UNIVERSITI PUTRA MALAYSIA

BIODIESEL SYNTHESIS FROM PFAD USING HETEROGENEOUS SULFONATED-GLUCOSE CATALYSTS

KEFAS HARUNA MAVAKUMBA

FK 2019 13

BIODIESEL SYNTHESIS FROM PFAD USING HETEROGENEOUS SULFONATED-GLUCOSE CATALYSTS

By

KEFAS HARUNA MAVAKUMBA

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

November 2018

COPYRIGHT

DEDICATION

This thesis is dedicated to the following persons:

My beloved parent;

My dearest wife and children

Abstract of thesis presented to the senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy.

BIODIESEL SYNTHESIS FROM PFAD USING HETEROGENEOUS SULFONATED-GLUCOSE CATALYSTS

By

KEFAS HARUNA MAVAKUMBA

November 2018

Chairman : Professor Robiah Binti Yunus, PhD
Faculty : Engineering

The use of heterogeneous catalysts for biodiesel production is known to mitigate technical issues associated with the use of homogeneous catalysts which are contributed mainly by costly separations and purification steps. However, the limitation in catalytic active sites and stability are issues that deter the effectiveness of the heterogeneous system. In principle, the sugar carbon based catalysts can address these problems. In this study, sulfonated carbonized glucose catalyst was synthesized and utilized for biodiesel synthesis through a single step esterification of non-edible palm fatty acid distillate (PFAD) in an oscillatory flow reactor (OFR). The optimum sulfonation conditions obtained from the use of RSM-CCRD in the catalyst synthesis were 11.25 % of $(NH_4)_2SO_4$ concentration, 5.34 hr of time, 25.16 ml of concentrated H_2SO_4 and 151.15 ^oC of temperature which achieved 93.30 % free fatty acid (FFA) conversion and 91.87 % FAME yield.

The optimized sulfonated catalyst underwent detailed characterization utilizing FTIR, XRD, TGA, TPD-NH_3, FESEM, EDX and BET. Results showed it had a stable amorphous polycyclic aromatic structure with BET surface area of 4.47 m^2/g and 5.92 mmol/g acid sites density thereby exhibiting high catalytic activity in the esterification reaction. The optimization of process conditions in the batch reactor achieved 93.23 % FFA conversion at optimized conditions of 4 wt.% of sulfonated catalyst, 65 ^oC reaction temperature, 10:1 methanol to PFAD molar ratio and 4 h of reaction time. The catalyst was active up to five cycles re-uses without reactivation.

The kinetics study of the esterification of PFAD and methanol using the sulfonated glucose acid catalyst performed in the batch reflux reactor proved that it was an

irreversible reaction due to the use of excess methanol. The experimental data was best interpreted with bimolecular (equimolar) second order model. The rate constant of the reaction (k) from the kinetics study determined at various temperatures ranged from 0.0002 to 0.00053 and the activation energy was calculated to be 55.08 $kJmol^{-1}$. The developed kinetics model and the experimental data are in good agreement.

The biodiesel production with optimized solid acid catalyst in OFR was successfully performed. The OFR achieved maximum of 97.1 % FFA conversion to FAME and >94 % yield. The optimum operating conditions at optimum conversion were 2.5 wt.% of sulfonated catalyst, 60 ^{o}C temperature, 9:1 methanol to PFAD molar ratio, 6 Hz oscillation frequency, and 50 min reaction time. The sulfonated catalyst showed reasonable catalytic activity for up to four cycle's reuse in the OFR achieving about 80 % conversion at the fourth cycle. The performance of OFR was better than the reflux batch reactor in terms of conversion and operating conditions due to the efficient fluid mixing mechanism which resulted in reaction time reduction as well as enhancing heat and mass transfer.

In addition, the properties of the PFAD FAME produced from the OFR showed a pour point and cloud point of 12 ^{o}C and 15 ^{o}C, respectively. The low temperature characteristics of the biodiesel were slightly above the ASTM standard due to high FFA constituent of the PFAD. Most of the other properties are within standard specifications for ASTM D6751 and EN 14214. The biodiesel produced is not suitable for winter grade biodiesel due to its high pour point.

In conclusion, the synthesized modified sulfonated glucose catalyst has proven to be a catalytically active and stable heterogeneous acid catalyst for biodiesel synthesis from high FFA PFAD feedstock especially in the OFR system.

Abstrak tesis yang disampaikan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS BIODIESEL DARIPADA PFAD DENGAN MENGGUNAKAN PEMANGKIN GLUKOSA SULFONAT HETEROGEN

Oleh

KEFAS HARUNA MAVAKUMBA

November 2018

Pengerusi : Profesor Robiah Binti Yunus, PhD
Fakulti : Kejuruteraan

Penggunaan pemangkin heterogen adalah untuk mengurangkan isu-isu teknikal yang berkaitan dengan penggunaan pemangkin homogen dalam sintesis biodiesel disebabkan oleh langkah pemisahan dan pembersihan yang agak mahal. Walaupun penggunaan pemangkin heterogen mungkin telah mengurangkan masalah ini, keterbatasan pada tapak aktif dan kestabilan aktif disebabkan oleh pendedahan kepada medium persekitaran mungkin tidak sesuai untuk industri. Secara dasarnya, pemangkin berasaskan glukosa berkabonasi dapat mengatasi permasalahan ini. Dalam kajian ini, pemangkin sulfonat asid pepejal glukosa berkarbonasi telah disintesis melalui satu langkah tindak balas esterifikasi distilat asid lemak sawit tidak boleh dimakan (PFAD) dengan metanol dalam reaktor aliran ayunan (OFR). Keadaan sulfonasi yang optimum diperolehi dengan menggunakan kaedah permukaan gerak balas dengan reka bentuk putaran komposit pusat (RSM-CCRD), dengan kepekatan $(NH_4)_2SO_4$ sebanyak 11.25 %, masa selama 5.34 jam, isipadu H_2SO_4 sebanyak 25.16 ml dan suhu 151.15 ^oC yang mana telah mencapai 93.30 % penukaran asid lemak bebas (FFA) dan 91.87 % penghasilan FAME.

Pemangkin sulfonat yang telah optimum dicirikan dengan menggunakan FTIR, XRD, TGA, TPD-NH_3, FESEM, EDX dan BET. Pemangkin yang dioptimumkan mempunyai struktur aromatik polietiklik amorf yang stabil dengan luas permukaan BET sebanyak 4.47 m^2/g dan ketumpatan tapak asid sebanyak 5.92 mmol/g dengan itu mempamerkan aktiviti pemangkin yang tinggi dalam reaksi esterifikasi. 93.23% asid lemak terbebas (FFA) berjaya diperoleh melalui parameter proses yang optimum pada suhu tindak balas 65 °C, 10:1 nisbah metanol kepada PFAD selama 4 jam masa tindak balas dengan kehadiran 4 % pemangkin sulfonat. Pemangkin masih boleh digunakan sebanyak lima kitaran tanpa perlu diaktifkan.

Kajian kinetik bagi esterifikasi PFAD menggunakan pemangkin asid pepejal glukosa karbonil sulfonat yang dijalankan di dalam reaktor refluks menunjukkan tindak balas tidak berbalik kerana penggunaan metanol yang berlebihan. Data kajian diintepretasi dengan baik menggunakan model order kedua bimolekular (equimolar). Pemalar kadar tindak balas (k) dari kajian kinetik yang diperoleh pada pelbagai suhu adalah dari 0.0002 sehingga 0.00053 dan tenaga pengaktifan sebanyak 55.08 $kJmol^{-1}$ berjaya dikira. Model kinetik yang dihasilkan adalah bertepatan dengan data yang diperoleh daripada eksperimen.

Penghasilan biodiesel dengan pemangkin asid pepejal yang optimum menggunakan OFR berjaya dilaksanakan. OFR mencapai penukaran maksimum FFA kepada FAME sebanyak 97.1% dan hasil melebihi 94 %. Keadaan operasi yang optimum ialah 2.5 % berat pemangkin sulfonat, suhu 60 ^oC, 9: 1 nisbah molar metanol kepada PFAD, frekuensi ayunan 6 Hz, dan masa reaksi 50 min pada penukaran optimum. Ujian keupayaan penggunaan semula pemangkin dalam OFR menunjukkan aktiviti pemangkin yang tinggi sehingga empat kitaran penggunaan dan berjaya mencapai 80% penukaran pada kitaran keempat. Prestasi OFR adalah lebih baik daripada reaktor kelompok refluks dari segi penukaran dan keadaan operasi disebabkan oleh kejayaan mencapai pencampuran bendalir yang seragam dan efisien melalui gerak cairan berayun yang berinteraksi di plat orifis di dalam tiub lantas mengurangkan masa untuk melengkapan tindak balas serta pemindahan haba dan pemindahan jisim dipertingkatkan.

Sebagai tambahan, ciri-ciri PFAD FAME yang dihasilkan dari OFR menunjukkan keputusan titik tuang dan titik awan masing-masing 12^oC dan 15^oC. Ciri-ciri ini telah melepasi sedikit standard ASTM kerana kandungan FFA tinggi di dalam PFAD manakala kebanyakan ciri-ciri lain telah menepati spesifikasi standard untuk ASTM D6751 dan EN 14214. Biodiesel yang dihasilkan adalah tidak sesuai untuk gred biodiesel musim sejuk kerana titik tuang yang tinggi.

Kesimpulannya, penggunaan pemangkin asid pepejal glukosa sulfonat yang diubahsuai telah terbukti sebagai pemangkin aktif dan asid pemangkin heterogen yang stabil bagi sintesis biodiesel dari FFA PFAD terutamanya bagi sistem OFR.

ACKNOWLEDGEMENTS

I thank God Almighty and all praise goes to Him for giving me the wisdom, strength, protection and ability to complete my PhD study.

My profound gratitude and heartfelt thanks to my dedicated supervisor, Prof Dr. Robiah Binti Yunus for her continuous support, high level of patience, tolerance, motivation, immense knowledge and excellent supervision. Her continuous guidance and meaningful advice were of help to me throughout the course of this study.

My sincere thanks go to my co-supervisors, Dr Umer Rashid and Prof Taufiq Yap Yun Hin for their insightful comments, assistance, encouragement and support which are highly appreciated.

