UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF CARBOHYDRATE-DERIVED SOLID ACID CATALYSTS FOR BIODIESEL PRODUCTION FROM PALM FATTY ACID DISTILLATE

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By

MOHD LOKMAN BIN IBRAHIM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for Degree of Doctor of Philosophy

March 2016

DEDICATION

Special Dedicated to my Mother
Aminah Bte Semail (1965 – 2013)

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor Philosophy

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March 2016

Chairman : Prof. Taufiq Yap Yun Hin, PhD
Faculty : Science

High concerns on the energy security and uncontrolled emissions of greenhouse gas had forced all countries to turn towards the utilization of environmentally-friendly and renewable biofuels. In this work, the usage of inexpensive and non-edible oil feedstock such as palm fatty acid distillate (PFAD) for the biodiesel production is recommended.

A highly potential heterogeneous carbon-based solid acid catalyst derived from carbohydrates was successfully developed and applied for biodiesel production. The carbohydrate-derived solid acid catalysts were synthesized by sulfonation of incomplete carbonized carbohydrates using concentrated sulfuric acid. The prepared catalysts underwent a detailed characterization analyses in terms of its active site's functional groups, morphological structure, thermal stability, surface area and density of the acid sites. The catalytic activity of all prepared catalysts had demonstrated the highest conversion of PFAD to biodiesel under the following reaction condition: catalyst loading of 2 wt.%, methanol-to-PFAD molar ratio of 10:1, reaction temperature of 75 °C and the reaction time was 3 h.

In order to improve the esterification reaction process, an efficient microwave batch reactor was fabricated. A study on a microwave-assisted acceleration of esterification rate of PFAD using glucose-derived solid acid catalyst was carried out. It was found that the radio frequency of microwave energy could enhance the reaction rate faster than the conventional heating technique. The results revealed the potential of microwave irradiation; which offers faster esterification rate with advantages of enhancing the FAME yield and reducing the production cost.

Another study was carried out to investigate the effect of high temperature on the esterification reaction of PFAD. The supercritical reactor was used to heat up the reaction system up to sub- and super-critical conditions. The results from the optimization of reaction variables were; reaction temperature of 290 °C, methanol-to-PFAD molar ratio of 6:1, catalyst amount of 1 wt.% and reaction time of 5 min. The esterification of PFAD in supercritical methanol with the presence of glucose- and starch-derived solid acid catalysts at this condition resulted 95.4% and 97.3% of FAME yield, respectively - both catalysts yielded significantly higher conversion compared to

un-catalyzed supercritical methanol reaction with the ability to be recycled up to 10 times.

As a conclusion, it revealed that the sulfonated carbohydrate-derived acid catalysts had high potentials by showing high catalytic activity with better stability and were suitable for the biodiesel production from low-quality feedstock with high FFA content, especially PFAD. The improvement on the reaction rate by applying the invented microwave-assisted and supercritical methanol reactions showed positive outcome – which in turn, proved the fast reaction with high FAME yield.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

SINTESIS MANGKIN ASID PEPEJAL TERBITAN KARBOHIDRAT UNTUK PENGHASILAN BIODIESEL DARIPADA BAHAN ASID LEMAK SAWIT SULINGAN

Oleh

MOHD LOKMAN BIN IBRAHIM

Mac 2016

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Kebimbangan terhadap sumber bekalan tenaga, harga bahan api yang tidak menentu, dan pembebasan gas rumah hijau yang tidak terkawal menyebabkan kebanyakan negara beralih ke arah penggunaan bahan api-bio yang boleh diperbaharui dan mesra alam. Dalam kajian ini, penggunaan bahan mentah yang murah dan tidak boleh dimakan seperti asid lemak sawit sulingan (PFAD) untuk penghasilan biodiesel telah dikaji dan diguna pakai.

Bahan mangkin heterogen asid pepejal terbitan karbohidrat berasaskan karbon telah berjaya disintesis dan digunakan untuk menghasilkan biodiesel. Bahan mangkin ini telah dihasilkan melalui proses pengsulfuran karbohidrat iaitu pemanasan karbohidrat bersama asid sulfuric pekat. Beberapa pencirian bahan mangkin telah dilakukan dengan menggunakan pelbagai teknik seperti analisis kumpulan berfungsi, morfologi permukaan, kestabilan terma, luas permukaan dan kuantiti tapak asid. Aktiviti pemangkinan semua katalis yang disediakan menunjukkan penukaran tertinggi bahan PFAD kepada biodiesel dengan keadaan: 2% bahan mangkin, nisbah molar metanol kepada PFAD (10:1), suhu tindak balas ialah 75 °C dan masa tindak balas ialah 3 jam.

