

CHAPTER ONE

INTRODUCTION

1.0 Background History

Global attention is fast shifting to the application of biomass as a source of fuel for the nearest future especially for transportation due to the projected decline in fossil fuel reserves, rise in petroleum prices and the attendant environmental impact of its exploration, processing and especially the exhaust gases from petrol and diesel engines (Immer et al. 2010; Li et al., 2012). As an alternative to these fossil fuel shortcomings, production of both bio-ethanol fuel (BEF) from carbohydrate especially corn via enzymatic transformation, and fatty acid methyl ester (FAME) biodiesel from transesterification of triglycerides with methanol have received tremendous attention in recent years. However, the conflict of BEF with carbohydrate feedstock has limited the expected popularity of its production since most developing countries still largely rely on carbohydrate as the commonest staple source of food. On the other hand, the shortcomings of FAME biodiesel such as higher viscosity and cloud point temperature, poor oxidation stability, poor storage ability, glycerol by-product menace and lower energy density is challenging its future economic and technical reliability (Danuthaia et al., 2011; Kovacs et al., 2011). Consequently, it is blended with conventional petroleum diesel to produce a blended fuel of 20% biodiesel and coded B20 in the United State of America.

In an attempt to achieve a 100% renewable fuel, catalytic deoxygenation of triglycerides and free fatty acids (FFAs) has been proposed and is currently being widely studied both in the presence of hydrogen gas – hydrodeoxygenation (HDO) (Danuthaia et al., 2011; Immer et al., 2010; Kovacs et al., 2011; Liu et al., 2009; Mortensena et al., 2011) and in the absence of hydrogen gas - decarboxylation and

decarbonylation (Decarbs) (Arend et al., 2011; Do et al., 2009). Details of the two processes that had been carefully reviewed (Mortensen et al., 2011) and compared (Do et al., 2009) showed that HDO is more prospective because its products are mostly paraffin with similar properties to the conventional diesel fuel compared to mixtures of paraffin and other condensation products such as esters and ketones observed in Decarbs which adversely reduces the energy density (Do et al., 2009; Immer et al. 2010; Kovacs et al., 2011). In addition, HDO process can be adapted into hydrotreating units (HDTU) of existing conventional refineries without serious modification (Sousa et al., 2012). Finally, the fast rate of catalyst deactivation in Decarbs processes has eventually made it less attractive as compared to the HDO (Arend et al., 2011; Danuthaia et al., 2011).

In attempt to deepen knowledge into the HDO process, effects such as reaction variables, i.e. temperature, H₂ gas flow rate, pressure and type of the catalyst have been well studied (Danuthaia et al., 2011; Immer et al. 2010; Kovacs et al., 2011; Sousa et al., 2012). However, since it has been considered that the existing HDTU of conventional refineries can be adapted, studies on developing suitable catalysts such as types of the support and metals (Park et al., 2011), catalyst preparation procedure (Li et al., 2012; Sousa et al., 2012) and effect of additives such as sulfur (Sotelo-Boyás et al., 2011) and phosphorus (Yang et al., 2012) are currently at the fore. Various sulfide catalysts such as NiMo/Al₂O₃ and CoMo/Al₂O₃ have been synthesized and tested on various feed stocks and their results according to the authors (Guzman et al., 2010; Simáček and Kubicka, 2010) showed enhanced HDO efficiency compared to the non-sulfide ones, and in addition isomerized products were also observed. As an alternative to sulfide modification, NiMo/Al₂O₃ catalyst was modified with fluorine to increase the acidity and it was reported to be highly favorable for paraffin skeletal isomerization, although it gradually loses its isomerization activity due to leaching of the fluoride

contents (Kovacs et al., 2011). Generally, the presence of isomerized product is considered an advantage due to the ability of iso-paraffin to lower the biofuel freezing point since normal-paraffin (C₁₆–C₁₈) has comparable high freezing point (between 18 °C and 28 °C) which is a disadvantage to their cold flow properties such as cold filter plugging point (Kovacs et al., 2011).