I wish to extend my thanks to the staff and technician of Institute of Advanced Technology, Engineering laboratory and Putra Catalysis laboratory for assisting me directly or indirectly throughout my study period. Also, my thanks go to my colleagues, Dr Azhari, Dr Lim, Atiqah, Liyana, Saiful, Dr Chang, Aznizan, Hussein, Hafez, Dalila, Ika, Aklisah, Feaqah, Ibrahim, Kania, etc and my friends for their constant support, motivation and encouragement.

I would like to thank my family: my parents, my wife and children, siblings, the LFCA Yola, for their prayers and encouragement throughout my stay in Malaysia and my life in general.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Robiah Binti Yunus, PhD
Professor
Faculty of Engineering
University Putra Malaysia
(Chairman)

Umer Rashid, PhD
Associate Professor
Institute of Advanced Technology
Universiti Putra Malaysia
(Member)

Taufiq-Yap Yun Hin, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

_____
ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- the intellectual properties from this thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/ fabrication in the thesis, scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studied) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature:_____ Date:_____

Name and Matric No: Kefas Haruna Mavakumba, GS42125

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rule 2003 (Revision 2012-2013) are adhered to.

Signature: _____
Name of Chairman of Supervisory Committee: Professor Dr. Robiah Binti Yunus

Signature: _____
Name of Member of Supervisory Committee: Associate Professor Dr. Umer Rashid

Signature: _____
Name of Member of Supervisory Committee: Professor Dr. Taufiq-Yap Yun Hin

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ANOVA	Analysis Of Variance
AOCS	American Oil Chemist's Society
ASTM	American Standard Testing Method
BET	Brunauer Emmett Teller
CCD	Central Composite Design
CCR	Canradson Carbon Residue
CCRD	Central Composite Rotatable Design
CFPP	Cold Filter Plugging Point
CHNS	Carbon Hydrogen Nitrogen Sulfur
CPO	Crude Palm Oil
DF	Diesel Fuel
DIN	Deutsches Institut für Normung (The German Institute for Standardization)
EDX	Energy Dispersive X-ray
EN	Euro Norm
ER	Eley–Rideal
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
FESEM	Field Emission Scanning Electron Microscope
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectroscopy
GC-FID	Gas Chromatography-Flame Ionization Detector
GC-MS	Gas Chromatography-Mass Spectrometer
ICG	Incomplete Carbonized Glucose

ITMA	Institute of Advance Technology
JME	Jatropha Methyl Ester
LH	Langmuir–Hinshelwood
MPOB	Malaysian Palm Oil Board
MWCNTs	Multi-Walled Carbon Nanotubes
OFR	Oscillation Flow Reactor
PFAD	Palm Fatty Acid Distillate
PFADME	Palm Fatty Acid Distillate Methyl Ester/Biodiesel
PME	Palm Methyl Ester
PH	Pseudo-Homogeneous
PP	Popken
RDB	Refined, Blenched Deodorized
Ren	Reynolds Number
Reo	Oscillatory Reynolds Number
RSM-CCRD	Response Surface Methodology- Central Composite Rotatable Design
St	Strouhal Number
TAG	Triglycerides
TGA	Thermogravimetric Analyzer
TPD-NH_3	Temperature Programmed Desorption-Ammonia
USA	United States of America
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

Currently, the energy requirement of the world is mainly generated from non-renewable resources known as fossil fuels and the depletion of this sources is anticipated to occur in the near future (Borges and Díaz, 2012). For many decades, because of the excessive usage of the depleting oil reserves of the world by the ever-growing human population, energy crises have been confronting the world (Agarwal, 2007). It is known that the world economy is to a great extent contributed by the transportation of goods and services (Jothiramalingam and Wang, 2009; Sarkar *et al.*, 2012) and in related view, transportation is majorly dependant on energy coming from petroleum resources. In fact, 96 % of fossil fuels are used by the transportation sector with a yearly fuel consumption of 62 % world wide (Piriou *et al.*, 2013). This is also similar with other energy sources like natural gas, coal, nuclear energy and hydroelectricity (Sani *et al.*, 2014). Besides the rise in prices of fossil fuels, another disturbing issue is the environmental effect of fuels combustion emission on human life and the ecosystem. The use of petroleum products as fuels emits carbon dioxide gas (CO_2) into the atmosphere which contributes to an increase in earth's surface temperature due to increase in green house gas leading to serious climate change (Fauzi and Amin, 2013). These issues have necessitated the search to establish the renewable prominence which will supplement or replace fossil fuel. Biofuels have gained attention as an alternative to fossil fuel derivative which are sourced from different biomass. Nevertheless, it is required that biofuel should be economically benign, technically viable and readily accessible (Avhad and Marchetti, 2016).

Biodiesel, a promising substitute to petroleum diesel has received wide consideration in the last two decades because of its biodegradability, non toxic and renewable nature (Li *et al.*, 2010; Marchetti, 2013). In addition, biodiesel does not add to the total atmospheric CO_2 as CO_2 emitted from biodiesel combustion could be recycled by the process known as photosynthesis of the plant where the biodiesel is derived from. The influence of emissions from biodiesel combustion on the green house are therefore minimized (Peterson and Hustrulid, 1998). Moreover, biodiesel is known to contains 10 % oxygen, and its presence in the fuel accelerates combustion rate and reduces pollutants production such as carbon monoxide (CO), particulate matters and polycyclic aromatic compounds (Agarwal, 2007). Other advantageous benefits obtainable from the proper usage of biodiesel compared to the use of petroleum diesel includes ultra-low sulfur concentration, higher flash point, superior cetane number and better lubricating efficiency (Knothe, 2009; Marchetti, 2012). The characteristics mentioned above possessed by biodiesel makes it a proper substitute to petroleum diesel and presently the biodiesel blends are being utilized in many countries around the world in diesel engines.

Biodiesel is defined as the monoalkyl esters of long chain fatty acids obtained from renewable lipids such as vegetable oils and animal fats (Math *et al.*, 2010). The most commonly used method among the various routes for biodiesel production is the catalyst aided alcoholysis of lipid feedstock, which is the transesterification of triacylglycerol (TAGs) also known as triglycerides and esterification of free fatty acids (FFA). Various alcohol types utilized for biodiesel production include methanol, ethanol, propanol and butanol. Although, the most broadly used are methanol and ethanol. However, methanol is the frequently used alcohol for biodiesel synthesis because of its low cost and industrial availability (Lam *et al.*, 2010). The use of methanol in alcoholysis reaction of lipid, results in the formation of product known as fatty acid methyl esters (FAME) where as ethanol forms fatty acid ethyl esters (FAEE).

The choice of feedstock used for biodiesel synthesis especially for large scale production depends on its availability and geographical location. For instance, in the United States soybean oil is widely utilized (with feedstock up to 9431 million pounds in 2015), while in Europe rapeseed oil is frequently used (with 6.17 million tonnes making 55% of total production in 2014) and in Asia palm oil (Malaysia and Indonesia produced 17.5 and 20.9 million metric tonnes of crude palm oil, respectively in 2009) (Kapor *et al.*, 2017). Biodiesel is also produced from alternative feedstocks like refined, crude, waste, and non edible oils using various types of catalysts. Different properties of biodiesel emanate from different feedstock used and the commonly affected properties are viscosity, heating value, oxidation stability, density, low temperature properties and cetane number (Ferrero *et al.*, 2016; Ruhul *et al.*, 2016). Many vegetable oil types have been involved in the production of biodiesel such as palm kernel, sunflower, coconut, canola and sunflower oil (Demirbas, 2007). However, the main drawback of utilizing vegetable oil is food versus fuel issue and the high price of vegetable oil diesel (biodiesel) against petroleum diesel (Choudhury *et al.*, 2013; Talebian-Kiakalaieh *et al.*, 2013a). To counter these issues, research into the use of non edible or waste oils like palm fatty acid distillate (PFAD), rubber seed, jatropha and waste cooking oils have been intensified. In recent times, researches have been performed using PFAD feedstock as a starting material to synthesize biodiesel (Al-Jaberi *et al.*, 2017; Cho *et al.*, 2012; Chongkhong *et al.*, 2007; Lokman *et al.*, 2016; Yujaroen *et al.*, 2009). PFAD, a promising non edible feedstock with very large amount of free fatty acid for biodiesel production, is a by product obtained from palm oil refinery having a production capacity of about 649,459 tonnes which is equivalent to 3.25 % PFAD produced per one tonne of crude palm oil being processed in Malaysia (Kapor *et al.*, 2017).

The actual function of the catalyst in biodiesel production reaction is to accelerate the rate of reaction and the methyl esters yield. Generally, catalysts utilized in biodiesel production are categorized into three namely acids, alkalis and enzymes (Nelson *et al.*, 1996; Shimada *et al.*, 1999). The alkali and acid catalysts are either homogeneous or heterogeneous by nature. Based on their chemical presence in reaction, homogeneous catalysts are in liquid phase while heterogeneous catalysts are in solid phase, in a dissimilar phase from the reaction mixture (Borges and Díaz,

2012; Phan *et al.*, 2006). Homogenous catalysts either alkali or acids present a few disadvantages such as require washing of biodiesel with large amount of water to separate the catalyst resulting in waste water generation and biodiesel loss as well as equipment corrosion. To address these issues, the use of heterogeneous catalyst for the synthesis of biodiesel has been recently pursued. Heterogeneous catalysts have the advantages of easy removal from product and reusability (Sharma *et al.*, 2011). Heterogeneous base catalysts have been successful providing high yield of biodiesel. Nevertheless, their performance is affected when feedstock with high free fatty acids (FFA) content is utilized like the non-edible oils and PFAD. Thus solid acid catalysts are preferred as they are insensitive to water and FFA content of feedstock as well as can simultaneously catalyse esterification and transesterification reactions (Sani *et al.*, 2014). In addition to their reusability and easy separation, heterogeneous acid catalysts have minimal corrosion effect of process equipment as found with some homogeneous acid catalysts like sulphuric acid.

