CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The simulation results established a range of the thermodynamic feasible operating conditions for the reaction temperature, stoichiometry ratio and pressure for the hydrodeoxygenation (HDO) process of oleic acid (OA) and stearic acid into paraffinic biofuel. Although there are variations in the simulation and experimental results as expected, but the simulation results served as a veritable template and guide for the catalytic hydrodeoxygenation of OA. In order to validate the simulation results in experimental study, two different sets of supported catalysts were synthesized. The first set of catalysts were two nickel based catalysts supported on alumina, the first catalyst was nickel on alumina (Ni/Al_2O_3) prepared via incorporation of inorganic Ni precursor from nickel nitrate into Al_2O_3 and was. The second was an organometallic catalyst of nickel oxalate supported on alumina (NiOx/Al_2O_3) and it was synthesized via the incorporation nickel oxalate (NiOx) precursor prepared by functionalization of Ni with oxalic acid (OxA).

Both catalysts were characterized for physical and chemical properties and the results showed that Ni species present in Ni/Al_2O_3 was 8.2% while 9.3% was observed for NiOx/Al_2O_3 according to the energy dispersive X-ray (EDX) result. Although the Ni content of both samples were below the expected value 10% due to the degree of hydration at their synthesis stage, the comparably higher value of the NiOx/Al_2O_3 was due to the OxA functionalization because NiOx is highly insoluble. Furthermore, X-ray fluorescence, X-ray diffraction, Fourier transform infrared and Raman spectroscopy results showed that Ni species in NiOx/Al_2O_3 was highly dispersed due to the OxA functionalization which also modified the textural and morphological properties as seen in the N_2 adsorption/desorption and scanning electron microscopy results, respectively. The activities of both Ni/Al_2O_3 and NiOx/Al_2O_3 were validated on the HDO of OA based on the range of values from the simulation study. NiOx/Al_2O_3 did not only showed the best catalytic and reusability abilities, but it also possesses isomerization ability as a result of the OxA functionalization which increased its acidity. The NiOx/Al_2O_3 also has the highest rate constants evaluated using pseudo-first-order kinetics, but the lowest overall activation energies. A more critical analysis of the activation energy revealed that 38.5 kJ/mole and 63.6 kJ/mole would be saved if NiOx/Al_2O_3 is used instead of Ni/Al_2O_3.

In view of the enhanced HDO activity and the additional isomerization ability of the organometallic catalyst due to the increased acidity, fluoropalladium oxalate supported on zeolite catalyst (FPdOx/Zeol) was synthesized via functionalization of palladium oxalate with fluoride ion to further enhance its acidity. Both FPdOx/Zeol and the non-fluoro palladium oxalate (PdOx/Zeol) were characterized and their activities were tested on OA. According to the SEM, XRD and EDX characterization results, both catalysts showed loss of crystallinity with increase in the Si/Al ratio due to effect of OxA functionalization and calcination which removed the extra framework and framework alumina, respectively. However, the loss of crystallinity appears to be more intense in the FPdOx/Zeol catalyst due to the fluoride ion functionalization which was also verified by the presence of fluoride in the EDX result. In addition, both Raman spectroscopy and XRD results showed that Pd particles are more highly dispersed in FPdOx/Zeol than in PdOx/Zeol catalyst. Furthermore, the increased acidity due to fluoride ion functionalization enhanced the textural properties of FPdOx/Zeol compared to PdOx/Zeol which increases its surface area and porosity according BET result. Their catalytic activities showed that both FPdOx/Zeol and PdOx/Zeol have almost same HDO products, but FPdOx/Zeol possesses higher isomerization activities producing 28% iso-$C_{18}H_{38}$ compared to 11% produced by PdOx/Zeol.

