STUDY ON THE KINETICS OF CATION EXCHANGE RESINS AS CATALYSTS IN FREE FATTY ACID (FFA) ESTERIFICATION OF SIMULATED USED COOKING OIL

NURSOFIA BINTI MOHD YUNUS

Master

UNIVERSITI MALAYSIA PAHANG

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis project and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science.

_____

(Supervisor's Signature)

Full Name : Dr. Sumaiya Binti Zainal Abidin @ Murad

Position : Senior Lecturer

Date : 16th March 2018

_____

(Co-supervisor's Signature)

Full Name : Prof. Madya Dr. Chin Sim Yee

Position : Senior Lecturer

Date : 16th March 2018

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

_____

(Student's Signature)

Full Name : Nursofia Binti Mohd Yunus

ID Number : MKC15019

Date : 16th March 2018

STUDY ON THE KINETICS OF CATION EXCHANGE RESINS AS CATALYSTS IN FREE FATTY ACID (FFA) ESTERIFICATION OF SIMULATED USED COOKING OIL

NURSOFIA BINTI MOHD YUNUS

Thesis submitted in fulfilment of the requirements
for the award of the degree of
Master of Science

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

MARCH 2018

ACKNOWLEDGEMENTS

Bismillahi ar-rahmaan ar-rahim
In the name of Allah the Most Gracious and Most Merciful

First of all, my praise and thanks to you my Lord Allah, the Most Gracious, Most Merciful for enabling me to complete this research successfully. Thank you for blessing, protecting and guiding me throughout this period and for putting so many good people in my research journey.

A highest appreciation to be given to my supervisor, Dr. Sumaiya Binti Zainal Abidin @ Murad for granting me this great opportunity to work under her supervision. I have received a lot of her guidance and encouragements throughout this research work. Besides, she has been very helpful in providing clear insight to my research and arrange an effective weekly meeting for me. I would also like to thank my co-supervisor, Associate Professor Dr. Chin Sim Yee for her valuable suggestions and comments regarding this research work.

I offer my sincerest gratitude to Universiti Malaysia Pahang Research Grant (RDU RDU140357), TWAS-COMSTECH research grant (14-337) and Prototype Development Research Grant Scheme (PGRS 170320) for sponsoring this research work. Special gratitude also goes to all my UMP colleagues for their support, trust and friendship. I would like to thank Nurul Asmawati Binti Roslan (Postgraduate student) and Siti Amirah Binti Abdul Ghani (Undergraduate student) for helping me in finishing the research work. Without their help, I could not have finished my dissertation successfully.

I would also like to express our acknowledgement to Mitsubishi Chemical Corporation for kindly supplying the catalysts for this research work. I would like to acknowledge with appreciation to technical staff of FKKSA laboratory, who gave the permissions to use all the required machinery and necessary material to complete this research.

Finally, I would like thank my beloved parents, Mohd Yunus Bin Saidun and Meriam @ Rahanah Binti Busu for their support, love and faith in me. Without their prayer and motivation, I could have never reached this far.