In the past years, studies have been done on the utilization of heterogeneous acid catalysts for the production of biodiesel and few examples are sulphated zirconium oxide (SO_4^2-ZrO_2) (Park *et al.*, 2008), sulphated tin oxide (SO_4^2-/SnO_2) (Furuta *et al.*, 2004), heteropoly acids (Zhang *et al.*, 2009), and sulfonated carbonized catalyst (Deshmane *et al.*, 2013). Although, these heterogeneous catalysts have some few disadvantages such as high temperature of reaction, costly materials, long reaction time and leaching, this can be minimized depending on catalyst preparation. Lately, carbon based solid acid catalyst has gain research attention with reported advantages including high thermal stability, ability to be reused, uniform distribution of active sites, inexpensive and simple preparation (Konwar *et al.*, 2014). This catalyst comprises of small polycyclic aromatic sheets attached to $–SO_3H$ have shown greater potential to high FFA feedstocks (Nakajima and Hara, 2012). Therefore, based on the advantages of the carbon based catalyst, this study investigated the potential of sugar based catalyst prepared by modified sulfonation method using response surface methodology (RSM) approach. A commercial d-glucose was used as catalyst for the synthesis of biodiesel from palm fatty acid distillate feedstock.

1.2 Problem statements

Elevating issues hindering the wide spread usage and commercialization of biodiesel is connected to its higher cost of production compared to diesel fuel from petroleum which comes majorly from feedstock (vegetable oils) inadditon to other cost issues emanating from using expensive catalytic system (heterogeneous) and multiple-step processing technology. Hence the use of alternative approaches and technologies that make use of non-refined vegetable oil and waste oils are being considered and studied (Haas *et al.*, 2002; Marchetti, 2013; Phan and Phan, 2008). In a standpoint to reduce cost of biodiesel, palm fatty acid distillate (PFAD) a low cost feedstock has been utilized for biodiesel production and no longer contributes towards food vs fuel issue. Besides, it helps in improving environmental problems resulting from waste management issues in the palm oil industry.

Technical issues associated with the utilization of homogeneous catalysts to some extent would be reduced by the heterogeneous catalytic system. The key benefit of heterogeneous catalyst is that it does not dissolve or consume in the reaction, hence can be separated easily from the reaction products. However, heterogeneous catalysts also have disadvantages (drawbacks). Among others are the limitations of their catalytic active sites or centres and more severe reaction conditions are required to achieve similar reaction conversion as in homogeneous catalysed process. Also, the issue of slower rate of reaction of heterogeneous catalyzed process which could be connected to mass transfer resistance as a result of the presence of three phases of oil, alcohol and catalyst (Puna *et al.*, 2010). In addition, the poisoning of the catalyst active centres due to the exposure to the surrounding atmospheric medium could also influence the activity and stability of the catalysts.

Thus, these issues associated with heterogeneous catalysts entail detail investigation into physical and chemical properties of the solid catalysts. Furthermore, the high cost of materials used to synthesize the catalyst, and the long time synthesis and complicated procedure could also contribute to the total cost of production (Avhad and Marchetti, 2016). Therefore, to overcome these issues, the polycyclic aromatic carbon based acid catalyst which has proven to be stable and catalytically active is intoduced in this research. An example of carbon-based acid catalyst having the polycyclic aromatic carbon structure is the carbohydrate carbon-based heterogeneous acid catalyst (sugar catalyst) (Alves *et al.*, 2013) and is capable of converting high FFA feedstock.

Previously, reports have shown that the synthesis of carbonized glucose material by sulfonation with sulfuric takes a long time of 15 h to perform which implies being energy intensive. However, in this study, in a quest to reduce the long sulfonation time, a modified (new) sulfonation method to activate carbonized glucose material into acid catalyst with two sulfonating agents (ammonium sulphate and concentrated sulfuric acid) via RSM tool has been proposed. Four sulfonation variables were optimized with the design expert software and the procedure has been discussed in the thesis.

The alcoholysis of different natural oils to produce biodiesel is commonly carried out in stirred batch reactor. Batch modes are faced with limitations such as larger reactor volume required leading to higher capital investment and inconsistency in product quality due to difficulty in process control, mass and heat transfer problems amidst methanol and oil, and extreme conditions of operation, most especially long reaction time associated with the use heterogeneous catalyst (Fauzi and Amin, 2013). Changing to continuous process with the use of oscillatory flow technique induces the mixing between oil, methanol and catalyst and enables the process to be conducted continuously, which enhances yield, reduce residence time and improve the economics of the process. Also the short length to diameter of the reactor reduces capital cost and makes it to be scalable (Qiu *et al.*, 2010).

OFR is suitable for both batch and continuous modes of operation and recommended for biodiesel production (Ramning Amol *et al.*, 2013). It is also worth noting that the use of heterogeneous solid acid catalyst has yet to be explored in OFR. It is envisaged that the longer reaction time associated with solid acid catalyst will be improved with OFR and synthesized sulfonated catalyst.

1.3 Objectives of the study

The purpose of this research work is to synthesize sulfonated glucose catalyst by modifying the sulfonation method and assess its catalytic activity in biodiesel synthesis from PFAD. The specific objectives of this study are:

1. To synthesize sulfonated incomplete carbonized glucose catalyst for the esterification of PFAD.
2. To evaluate the effects of process conditions on esterification of PFAD in batch reflux reactor.
3. To perform kinetics study of esterification of PFAD catalysed by the synthesized catalyst in batch reflux reactor.
4. To assess the catalytic activity of synthesized sulfonated glucose catalyst in the esterification of PFAD in oscillatory flow reactor (OFR).

1.4 Scope of the study

The research work covers the preparation of sulfonated glucose carbon solid acid catalyst by modification of the sulfonation method. The sulfonated variables were optimized using the RSM-CCRD for the esterification of PFAD to fatty acid methyl ester. The sulfonation variables considered are time, ammonium sulphate, temperature and sulfuric acid whereas the response factor used to monitor each synthesis runs was percentage free fatty acid (FFA) conversion. All range for sulfonation parameters were chosen after some prelimnary work. The optimum sulfonated catalyst obtained from the RSM after validation was subjected to detailed characterization to establish its properties in order to understand its behaviour during esterification reaction to produce biodiesel.

Meanwhile, the PFAD feedstock used for the study was also characterized. In addition, the optimized sulfonated catalyst was first used for esterification to optimize the process operating conditions in the batch reactor. The process parameters namely reaction temperature, molar ratio of methanol to PFAD, reaction time and catalyst loading were optimized. Kinetics of esterification process under optimized operating conditions using the sulfonated glucose catalyst in the batch reactor was carried out to determine the order and rate of reaction. The effect of temperature from Arrhenius equation was also investigated. Thereafter, the solid acid catalyst was introduced into the OFR system and the process parameters were optimized. This was done in order to understand how the heterogeneous catalyst works in the OFR and to assess the benefits that the system offers in biodiesel

production. The esterification reaction was performed under atmospheric condition. Lastly, the fuel quality tests of the PFAD methyl ester synthesized from OFR were carried out including; kinematic viscosity, acid number, density, pour point, cloud point, flash point, water content, carbon residue, cetane number, calorific value, distillation temperature, sulphated ash, phosphorus and oxidation stability.

1.5 Thesis outline

This thesis is divided into five chapters. Chapter 1 is the introductory chapter which provides the background of the problem statement focusing on the significance of the biodiesel production and also highlights the objectives of the study. Chapter 2 presents the literature review of the various subjects pertinent to the research work. It covers a wide process overview, synthesis and analysis as accounted by previous authors. Biodiesel feedstocks, production methods, catalysts, processing technology for biodiesel production are discussed. Literatures on solid acid catalysts, parameters affecting biodiesel process, biodiesel properties and chemical kinetics of esterification reaction were also reviewed. Chapter 3 covers the materials and methods for synthesis and characterization of the solid acid catalyst, reaction process, product analysis, and kinetics study and fuel properties. Chapter 4 presents the experimental results and detailed discussions and analysis of the results. Finally, chapter 5 stands for conclusion of the research and recommendation for future research work.

REFERENCES

Adeyemi, N. A., Mohiuddin, A., and Jameel, T. (2011). Waste cooking oil transesterification: influence of impeller type, temperature, speed and bottom clearance on FAME yield. *African Journal of Biotechnology, 10* (44), 8914-8929.

Agarwal, A. K. (2007). Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in energy and combustion science, 33* (3), 233-271.

Agarwal, A. K., and Rajamanoharan, K. (2009). Experimental investigations of performance and emissions of Karanja oil and its blends in a single cylinder agricultural diesel engine. *Applied Energy, 86* (1), 106-112.

Agarwal, D., Kumar, L., and Agarwal, A. K. (2008). Performance evaluation of a vegetable oil fuelled compression ignition engine. *Renewable energy, 33* (6), 1147-1156.

Ahmad, M., Rashid, S., Khan, M. A., Zafar, M., Sultana, S., and Gulzar, S. (2009). Optimization of base catalyzed transesterification of peanut oil biodiesel. *African Journal of Biotechnology, 8* (3), 441-446.

Aksoy, H., Kahraman, I., Karaosmanoglu, F., and Civelekoglu, H. (1988). Evaluation of Turkish sulphur olive oil as an alternative diesel fuel. *Journal of the American Oil Chemists' Society, 65* (6), 936-938.

Al-Jaberi, S. H., Rashid, U., Al-Doghachi, F. A., Abdulkareem-Alsultan, G., and Taufiq-Yap, Y. (2017). Synthesis of MnO-NiO-SO4− 2/ZrO2 solid acid catalyst for methyl ester production from palm fatty acid distillate. *Energy conversion and management, 139*, 166-174.

Alhassan, F. H., Rashid, U., Yunus, R., Sirat, K., Lokman, I. M., and Taufiq-Yap, Y. H. (2015). Synthesis of ferric–manganese doped tungstated zirconia nanoparticles as heterogeneous solid superacid catalyst for biodiesel production from waste cooking oil. *International journal of green energy, 12* (9), 987-994.

Alhassan, F. H., Yunus, R., Rashid, U., Sirat, K., Islam, A., Lee, H., and Taufiq-Yap, Y. H. (2013). Production of biodiesel from mixed waste vegetable oils using Ferric hydrogen sulphate as an effective reusable heterogeneous solid acid catalyst. *Applied Catalysis A: General, 456*, 182-187.

Altun, Ş., Bulut, H., and Öner, C. (2008). The comparison of engine performance and exhaust emission characteristics of sesame oil–diesel fuel mixture with diesel fuel in a direct injection diesel engine. *Renewable energy, 33* (8), 1791-1795.

