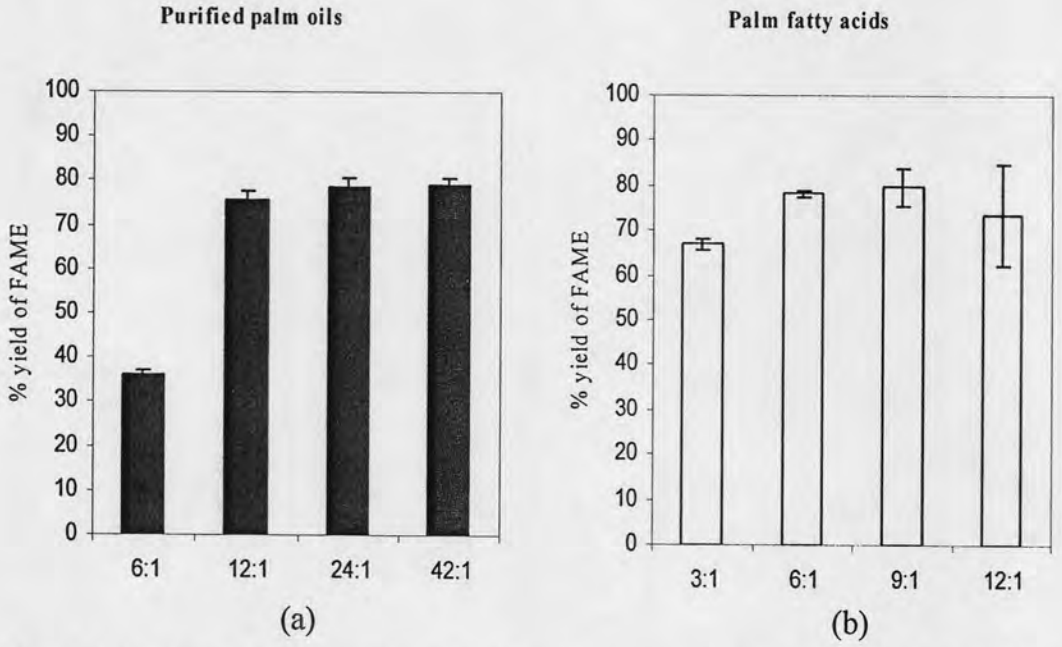

Figure 4.4 Effect of molar ratio of methanol to reactants on FAMEs yield, SO_4^{2-}/ZrO_2 catalysts:reactants mass ratio was 0.5, reaction temperature 290°C and reaction time was 10 minutes for transesterification (a) and 1 minute for esterification (b)

From the stoichiometric ratio of the reactants for transesterification, it requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. For esterification, it requires one mole of alcohol and fatty acid to yield one mole of fatty acid ester and water. In these reactions, the molar ratios of alcohol to vegetable oil and fat have been shown to be one of the most important factors. The FAMEs yield could be increased by using excess amount of alcohol to shift the equilibrium to the right-hand side. In this work, the effect of molar

ratio of methanol to reactants on FAMEs yield were determined for the range of molar ratio between 6:1-42:1 for purified palm oil and 3:1-12:1 for palm fatty acid. The reaction temperature was 290 °C and the amount of SO_4^{2-}/ZrO_2 catalysts (SZ1) was 0.5 wt % of the reactant. The FAMEs yields shown in the Figure 4.4 (a) and (b) were obtained after the reactions were carried out for 10 minutes of transesterification and 1 minute of esterification, respectively. It can be seen from this result that the FAMEs yield increased from about 37 % to 80 % and 68 % to 80 % as the molar ratio increase from 6:1 to 24:1 of purified palm oil and 3:1 to 6:1 of palm fatty acid, respectively. However, the FAMEs yield were only slightly increased when the ratio of methanol to reactants were higher than 24:1 for purified palm oil and slightly decreased when the ratios were higher than 6:1 for palm fatty acid. Therefore, the optimum molar ratio of methanol to reactants for catalytic transesterification of purified palm oil and catalytic esterification of palm fatty acid in supercritical methanol to biodiesel were 24:1 and 6:1, respectively.