TABLE OF CONTENT

DECLARATION

TITLE PAGE

ACKNOWLEDGEMENTS **ii**

ABSTRAK **iii**

ABSTRACT **iv**

TABLE OF CONTENT **v**

LIST OF TABLES **ix**

LIST OF FIGURES **x**

LIST OF SYMBOLS **xii**

LIST OF ABBREVIATIONS **xvi**

CHAPTER 1 INTRODUCTION **1**

1.1 Introduction 1

1.2 Problem statement 4

1.3 Research objectives 5

1.4 Research scope 5

1.5 Organisation of thesis 6

CHAPTER 2 LITERATURE REVIEW **8**

2.1 Introduction 8

2.2 Biodiesel for alternative fuel vehicles 8

2.3 Esterification as an alternative pre-treatment process for biodiesel feedstock 11

2.4 Feedstock for esterification process 13

2.4.1 Non-edible vegetable oil 13

2.4.2 Animal fats 16

2.4.3 Waste oils 17

2.5 Types of esterification catalyst 21

2.5.1 Homogeneous acid catalyst 21

2.5.2 Heterogeneous acid catalyst 22

2.6 Mass transfer resistance 36

2.7 Process variables of the esterification process 38

2.7.1 Catalyst loading 38

2.7.2 Reaction temperature 39

2.7.3 Alcohol type 40

2.7.4 Alcohol to oil ratio 42

2.8 Kinetic modelling of free fatty acid esterification 43

2.8.1 Pseudo homogeneous (P-H) model 44

2.8.2 Langmuir-Hinshelwood-Hougen-Watson (LHHW) model 46

2.8.3 Eley-Rideal (E-R) model 47

2.9 Summary 51

CHAPTER 3 METHODOLOGY 53

3.1 Introduction 53

3.2 Materials and chemicals 55

3.3 Catalyst preparation 56

3.4 Catalyst characterisation 56

3.4.1 Particle size distribution (PSD) analysis 56

3.4.2 Scanning electron microscopy (SEM) analysis 57

3.4.3 Field emission scanning electron microscopy (FESEM) and energy dispersive x-ray (EDX) spectroscopy 57

3.4.4 Fourier transform-infra red spectroscopy (FT-IR) analysis 57

3.4.5 Nitrogen physiorption analysis 58

3.4.6 Elemental analysis 58

3.4.7 Acid capacity analysis 58

3.5 Feedstock 59

3.5.1 Preparation of simulated used cooking oil (SUCO) 59

3.5.2 Acid value and FFA content analysis 59

3.6 Esterification reaction using batch reactor 60

3.7 Kinetic study of batch esterification of FFA 63

3.7.1 The kinetic models of FFA esterification 63

CHAPTER 4 ESTERIFICATION OF FREE FATTY ACID USING ION EXCHANGE RESINS 76

4.1 Introduction 76

4.2 Catalyst characterisation 76

4.2.1 Fourier transform infra-red spectroscopy (FT-IR) analysis 76

4.2.2 Surface area analysis 78

4.2.3 Elemental analysis 78

4.2.4 Catalyst morphology analysis 79

4.2.5 Acid capacity analysis 81

4.2.6 Particle size distribution (PSD) analysis 81

4.3 Esterification of FFA in SUCO using ion exchange resins as catalyst- catalyst screening study 83

4.4 Esterification of FFA in SUCO using OVAAT method 85

4.4.1 Effect of catalyst loading 85

4.4.2 Effect of reaction temperature 86

4.4.3 Effect of methanol to oil mass ratio 88

4.5 Reusability study 89

4.6 Comparison between RCP160M with conventional cation exchange resins 92

4.7 Summary 94

CHAPTER 5 KINETIC STUDIES OF THE FREE FATTY ACID ESTERIFICATION IN A BATCH MODE 96

5.1 Introduction 96

5.2 Effect of mass transfer resistance 96

5.3 Estimation of reactant rate constant 99

5.4 Evaluation of activation energy and pre-exponential factor 105

5.5 Summary 106

CHAPTER 6 CONCLUSION AND RECOMMENDATIONS 108

6.1 Conclusion 108

6.2 Recommendations 109

REFERENCES 111

APPENDIX A CALCULATION OF WEISZ-PRATE CRITERION (C_{WP}) AND MEARS CRITERION (C_M) 139

ACHIEVEMENTS 145

LIST OF TABLES

Table 2.1	Seed oil content of non-edible plants	14
Table 2.2	An esterification reaction of two-step esterification and transesterification reaction using used cooking oil	20
Table 2.3	The list of the esterification reaction catalysed by ion exchange resins	34
Table 2.4	The list of the kinetic model used in esterification of FFA	49
Table 3.1	List of materials and chemicals	55
Table 3.2	List of catalysts	55
Table 3.3	List of main components in the experimental setup for esterification reaction in a batch reactor	62
Table 3.4	List of conditions for each parameters in batch esterification of SUCO	62
Table 4.1	The FT-IR assignment of bands for cation exchange resins	77
Table 4.2	BET results of ion exchange resins	78
Table 4.3	Elemental analysis of ion exchange resins	79
Table 4.4	Acid capacity analysis of ion exchange resins	81
Table 4.5	Physicochemical properties of fresh and spent RCP160M	92
Table 4.6	Comparison of performance RCP160M with reported cation exchange resins	94
Table 5.1	The C_M values of different stirring speed	97
Table 5.2	The C_{WP} values for difference size of catalyst	99
Table 5.3	Kinetic parameters for esterification of SUCO using RCP160M	101
Table 5.4	Activation energy and pre-exponential factor for each model	105
Table 5.5	Comparison of activation energy with reported heterogeneous catalyst	106
Table 5.6	Reaction enthalpy and entropy	106

LIST OF FIGURES

Figure 1.1	Final energy consumption by fuel type in 2015	1
Figure 2.1	Final energy consumption by sectors in 2015	9
Figure 2.2	Chemical equation for esterification of FFA	12
Figure 2.3	Mechanism scheme of esterification of FFA	12
Figure 3.1	Summary of the experimental work	54
Figure 3.2	Schematic diagram of esterification of SUCO in a batch reactor	61
Figure 3.3	Kinetic study of FFA esterification using POLYMATH 6.10	75
Figure 4.1	FT-IR spectra of ion exchange resins	77
Figure 4.2	SEM images of a) RCP145H, b) RCP160M, c) PK208LH, d) PK216LH, e) PK228LH, f) SK1BH, g) SK104H	80
Figure 4.3	Particle size distribution of the cation exchange resins	82
Figure 4.4	Screening study on the performance of cation exchange resins (Reaction conditions: 5 wt. % catalyst loading; 60 ˚C reaction temperature; 450 rpm stirring speed; 12:1 methanol to oil mass ratio; 8 h reaction time)	84
Figure 4.5	Studies on the effect of different catalyst loadings (Reaction conditions: 300 rpm stirring speed; 60 ˚C reaction temperature; 12:1 methanol to oil mass ratio; 8 h reaction time)	86
Figure 4.6	Studies on the effect of reaction temperature (Reaction conditions: 300 rpm stirring speed; 4 wt. % catalyst loading; 12:1 methanol to oil mass ratio; 8 h reaction time)	87
Figure 4.7	Studies on the effect of methanol to oil mass ratio (Reaction conditions: 300 rpm stirring speed; 4 wt. %; 60 ˚C reaction temperature; 8 h reaction time)	89
Figure 4.8	Reusability of RCP160M catalyst by methanol and hexane washing (Experimental conditions: 300 rpm stirring speed; 4 wt. % catalyst loading; 60 ˚C reaction temperature; 18:1 methanol to oil mass ratio; 8 h reaction time)	91
Figure 4.9	Reusability of RCP160M catalyst by methanol washing (Experimental conditions: 300 rpm stirring speed, 4 wt. % catalyst loading, 60 ˚C reaction temperature, 18:1 methanol to oil mass ratio, 8 h reaction time)	91
Figure 5.1	Studies on the effect of different stirring speed (Reaction conditions: 5 wt. % catalyst loading; 60 ˚C reaction temperature; 12:1 methanol to oil mass ratio)	98
Figure 5.2	Studies on the effect of different range of catalyst size, small (300-700 µm), mixture (300-1000 µm), large (700-1000 µm) (Reaction conditions: 300 rpm stirring speed; 5 wt. % catalyst loading; 60 ˚C reaction temperature; 12: methanol to oil mass ratio)	99