Alves, C., Oliveira, A., Carneiro, S., Silva, A., Andrade, H. M. C., de Melo, S. V., and Torres, E. A. (2013). Transesterification of waste frying oil using a zinc aluminate catalyst. *Fuel Processing Technology, 106*, 102-107.

Atabani, A., Silitonga, A., Ong, H., Mahlia, T., Masjuki, H., Badruddin, I. A., and Fayaz, H. (2013). Non-edible vegetable oils: a critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production. *Renewable and Sustainable Energy Reviews, 18*, 211-245.

Atadashi, I., Aroua, M., and Aziz, A. A. (2010). High quality biodiesel and its diesel engine application: a review. *Renewable and Sustainable Energy Reviews, 14* (7), 1999-2008.

Avhad, M., and Marchetti, J. (2016). Innovation in solid heterogeneous catalysis for the generation of economically viable and ecofriendly biodiesel: A review. *Catalysis Reviews, 58* (2), 157-208.

Balat, M., and Balat, H. (2010). Progress in biodiesel processing. *Applied Energy, 87* (6), 1815-1835.

Bambase, M. E., Nakamura, N., Tanaka, J., and Matsumura, M. (2007). Kinetics of hydroxide-catalyzed methanolysis of crude sunflower oil for the production of fuel-grade methyl esters. *Journal of Chemical Technology and Biotechnology, 82* (3), 273-280.

Banerjee, A., and Chakraborty, R. (2009). Parametric sensitivity in transesterification of waste cooking oil for biodiesel production—a review. *Resources, Conservation and Recycling, 53* (9), 490-497.

Berrios, M., Siles, J., Martin, M., and Martin, A. (2007). A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil. *Fuel, 86* (15), 2383-2388.

Boey, P.-L., Ganesan, S., Maniam, G. P., Khairuddean, M., and Efendi, J. (2013). A new heterogeneous acid catalyst for esterification: optimization using response surface methodology. *Energy conversion and management, 65*, 392-396.

Bokhari, A., Chuah, L. F., Yusup, S., Ahmad, J., Shamsuddin, M. R., and Teng, M. K. (2015). Microwave-assisted methyl esters synthesis of Kapok (Ceiba pentandra) seed oil: parametric and optimization study. *Biofuel Research Journal, 2* (3), 281-287.

Borges, M., and Díaz, L. (2012). Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: a review. *Renewable and Sustainable Energy Reviews, 16* (5), 2839-2849.

Brunold, C., Hunns, J., Mackley, M., and Thompson, J. (1989). Experimental observations on flow patterns and energy losses for oscillatory flow in ducts containing sharp edges. *Chemical Engineering Science, 44* (5), 1227-1244.

Brunschwig, C., Moussavou, W., and Blin, J. (2012). Use of bioethanol for biodiesel production. *Progress in energy and combustion science, 38* (2), 283-301.

Bruwer, J. J., Boshoff, B. V. D., Hugo, F. J. C., and Englebrecht, A. (1980). The utilization of sunflower seed oil as a renewable fuel for diesel engines, Proceedings of the ASAE National Energy Symposium, ASAE Publication, St Joseph.

Canakci, M., and Gerpen, J. V. (2003). "A pilot plant to produce biodiesel from high free fatty acid feedstocks," Transactions of the American Society of Agricultural Engineers, vol. 46, no. 4, pp. 945–954. .

Canakci, M., and Van Gerpen, J. (2001). Biodiesel production from oils and fats with high free fatty acids. *Transactions of the ASAE, 44* (6), 1429.

Chang, A. S., Sherazi, S. T. H., Kandhro, A. A., Mahesar, S. A., Chang, F., Shah, S. N., Laghari, Z. H., and Panhwar, T. (2016). Characterization of Palm Fatty Acid Distillate of Different Oil Processing Industries of Pakistan. *Journal of oleo science, 65* (11), 897-901.

Charoenchaitrakool, M., and Thienmethangkoon, J. (2011). Statistical optimization for biodiesel production from waste frying oil through two-step catalyzed process. *Fuel Processing Technology, 92* (1), 112-118.

Cheah, K., Toh, T., and Koh, P. (2010). Palm fatty acid distillate biodiesel. *International news on fats, oils, and related materials, 21* (5), 264-266.

Chen, J., Chen, J., Zhang, X., Gao, J., and Yang, Q. (2016). Efficient and stable PS-SO3H/SiO2 hollow nanospheres with tunable surface properties for acid catalyzed reactions. *Applied Catalysis A: General, 516*, 1-8.

Cheng, Y., Feng, Y., Ren, Y., Liu, X., Gao, A., He, B., Yan, F., and Li, J. (2012). Comprehensive kinetic studies of acidic oil continuous esterification by cation-exchange resin in fixed bed reactors. *Bioresource technology, 113*, 65-72.

Chin, L., Abdullah, A., and Hameed, B. (2012). Sugar cane bagasse as solid catalyst for synthesis of methyl esters from palm fatty acid distillate. *Chemical engineering journal, 183*, 104-107.

Chin, L., Hameed, B., and Ahmad, A. (2009). Process optimization for biodiesel production from waste cooking palm oil (Elaeis guineensis) using response surface methodology. *Energy & Fuels, 23* (2), 1040-1044.

Cho, H. J., Kim, J.-K., Hong, S. W., and Yeo, Y.-K. (2012). Development of a novel process for biodiesel production from palm fatty acid distillate (PFAD). *Fuel Processing Technology, 104*, 271-280.

Chongkhong, S., Tongurai, C., and Chetpattananondh, P. (2009). Continuous esterification for biodiesel production from palm fatty acid distillate using economical process. *Renewable energy, 34* (4), 1059-1063.

Chongkhong, S., Tongurai, C., Chetpattananondh, P., and Bunyakan, C. (2007). Biodiesel production by esterification of palm fatty acid distillate. *Biomass and bioenergy, 31* (8), 563-568.

Choudhury, H. A., Malani, R. S., and Moholkar, V. S. (2013). Acid catalyzed biodiesel synthesis from Jatropha oil: mechanistic aspects of ultrasonic intensification. *Chemical engineering journal, 231*, 262-272.

Coker, A. K. (2001). *Modelling of chemical kinetics and reactor design, Gulf Publishing Company, Houston.*

Darnoko, D., and Cheryan, M. (2000). Kinetics of palm oil transesterification in a batch reactor. *Journal of the American Oil Chemists' Society, 77* (12), 1263-1267.

Dawodu, F. A., Ayodele, O., Xin, J., Zhang, S., and Yan, D. (2014). Effective conversion of non-edible oil with high free fatty acid into biodiesel by sulphonated carbon catalyst. *Applied Energy, 114*, 819-826.

Dehkhoda, A. M., West, A. H., and Ellis, N. (2010). Biochar based solid acid catalyst for biodiesel production. *Applied Catalysis A: General, 382* (2), 197-204.

Dehkordi, A. M., and Ghasemi, M. (2012). Transesterification of waste cooking oil to biodiesel using Ca and Zr mixed oxides as heterogeneous base catalysts. *Fuel Processing Technology, 97*, 45-51.

Demirbas, A. (2007). Importance of biodiesel as transportation fuel. *Energy policy, 35* (9), 4661-4670.

Demirbas, A. (2009). Progress and recent trends in biodiesel fuels. *Energy conversion and management, 50* (1), 14-34.

Demirbaş, A. (2003). Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. *Energy conversion and management, 44* (13), 2093-2109.

Deshmane, C. A., Wright, M. W., Lachgar, A., Rohlfing, M., Liu, Z., Le, J., and Hanson, B. E. (2013). A comparative study of solid carbon acid catalysts for the esterification of free fatty acids for biodiesel production. Evidence for the leaching of colloidal carbon. *Bioresource technology, 147*, 597-604.

Deshmane, V. G., Gogate, P. R., and Pandit, A. B. (2008). Ultrasound-assisted synthesis of biodiesel from palm fatty acid distillate. *Industrial & Engineering Chemistry Research, 48* (17), 7923-7927.

Di Serio, M., Tesser, R., Pengmei, L., and Santacesaria, E. (2007). Heterogeneous catalysts for biodiesel production. *Energy & Fuels, 22* (1), 207-217.

Dias, J. M., Alvim-Ferraz, M. C., and Almeida, M. F. (2008). Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality. *Fuel, 87* (17-18), 3572-3578.

do Nascimento, L. A. S., Angélica, R. S., Da Costa, C. E., Zamian, J. R., and da Rocha Filho, G. N. (2011). Conversion of waste produced by the deodorization of palm oil as feedstock for the production of biodiesel using a catalyst prepared from waste material. *Bioresource technology, 102* (17), 8314-8317.

Dossin, T. F., Reyniers, M.-F., and Marin, G. B. (2006). Kinetics of heterogeneously MgO-catalyzed transesterification. *Applied Catalysis B: Environmental, 62* (1-2), 35-45.

Dunn, R., Shockley, M., and Bagby, M. (1996). Improving the low-temperature properties of alternative diesel fuels: vegetable oil-derived methyl esters. *Journal of the American Oil Chemists' Society, 73* (12), 1719-1728.

Dunn, R. O., and Knothe, G. (2003). Oxidative stability of biodiesel in blends with jet fuel by analysis of oil stability index. *Journal of the American Oil Chemists' Society, 80* (10), 1047-1048.

Embong, N. H., Maniam, G. P., Rahim, M. H. A., Lee, K. T., and Huisingh, D. (2016). Utilization of palm fatty acid distillate in methyl esters preparation using SO42−/TiO2–SiO2 as a solid acid catalyst. *Journal of cleaner production, 116*, 244-248.

Encinar, J., González, J., and Rodríguez-Reinares, A. (2007). Ethanolysis of used frying oil. Biodiesel preparation and characterization. *Fuel Processing Technology, 88* (5), 513-522.

Enweremadu, C., and Mbarawa, M. (2009). Technical aspects of production and analysis of biodiesel from used cooking oil—a review. *Renewable and Sustainable Energy Reviews, 13* (9), 2205-2224.

Eze, V. C., Phan, A. N., Pirez, C., Harvey, A. P., Lee, A. F., and Wilson, K. (2013). Heterogeneous catalysis in an oscillatory baffled flow reactor. *Catalysis Science & Technology, 3* (9), 2373-2379.