Dalam usaha untuk meningkatkan proses tindak balas pengesteran, satu reactor dengan gelombang mikro telah difabrikasi. Kajian kesan kadar pecutan gelombang mikro terhadap pengesteran bahan PFAD dengan menggunakan mangkin asid pepejal terbitan glukosa telah dijalankan. Keputusan yang diperolehi menunjukkan bahawa tenaga radio berfrekuensi gelombang mikro boleh meningkatkan kadar tindak balas berbanding dengan teknik pemanasan konvensional. Secara keseluruhan kajian yang dilakukuan menunjukkan bahawa sinaran gelombang mikro mampu mempercepatkan kadar pengesteran dan meningkatkan produktiviti serta mengurangkan kos pengeluaran.

Kajian seterusnya telah dijalankan untuk mengkaji kesan penggunaan suhu yang tinggi terhadap tindak balas pengesteran PFAD. Reaktor super-genting telah digunakan untuk tindak balas pemanasan sehingga mencapai pada tahap sub- dan super-genting. Suhu tindak balas pada 290 °C, nisbah molar methanol kepada bahan PFAD ialah 6:1, berat mangkin sebanyak 1% dan dengan masa tindak balas selama 5 min telah dikenalpasti sebagai keadaan tindak balas yang paling optimum. Didapati, pengesteran bahan PFAD kepada biodisel dalam keadaan super-genting dengan penggunaan mangkin asid pepejal terbitan glukosa dan kanji, masing-masing memberikan peratus hasil pada 95.4% dan 97.3% - Kedua-dua bahan mangkin memberikan peratus penukaran yang lebih tinggi berbanding tindakbalas super-genting yang dijalankan tanpa penggunaan mangkin. Selain itu, bahan mangkin yang digunakan dalam penyelidikan ini didapati mempunyai sifat kebolehulangan yang sangat baik dengan 10 kali kitaran.

Akhir sekali, dapat disimpulkan bahawa mangkin asid pepejal terbitan karbohidrat mempunyai aktiviti pemangkinan dan kestabilan yang sangat baik. Bahan mangkin ini sesuai digunakan dalam penukaran bahan mentah berkualiti rendah dengan kandungan FFA yang tinggi seperti PFAD. Kadar tindak balas yang cepat dengan hasil FAME yang tinggi berjaya diperolehi jika menggunakan teknik gelombang micro dan super-genting. Kedua-dua pendekatan ini juga dilihat sebagai suatu alternative baru yang memberi kesan positif - pada masa yang sama meningkatkan kadar tindak balas dan hasil produk biodiesel.

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LIST OF ABBREVIATIONS

P_c	Critical pressure
T_c	Critical temperature
MW	Molecular weight
T	Reaction temperature
t	Reaction time
S_{BET}	BET surface area
P_o	Vapour pressure
P/P_o	Relative pressure
P	Reaction pressure
R	Alkyl group
c	BET Constant
M	Molarity
m	mol
°C	Degree celcius
h	Hour
min	Minutes
μL	Microliter
mg	Miligram
PFAD	Palm Fatty Acid Distillate
CPO	Crude Palm Oil
ANOVA	Analysis of VAriance
ASTM	American Society for Testing and Materials
EN	European Standard
CCD	Central Composite Design
FFA	Free fatty acid
TGs	Triglycerides
MGs	Monoglycerides
DGs	Diglycerides
DOE	Design of Experiment
FAME	Fatty acid methyl ester
GC-FID	Gas Chromatography-Flame Ionization Detector\
GC-MS	Gas Chromatography- Mass Spectrometer
AV	Acid value
SV	Saponification value
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
CH_3OH	Methanol
C_2H_5OH	Ethanol
H_2SO_4	Sulphuric acid
KBr	Potassium bromide
XRD	X-ray Diffraction analysis
TG-DTG	Thermal Gravimetry-Differential Thermal Gravimetric
FESEM	Field Emission Scanning Electron Microscopy
BET	Brunauer-Emmett-Teller
FTIR	Fourier Transform Infrared Spectroscopy
NH_3-TPD	Ammonia-Temperature Programmed Desorption
$NaHCO_3$	Sodium Hydrogen Carbonate

HCl	Hydrochloric Acid
GHG	Life-cycle Greenhouse Gas
NO_x	Nitrogen dioxide
XPS	X-ray Photoelectron Spectroscopy
PP	Pour Point
CP	Cloud Point
RSM	Response Surface Methodology
CHNOS	Carbon Hydrogen Nitrogen Oxygen Sulfur element analysis
EDX	Energy Dispersive X-ray
-PWM	-Pulse Width Modulation

CHAPTER 1

INTRODUCTION

1.1 Green Technology and Alternative Fuels

Currently, the negative environmental impact from the burning of fossil fuels, coals, and compressed natural gas has become one of the major problems occurring worldwide (Amigun *et al.*, 2008; Demirbas, 2008). Climate changes occur when the greenhouse effect increases from the burning of fossil fuels as evidenced by flash floods, windstorms, heat waves, and sudden droughts in a number of countries (Lam & Lee, 2011). Furthermore, the global energy demand is increasing while energy sources from fossil fuels are rapidly diminishing.