Figure 5.3 The Arrhenius plot at 300 rpm stirring speed, 4 wt. % catalyst loading, 60 ˚C reaction temperature, 18:1 methanol to oil mass ratio, a) P-H model, b) LHHW model, c) E-R (Case I) model and d) E-R (Case II) model 103

Figure 5.4 The comparison of experimental and calculated data of FFA conversion versus time (min). Experimental conditions: Catalyst: RCP160M; 12:1 methanol to oil mass ratio, 4 wt. % catalyst loading and 300 rpm in 8 h reaction time. 104

LIST OF SYMBOLS

TPA	12-tungstophosphoric acid
H_3PW/ZrO_2	12-tungstophosphoric acid supported on zirconia
Ea	Activation energy
K_A	Adsorption coefficient of FFA
K_B	Adsorption coefficient of methanol
K_C	Adsorption coefficient of esters
K_D	Adsorption coefficient of water
Al	Aluminium
Al_2O_3	Aluminium oxide
Å	Ångstrøm (0.1 nanometre)
C_{AB}	Bulk concentration of limiting reactant
CaO	Calcium oxide
C	Carbon
CO_2	Carbon dioxide
ρ_b	Catalyst density
R_c	Catalyst radius
Cm	Centimetre
Ce	Cerium
Cs	Caesium
R^2	Coefficient of determination
M	Concentration
C_A	Concentration of free fatty acid
C_C	Concentration of esters
C_{HCl}	Concentration of hydrochloric acid
C_B	Concentration of methanol
C_{NaOH}	Concentration of sodium hydroxide
C_V	Concentration of vacant sites on surface
C_D	Concentration of water
C_{li}	Concentration of the limiting reactant in mixture
x	Conversion
cm^3	Cubic centimetre

^oC	Degree celsius
ID	Diameter
D_{eff}	Effective diffusivity
ΔH	Enthalphy
ΔS	Entrophy
K_{eq}	Equilibrium constant
$Fe_2(SO_4)_2/C$	Ferric sulphate on carbon
$C_{NaOH\ final}$	Final concentration of sodium hydroxide
k_f	Forward rate constant
R	Gas constant
g	Gram
h	Hour/hours
HF	Hydrofluoric acid
H	Hydrogen
H^+	Hydrogen ion/ proton
$C_{NaOH\ initial}$	Initial concentration of sodium hydroxide
$V_{initial}$	Initial volume
J	Joule
K	Kelvin
kJ	Kilojoule
kv	Kilovolt
La_2O_3	Lanthanum oxide
$>$	Larger than
$<$	Less than
L	Litre
MnO	Manganese oxide
m_c	Mass of catalyst
K_c	Mass transfer coefficient
C_M	Mears Criterion
Mpa	Megapascal
μm	Micrometre
mg	Milligram
ml	Millilitre

mmol	Millimoles
Mm	Millimetre
mmHg	Millimetre of mercury
min	Minute/minutes
mol	Molarity
Nd_2O_3	Neodymium oxide
NiO	Nickel (II) oxide
N_2	Nitrogen
ppm	Parts per million
%	Percent
H_3PO_4	Phosphoric acid
±	Plus or minus
psi	Pound per square inch
KOH	Potassium hydroxide
A/a	Pre-exponential factor
r_{AD}	Rate of adsorption
r_{DC}	Rate of desorption
r_s	Rate of surface reaction
r_A	Reaction rate
rpm	Revolution per minute
Si	Silica
NaOH	Sodium hydroxide
SiO_2	Silicon dioxide
m^2	Square metre
NH_2SO_3H	Sulfamic acid
$-SO_3H$	Sulfonic group
S	Sulphur
H_2SO_4	Sulphuric acid
SO_2	Sulphuric oxide
SO_4^2	Sulphated
SO_4^2/SnO_2	Sulphated tin oxide
SO_4^{2-}/TiO_2	Sulphated titanium oxide
SO_4^{2-}/ZrO_2	Sulphated zirconium oxide