Fauzi, A. H. M., and Amin, N. A. S. (2013). Catalysis in biodiesel synthesis: challenges and future perspectives *Advances in Biofuels* (pp. 127-152): Springer.

Felizardo, P., Correia, M. J. N., Raposo, I., Mendes, J. F., Berkemeier, R., and Bordado, J. M. (2006). Production of biodiesel from waste frying oils. *Waste management, 26* (5), 487-494.

Fermoso, J., Gil, M. V., Arias, B., Plaza, M. G., Pevida, C., Pis, J., and Rubiera, F. (2010). Application of response surface methodology to assess the combined effect of operating variables on high-pressure coal gasification for H2-rich gas production. *international journal of hydrogen energy, 35* (3), 1191-1204.

Fernández-Ramos, A., Miller, J. A., Klippenstein, S. J., and Truhlar, D. G. (2006). Modeling the kinetics of bimolecular reactions. *Chemical reviews, 106* (11), 4518-4584.

Ferrero, G. O., Rojas, H. J., Argaraña, C. E., and Eimer, G. A. (2016). Towards sustainable biofuel production: Design of a new biocatalyst to biodiesel synthesis from waste oil and commercial ethanol. *Journal of cleaner production, 139*, 495-503.

Forson, F., Oduro, E., and Hammond-Donkoh, E. (2004). Performance of jatropha oil blends in a diesel engine. *Renewable energy, 29* (7), 1135-1145.

Freedman, B., Pryde, E., and Mounts, T. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists Society, 61* (10), 1638-1643.

Furuta, S., Matsuhashi, H., and Arata, K. (2004). Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure. *Catalysis communications, 5* (12), 721-723.

Gaikwad, N. D., and Gogate, P. R. (2015). Synthesis and application of carbon based heterogeneous catalysts for ultrasound assisted biodiesel production. *Green Processing and Synthesis, 4* (1), 17-30.

Ganapathy, T., Murugesan, K. a., and Gakkhar, R. (2009). Performance optimization of Jatropha biodiesel engine model using Taguchi approach. *Applied Energy, 86* (11), 2476-2486.

Gao, C., Zhai, Y., Ding, Y., and Wu, Q. (2010). Application of sweet sorghum for biodiesel production by heterotrophic microalga Chlorella protothecoides. *Applied Energy, 87* (3), 756-761.

Glisic, S., and Skala, D. (2009). The problems in design and detailed analyses of energy consumption for biodiesel synthesis at supercritical conditions. *The journal of supercritical fluids, 49* (2), 293-301.

Goering, C., Schwab, A., Daugherty, M., Pryde, E., and Heakin, A. (1982). Fuel properties of eleven vegetable oils. *Transactions of the ASAE, 25* (6), 1472-1477.

Gui, M. M., Lee, K., and Bhatia, S. (2008). Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. *Energy, 33* (11), 1646-1653.

Gunawan, E. R., Basri, M., Rahman, M. B. A., Salleh, A. B., and Rahman, R. N. Z. A. (2005). Study on response surface methodology (RSM) of lipase-catalyzed synthesis of palm-based wax ester. *Enzyme and Microbial Technology, 37* (7), 739-744.

Guo, F., Xiu, Z.-L., and Liang, Z.-X. (2012). Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. *Applied Energy, 98*, 47-52.

Haas, M. J., Bloomer, S., and Scott, K. (2002). Process for the production of fatty acid alkyl esters: Google Patents.

Haas, M. J., Michalski, P. J., Runyon, S., Nunez, A., and Scott, K. M. (2003). Production of FAME from acid oil, a by-product of vegetable oil refining. *Journal of the American Oil Chemists' Society, 80* (1), 97-102.

Habib, N. S. H. A., Yunus, R., Rashid, U., Taufiq-Yap, Y. H., Abidin, Z. Z., Syam, A. M., and Irawan, S. (2014). Transesterification Reaction for Synthesis of Palm–based Ethylhexyl Ester and Formulation as Base Oil for Synthetic Drilling Fluid. *Journal of oleo science, 63* (5), 497-506.

Hara, M., Yoshida, T., Takagaki, A., Takata, T., Kondo, J. N., Hayashi, S., and Domen, K. (2004). A carbon material as a strong protonic acid. *Angewandte Chemie International Edition, 43* (22), 2955-2958.

Harvey, A., Mackley, M., and Stonestreet, P. (2001). Operation and optimization of an oscillatory flow continuous reactor. *Industrial & Engineering Chemistry Research, 40* (23), 5371-5377.

Harvey, A. P., Mackley, M. R., and Seliger, T. (2003). Process intensification of biodiesel production using a continuous oscillatory flow reactor. *Journal of Chemical Technology and Biotechnology, 78* (2-3), 338-341.

Hayyan, A., Alam, M. Z., Mirghani, M. E., Kabbashi, N. A., Hakimi, N. I. N. M., Siran, Y. M., and Tahiruddin, S. (2010). Sludge palm oil as a renewable raw material for biodiesel production by two-step processes. *Bioresource technology, 101* (20), 7804-7811.

Hewgill, M., Mackley, M., Pandit, A., and Pannu, S. (1993). Enhancement of gas-liquid mass transfer using oscillatory flow in a baffled tube. *Chemical Engineering Science, 48* (4), 799-809.

Hidayat, A., Wijaya, K., and Budiman, A. (2015a). Esterification of free fatty acid on palm fatty acid distillate using activated carbon catalysts generated from coconut shell. *Procedia Chemistry, 16*, 365-371.

Hidayat, A., Wijaya, K., Nurdiawati, A., Kurniawan, W., Hinode, H., Yoshikawa, K., and Budiman, A. (2015b). Esterification of palm fatty acid distillate with high amount of free fatty acids using coconut shell char based catalyst. *Energy Procedia, 75*, 969-974.

Highina, B., Bugaje, I., and Ngala, G. (2014). Perfomance evaluation of continuous oscillatory baffled reactor arrangementon production of biodiesel from jatropha oil using heterogenous catalyst. *World Journal of Renewable Energy and Engineering, 1* (1), 1-7.

Highina, B., Bugaje, I., and Umar, B. (2011). Biodiesel production from Jatropha caucus oil in a batch reactor using zinc oxide as catalyst. *Journal of Petroleum Technology and Alternative Fuels, 2* (9), 146-149.

Howes, T., Mackley, M., and Roberts, E. (1991). The simulation of chaotic mixing and dispersion for periodic flows in baffled channels. *Chemical Engineering Science, 46* (7), 1669-1677.

Hoydonckx, H., De Vos, D., Chavan, S., and Jacobs, P. (2004). Esterification and transesterification of renewable chemicals', Topics in Catalysis, 27, (1-4), pp. 83-96.

Huang, D., Zhou, H., and Lin, L. (2012). Biodiesel: an alternative to conventional fuel. *Energy Procedia, 16*, 1874-1885.

Huang, G., Chen, F., Wei, D., Zhang, X., and Chen, G. (2010). Biodiesel production by microalgal biotechnology. *Applied Energy, 87* (1), 38-46.

Hulett, J. (1964). Deviations from the Arrhenius equation. *Quarterly Reviews, Chemical Society, 18* (3), 227-242.

Ibrahim, I. M. (2016). Syhthesis of carbohydrate-derived solid acid catalysts for biodiesel production from palm fatty acid distillate. Unpublished PhD dissertation, University Putra Malaysia, Malaysia.

Issariyakul, T., and Dalai, A. K. (2014). Biodiesel from vegetable oils. *Renewable and Sustainable Energy Reviews, 31*, 446-471.

Issariyakul, T., Kulkarni, M. G., Dalai, A. K., and Bakhshi, N. N. (2007). Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. *Fuel Processing Technology, 88* (5), 429-436.

Jain, S., and Sharma, M. (2011). Oxidation stability of blends of Jatropha biodiesel with diesel. *Fuel, 90* (10), 3014-3020.

Jayed, M., Masjuki, H., Kalam, M., Mahlia, T., Husnawan, M., and Liaquat, A. (2011). Prospects of dedicated biodiesel engine vehicles in Malaysia and Indonesia. *Renewable and Sustainable Energy Reviews, 15* (1), 220-235.

Jiang, S., Zhang, F., and Pan, L. (2010). Sodium phosphate as a solid catalyst for biodiesel preparation. *Brazilian Journal of Chemical Engineering, 27* (1), 137-144.

Jothiramalingam, R., and Wang, M. K. (2009). Review of recent developments in solid acid, base, and enzyme catalysts (heterogeneous) for biodiesel production via transesterification. *Industrial & Engineering Chemistry Research, 48* (13), 6162-6172.

Kapilakarn, K., and Peugtong, A. (2007). A comparison of costs of biodiesel production from transesterication. *International Energy Journal, 8* (1)

Kapor, N. Z. A., Maniam, G. P., Rahim, M. H. A., and Yusoff, M. M. (2017). Palm fatty acid distillate as a potential source for biodiesel production-a review. *Journal of cleaner production, 143*, 1-9.

Kastner, J. R., Miller, J., Geller, D. P., Locklin, J., Keith, L. H., and Johnson, T. (2012). Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon. *Catalysis Today, 190* (1), 122-132.

Kazemian, H., Turowec, B., Siddiquee, M. N., and Rohani, S. (2013). Biodiesel production using cesium modified mesoporous ordered silica as heterogeneous base catalyst. *Fuel, 103*, 719-724.

Keera, S., El Sabagh, S., and Taman, A. (2011). Transesterification of vegetable oil to biodiesel fuel using alkaline catalyst. *Fuel, 90* (1), 42-47.

Kefas, H. M., Yunus, R., Rashid, U., and Taufiq-Yap, Y. H. (2018). Modified sulfonation method for converting carbonized glucose into solid acid catalyst for the esterification of palm fatty acid distillate. *Fuel, 229*, 68-78.

Kelkar, M. A., Gogate, P. R., and Pandit, A. B. (2008). Intensification of esterification of acids for synthesis of biodiesel using acoustic and hydrodynamic cavitation. *Ultrasonics Sonochemistry, 15* (3), 188-194.

Kim, D., Choi, J., Kim, G.-J., Seol, S. K., Ha, Y.-C., Vijayan, M., Jung, S., Kim, B. H., Lee, G. D., and Park, S. S. (2011). Microwave-accelerated energy-efficient esterification of free fatty acid with a heterogeneous catalyst. *Bioresource technology, 102* (3), 3639-3641.