Fossil fuels are one of the non-renewable energy resources, which will be exhausted in several decades if large-scale of energy source is used continuously (Aguilera *et al.*, 2009). As shown in Figure 1.1, the world production of fossil oil is at the peak of the production, and it was expected to diminish as reaching the year 2050. As a result of those scenarios, replacing petroleum consumption, minimizing future costs, and eliminating the negative impact on health and the environment are crucial. Thus, the replacement of non-renewable energy source with renewable resources is imperative to fulfill the needs of the energy demand without causing harm to the environment and mankind.

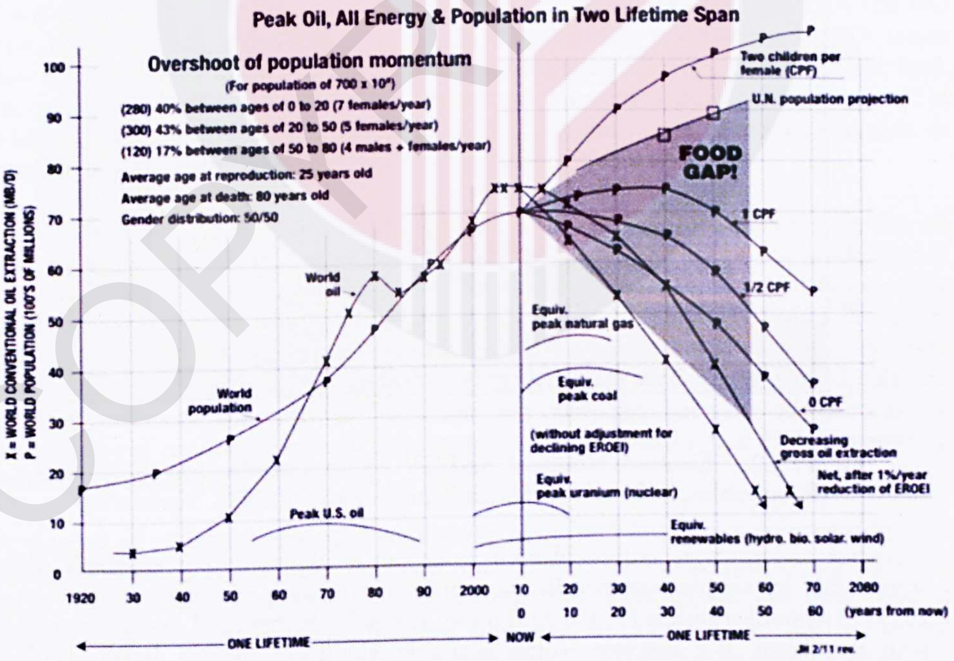

Figure 1.1 Estimation of fossil oil production in comparison with world population (ASPO-USA Supplement, November 2011)

Because of that crisis, different types of energy are being utilized to cover up the high demand of petroleum-based fuel such as the wind turbines, river dams, solar panels, geothermal power and biofuels. Since past decades the production of bio-fuel, ethanol and hydro treated vegetable oil are increased significantly and became the most common alternative fuels, as shown in Figure 1.2. In this work, only the potential of bio-fuel derived natural renewable resource or known as biodiesel has been focused and investigated as the alternative fossil-fuel replacement.

1.2 Biodiesel and its Benefit

Basically, biomass can be converted to biofuels such as biogas, biodiesel, and bioethanol (Peng-Lim *et al.*, 2012). The feedstocks of biofuel are differentiating each other and the availability of feedstock is highly dependent on agro-climatic conditions of the region. As reported by Lam & Lee (2011), biodiesel has similar properties as fossil fuels in terms of the chemical structure and energy content. Thus, biodiesels became the most suitable bio-fuels to replace non-renewable diesel fuel as the energy source for transportation and industries. Furthermore, the modification of the engine system is not required due to the compatibility of biodiesel in normal diesel engine and it has been used widely in Europe and the United States (Xue *et al.*, 2011).

