

## CHAPTER IX

### CONCLUSIONS AND RECOMMENDATIONS

#### 9.1 Conclusions

The improvement of biodiesel oxidative stability by partial hydrogenation of polyunsaturated fatty acid methyl esters (FAMES) was studied. This research can be divided into two parts based on the type of biodiesel feedstock. In the first part, partial hydrogenation of polyunsaturated FAMES derived from palm oil was investigated and the Pd supported on carbon were used as a catalyst. The influences of Pd precursor, catalyst calcination condition, type of carbon support, and particle size of carbon support were studied. The results revealed that Pd particle size plays an important role on the hydrogenation activity of the catalyst. The Pd supported on activated carbon prepared from  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and calcined under  $\text{N}_2$  at  $500^\circ\text{C}$ , which possessed Pd particle size of  $\sim 17$  nm, provided suitable performance for the partial hydrogenation of palm oil-derived polyunsaturated FAMES, and resulted in an improvement of the oxidative stability with small effect to the cold flow properties. Moreover, due to the location of Pd metals, which locate outside the pore of carbon; therefore, internal mass transfer limitation can be neglected and the particle size of carbon support has an important effect on the catalytic activity. The Pd supported on smaller particle size of activated carbon shows the higher hydrogenation activity, which can be explained from its higher surface area and higher Pd dispersion. In addition, the effects of type of reactor (batch and continuous flow) and reaction conditions in continuous flow reactor (temperature, hydrogen partial pressure, and biodiesel feed flow rate) were investigated. It was found that the partial hydrogenation in a continuous flow reactor provided hydrogenation rate 4–5 times higher than in a batch type reactor. However, the partial hydrogenation in a batch-type reactor provided higher selectivity towards C18:1 at a high conversion. This is due to the contact possibility between oil and the catalyst surface in a batch reactor being lower than that of a continuous flow reactor that suppresses the deeper hydrogenation of intermediate products (C18:1) into saturated products (C18:0). The

higher reaction temperature and hydrogen partial pressure, and lower biodiesel feed flow rate exhibited higher conversion of polyunsaturated C18:2 and C18:3 FAMEs.

The second part is the study on partial hydrogenation of polyunsaturated FAMEs derived from rapeseed oil using Pd supported on mesoporous amorphous materials ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ) as a catalyst. The effects of  $\text{SiO}_2$  pore size and support acidic properties were studied. The results showed that pore size of the  $\text{SiO}_2$  support had a significant effect on the activity and *cis-trans* selectivity of the catalyst, which affects the pore diffusion of the reactants and contact probability between the reactants and Pd active sites. The Pd on ~45 nm pore size  $\text{SiO}_2$  exhibits the highest hydrogenation activity, whereas; *cis-trans* selectivity depends on contact probability between reactant and catalyst. The selectivity towards *cis*-monounsaturated FAME was found to be high for Pd on ~2 nm (Q3) and ~68 nm (Q50) pore size  $\text{SiO}_2$  due to the low contact probability between FAME molecules and active sites in very small and large pores. Despite from the small pore size of  $\text{SiO}_2\text{-Q3}$ , the adsorption of FAME molecules on its protonic sites also promoted high *cis*-selectivity. Furthermore, the acidic properties of the support showed a significant effect on the sulfur (S) tolerance. The acidic supports ( $\text{SiO}_2\text{-Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ ) revealed a higher degree of S tolerance due to an electron deficiency of Pd metal caused by their acidic sites. In addition, the selectivity towards *cis*-isomers of the Pd catalysts could be increased by using acidic supports and the addition of S. Finally the influence of metal type: Pt, Pd, and Ni, on catalytic activity and *cis-trans* selectivity was considered. It was found that Pd is the best catalyst in terms of partial hydrogenation, which results in a lower saturated FAMEs composition when compared with the Pt and Ni catalysts at the same conversion. In addition, Pd shows the highest hydrogenation activity, which provides an advantage in terms of mild operating conditions.

## 9.2 Recommendations

According to the overall conclusions of this work, Pd is the best catalyst in terms of partial hydrogenation, resulting in a lower saturated FAMES composition when compared to the Pt and Ni catalysts and good optimization between oxidative stability and cold flow properties. Moreover, it was found that using very small and large pore size supports, can lower the selectivity towards *trans*-monounsaturated FAMES. Here, main reaction sites are located over the outer surface of the catalyst particles for the former one, and over the pore walls inside the catalyst particles for the latter one. Comparing between the small and large pore size support, the former one is better in terms of attrition resistance, which is an important point for industry. Therefore, Pd supported on the sintered or formed supports made of ceramic (metal oxides) or metallic materials, which have large pores for making ease of the reactants diffusion into the supports and high mechanical strength, would be recommended for the high hydrogenation activity and controlling the formation of *trans*-isomers. In addition, it was found that using acidic support could improve the sulfur tolerance and decrease *trans*-isomers selectivity of the Pd catalyst. Thus, elucidation of the effect of Bronsted and Lewis acid on these catalytic performances would be necessary for designing the acid supports. The effect of super acid on these catalytic performances would be of great value, because some additional catalytic performances, such as skeletal isomerization of FAME molecules, would be expected. Since there are less data of the effect of different acidic supports on partial hydrogenation of polyunsaturated FAMES, using a wide variety of acidic and basic support would be interesting. Furthermore, studying the partial hydrogenation of FAMES derived from high polyunsaturated FAMES content feedstock such as soybean and fish oil, using powerful Pd catalysts to improve its oxidative stability is challenging. Finally, the study in stability and reusability of the catalyst is importance in industrial point of view.