Kim, H.-J., Kang, B.-S., Kim, M.-J., Park, Y. M., Kim, D.-K., Lee, J.-S., and Lee, K.-Y. (2004). Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis Today, 93*, 315-320.

Knothe, G. (2001). Historical perspectives on vegetable oil-based diesel fuels. Inform, 11, 1103–7.

Knothe, G. (2009). Improving biodiesel fuel properties by modifying fatty ester composition. *Energy & Environmental Science, 2* (7), 759-766.

Knothe, G., and Dunn, R. O. (2001). Biofuels derived from vegetable oils and fats. *Oleochemical manufacture and applications*, 106-163.

Knothe, G., Gerpen J V, and krahl, J. (2005). *The Biodiesel Handbook. In G. Knothe. History of vegetable oil-based diesel fuels (pp 2-10) Urbana: AOCS press publishers.*

Komers, K., Stloukal, R., Machek, J., and Skopal, F. (2001). Biodiesel from rapeseed oil, methanol and KOH. 3. Analysis of composition of actual reaction mixture. *European Journal of Lipid Science and Technology, 103* (6), 363-371.

Konwar, L. J., Boro, J., and Deka, D. (2014). Review on latest developments in biodiesel production using carbon-based catalysts. *Renewable and Sustainable Energy Reviews, 29*, 546-564.

Kumari, A., Mahapatra, P., Garlapati, V. K., and Banerjee, R. (2009). Enzymatic transesterification of Jatropha oil. *Biotechnology for Biofuels, 2* (1), 1.

Kusdiana, D., and Saka, S. (2001). Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. *Fuel, 80* (5), 693-698.

Lacoste, F., and Lagardere, L. (2003). Quality parameters evolution during biodiesel oxidation using Rancimat test. *European Journal of Lipid Science and Technology, 105* (3-4), 149-155.

Lal, K. (1994). U.S. Patent 5,338,471.

Lam, M. K., Lee, K. T., and Mohamed, A. R. (2010). Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. *Biotechnology advances, 28* (4), 500-518.

Lang, X., Dalai, A. K., Bakhshi, N. N., Reaney, M. J., and Hertz, P. (2001). Preparation and characterization of bio-diesels from various bio-oils. *Bioresource technology, 80* (1), 53-62.

Lavenspiel, O. (1999). *Chemical reaction engineering, John Wiley and Sons Inc., United States.*

Lee, H., Yunus, R., Juan, J. C., and Taufiq-Yap, Y. H. (2011). Process optimization design for jatropha-based biodiesel production using response surface methodology. *Fuel Processing Technology, 92* (12), 2420-2428.

Lee, K. T., and Ofori-Boateng, C. (2013). *Sustainability of biofuel production from oil palm biomass*: Springer.

Leung, D., and Guo, Y. (2006). Transesterification of neat and used frying oil: optimization for biodiesel production. *Fuel Processing Technology, 87* (10), 883-890.

Leung, D. Y., Wu, X., and Leung, M. (2010). A review on biodiesel production using catalyzed transesterification. *Applied Energy, 87* (4), 1083-1095.

Li, Q., Zheng, J., and Yan, Y. (2010). Biodiesel preparation catalyzed by compound-lipase in co-solvent. *Fuel Processing Technology, 91* (10), 1229-1234.

Li, S., Wang, Y., Dong, S., Chen, Y., Cao, F., Chai, F., and Wang, X. (2009). Biodiesel production from Eruca Sativa Gars vegetable oil and motor, emissions properties. *Renewable energy, 34* (7), 1871-1876.

Lim, S., and Teong, L. K. (2010). Recent trends, opportunities and challenges of biodiesel in Malaysia: an overview. *Renewable and Sustainable Energy Reviews, 14* (3), 938-954.

Lin, L., Cunshan, Z., Vittayapadung, S., Xiangqian, S., and Mingdong, D. (2011). Opportunities and challenges for biodiesel fuel. *Applied Energy, 88* (4), 1020-1031.

Lin, L., Ying, D., Chaitep, S., and Vittayapadung, S. (2009). Biodiesel production from crude rice bran oil and properties as fuel. *Applied Energy, 86* (5), 681-688.

Liu, F., Meng, X., Zhang, Y., Ren, L., Nawaz, F., and Xiao, F.-S. (2010a). Efficient and stable solid acid catalysts synthesized from sulfonation of swelling mesoporous polydivinylbenzenes. *Journal of Catalysis, 271* (1), 52-58.

Liu, K.-S. (1994). Preparation of fatty acid methyl esters for gas-chromatographic analysis of lipids in biological materials. *Journal of the American Oil Chemists' Society, 71* (11), 1179-1187.

Liu, X.-Y., Huang, M., Ma, H.-L., Zhang, Z.-Q., Gao, J.-M., Zhu, Y.-L., Han, X.-J., and Guo, X.-Y. (2010b). Preparation of a carbon-based solid acid catalyst by sulfonating activated carbon in a chemical reduction process. *Molecules, 15* (10), 7188-7196.

Liu, Y., Lotero, E., and Goodwin Jr, J. G. (2006a). A comparison of the esterification of acetic acid with methanol using heterogeneous versus homogeneous acid catalysis. *Journal of Catalysis, 242* (2), 278-286.

Liu, Y., Lotero, E., and Goodwin Jr, J. G. (2006b). Effect of carbon chain length on esterification of carboxylic acids with methanol using acid catalysis. *Journal of Catalysis, 243* (2), 221-228.

Lokman, I. M., Goto, M., Rashid, U., and Taufiq-Yap, Y. H. (2016). Sub-and supercritical esterification of palm fatty acid distillate with carbohydrate-derived solid acid catalyst. *Chemical engineering journal, 284*, 872-878.

Lokman, I. M., Rashid, U., and Taufiq-Yap, Y. H. (2015a). Production of biodiesel from palm fatty acid distillate using sulfonated-glucose solid acid catalyst: Characterization and optimization. *Chinese Journal of Chemical Engineering, 23* (11), 1857-1864.

Lokman, I. M., Rashid, U., Taufiq-Yap, Y. H., and Yunus, R. (2015b). Methyl ester production from palm fatty acid distillate using sulfonated glucose-derived acid catalyst. *Renewable energy, 81*, 347-354.

Lotero, E., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D. A., and Goodwin, J. G. (2005). Synthesis of biodiesel via acid catalysis. *Industrial & Engineering Chemistry Research, 44* (14), 5353-5363.

Lou, W.-Y., Zong, M.-H., and Duan, Z.-Q. (2008). Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts. *Bioresource technology, 99* (18), 8752-8758.

Ma, F., and Hanna, M. A. (1999). Biodiesel production: a review. *Bioresource technology, 70* (1), 1-15.

Macedo, C., Abreu, F. R., Tavares, A. P., Alves, M. B., Zara, L. F., Rubim, J. C., and Suarez, P. A. (2006). New heterogeneous metal-oxides based catalyst for vegetable oil trans-esterification. *Journal of the Brazilian Chemical Society, 17* (7), 1291-1296.

Mackay, M., Mackley, M., and Wang, Y. (1991). Oscillatory flow within tubes containing wall or central baffles. *Chemical engineering research and design, 69* (6), 506-513.

Mackley, M., and Ni, X. (1991). Mixing and dispersion in a baffled tube for steady laminar and pulsatile flow. *Chemical Engineering Science, 46* (12), 3139-3151.

Mackley, M., Smith, K., and Wise, N. (1993). The mixing and separation of particle suspensions using oscillatory flow in baffled tubes. *Trans. IChemE, 71* (Part A), 649-656.

Mackley, M., Tweddle, G., and Wyatt, I. (1990). Experimental heat transfer measurements for pulsatile flow in baffled tubes. *Chemical Engineering Science, 45* (5), 1237-1242.

Mar, W. W., and Somsook, E. (2012). Sulfonic-functionalized carbon catalyst for esterification of high free fatty acid. *Procedia Engineering, 32*, 212-218.

Marchetti, J., and Errazu, A. (2008). Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides. *Biomass and bioenergy, 32* (9), 892-895.

Marchetti, J., Miguel, V., and Errazu, A. (2007). Possible methods for biodiesel production. *Renewable and Sustainable Energy Reviews, 11* (6), 1300-1311.

Marchetti, J. M. (2012). A summary of the available technologies for biodiesel production based on a comparison of different feedstock's properties. *Process Safety and Environmental Protection, 90* (3), 157-163.

Marchetti, J. M. (2013). Influence of economical variables on a supercritical biodiesel production process. *Energy conversion and management, 75*, 658-663.

Math, M., Kumar, S. P., and Chetty, S. V. (2010). Technologies for biodiesel production from used cooking oil—A review. *Energy for sustainable Development, 14* (4), 339-345.

Mathiyazhagan, M., Ganapathi, A., Jaganath, B., Renganayaki, N., and Sasireka, N. (2011). Production of biodiesel from non-edible plant oils having high FFA content. *International Journal of Chemical and Environmental Engineering, 2* (2)

Mazubert, A., Poux, M., and Aubin, J. (2013). Intensified processes for FAME production from waste cooking oil: a technological review. *Chemical engineering journal, 233*, 201-223.

Mbaraka, I. K., and Shanks, B. H. (2005). Design of multifunctionalized mesoporous silicas for esterification of fatty acid. *Journal of Catalysis, 229* (2), 365-373.

Mengyu, G., Deng, P., Li, M., En, Y., and Jianbing, H. (2009). The kinetics of the esterification of free fatty acids in waste cooking oil using Fe2 (SO4) 3/C catalyst. *Chinese Journal of Chemical Engineering, 17* (1), 83-87.

Menzinger, M., and Wolfgang, R. (1969). The meaning and use of the Arrhenius activation energy. *Angewandte Chemie International Edition, 8* (6), 438-444.

Metre, A. V., and Nath, K. (2015). Super phosphoric acid catalyzed esterification of Palm Fatty Acid Distillate for biodiesel production: physicochemical parameters and kinetics. *Polish Journal of Chemical Technology, 17* (1), 88.