4.6 Effect of catalysts recycling

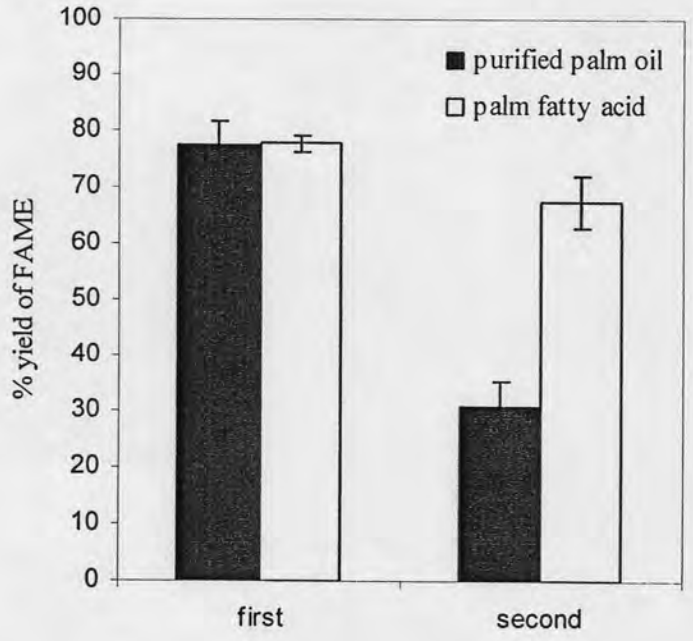

Figure 4.5 Effect of recycling catalysts on FAMEs yield, molar ratio of methanol to purified palm oil was 42:1, molar ratio of methanol to palm fatty acid was 6:1, SO_4^{2-}/ZrO_2 catalysts:reactants mass ratio was 0.5, reaction temperature 290 °C and reaction time was 10 minutes for transesterification and 1 minute for esterification

From an economic observation, the cost of catalyst is one of the most important factors that control the cost of biodiesel production. Therefore, the stability and reusability of the catalyst are of great importance for industrial applications. The limitation of SO_4^{2-}/ZrO_2 catalyst is its rapid deactivation. The FAMEs yield decreased when recycling the catalyst. In this work, catalysts recycling were examined for transesterification of purified palm oil and esterification of palm fatty acid in supercritical methanol. The reaction was carried out at 290 °C. The SO_4^{2-}/ZrO_2 catalysts (SZ1):reactants mass ratio of 0.5 % was used for the reaction, and the molar ratio of 42:1 was used for purified palm oil and 6:1 for palm fatty acid. The FAMEs yields shown in the Figure 4.5 were obtained after the reactions were carried out for 10 min and 1 min for transesterification and esterification respectively.

After the first reaction cycle, the SO_4^{2-}/ZrO_2 catalyst was washed with hexane and dried overnight at 100 °C. It can be seen from this result that the FAMEs yield of first cycle decreased from around 78-79 % to only 31 % in the second cycle transesterfication of purified palm oil and to 68 % in the second cycle for the esterification of palm fatty acid. It is probable that the observed catalyst deactivation was the result of side blockage by adsorbed intermediates or product species that were considerably more polar than the original reagents (Lo´pez et al., 2005), and/or carbon deposition (Suwannakarn et al., 2008). The decrease in the reaction rate may also be attributed to sulfur leaching, poisoning (e.g., by water), pore filling or a combination of these deactivation mechanisms (Lo´pez et al., 2008). The loss of sulfur species has especially been considered for SO_4^{2-}/ZrO_2 catalyst in reaction mixture. According to Corma (1997) and Kiss et al. (2006), the catalyst was deactivated due to sulfate loss caused by the water present in the reaction mixture. Moreover, one might consider that the highly electronegative sulfate ions can be lost from the catalyst in the present of an alcohol (Lo´pez et al., 2008). Suwannakarn et al. (2008) reported the effect of alcohol on SO_4^{2-}/ZrO_2 catalyst deactivation, SO_4^{2-}/ZrO_2 catalyst samples were immersed in the three different alcohols (methanol, ethanol and buthanol). They found that alcohols with large alkyl chain length have slower leaching of the active site in SO_4^{2-}/ZrO_2 catalyst. The rate and degree of sulfate leaching from the solid surface may depend on the catalyst SO_4^{2-} loading, calcinations temperature, reaction temperature, and reaction media (Lo´pez et al., 2008). However, the activity of used SO_4^{2-}/ZrO_2 catalyst can be easily regenerated by re-impregnation with sulfuric acid

and re-calcinations. The regenerated catalysts that have the same activity as in fresh catalyst can be obtained (Jitputti et al., 2006).