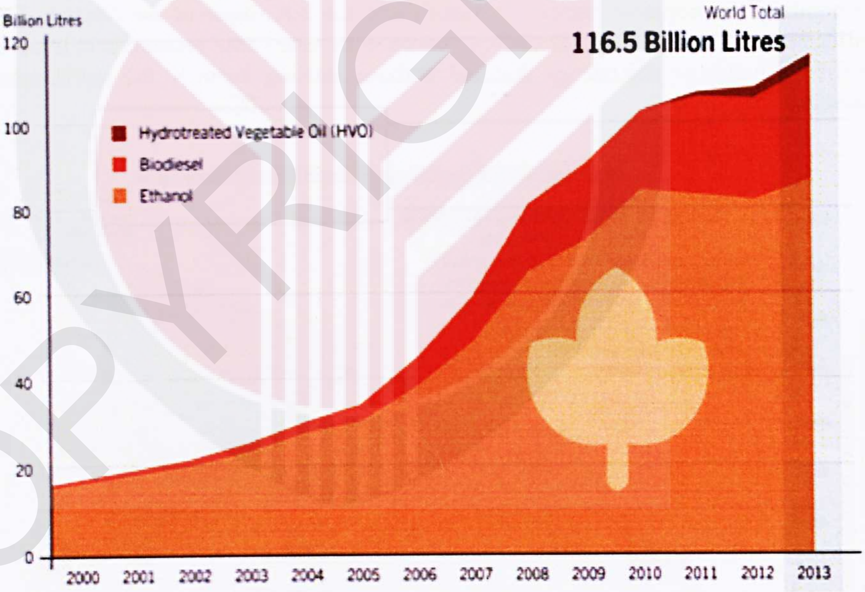

Figure 1.2 **Ethanol, biodiesel, and HVO global production, 2000-2013**
(Renewables, 2014 Global Status Report - Paris: REN21, Secreteriat)

Biodiesel or known as fatty acid alkyl ester can be derived from vegetable oils or animal fats by simple transesterification and esterification processes (Rashid *et al.*, 2013). Biodiesel is meant for standard diesel engines whether used directly or blended with petroleum. For instance, some available biodiesels include B100 (100% of biodiesel), B20 (blended with 20% of biodiesel) and B5 (blended with 5% of biodiesel) (Dubé *et al.*, 2007; Szybist *et al.*, 2007). Biodiesel was introduced as early as 1853 by Patrick Duffy (Duffy, 1853), which was about 40 years before Rudolf Diesel had developed the first model of a diesel engine on the 10th August 1893 (Henriques, 1898).

Al Zuhair (2007) and Agarwal *et al.* (2007) reported that the biodiesel has an excellent combustion emission profile by producing lower emission of carbon monoxide, unburned hydrocarbon and particulate matters. The combustion of biodiesel produces low concentration of CO_2 to the atmosphere, thus eliminating the green house effect. The properties of biodiesels such as biodegradable in nature, low toxicity, lower sulfur content, high volatility, high flammability, high cetane number (shorter ignition delays) and better lubricity have made it acceptable as an emerging renewable energy resource for replacement of petroleum-based fuel (Boehman, 2005; Knothe *et al.*, 2006; Sharma & Singh, 2010).

1.3 Biodiesel Production Process

The most important factors for choosing the technology to be employed for biodiesel production is quality of the oil; consisting with different amount of free fatty acid (FFA), moisture and saturation level of vegetable oils and animal fats. The common virgin oil such as palm oil, soybean oil and canola oil are the most expensive feedstock and not compatible for low-cost biodiesel production. As reported some years ago, 70% from the total cost of biodiesel production is originated from the price of the feedstock and followed by the costs of the solvent, energy power and maintenance (Ma & Hanna, 1999). For that reason, an ideal way to reduce the cost of biodiesel production is by using the cheaper feedstock such as animal fats, greases and waste oils.

Canakci & Gerpen (2001) studied the production of biodiesel from high FFA fats and oils. They reported that 2.5 billion pounds of restaurant's and fast-food stall's waste fats were collected yearly. The authors also mentioned the price of the animal feed, tallow, grease, blood and hydrolyzed feather meal were less than $0.02 per pound. In addition to these findings, it was also stated that the usage of waste materials is possible for lowering the cost of biodiesel production by 50 to 70%.

In this work, a high FFA content of non-edible by-product from refinery of palm oil known as palm fatty acid distillate (PFAD) was chosen as the test oil for production of fatty acid methyl ester (FAME) or known as biodiesel. In 2014, Malaysia is exporting 25.02 million metric tons of crude palm oil with the total income of RM63.36 billion, and known as the second largest country of crude palm oil producer after Indonesia; besides producing 1.11 million metric tons of PFAD as the side-product of palm oil refinery process (Zain, 2015). The crude oil refining process is the process for purification of crude palm oil and it is required to remove the FFA or PFAD to produce refined vegetable oil.

A number of research groups had studied the usage of PFAD as starting materials for biodiesel production including Yujaroen *et al.*, (2009), Cho *et al,* (2012), Chongkhong *et al.*, (2007) and Chongkhong *et al.*, (2009). Nowadays, PFAD has been used in animal feed industry, cosmetic industry and soap industry (Mielke, 2010). In our investigation, we found out that the utilization of PFAD as the biodiesel's feedstock could maximize the biodiesel productivity by enhancing the production yield, lowering the production cost and also had potential in improving the management of abundance waste materials, which can lead to the environmental pollution.