$Fe(SO_4)_3/C$	Supported ferric sulphate on carbon
T	Temperature
TCD	Thermal conductivity detector
TiO_2	Titanium oxide
C_t	Total concentration of active sites on surface
WO_3	Tunsteng trioxide
vol	Volume
V_{HCl}	Volume of hydrochloric acid
V_{NaOH}	Volume of sodium hydroxide
v/v	Volume per volume
wt. %	Weight percent
w/w	Weight per weight
C_{wp}	Weisz Prater Criterion
Yb_2O_3	Ytterbium (III) oxide
ZnO	Zinc oxide
ZrO_2	Zirconium oxide

LIST OF ABBREVIATIONS

TPA	12-Tungstopphosphoric acid
ASTM	American Society for Testing and Materials
A-SZr	Aerogel sulphated zirconia catalyst
BET	Brunauer-Emmett-Teller
CAHZ	Dealuminated HSZM-5 with citric acid
CHNS	Elemental analysis
CSTR	Continuous stirred tank reactor
DDPO	Deodorisation processes of palm oil
EDX	Energy dispersive x-ray spectroscopy
E-R	Eley-Rideal
FAME	Fatty acid methyl ester
FAU	Faujasite
FESEM	Field emission scanning electron microscopy
FFA	Free fatty acid
FS/OMC	Ferric sulfate supported on ordered mesoporous carbon
FT-IR	Fourier-Transform Infrared Spectroscopy
H	Hydrogen
HPA	Heteropolyacid
HPAs	Heteropolyacids
HZ	HZSM-5 zeolite
IM-1	Intermediate 1
IM-2	Intermediate 2
LA	Lanthanum oxide
L-M	Levenberg-Marquardt
MFI	ZSM-5
MK700	Kaolin waste
LHHW	Langmuir-Hinshelwood-Hougen-Watson
MOR	Mordenite
N	Nitrogen
OBR	Oscillatory baffled reactor
OSHA	Occupational Safety and Health Administration

OVAAT	One-variable-at-a-time
PBR	Packed bed reactor
PFR	Plug flow reactor
PMo	Molybdophosphoric acid
PSD	Particle size distribution
PSS	Polystyrene waste
P-H	Pseudo-homogeneous
R&D	Research and development
RBFA	Rice bran fatty acid
RBO	Rice bran oil
RHC	Rice husk char
S	Sulphur
SCER	Sulfonated cation exchange resins
SEM	Scanning Electron Microscopy
SiW	Tungstosilicic acid
SLO	Sulphated lanthanum oxide
ST-DVB	Styrene and divinyl benzene
SUCO	Simulated used cooking oil
SZ	Sulphated zirconia
TFR	Tubular flow reactor
TiZ	Titania zirconia
TPD	Thermal desorption spectroscopy
TW	Tungstophoric acid
UCO	Used cooking oil
USDA	United States Department of Agriculture
WZ	Tungstated zirconia
X-SZr	Xerogel sulphated zirconia catalyst

STUDY ON THE KINETICS OF CATION EXCHANGE RESINS AS CATALYSTS IN FREE FATTY ACID (FFA) ESTERIFICATION OF SIMULATED USED COOKING OIL

NURSOFIA BINTI MOHD YUNUS

Thesis submitted in fulfilment of the requirements
for the award of the degree of
Master of Science

