



Catalytic Hydro-cracking of Bio-oil to Bio-fuel

Amir Ahmad Forghani

(1200751)

Thesis submitted for the degree of Doctor of Philosophy

School of Chemical Engineering

Faculty of Engineering, Computer & Mathematical Sciences

The University of Adelaide, Australia

December 2014

Table of contents

Abstract	iv
Declaration	vi
Acknowledgments	vii
Chapter 1- Introduction	1
1.1. Background	2
1.2. Aims	5
1.3. Thesis outline	6
1.4. Papers arising from this thesis	7
1.5. Format	9
References	10
Chapter 2- Literature review	12
2.1. Bio-oil upgrading processes and applied catalysts	13
2.2. Application of metal based catalysts in bio-oil conversion	16
2.2.1. Application of supported metal sulfide catalysts	16
2.2.2. Application of sulfured-free metal catalysts	18
2.3. Mathematical modelling of the Catalytic bio-oil upgrading reactors	19
References	22
Chapter 3: Mathematical modelling of a hydrocracking reactor for triglyceride conversion to biofuel: model establishment and validation	27

Chapter 4: Performance investigation of a hydro-cracking reactor for triglyceride conversion to bio-fuel production	40
Chapter 5: Catalytic Conversion of Oleic Acid in Bio-oil to Liquid Hydrocarbon Fuels	80
Chapter 6: Hydro-conversion of Oleic Acid in Bio-oil to Liquid Hydrocarbons: an Experimental and Modelling Investigation	104
Chapter 7: Conclusions & Future works	138
7.1. Conclusions	139
7.1.1. Investigation of the hydro-cracking reactor performance and sensitivity analysis	139
7.1.2. Hydro-cracking with non-expensive sulfured free zeolite catalysts	140
7.2. Recommendations for future works	141
Appendix: Conference Presentations	143

Abstract

Over the last hundred years, the fossil fuels consumption is increasing dramatically and this lead to a significant increase in greenhouse gas emissions, the depletion of natural reserves of fossil fuels and increase the fuel production cost. Consequently, renewable and sustainable fuel sources such as bio-oil are receiving increased attention. In bio-based oil such as micro-algae oil, triglycerides and fatty acids are sustainable resources with high energy densities that can be converted into liquid hydrocarbon fuels, efficiently. One of the efficient ways for bio-oil conversion to applicable fuels is hydro-cracking. Hydro-cracking with acidic catalysts is a single step and energy efficient process for bio-oil upgrading towards bio-fuels. Zeolitic structures such as ZSM-5 and beta-zeolite are prevalent acidic catalysts in hydro-treating processes due to their strong acidity, their crystalline porous structure and their high hydrothermal stability. The aim of this research is checking the feasibility of hydro-cracking synthesis towards the light (LC) and middle (MC) range of hydrocarbons over the zeolite based catalysts. Two different types of zeolite catalysts, ZSM-5 and beta-zeolite, were chosen and they were impregnated with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and calcined at $500\text{ }^\circ\text{C}$. The prepared catalysts were tested with oleic acid which is the main component of plant-derived oil. The catalysts were injected in a lab-scale trickle bed reactor in certain operating conditions. The oleic acid conversion over beta-zeolite was greater than ZSM-5 due to higher pore size distribution and acidity of beta-zeolite compared with ZSM-5. Also the reaction rate constant and Arrhenius equations for beta-zeolite and ZSM-5 were identified. The second step

of this research is investigating the hydro-cracking performance with performing a mathematical modelling. The model predictions showed reasonable correlation with experimental data and conversion rates. The total conversion for the hydro-cracking reactor model was 82.54 % for 4 major classes of hydrocarbons (light [LC], middle [MC], heavy [HC] and oligomerised [OC]). In addition, the concentration distribution and temperature profile along the reactor were investigated. At the end, a comprehensive sensitivity analysis was performed to analyse the hydro-cracking reactor performance.

Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

The author acknowledges that copyright of published works contained within this thesis resides with the copyright holder(s) of those works.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library Search and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Acknowledgment

I would not have been able to complete this journey without the aid, support and contribution of many people.

I would firstly like to acknowledge the support given to me by my supervisors Associate Professor David M. Lewis and Associate Professor Phillip Pendleton who helped me in all time of my research and writing of this thesis. I thank A/Prof. David Lewis for his patience, support and guide through up and down times of my PhD thesis. I thank A/Prof. Phillip Pendleton for his motivation, enthusiasm, immense and comprehensive knowledge in the field material sciences and the characterisation procedures during my PhD.

I would like to acknowledge Adelaide Scholarship International (ASI) for their financial support. Also I would like to appreciate Prof. Peter Ashman for approving a short term scholarship of chemical engineering school. I would also like to thank the current and former staffs of the School of Chemical Engineering and Centre for energy Technology (CET).

I am deeply appreciating my parents who always encourage and support me through my life. I am also appreciating my sister, Bahar for her support during my PhD. I would like to express my special gratitude and thank to Nastaran, for being the most loving, patient and understanding wife for over this period.