1.4 Catalyst

The utilization of catalyst in biodiesel production is important in order to increase the FAME yield and improve the production process. Basically, catalyst is defined as any substance with a potential to increase or to speed up the reaction rate of certain chemical reaction by providing the alternative way with lower activation energy as shown in Figure 1.3. There are two main types of catalysts which were normally used in the biodiesel production process; homogeneous and heterogeneous catalyst. Homogeneous catalyst is the catalyst that has the same phase with the reactant or the sample feedstock. Meanwhile, the heterogeneous catalyst is the catalyst which has a different phase from the reactants (Astruc *et al*., 2005; Phan *et al*., 2006).

The homogeneous base and acid catalysts are the common catalyst for biodiesel production. However, it could cause many obstacles such as the equipment corrosion, difficulties in separation and abundance of toxic wastewater after biodiesel purification process. To overcome the stated problems, the heterogeneous solid catalyst is used and it allows more environmentally friendly process for biodiesel production (Islam *et al*., 2012), it also had the potential to eliminate the separation, purification, corrosion and environmental problems.

A number of heterogeneous solid acid catalysts have been introduced in past decades, for instance carbon-based catalyst (Deshmane *et al*., 2013; Wang *et al*., 2013), metal-based catalyst (Islam *et al*., 2012; Jacobson *et al*., 2008) and polymer-based catalyst (Yamaguchi *et al*., 2009). However, each catalyst has individual drawbacks and limitation in certain reaction conditions; they include expensive materials, complicated preparation step, less activity and stability.

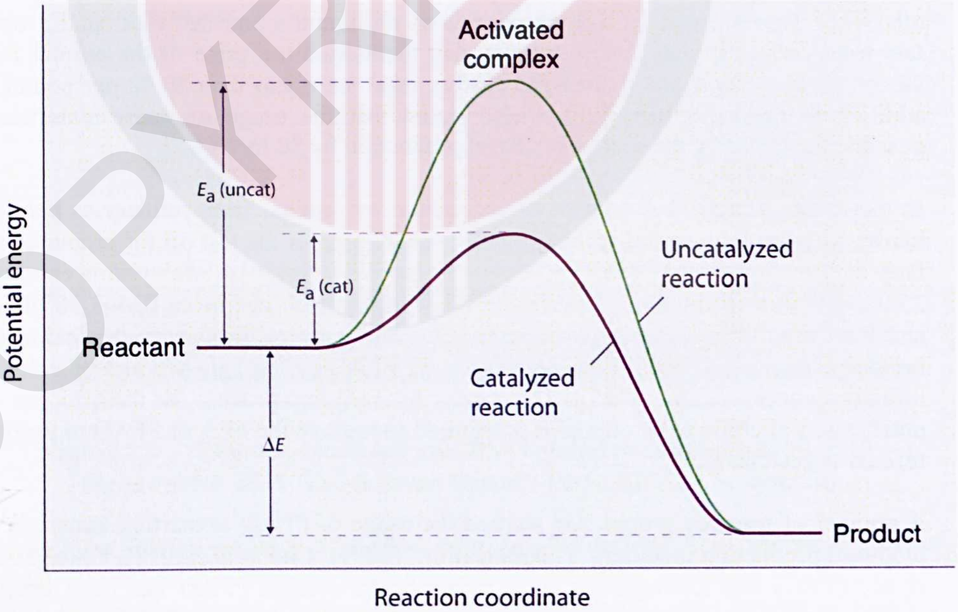

Figure 1.3 **The effect of catalyst on the activation energy of the reaction** (Clark, 2012)

Recently, the heterogeneous poly-aromatic carbon-based solid acid catalyst becomes an attractive catalyst due to its cheaper cost preparation, good stability of carbon structure, high surface area, modification ability, and high catalytic activity. Thus, it would be a good catalyst for low-cost biodiesel production. Carbon-based solid acid catalyst can be easily synthesized from cheap biomass materials such as wheat (Wang *et al.*, 2013), carbohydrates (Deshmane *et al.*, 2013), oil-cake wastes (Konwar, Das, et al., 2014) and empty fruit bunch (Yaakob *et al.*, 2012). Different carbon precursors give different catalytic profiles with different reaction performance. A fundamental study needs to be done to understand the activity related to the network of carbon structure and its criteria and properties.

In this work, a number of carbon-based solid acid catalysts were prepared from the carbohydrate species. The performance of each catalyst was investigated by carry out the reaction of PFAD with methanol at different operating condition and different type of reactors.