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

MARCH 2018

ABSTRAK

Minyak masak terpakai (UCO) adalah salah satu pengganti yang berpotensi sebagai bahan mentah untuk menghasilkan biodiesel kerana kosnya yang rendah. Walaupun mempunyai banyak kelebihan, UCO mengandungi asid lemak bebas yang sangat tinggi dan menyumbang kepada tindak balas saponifikasi apabila ia digunakan dalam tindak balas transesterifikasi. Resin pertukaran ion telah digunakan secara meluas dalam tindak balas esterifikasi asid lemak bebas bagi membantu mengurangkan kandungan asid lemak bebas di dalam UCO. Pemangkin ini telah menunjukkan prestasi yang sangat baik dalam masa yang singkat. Walau bagaimanapun, resin pertukaran ion konvensional mempunyai kawasan asid yang rendah, kawasan permukaan dan isipadu liang yang sederhana, dan juga ketahanan dan kestabilan yang rendah. Oleh itu, dalam kajian ini, pemangkin-pemangkin seperti RCP160M, RCP145H, PK228LH, PK216LH, PK208LH, SK104H dan SK1BH dengan tekstur dan morfologi yang berbeza telah digunakan sebagai pemangkin untuk pengesteran asid lemak bebas dalam minyak masak terpakai. Ciri-ciri fizikokimia pemangkin-pemangkin ini telah dikaji menggunakan analisis *Fourier transform-infra red spectroscopy (FT-IR), nitrogen physisorption, scanning electron microscopy (SEM), elemental analyis (CHNS), titration and particle size distribution (PSD).* Pemangkin-pemangkin ini telah disaringkan terlebih dahulu untuk menentukan pemangkin yang terbaik pada kadar kacauan 450 rpm, 5 wt. % pemangkin pemangkin, 60 ˚C dan 12:1 nisbah jisim metanol dan minyak. Pemangkin yang terbaik telah digunakan dalam kajian seterusnya dengan memberi tumpuan kepada kesan rintangan pemindahan jisim dan juga parameter-parameter yang berlainan seperti kesan muatan pemangkin, suhu proses dan nisbah jisim metanol dan minyak. Kajian ini telah diteruskan dengan menghasilkan tiga jenis model; Pseudo homogeneous (P-H), Langmuir-Hinshelwood-Hougen-Watson (LHHW) dan Eley-Rideal (Kes I dan Kes II) untuk menentukan kadar pemalar dan tenaga pengaktifan reaksi dengan menggunakan program POLYMATH 6.10. Keputusan kajian menunjukkan bahawa RCP160M menunjukkan prestasi yang terbaik sebagai pemangkin dalam proses pra-rawatan minyak masak terpakai bagi penghasilan biodiesel kerana ia telah berjaya mengatasi pemangkin-pemangkin lain dengan menunjukkan penukaran asid lemak bebas yang paling tinggi dalam proses pengesteran. Prestasi RCP160M yang cemerlang adalah disebabkan oleh luas permukaan pemangkin dan isi padu liang yang tinggi berbanding pemangkin-pemangkin yang lain. Sebanyak 95 % daripada asid lemak bebas telah berjaya ditukarkan pada kadar kacauan 300 rpm, 4 wt. % jumlah pemangkin, 60 ˚C suhu proses dan 18:1 nisbah jisim metanol dan minyak. Semasa proses kitaran semula RCP160M dalam proses pengesteran, sebanyak 5-15 % aktiviti RCP160M telah berkurang untuk satu kitaran. Pengurangan ini mungkin disebabkan oleh liang pemangkin telah tersumbat oleh minyak semasa tindak balas berlaku dan menghalang reaktan untuk memasuki kawasan aktif pemangkin. Selain itu, pengurangan kawasan yang aktif sewaktu proses mencuci juga merupakan salah satu faktor pengurangan aktiviti pemangkin. Dalam pada itu, keputusan kinetik mendapati bahawa data eksperimen bagi proses pengesteran menggunakan RCP160M telah berjaya dikaitkan dengan model E-R (II) dengan tenaga pengaktifan sebanyak 37.2 kJ/mol. Keputusan kinetik ini menunjukkan bahawa penyerapan molekul bukan polar (asid lemak bebas) adalah lebih baik daripada penyerapan molekul polar (methanol) pada permukaan pemangkin. Melalui kajian ini, pembaikan prosedur untuk regenerasi RCP160M perlu diteruskan pada masa hadapan kerana pemangkin ini adalah pemangkin yang berpotensi dalam penghasilan biodiesel.

ABSTRACT

Used cooking oil (UCO) is one of the potential substitutes for conventional biodiesel feedstock due to its low cost. In spite of its advantage, UCO has high free fatty acid (FFA) level which contributes to saponification reaction when it was directly utilised in base catalysed transesterification reaction. Ion exchange resins have been widely used in FFA esterification reaction to reduce the FFA content as this type of catalyst exhibits good catalyst performance in a short period of time. Nevertheless, conventional ion exchange resin has low acidic sites, moderate specific surface area and pore volume, poor durability and thermal stability. Therefore, in this study styrene-divinylbenzene (DVB) resins; RCP160M, RCP145H, PK228LH, PK216LH, PK208LH, SK104H and SK1BH with different textural and morphological properties were used as catalysts for the esterification of FFA in simulated used cooking oil (SUCO). These resins were characterised using Fourier transform-infrared spectroscopy (FT-IR), nitrogen physisorption, scanning electron microscopy (SEM), elemental analyser (CHNS), titration and particle size distribution (PSD) analyser to determine their physicochemical properties. These catalysts were screened to determine the best performance catalyst under reaction conditions of 300 rpm stirring speed, 5 wt. % catalyst loading, 60 ˚C and 12:1 methanol to oil mass ratio. The best performance catalyst was used in the subsequent studies focusing on the effect of mass transfer resistance, the effect of catalyst loading, reaction temperature, and methanol to oil mass ratio to investigate the best conditions in a batch mode system. The study proceeded with the kinetics of FFA esterification by developing three kinetic models; Pseudo homogeneous (P-H), Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley-Rideal (Case I and Case II) to determine rate constant and activation energy of the reaction using POLYMATH 6.10 program. The results revealed that RCP160M was found to give the best catalytic performance as it outperformed the other catalysts and achieved maximum FFA conversions. This may attributed to the high specific surface area and total pore volume of RCP160M. 95 % of FFA conversion was achieved at the best reaction conditions with a stirring speed of 300 rpm, catalyst loading of 4 wt. %, a reaction temperature of 60 ˚C, and methanol to oil mass ratio of 18:1. During the reusability study, the catalytic activity of RCP160M decreased about 5-15 % for each cycle. The decrease of FFA conversion was due to pore blockage by oil during the reaction and simultaneously blocked the reactants from accessing the active sites. Besides, the loss of active sites during washing process might possibly occur between the reuse cycles. The kinetic results revealed that the experimental data were best-fitted to the E-R model (Case II) with the activation energy of 37.2 kJ/mol. This study showed that the reaction was limited by surface reaction where the adsorption of non-polar FFA molecules was more favourable than the adsorption of polar methanol molecules. In future, it was recommended that further work is necessary to improve the regeneration procedure of RCP160M as this catalyst can be potentially used as a catalyst for biodiesel production.