4.7 Effect of reaction temperature

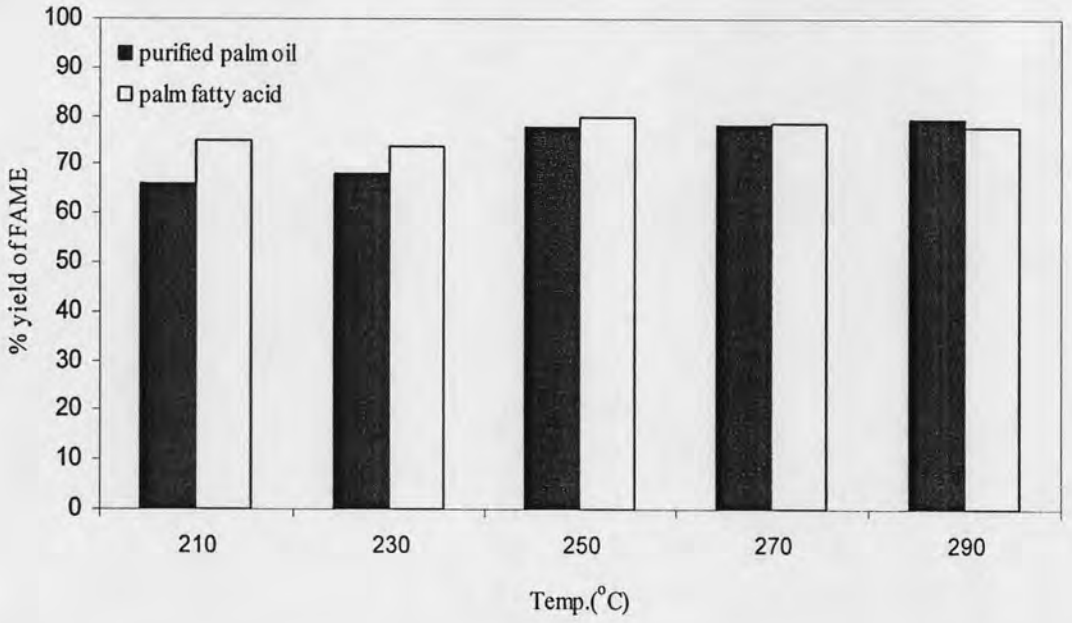

Figure 4.6 Effect of reaction temparature on FAMEs yield, molar ratio of methanol to purified palm oil was 42:1, molar ratio of methanol to palm fatty acid was 6:1, SO_4^{2-}/ZrO_2 catalysts:reactants mass ratio was 0.5 and reaction time were 10 minutes for transesterification and esterification

Reaction temperature can influence the reaction rate and the FAMEs yield because the intrinsic rate constant is usually a strong function of temperature (Liu et al., 2008). In this work, the reactions were carried out for 10 min with methanol at the molar ratio of 42:1 for purified palm oil, and 6:1 for palm fatty acid with 0.5 wt % SO_4^{2-}/ZrO_2 catalysts (SZ1). The reaction temperatures were varied in the range of 210-290 °C and the FAMEs yields are shown in Figure 4.6. The results indicate that the FAMEs yield increased initially with reaction temperature for both purified palm oil and palm fatty acid. When the temperature was between 210-250 °C, the FAMEs yield slightly increased with temperature from 66 % to 78 % and 75 % to 80 % for transesterification and esterification, respectively. While at 250 °C and higher, the FAMEs yields for both reactions were relatively constant at around 80 %.

Table 4.4 The FAMEs yield of Non-catalytic supercritical methanolysis after 10 minutes (Jomtib, 2006; Yujaroen, 2006)

Reactant	MeOH:reactant	% yield of FAMEs	
		250 °C	300 °C
Purified palm oil	45:1	~2	~15
Palm fatty acid	6:1	~20	~70

When compare the catalytic (Figure 4.6) and non-catalytic (Table 4.4) transesterification of purified palm oil and esterification of palm fatty acid in supercritical methanol at the same reaction time of 10 minutes, the reactions with catalysts were found to give much higher FAMEs yield than those without catalysts. When compare the results at the equal reaction temperature of 250 °C, the non-catalytic supercritical reactions were found to give lower FAMEs yield than that with catalyst for both transesterification and esterification. Generally, the increase in temperature causes the polarity of methanol to decrease, as a result of the breakdown of the hydrogen bonding of methanol, leading to increased solubility of vegetable oils and fatty acids in methanol. Adding SO_4^{2-}/ZrO_2 catalyst to the reaction mixture can increase the efficiency of reaction and decrease the vigorous conditions. Form the results observed in this study, the reaction temperature was decreased from 300 °C to 250°C. Therefore, the optimum reaction temperature for both catalytic transesterification of purified palm oil and catalytic esterification of palm fatty acid in supercritical methanol to biodiesel was considered to be around 250 °C.