Mielke, T. (2010). *The Price Outlook of Palm and Lauric Oils and Impacts from the Global Vegetable Oil Markets: A Fundamental Approach. Palm and Lauric Oils Conference & Exhibition Price Outlook (POC), Kuala Lumpur, Malaysia.*

Mittelbach, M. (1996). Diesel fuel derived from vegetable oils, VI: Specifications and quality control of biodiesel. *Bioresource technology, 56* (1), 7-11.

Mittelbach, M., and Gangl, S. (2001). Long storage stability of biodiesel made from rapeseed and used frying oil. *Journal of the American Oil Chemists' Society, 78* (6), 573-577.

Mo, X., López, D. E., Suwannakarn, K., Liu, Y., Lotero, E., Goodwin Jr, J. G., and Lu, C. (2008). Activation and deactivation characteristics of sulfonated carbon catalysts. *Journal of Catalysis, 254* (2), 332-338.

Mofijur, M., Masjuki, H., Kalam, M., Atabani, A., Shahabuddin, M., Palash, S., and Hazrat, M. (2013). Effect of biodiesel from various feedstocks on combustion characteristics, engine durability and materials compatibility: A review. *Renewable and Sustainable Energy Reviews, 28*, 441-455.

Moser, B. R. (2009). Biodiesel production, properties, and feedstocks. *In Vitro Cellular & Developmental Biology-Plant, 45* (3), 229-266.

Nadkarni, R. A. (2007). Guide to ASTM test methods for the analysis of petroleum products and lubricants/R.A. Kishore Nadkarni-2nd ed. p.cm.(ASTM manual series; no mnl 44-2nd)West Conshohocken, PA. Retrieved from www.astm.org.

Naik, M., Meher, L., Naik, S., and Das, L. (2008). Production of biodiesel from high free fatty acid Karanja (Pongamia pinnata) oil. *Biomass and bioenergy, 32* (4), 354-357.

Nakajima, K., and Hara, M. (2012). Amorphous carbon with SO3H groups as a solid Brønsted acid catalyst. *ACS catalysis, 2* (7), 1296-1304.

Nakajima, K., Hara, M., and Hayashi, S. (2007). Environmentally benign production of chemicals and energy using a carbon-based strong solid acid. *Journal of the American Ceramic Society, 90* (12), 3725-3734.

Nakpong, P., and Wootthikanokkhan, S. (2010). High free fatty acid coconut oil as a potential feedstock for biodiesel production in Thailand. *Renewable energy, 35* (8), 1682-1687.

Nas, B., and Berktay, A. (2007). Energy potential of biodiesel generated from waste cooking oil: an environmental approach. *Energy Sources, Part B: Economics, Planning, and Policy, 2* (1), 63-71.

Nelson, L. A., Foglia, T. A., and Marmer, W. N. (1996). Lipase-catalyzed production of biodiesel. *Journal of the American Oil Chemists' Society, 73* (9), 1191-1195.

Ng, J.-H., Ng, H. K., and Gan, S. (2010). Advances in biodiesel fuel for application in compression ignition engines. *Clean technologies and environmental policy, 12* (5), 459-493.

Ni, X., Jian, H., and Fitch, A. (2002). Computational fluid dynamic modelling of flow patterns in an oscillatory baffled column. *Chemical Engineering Science, 57* (14), 2849-2862.

Noshadi, I., Amin, N., and Parnas, R. S. (2012). Continuous production of biodiesel from waste cooking oil in a reactive distillation column catalyzed by solid heteropolyacid: optimization using response surface methodology (RSM). *Fuel, 94*, 156-164.

Oils & Fats International. (2018). Indonesia, Malaysia palm oil output projected to grow in 2018. https://www.ofimagazine.com/news/indonesia-malaysia-palm-oil-output-projected-to-grow-in-2018 (accessed December 2018).

Okamura, M., Takagaki, A., Toda, M., Kondo, J. N., Domen, K., Tatsumi, T., Hara, M., and Hayashi, S. (2006). Acid-catalyzed reactions on flexible polycyclic aromatic carbon in amorphous carbon. *Chemistry of Materials, 18* (13), 3039-3045.

Omar, W. N. N. W., and Amin, N. A. S. (2011a). Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. *Fuel Processing Technology, 92* (12), 2397-2405.

Omar, W. N. N. W., and Amin, N. A. S. (2011b). Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. *Biomass and bioenergy, 35* (3), 1329-1338.

Ong, H. R., Khan, M. R., Chowdhury, M., Yousuf, A., and Cheng, C. K. (2014). Synthesis and characterization of CuO/C catalyst for the esterification of free fatty acid in rubber seed oil. *Fuel, 120*, 195-201.

Pahl, G. (2005). Biodiesel: Growing a New Energy Economy. White River Junction, VT. Chelsea Green Publishing Company.

Park, Y.-M., Lee, D.-W., Kim, D.-K., Lee, J.-S., and Lee, K.-Y. (2008). The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel. *Catalysis Today, 131* (1-4), 238-243.

Pasias, S., Barakos, N., Alexopoulos, C., and Papayannakos, N. (2006). Heterogeneously catalyzed esterification of FFAs in vegetable oils. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology, 29* (11), 1365-1371.

Peng-Lim, B., Ganesan, S., Maniam, G. P., and Khairuddean, M. (2012). Sequential conversion of high free fatty acid oils into biodiesel using a new catalyst system. *Energy, 46* (1), 132-139.

Peterson, C. L., and Hustrulid, T. (1998). Carbon cycle for rapeseed oil biodiesel fuels. *Biomass and bioenergy, 14* (2), 91-101.

Phan, A. N., Harvey, A., and Lavender, J. (2011). Characterisation of fluid mixing in novel designs of mesoscale oscillatory baffled reactors operating at low flow rates (0.3–0.6 ml/min). *Chemical Engineering and Processing: Process Intensification, 50* (3), 254-263.

Phan, A. N., and Phan, T. M. (2008). Biodiesel production from waste cooking oils. *Fuel, 87* (17-18), 3490-3496.

Phan, N. T., Van Der Sluys, M., and Jones, C. W. (2006). On the nature of the active species in palladium catalyzed Mizoroki–Heck and Suzuki–Miyaura couplings–homogeneous or heterogeneous catalysis, a critical review. *Advanced Synthesis & Catalysis, 348* (6), 609-679.

Ping, B. T. Y., and Yusof, M. (2009). Characteristics and properties of fatty acid distillates from palm oil. *Oil Palm Bulletin, 59*, 5-11.

Piriou, B., Vaitilingom, G., Veyssière, B., Cuq, B., and Rouau, X. (2013). Potential direct use of solid biomass in internal combustion engines. *Progress in energy and combustion science, 39* (1), 169-188.

Poppe, J. K., Garcia-Galan, C., Matte, C. R., Fernandez-Lafuente, R., Rodrigues, R. C., and Ayub, M. A. Z. (2013). Optimization of synthesis of fatty acid methyl esters catalyzed by lipase B from Candida antarctica immobilized on hydrophobic supports. *Journal of Molecular Catalysis B: Enzymatic, 94*, 51-56.

Pramanik, K. (2003). Properties and use of Jatropha curcas oil and diesel fuel blends in compression ignition engine. *Renewable energy, 28* (2), 239-248.

Prankl, H., and Schindlbauer, H. Oxidation Stability of Fatty Acid Methyl Esters, Proceedings of 10th European Conference on Biomass for Energy and Industry, Würzburg, Germany, June 8-11, 1998. BLT Wieselburg, 1998.

Puna, J., Gomes, J., Correia, M. J. N., Dias, A. S., and Bordado, J. (2010). Advances on the development of novel heterogeneous catalysts for transesterification of triglycerides in biodiesel. *Fuel, 89* (11), 3602-3606.

Qiu, Z., Zhao, L., and Weatherley, L. (2010). Process intensification technologies in continuous biodiesel production. *Chemical Engineering and Processing: Process Intensification, 49* (4), 323-330.

Ramadhas, A., Jayaraj, S., and Muraleedharan, C. (2004). Use of vegetable oils as IC engine fuels—a review. *Renewable energy, 29* (5), 727-742.

Ramadhas, A. S., Jayaraj, S., and Muraleedharan, C. (2005). Biodiesel production from high FFA rubber seed oil. *Fuel, 84* (4), 335-340.

Ramning Amol, M., Dhote Priya, S., and Ganvir, V. (2013). Production of Neem Oil Methyl Ester (NOME) from Oscillatory Baffled Reactor. *Research Journal of Recent Sciences, 2*, 223-228.

Rashid, U., Ahmad, J., Yunus, R., Ibrahim, M., Masood, H., and Syam, A. M. (2014). Momordica Charantia seed oil methyl esters: a kinetic study and fuel properties. *International journal of green energy, 11* (7), 727-740.

Rashid, U., Anwar, F., Ashraf, M., Saleem, M., and Yusup, S. (2011). Application of response surface methodology for optimizing transesterification of Moringa oleifera oil: Biodiesel production. *Energy conversion and management, 52* (8-9), 3034-3042.

Rattanaphra, D., Harvey, A. P., Thanapimmetha, A., and Srinophakun, P. (2011). Kinetic of myristic acid esterification with methanol in the presence of triglycerides over sulfated zirconia. *Renewable energy, 36* (10), 2679-2686.

Refaat, A. (2010). Different techniques for the production of biodiesel from waste vegetable oil. *International Journal of Environmental Science & Technology, 7* (1), 183-213.

Refaat, A., Attia, N., Sibak, H. A., El Sheltawy, S., and ElDiwani, G. (2008). Production optimization and quality assessment of biodiesel from waste vegetable oil. *International Journal of Environmental Science & Technology, 5* (1), 75-82.

Reis, N., Harvey, A., Mackley, M., Vicente, A., and Teixeira, J. (2005). Fluid mechanics and design aspects of a novel oscillatory flow screening mesoreactor. *Chemical engineering research and design, 83* (4), 357-371.

Ruhul, M. A., Abedin, M. J., Rahman, S. A., Masjuki, B. H. H., Alabdulkarem, A., Kalam, M. A., and Shancita, I. (2016). Impact of fatty acid composition and physicochemical properties of Jatropha and Alexandrian laurel biodiesel blends: an analysis of performance and emission characteristics. *Journal of cleaner production, 133*, 1181-1189.

Sahoo, P., and Das, L. (2009). Process optimization for biodiesel production from Jatropha, Karanja and Polanga oils. *Fuel, 88* (9), 1588-1594.