REFERENCES

Abbas, A. S., Albayati, T. M., & Alismaeel, Z. T. (2016). Kinetics and mass transfer study of oleic acid esterification over prepared nanoporous HY zeolite. *Iraqi Journal of Chemical and Petroleum Engineering, 17*, 47-60.

Abdala, A. C. d. A., dos Santos Garcia, V. A., Trentini, C. P., Cardozo Filho, L., da Silva, E. A., & da Silva, C. (2014). Continuous Catalyst-Free Esterification of Oleic Acid in Compressed Ethanol. *International Journal of Chemical Engineering, 2014*, 1-5.

Abdullah, N. H., Hasan, S. H., & Yusoff, N. R. M. (2013). Biodiesel Production Based on Waste Cooking Oil (WCO). *International Journal of Materials Science and Engineering*, 94-99.

Abdulrahman, R. K., Zangana, M. H., Ali, J. A., Aziz, R. I., Karem, R. M., & Hussain, B. M. (2016). Biofuel From Cow Tallow: A Case Study. *European Scientific Journal, 12*.

Abidin, S. Z. (2012). Production of biodiesel from used cooking oil (UCO) using ion exchange resins as catalyst. (Doctor of Philosophy), Loughborough University, United Kingdom.

Abidin, S. Z., Haigh, K. F., & Saha, B. (2012). Esterification of Free Fatty Acids in Used Cooking Oil Using Ion-Exchange Resins as Catalysts: An Efficient Pretreatment Method for Biodiesel Feedstock. *Industrial & Engineering Chemistry Research, 51*, 14653-14664.

Aghabarari, B., dorostkar, N., Ghiaci, M., Amini, S. G., Rahimi, E., & Martinez-Huerta, M. V. (2014). Esterification of fatty acids by new ionic liquids as acid catalysts. *Journal of the Taiwan Institute of Chemical Engineers, 45*, 431-435.

Aguieiras, E. C., Ribeiro, D. S., Couteiro, P. P., Bastos, C. M., de Queiroz, D. S., Parreira, J. M., & Langone, M. A. (2016). Investigation of the Reuse of Immobilized Lipases in Biodiesel Synthesis: Influence of Different Solvents in Lipase Activity. *Applied Biochemistry and Biotechnology, 179*, 485-496.

Akbay, E. Ö., & Altıokka, M. R. (2011). Kinetics of esterification of acetic acid with n-amyl alcohol in the presence of Amberlyst-36. *Applied Catalysis A: General, 396*, 14-19.

Akyalçın, S., & Altıokka, M. R. (2012). Kinetics of esterification of acetic acid with 1-octanol in the presence of Amberlyst 36. *Applied Catalysis A: General, 429-430*, 79-84.

Al-Jaberi, S. H. H., Rashid, U., Al-Doghachi, F. A. J., Abdulkareem-Alsultan, G., & Taufiq-Yap, Y. H. (2017). Synthesis of MnO-NiO-SO 4 −2 /ZrO 2 solid acid catalyst for methyl ester production from palm fatty acid distillate. *Energy Conversion and Management, 139*, 166-174.

Alcañiz-Monge, J., Trautwein, G., & Marco-Lozar, J. P. (2013). Biodiesel production by acid catalysis with heteropolyacids supported on activated carbon fibers. *Applied Catalysis A: General, 468*, 432-441.

Al-Mofleh, A., Taib, S., & Salah, W. A. (2010). Malaysian Energy Demand and Emissions from the Transportation Sector. *Transport, 25*(4), 448-453.

Ali, S. H., Tarakmah, A., Merchant, S. Q., & Al-Sahhaf, T. (2007). Synthesis of esters: Development of the rate expression for the Dowex 50 Wx8-400 catalyzed esterification of propionic acid with 1-propanol. *Chemical Engineering Science, 62*, 3197-3217.

Alptekin, E., Canakci, M., & Sanli, H. (2011). *Methyl ester production from chicken fat with high FFA*. Paper presented at the World Renewable Energy Congress, 8-13 May, Sweden.

Andreani, L., & Rocha, J. D. (2012). Use of ionic liquids in biodiesel production: A review. *Brazilian Journal of Chemical Engineering, 29*, 1-13.

Aranda, D. A. G., Gonçalves, J. d. A., Peres, J. S., Ramos, A. L. D., de Melo, C. A. R., Antunes, O. A. C., . . . Taft, C. A. (2009). The use of acids, niobium oxide, and zeolite catalysts for esterification reactions. *Journal of Physical Organic Chemistry, 22*, 709-716.