Recently, Li et al., (2012) in a study on series of NiMo/ γ -Al₂O₃ catalysts with organic functionalization using different quantities of urea reported that urea improves the solubility of Mo and Ni salt in the support and also facilitates the formation of molybdate and polymolybdate complexes. This phenomenon in turn enhances the catalysts' morphology and textural properties and the catalytic activity due to better porosity, well dispersed active particles, increased octahedral molybdenum/nickel oxides and proper acidity. Similarly, Sousa et al., (2012) reported that expedient synthesis (such as temperature programmed carburization methodology) of supported molybdenum carbide (Mo₂C/Al₂O₃) as single metal catalyst gives excellent hydrotreating activity as an alternative to the sulfide and bi-metal catalysts.

1.1 Problem Statement

In view of the aforementioned studies, there is need to expediently synthesize supported organometallic catalysts that can combined the high porosity of inorganic supports such as zeolite and alumina, as well as the lipophilicity of organo-zeolite/alumina through the incorporation of organic acid functionalized active metals. This novel catalyst preparation protocol has been scarcely reported. Therefore in this study, a novel organometallic catalyst synthesis protocol was developed via the functionalization of selected HDO active metal (Ni, Mo, Pt and Pd) catalyst with oxalic acid to form their respective metal-oxalate ligands which are in turn incorporated into

zeolite and alumina supports. As an improvement over some earlier synthesized organometallic catalysts, fluoride ion was also used to functionalize the catalysts to further enhance their acidity since acidified catalyst are known to have ability for normal-paraffin skeletal isomerization of the already hydrodeoxygenated biofuel which is considered a value-added-component in the final biofuel.

1.2 Research Aims and Objectives

The aim of this research work is to expediently synthesize catalysts having high biofuel throughput with minimal active metal leaching for the hydrodeoxygenation of bio-oil (using oleic acid (OA) and stearic acid (SA) as the model compounds) into paraffinic biofuel with isomerized component. This aim will be achieved through the following objectives.

- i. To Carryout thermodynamic simulation of bio-oil hydrodeoxygenation process using Aspen Hysys process simulator to determine the process feasibility and to establish the feasible operating condition (FOC) range.
- ii. To synthesize, characterize and screen the catalytic activities of organometallic and non-organometallic catalysts on the HDO of OA process kinetics and determine the Arrhenius parameters based on mathematical modeling of hydrodeoxygenation process using 2D Table curve and MathCAD software.
- iii. To study the effect of fluoride ion functionalization on organometallic catalysts ability on the n-paraffin skeletal isomerization of the HDO product and study the effect of operational variables using different zeolite and alumina supported organometallic catalyst.
- iv. To study the process chemistry of the HDO of OA based on the Fourier Transform Infrared (FTIR) spectroscopy of the evolved product.

- v. To study the optimization process of the HDO of OA using response surface methods (RSM) and finally to study the reusability of the synthesized catalysts.

1.3 Scope of study

The scope of this research reports covers thermodynamic simulation to establish the feasibility of the HDO process of SA and OA followed by synthesis, characterization and testing of various organometallic and non-organometallic catalysts. In the first step, two alumina supported nickel catalysts were synthesized, the first was via incorporation of nickel nitrate into alumina ($\text{Ni}/\text{Al}_2\text{O}_3$) and the second was via incorporation of nickel oxalate prepared via functionalization of nickel with oxalic acid (OxA) into alumina ($\text{NiOx}/\text{Al}_2\text{O}_3$). The activities of both catalysts were tested on the HDO of OA. $\text{NiOx}/\text{Al}_2\text{O}_3$ showed the best HDO activity and in addition it produces isomerized fraction due to the effect of OxA functionalization which increased its acidity. A study on their HDO kinetics showed that the activity of $\text{NiOx}/\text{Al}_2\text{O}_3$ doubles that of $\text{Ni}/\text{Al}_2\text{O}_3$. Sequel to this observation and in order to enhance the isomerization ability of the organometallic catalysts, they were further functionalized with fluoride ion to enhance their acidity. The activity of palladium oxalate and fluoropalladium oxalate both supported on zeolite were tested and they both showed impressive HDO activity, but the latter showed enhanced isomerization ability. Consequently, all other metal-oxalate catalysts were further functionalized with fluoride ion and characterized using X-ray fluorescence (XRF), energy dispersive X-ray (EDX), scanning electron microscope (SEM), surface area analyzer (BET method), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and thermogravimetric analysis (TGA). Preliminary study on the possible auto catalytic or cracking ability of the reactor and its accessories were undertaken prior to the effect of operational variables – time, temperature, pressure, catalyst loading and gas flow rate.