Sequel to the enhanced physical and chemical properties and catalytic activity of FPdOx/Zeol, molybdenum and platinum were equally functionalized with fluoride ion and oxalic acid, in addition, a bimetallic catalyst of Ni and Mo were also functionalized and all the catalysts were supported on zeolite and characterized. A comparative study of all the catalysts on the HDO of OA showed that the bimetallic catalyst of Ni and Mo supported on zeolite has the highest HDO activity and even the highest reusability ostensibly due to the synergy of the two metals and the synthesis protocol. However, fluoromolybdenum oxalate catalyst has the highest isomerization ability due to its comparably high acidity as attested to by its fluoride content in the EDX result. All the studied catalysts on the HDO of OA showed that stearic acid is a common intermediate product which implied that there is sequential hydrogenation of OA to saturate its double bond prior to extraction of its O_2 molecules as water. This observation was further confirmed in a comprehensive study on the HDO of OA process chemistry based on the FTIR of the evolved product using FPdOx/Zeol catalyst. The optimization study based on response surface methods (RSM) using platinum catalyst showed that about 58 min, 27.8 mg FPtOx/Zeol loading, 18 bar and 364 °C are the optimum operating conditions to produce 28.39% iso-$C_{18}H_{38}$ and 68.93% n-$C_{18}H_{38}$ and the results were validated in repeated experiments.

The reusability studies of Ni/Al_2O_3 and NiOx/Al_2O_3 on the HDO of OA was carried out at 360 °C, 20 bar, 20 mg catalyst, 100 mL/min gas flow and 45 min. The results of

$NiOx/Al_2O_3$ showed consistency for both n-$C_{18}H_{38}$ and iso- $C_{18}H_{38}$ in three consecutive runs after which only iso-$C_{18}H_{38}$ showed 4% drop after the 4th run. On the other hand, Ni/Al_2O_3 showed a marginal drop of about 3% in the n-$C_{18}H_{38}$ production in the second run, but a drastic reduction of 8% in the third reuse. Similar high reusability like the $NiOx/Al_2O_3$ was observed for all other fluoride ion and oxalic acid functionalized catalysts supported on Zeol. Their high reusability was undoubtedly due to the OxA functionalization which intercalated in them the exceptional high reusability quality of organometallic catalysts due to the presence of the metal-oxalate ligand complex which are known to be highly reactive and reaction specific thus minimizing reaction time and prolonging the catalyst life span. Similarly, the presence of those strong M^+ - oxalate ligand in the OxA functionalized catalysts increases the active metal resistance to leaching out of the support which also minimizes the tendencies of multiple side reactions that could deactivate the catalysts.

These results are credible and would serve as a basis for further research towards industrial application and commercialization. In addition, the application of Aspen Hysys as a process thermodynamic simulation tool which is capable of predicting the properties of the feed and product is seemingly a pointer to the solution of a cheaper biofuel production.

5.2 Recommendation

In view of the observations in this study and the future projections, the following suggestions become expedient towards further research and successful commercialization of the catalytic HDO process of OA into high grade paraffin biofuel.

1. There is need to study a more complex feed stock such as real mother liquor obtained from pyrolysis of agricultural waste like saw dust for the HDO process using the these organometallic catalysts. Feed stocks such as the African Shea butter which is essentially carboxylic acids such as oleic, stearic, linoleic and linolenic acid should also be carefully considered in future for the HDO process.
2. A more robust GC-MS database with wide range of compounds should be procured for future studies. This becomes essentially imperative especially when taking the first recommendation in consideration so as to determine all the species present per time in order to be able to adequately study the HDO process mechanism.
3. The need to study the HDO process in continuous mode (such as trickle bed or differential reactor) cannot be overemphasized especially if the possibility of adapting the process into existing conventional fossil fuel refinery should be considered in order to reduce the cost of production. Future works should also include catalyst deactivation studies.
4. As an extension, it is recommended that some of the facilities in the department should be upgraded and if possible more state-of-the-art facilities should be procured. This will enhance the drive of the University of Malaya to conduct fundamental researches which are easily publishable in Tier one ISI journals. In addition, postgraduate students access to analytical and instrumentation laboratories should not be restricted especially during lunch time, closing hours and even during the weekends.