Arbain, N.H., Salimon, J. 2011. The Effects of Various Acid Catalyst on the Esterification of Jatropha Curcas Oil based Trimethylolpropane Ester as Biolubricant Base Stock, *E-Journal of Chemistry, 8*, 33–41.

Arora, R., Kapoor, V., & Toor, A. P. (2014). *Esterification of Free Fatty Acids in Waste Oil Using a Carbon-based Solid Acid Catalyst*. Paper presented at the 2nd International Conference on Emerging Trends in Engineering and Technology (ICETET 2014), London, United Kingdom.

Arora, R., Toor, A. P., & Wanchoo, R. K. (2015). Esterification of High Free Fatty Acid Rice Bran Oil: Parametric and Kinetic Study. *Chemical and Biochemical Engineering Quarterly, 29*, 617-623.

Atabani, A. E., Silitonga, A. S., Ong, H. C., Mahlia, T. M. I., Masjuki, H. H., Badruddin, I. A., & 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.

Badday, A. S., Abdullah, A. Z., & Lee, K.-T. (2014). Transesterification of crude Jatropha oil by activated carbon-supported heteropolyacid catalyst in an ultrasound-assisted reactor system. *Renewable Energy, 62*, 10-17.

Baig, A., & Ng, F. T. T. (2010). A Single-Step Solid Acid-Catalyzed Process for the Production of Biodiesel from High Free Fatty Acid Feedstocks. *Energy & Fuels, 24*, 4712-4720.

Bakkiyaraj, S., Syed, M. B., Devanesan, M. G., & Thangavelu, V. (2016). Production and optimization of biodiesel using mixed immobilized biocatalysts in packed bed reactor. *Environmental Science and Pollution Research Int, 23*, 9276-9283.

Bala, V. S. S., Thiruvengadaravi, K. V., Kumar, P. S., Premkumar, M. P., Kumar, V. V., Sankar, S. S., Kumar, M. H., & Sivanesan, S. (2012). Removal of free fatty acids in Pongamia Pinnata (Karanja) oil using divinylbenzene-styrene copolymer resins for biodiesel production. *Biomass and Bioenergy, 37*, 335-341.

Balat, M. (2011). Potential alternatives to edible oils for biodiesel production – A review of current work. *Energy Conversion and Management, 52*, 1479-1492.

Banani, R., Youssef, S., Bezzarga, M., & Abderraba, M. (2015). Waste frying oil with high levels of free fatty acids as one of the prominent sources of biodiesel production. *Journal of Material and Environmental Science, 6*, 1178-1185.

Banković-Ilić, I. B., Stamenković, O. S., & Veljković, V. B. (2012). Biodiesel production from non-edible plant oils. *Renewable and Sustainable Energy Reviews, 16*, 3621-3647.

Baroi, C., & Dalai, A. K. (2014). Esterification of free fatty acids (FFA) of Green Seed Canola (GSC) oil using H-Y zeolite supported 12-Tungstophosphoric acid (TPA). *Applied Catalysis A: General, 485*, 99-107.

Baroi, C., Mahto, S., Niu, C., & Dalai, A. K. (2014). Biofuel production from green seed canola oil using zeolites. *Applied Catalysis A: General, 469*, 18-32.

Berchmans, H. J., & Hirata, S. (2008). Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. *Bioresoure Technology, 99*, 1716-1721.

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

Bhatti, H., Hanif, M., Qasim, M., & Ataurrehman. (2008). Biodiesel production from waste tallow. *Fuel, 87*, 2961-2966.

Blandamer, M. J., Burgess, J., Robertson, R. E., & Scott, J. M. W. (1982). Dependence of equilibrium and rate constants on temperature and pressure. *Chemical Reviews, 82*, 259-286.

Boffito, D. C., Crocellà, V., Pirola, C., Neppolian, B., Cerrato, G., Ashokkumar, M., & Bianchi, C. L. (2013). Ultrasonic enhancement of the acidity, surface area and free fatty acids esterification catalytic activity of sulphated ZrO2–TiO2 systems. *Journal of Catalysis, 297*, 17-26.

Bond, G. C. (1974). *Heterogeneous Catalysis; Principles and Applications* (Vol. 18). University of California: Clarendon Press; Oxford.

Bollin, P.M. 2011. The Production of Fatty Acid Methyl Esters. Master Thesis, The University of Toledo.

Borges, M. E., & 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*, 2839-2849.

Brahmkhatri, V., & Patel, A. (2011). 12-Tungstophosphoric acid anchored to SBA-15: An efficient, environmentally benign reusable catalysts for biodiesel production by esterification of free fatty acids. *Applied Catalysis A: General, 403*, 161-172.

Brahmkhatri, V., & Patel, A. (2012). An efficient green catalyst comprising 12-tungstophosphoric acid and MCM-41: synthesis characterization and diesterification of succinic acid, a potential bio-platform molecule. *Green Chemistry Letters and Reviews, 5*, 161-171.