As a follow up to the study on the effect of operating condition, the HDO of OA process chemistry was studied based on the in-situ analysis of the evolved products FTIR. Finally, the HDO process of OA was optimized for one of the most expensive active metals (platinum) and the reusability of all the tested catalysts were studied.

1.4 Organization of the Thesis

Chapter One presents general background information and history of biofuel especially owing to the fast depletion rates of fossil fuel reserves and the attendant hazardous effects of its exhaust gases on humans and environments. It also features the challenges encountered in past research studies and the proposed solution. Others include the problem statement, scope of work and the organization of the thesis.

Chapter Two reviews the historical background of this study which included the successes and failures recorded in the literature in the search for renewable energy as an alternative to fossil fuel. Different biofuel production methods and routes such decarboxylation, decarbonylation and hydrodeoxygenation were critically reviewed, and hydrodeoxygenation route was identified to be superior in view of the high quality paraffin that were produced which shared similar constitution and chemistry with those found in conventional diesel fuel. The review also includes the active metals and different supports that have been previously employed. In addition, the effect of operational variables on the process were reviewed as well as the possibility of combining hydrodeoxygenation and isomerization processes in one single unit via expedient synthesis of acidified catalysts.

Chapter Three features the materials and methods used in this report. This includes the list of chemicals and their suppliers, basic information on the model compounds and the catalyst supports. Catalyst preparation was detailed under two

sections; the first was the synthesis of the catalyst precursors via functionalization of the active metals with oxalic acid (and fluoride ion where applicable) and the second was the incorporation of the catalyst precursor into either alumina or zeolite. Post catalyst preparation steps like filtering, washing, drying and calcinations were described. Different catalyst characterization techniques used to determine both the qualitative and quantitative analysis of the catalysts were also described. The range of values of process parameters affecting the HDO of OA and SA were presented and finally, D-Optimal design, a form of response surface methods (RSM) was designed to optimize the HDO process.

Chapter Four presents the results and discussions in Parts from Part One to Nine using publication format, each Part was a manuscript published/reviewed/under review in Tier 1 Web of Science (formally known as ISI) indexed journals except Part One which was an extract of a conference proceeding (8th Conference on Sustainable Development of Energy, Water and Environment Systems – SDEWES Conference 2013, Dubrovnik Croatia) published in a Scopus indexed journal. The discussed results include the thermodynamic feasibility of the hydrodeoxygenation process of stearic acid and oleic acid - Part One. The effects of oxalic acid and fluoride ion functionalization, catalyst characterizations, effect of variation of process parameters (Part Two – Five, and Seven). Others includes the results of the OA process chemistry, kinetic and Arrhenius parameters of the OA HDO process (Part Two, Six and Seven) and the HDO process optimization using D-Optimal Design, a form of response surface methods (RSM) using Design Expert software from Stat Ease Inc (Part Eight). Finally, the catalyst reusability result was presented in all the Parts (except Part One and Six) to determine the catalysts stability.

Chapter five present the conclusions to each of the published/under-review manuscripts discretely as well as general recommendations based on the observations in course of this study.