Sánchez-Cantú, M., Pérez-Díaz, L. M., Pala-Rosas, I., Cadena-Torres, E., Juárez-Amador, L., Rubio-Rosas, E., Rodríguez-Acosta, M., and Valente, J. S. (2013). Hydrated lime as an effective heterogeneous catalyst for the transesterification of castor oil and methanol. *Fuel, 110*, 54-62.

Sani, Y. M., Daud, W. M. A. W., and Aziz, A. A. (2014). Activity of solid acid catalysts for biodiesel production: a critical review. *Applied Catalysis A: General, 470*, 140-161.

Sarin, R., Sharma, M., Sinharay, S., and Malhotra, R. K. (2007). Jatropha–palm biodiesel blends: an optimum mix for Asia. *Fuel, 86* (10-11), 1365-1371.

Sarkar, N., Ghosh, S. K., Bannerjee, S., and Aikat, K. (2012). Bioethanol production from agricultural wastes: an overview. *Renewable energy, 37* (1), 19-27.

Sawitri, D. R., and Sutijan, A. B. (2016). Kinetics study of free fatty acids esterification for biodiesel production from palm fatty acid distillate catalysed by sulphated zirconia. *ARPN Journal of Engineering and Applied Sciences, 11* (16), 9951-9957.

Sharma, Y. C., Singh, B., and Korstad, J. (2011). Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel. *Biofuels, Bioproducts and Biorefining, 5* (1), 69-92.

Shimada, Y., Watanabe, Y., Samukawa, T., Sugihara, A., Noda, H., Fukuda, H., and Tominaga, Y. (1999). Conversion of vegetable oil to biodiesel using immobilized Candida antarctica lipase. *Journal of the American Oil Chemists' Society, 76* (7), 789-793.

Shu, Q., Gao, J., Nawaz, Z., Liao, Y., Wang, D., and Wang, J. (2010a). Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst. *Applied Energy, 87* (8), 2589-2596.

Shu, Q., Nawaz, Z., Gao, J., Liao, Y., Zhang, Q., Wang, D., and Wang, J. (2010b). Synthesis of biodiesel from a model waste oil feedstock using a carbon-based solid acid catalyst: reaction and separation. *Bioresource technology, 101* (14), 5374-5384.

Shu, Q., Zhang, Q., Xu, G., Nawaz, Z., Wang, D., and Wang, J. (2009a). Synthesis of biodiesel from cottonseed oil and methanol using a carbon-based solid acid catalyst. *Fuel Processing Technology, 90* (7-8), 1002-1008.

Shu, Q., Zhang, Q., Xu, G., and Wang, J. (2009b). Preparation of biodiesel using s-MWCNT catalysts and the coupling of reaction and separation. *Food and Bioproducts Processing, 87* (3), 164-170.

Shuit, S. H., and Tan, S. H. (2014). Feasibility study of various sulphonation methods for transforming carbon nanotubes into catalysts for the esterification of palm fatty acid distillate. *Energy conversion and management, 88*, 1283-1289.

Singh, S., and Singh, D. (2010). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: a review. *Renewable and Sustainable Energy Reviews, 14* (1), 200-216.

Sinha, S., Agarwal, A. K., and Garg, S. (2008). Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. *Energy conversion and management, 49* (5), 1248-1257.

Soltani, S., Rashid, U., Yunus, R., and Taufiq-Yap, Y. H. (2016). Biodiesel production in the presence of sulfonated mesoporous ZnAl2O4 catalyst via esterification of palm fatty acid distillate (PFAD). *Fuel, 178*, 253-262.

Speight, J. (2008). Synthetic fuels handbook: properties, process and performance, United States.

Srivastava, A., and Prasad, R. (2000). Triglycerides-based diesel fuels. *Renewable and Sustainable Energy Reviews, 4* (2), 111-133.

Stonestreet, P., and Van der Veeken, P. (1999). The effects of oscillatory flow and bulk flow components on residence time distribution in baffled tube reactors. *Chemical engineering research and design, 77* (8), 671-684.

Syam, A. M. (2011). Continous production of Jatrpha Curcas L. biodiesel using oscillation flow reactor. Unpublished PhD dissertation, Universiti Putra Malaysia, Malaysia.

Syam, A. M., Yunus, R., Ghazi, T. I., and Choong, T. S. (2012). Synthesis of Jatropha curcas oil-based biodiesel in a pulsed loop reactor. *Industrial crops and products, 37* (1), 514-519.

Takagaki, A., Toda, M., Okamura, M., Kondo, J. N., Hayashi, S., Domen, K., and Hara, M. (2006). Esterification of higher fatty acids by a novel strong solid acid. *Catalysis Today, 116* (2), 157-161.

Talebian-Kiakalaieh, A., Amin, N. A. S., and Mazaheri, H. (2013a). A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy, 104*, 683-710.

Talebian-Kiakalaieh, A., Amin, N. A. S., Zarei, A., and Noshadi, I. (2013b). Transesterification of waste cooking oil by heteropoly acid (HPA) catalyst: optimization and kinetic model. *Applied Energy, 102*, 283-292.

Tesser, R., Casale, L., Verde, D., Di Serio, M., and Santacesaria, E. (2009). Kinetics of free fatty acids esterification: batch and loop reactor modeling. *Chemical engineering journal, 154* (1-3), 25-33.

Tesser, R., Di Serio, M., Guida, M., Nastasi, M., and Santacesaria, E. (2005). Kinetics of oleic acid esterification with methanol in the presence of triglycerides. *Industrial & Engineering Chemistry Research, 44* (21), 7978-7982.

Tiwari, A. K., Kumar, A., and Raheman, H. (2007). Biodiesel production from jatropha oil (Jatropha curcas) with high free fatty acids: an optimized process. *Biomass and bioenergy, 31* (8), 569-575.

Toda, M., Takagaki, A., Okamura, M., Kondo, J. N., Hayashi, S., Domen, K., and Hara, M. (2005). Green chemistry: biodiesel made with sugar catalyst. *Nature, 438* (7065), 178.

Tomasevic, A., and Siler-Marinkovic, S. (2003). Methanolysis of used frying oil. *Fuel Processing Technology, 81* (1), 1-6.

Tonetto, G. M., and Marchetti, J. M. (2010). Transesterification of soybean oil over Me/Al 2 O 3 (Me= Na, Ba, Ca, and K) catalysts and monolith K/Al 2 O 3-cordierite. *Topics in Catalysis, 53* (11-12), 755-762.

Torres-Jimenez, E., Jerman, M. S., Gregorc, A., Lisec, I., Dorado, M. P., and Kegl, B. (2011). Physical and chemical properties of ethanol–diesel fuel blends. *Fuel, 90* (2), 795-802.

Uzun, B. B., Kılıç, M., Özbay, N., Pütün, A. E., and Pütün, E. (2012). Biodiesel production from waste frying oils: Optimization of reaction parameters and determination of fuel properties. *Energy, 44* (1), 347-351.

Valeri, D., and Meirelles, A. J. (1997). Viscosities of fatty acids, triglycerides, and their binary mixtures. *Journal of the American Oil Chemists' Society, 74* (10), 1221-1226.

Van Gerpen, J. (2005). Biodiesel processing and production. *Fuel Processing Technology, 86* (10), 1097-1107.

van Leeuwen, P. W. (2001). Decomposition pathways of homogeneous catalysts. *Applied Catalysis A: General, 212* (1-2), 61-81.

Vicente, G., Martınez, M., and Aracil, J. (2004). Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresource technology, 92* (3), 297-305.

Vieira, S. S., Magriotis, Z. M., Santos, N. A., Saczk, A. A., Hori, C. E., and Arroyo, P. A. (2013). Biodiesel production by free fatty acid esterification using lanthanum (La3+) and HZSM-5 based catalysts. *Bioresource technology, 133*, 248-255.

Wan, T., Yu, P., Wang, S., and Luo, Y. (2009). Application of sodium aluminate as a heterogeneous base catalyst for biodiesel production from soybean oil. *Energy & Fuels, 23* (2), 1089-1092.

Wang, Y., Ou, S., Liu, P., Xue, F., and Tang, S. (2006). Comparison of two different processes to synthesize biodiesel by waste cooking oil. *Journal of Molecular Catalysis A: Chemical, 252* (1-2), 107-112.

Wu, Y.-p. G., Lin, Y.-f., and Chang, C.-T. (2007). Combustion characteristics of fatty acid methyl esters derived from recycled cooking oil. *Fuel, 86* (17-18), 2810-2816.

Xie, W., Peng, H., and Chen, L. (2006). Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. *Applied Catalysis A: General, 300* (1), 67-74.

Yujaroen, D., Goto, M., Sasaki, M., and Shotipruk, A. (2009). Esterification of palm fatty acid distillate (PFAD) in supercritical methanol: Effect of hydrolysis on reaction reactivity. *Fuel, 88* (10), 2011-2016.

Yusuf, N. N., Kamarudin, S. K., and Yaakob, Z. (2012). Overview on the production of biodiesel from Jatropha curcas L. by using heterogenous catalysts. *Biofuels, Bioproducts and Biorefining, 6* (3), 319-334.

Zhang, X., Li, J., Chen, Y., Wang, J., Feng, L., Wang, X., and Cao, F. (2009). Heteropolyacid nanoreactor with double acid sites as a highly efficient and reusable catalyst for the transesterification of waste cooking oil. *Energy & Fuels, 23* (9), 4640-4646.

Zhao, J., Yang, L., Li, F., Yu, R., and Jin, C. (2009). Structural evolution in the graphitization process of activated carbon by high-pressure sintering. *Carbon, 47* (3), 744-751.

Zheng, M., Skelton, R., and Mackley, M. (2007). Biodiesel reaction screening using oscillatory flow meso reactors. *Process Safety and Environmental Protection, 85* (5), 365-371.

Zheng, S., Kates, M., Dubé, M., and McLean, D. (2006). Acid-catalyzed production of biodiesel from waste frying oil. *Biomass and bioenergy, 30* (3), 267-272.

Zong, M.-H., Duan, Z.-Q., Lou, W.-Y., Smith, T. J., and Wu, H. (2007). Preparation of a sugar catalyst and its use for highly efficient production of biodiesel. *Green Chemistry, 9* (5), 434-437.