1.5 Problem Statements

The growing of the motorization and industrialization worldwide has led to the high demand of the petroleum-based fuel. Today, the sources of petroleum fuel are drained and exhausted. High-energy demand and the depletion of petroleum source had caused the great increase in price of fossil fuel, which only makes the replacing of fossil fuel with bio-fuel more crucial than ever. However, biodiesel too, carries a high price tag in the industry because of the expensive feedstock, expensive reactor and high maintenance. The use of non-edible waste material helps in reducing the cost of biodiesel production. In this work, PFAD oil has been used as the biodiesel's starting material, which was believed to have a significant potential as the next biodiesel feedstock. Indirectly, the waste management from palm oil factory also could be improved.

In the production of biodiesel, a catalyst is very important to improve the efficiency of the process. Heterogeneous catalyst was used instead of homogeneous catalyst due to the difficulties in separation and corrosion problem. However, the catalytic activity and the stability of the heterogeneous catalyst are the key factors in synthesizing a novel catalyst. To overcome this matter, the poly-aromatic carbon-based solid acid catalysts were introduced in this research, which had proved to have high catalytic activity and good stability.

The extended reaction time by classical methanol reflux method reduces the efficiency of the process. In this work, several approaches were carried out to increase the reaction rate; there are by the bombardment of microwave irradiation directly to the molecular level of the reaction mixture, and by heating the reaction mixture up to the supercritical point, where the boundaries between methanol and oil are removed. The basic understandings on these approaches will be discussed and reported in this thesis.

1.6 Hypothesis of the Research

The catalytic activity of the heterogeneous catalyst is strongly related to their surface characteristic and density of the active site. In this work, the carbohydrate-derived solid acid catalysts were activated with the sulfuric acid to generate the sulfonic functional group on the poly-aromatic carbon structure. Theoretically, high density of acid active site will escalates the activity of the catalysts, thus, more acid sites introduced on the structure of carbohydrate-derived solid acid catalyst resulted more catalytic activity.

Normally, the biodiesel is produced in an open system by simple methanol-reflux process at 65 °C for several hours. In this research, the potential of the microwave and the supercritical methanol rectors were introduced with the objective to enhance the reaction rate of both esterification and transesterification processes. The particular reactors had been used previously for the non-catalytic reaction of biodiesel production; however, the reaction rate had not improved significantly. The main idea is to introduce the heterogeneous solid catalyst into the reactor system. It was suggested that, the existence of the carbohydrate-derived solid acid catalyst in the reaction system helps to increase the reaction rate significantly and enhanced the yield of the biodiesel, hence reduces the time consumption needed to complete the reaction.

1.7 Objectives of the Research

The purpose of this research is to study the biodiesel production from PFAD, which is catalyzed by highly efficient heterogeneous solid acid catalyst derived from carbohydrates. There are 6 main objectives have been highlighted and concentrated:

1. To synthesis and characterize the heterogeneous carbohydrate-derived solid acid catalyst.
2. To evaluate the potential of PFAD as low-quality biodiesel feedstock.
3. To optimize the parameter condition for esterification of PFAD.
4. To investigate the effect of microwave-irradiation on esterification of PFAD.
5. To study the effect of supercritical temperature on esterification of PFAD.
6. To evaluate and investigate the properties of PFAD biodiesel.

1.8 Scope of the Research

This research covers the development of the low-cost biodiesel production process by using the low quality biodiesel feedstock such as PFAD as the main oil test. The PFAD is the by-product from the refinery process of crude palm oil containing large numbers of FFA in the range of 80-90 wt.%. Theoretically, direct esterification of PFAD with the methanol produces fatty acid methyl ester (FAME), water and small amount of glycerol as side product. Heterogeneous carbon-based solid acid catalysts derived from carbohydrate species were used to catalyze the reaction system instead of homogeneous catalyst. Detail characterization analysis of the catalyst and optimization process of the catalytic reaction were carried out and discussed in this thesis with the main purpose to understand the behavior of the catalyst toward the production of biodiesel. The microwave and supercritical methanol reactors were used to study the possibility and the potential to increase the reaction rate of the process and to shorten the reaction time. The biodiesel produced from this research have been analyzed through the quality assessment analysis according to the American Society for Testing and Materials (ASTM) and European (EN) standard methods.

1.9 Significant of the Research

In this work, a series of carbohydrate-derived solid acid catalysts were prepared and characterized, which was believed, had high potential to be used for the biodiesel production from high FFA feedstock, due to high catalytic activity, stability and recycle ability without any negative impact to the instrument and environment. The influence of different type of reactors was investigated in order to determine the most potential method to improve the reaction process, such as the microwave reactor equipped with temperature and power controller and the application of supercritical methanol reactor was used to study the behavior of the reaction mixture at supercritical state. The explanation on the heterogeneous carbohydrate-derived solid acid catalyst and both reactors in the production of the biodiesel from low-quality feedstock are the main cores in this work. Figure 1.4 shows the overall overview of the research flow in this work, which covers: (1) preparation and characterization of 5 types of carbohydrate-derived solid acid catalysts, (2) the collection and analysis of biodiesel feedstock, (3) catalytic evaluation of the catalyst, (4) optimization of the reaction conditions, (5) biodiesel production using the alternative methods (e.g., microwave-irradiation and supercritical-solvent techniques) and (6) Quality assessment of the product.

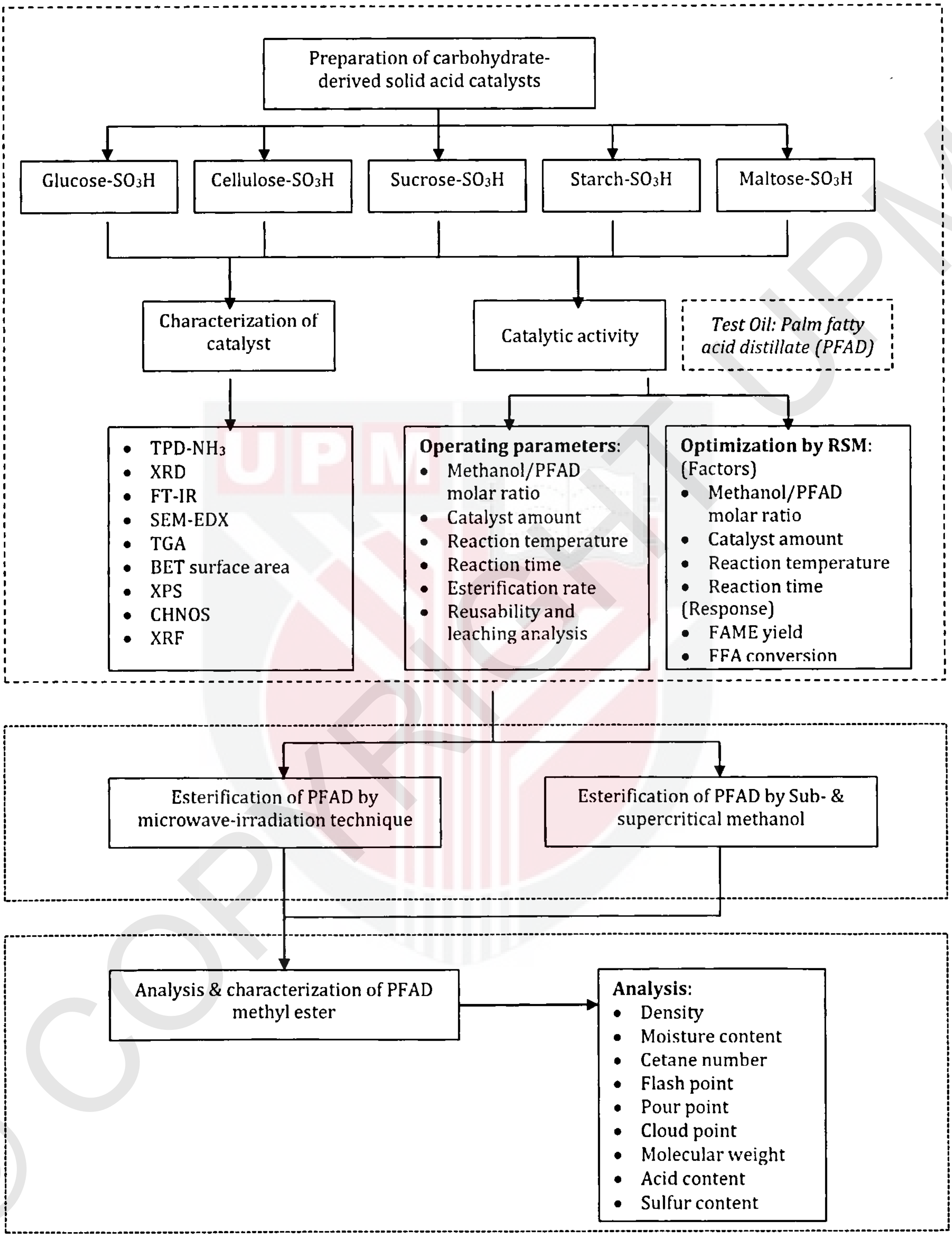

Figure 1.4 Overview of research workflow

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BIODATA OF STUDENT

The name is Mohd Lokman Ibrahim, was born on 25th June 1986 in Machang, Kelantan. He had completed primary education at SK Manek Urai Baru, Kuala Krai, Kelantan from 1993 to 1998. Completed high school at SMK Seri Intan, Machang, Kelantan on 2003. He graduated from matriculation education at Kolej MARA Kulim, Kedah in 2005 and furthers his 3 years first degree in Bachelor of Science majoring in Chemistry at Universiti Teknologi Malaysia (UTM) and graduated on 2008. He continued his Degree of Masters in Chemistry at Department of Chemistry Faculty of Science, UTM under supervision of the late Prof. Dr. Alias Mohd Yusof and graduated in 2011. He got 2 years experience working as the research officer in Institute of Pharmaceutical & Nutraceutical Malaysia (IPHARM), Pulau Pinang. Then, he pursued his Doctor of Philosophy in Catalysis at Catalysis Science & Technology Research Centre (PutraCAT), Department of Chemistry, Faculty of Science under supervision of Prof Dr. Taufiq Yap Yun Hin. His Ph.D study has been supported by Universiti Teknologi MARA and Malaysia's Ministry of Higher Education. He experienced with two-month attachment studies at Prof Motonobu Goto's Laboratory, Department of Chemical Engineering, University of Nagoya, Japan. His contribution in research has received recognition when his research papers were accepted and published in high impact factor journal.

LIST OF PUBLICATIONS

A. Publication:

Ibrahim M. Lokman, Umer Rashid, Robiah Yunus, and Yun Hin Taufiq-Yap. (2014). Carbohydrate-derived Solid Acid Catalysts for Biodiesel Production from Low-Cost Feedstocks: A Review. *Catalysis Reviews: Science and Engineering,* **56**: *187–219.* **(Impact factor: 8.471, Q1)**. http://dx.doi.org/10.1080/01614940.2014.891842

Ibrahim M. Lokman, Umer Rashid, Yun Hin Taufiq-Yap. (2015). Meso- and macroporous sulfonated starch solid acid catalyst for esterification of palm fatty acid distillate. *Arabian Journal of Chemistry*. xx:xxx-xxx. **(Impact factor: 3.725, Q1)**. http://dx.doi:10.1016/j.arabjc.2015.06.034

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Ibrahim M. Lokman, Umer Rashid, Zulkarnain Zainal, Yun Hin Taufiq-Yap. (2014). Microwave-assisted biodiesel production by esterification of palm fatty acid distillate. *Journal of Oleo Science.* **63**(9): 849-855. **(Impact factor: 1.242, Q3)**. http://dx.doi:10.5650/jos.ess14068

Ibrahim M. Lokman, Umer Rashid, Yun Hin Taufiq-Yap. (2015). Microwave-assisted Methyl Ester Production from Palm Fatty Acid Distillate over Heterogeneous Carbon-based Solid Acid Catalyst. *Chemical Engineering Technology*. 38: 1837-1844 **(Impact factor: 2.442, Q1).** http://dx.doi.org/10.1002/ceat.201500265

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B. Paper Presented at Conference:

Ibrahim M. Lokman, Saman A.F., Umer Rashid, Taufiq-Yap, Y.H. Quality evaluation of methyl ester derived from palm fatty acid distillate. The 6th Basic Science International Conference. Malang, Indonesia. 2-3 March 2016.

Ibrahim M. Lokman, Umer Rashid, Taufiq-Yap, Y.H. Methanolysis of palm fatty acid distillate (PFAD) using starch-derived solid acid catalyst: Optimization process of reaction parameters Malaysia International Conference on Oils and Fats 2014. Hotel Bangi-Putrajaya. August 20-21, 2014.

Ibrahim M. Lokman, Umer Rashid, Taufiq-Yap, Y.H. Synthesis of Glucose-Derived Solid Acid Catalyst for Production of Biodiesel from Palm Fatty Acid Distillate.The Seventh Jordan International Chemical Engineering (JiChE 07) Conference.4th to 6th November 2014. Amman, Jordan.

Ibrahim M. Lokman, Umer Rashid, Taufiq-Yap, Y.H. Low-cost biodiesel production from palm fatty acid distillate (PFAD) using glucose-derived solid acid catalyst: Optimization process of reaction parameters. International Symposium on EcoTopia Science. Nagoya Universiti, Nagoya, Japan. December 13-15, 2013.

C. Award:

Silver Medal, PRPI 14, Pameran Rekacipta, Penyelidikan dan Inovasi 2014, Universiti Putra Malaysia. (Ibrahim M. Lokman, Umer Rashid, Taufiq-Yap, Y.H.) Research entitled: Solvothermal Technology for Biodiesel Production.

D. List of Seminar and Workshop Attended:

Workshop on Advanced Materials and Nanotechnology 2015 (WAMN 2015), 4 – 5th November 2015, Institute of Advanced Technology, UPM.

Surface Science and Catalysts Characterization Workshop, 23-24 September 2014, Bangunan Pentadbiran, UPM.

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