Briggs, H. G., & Leong, H. K. (2016). *Malaysia Stoctacking Report on Sustainable Transport and Climate Change*. Retrieved from http://www.mot.gov.my/ SiteCollectionDocuments/Darat/MY_StockTakingReport_Final.pdf

Buasri, A., Chaiyut, N., Loryuenyong, V., Rodklum, C., Chaikwan, T., & Kumphan, N. (2012). Continuous Process for Biodiesel Production in Packed Bed Reactor from Waste Frying Oil Using Potassium Hydroxide Supported on Jatropha curcas Fruit Shell as Solid Catalyst. *Applied Sciences, 2,* 641-653.

Bueso, F., Moreno, L., Cedeno, M., & Manzanarez, K. (2015). Lipase-catalyzed biodiesel production and quality with Jatropha curcas oil: exploring its potential for Central America. *Journal of Biology Engineering, 9,* 12.

Caetano, C. S., Fonseca, I. M., Ramos, A. M., Vital, J., & Castanheiro, J. E. (2008). Esterification of free fatty acids with methanol using heteropolyacids immobilized on silica. *Catalysis Communications, 9,* 1996-1999.

Capeletti, M. R., Balzano, L., de la Puente, G., Laborde, M., & Sedran, U. (2000). Synthesis of acetal (1,1-diethoxyethane) from ethanol and acetaldehyde over acidic catalysts. *Applied Catalysis A: General, 198,* LI-L4.

Canakci, M. (2007). The potential of restaurant waste lipids as biodiesel feedstocks. *Bioresource Technology, 98*(1), 183-190.

Chabukswar, D. D., Heer, P. K. K. S., & Gaikar, V. G. (2013). Esterification of Palm Fatty Acid Distillate Using Heterogeneous Sulfonated Microcrystalline Cellulose Catalyst and Its Comparison with H2SO4Catalyzed Reaction. *Industrial & Engineering Chemistry Research, 52,* 7316-7326.

Chakrabarti, A., and Sharma, M. 1993. Cationic Ion Exchange Resins as Catalyst. *Reaction Polymer, 20,* 1-45.

Chakraborty, R., Gupta, A. K., & Chowdhury, R. (2014). Conversion of slaughterhouse and poultry farm animal fats and wastes to biodiesel: Parametric sensitivity and fuel quality assessment. *Renewable and Sustainable Energy Reviews, 29,* 120-134.

Chai, F., Cao, F. H., Zhai, F. Y., Chen, Y., Wang, X. H., & Su, Z. M. (2007). Transesterification of vegetable oil to biodiesel using a heteropolyacid solid catalyst. *Advanced Synthesis & Catalysis, 349,* 1057-1065.

Chai, M., Tu, Q., Lu, M., & Yang, Y. J. (2014). Esterification pretreatment of free fatty acid in biodiesel production, from laboratory to industry. *Fuel Processing Technology, 125*, 106-113.

Chakraborty, R., Gupta, A. K., & Chowdhury, R. (2014). Conversion of slaughterhouse and poultry farm animal fats and wastes to biodiesel: Parametric sensitivity and fuel quality assessment. *Renewable and Sustainable Energy Reviews, 29*, 120-134.

Chen, H-C., Ju, H-Y., Wu, T-T., Liu, Y-C., Lee, C-C., Chang, C., Chung, Y-L., & Shieh, C. J. (2011). Continuous production of lipase-catalyzed biodiesel in a packed-bed reactor: optimization and enzyme reuse study. *Journal of Biomedicine and Biotechnology, 2011*, 1-6.

Chen, J-W., Wu, W-T. 2003. Regeneration of Immobilised Candida Antarctica Lipase for Transesterification. *Journal of Bioscience and Bioengineering, 95*, 466-469.

Chen, Y-H., Wang, L-C., Tsai, C-H., & Shang, N-C. (2010). Continuous-flow esterification of free fatty acids in a rotating packed bed. *Industrial & Engineering Chemistry Research, 49*, 4117-4122.

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

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

Chin, S. Y., Ahmad, M. A. A., Kamaruzaman, M. R., & Cheng, C. K. (2015). Kinetic studies of the esterification of pure and dilute acrylic acid with 2-ethyl hexanol catalysed by Amberlyst 15. *Chemical Engineering Science, 129*, 116-125.

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

Chowdhury, A., Sarkar, D., & Mitra, D. (2016). Esterification of Free Fatty Acids Derived from Waste Cooking Oil with Octanol: Process Optimization and Kinetic Modeling. *Chemical Engineering & Technology, 39*, 730-740.

Chung, K-H., & Park, B-G. (2009). Esterification of oleic acid in soybean oil on zeolite catalysts with different acidity. *Journal of Industrial and Engineering Chemistry, 15*, 388-392.

Chung, K. H., Chang, D. R., & Park, B. G. (2008). Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts. *Bioresoure Technology, 99*, 7438-7443.

Corro, G., Tellez, N., Ayala, E., & Marinez-Ayala, A. (2010). Two-step biodiesel production from Jatropha curcas crude oil using SiO2·HF solid catalyst for FFA esterification step. *Fuel, 89*, 2815-2821.

Corro, G., Tellez, N., Bañuelos, F., & Mendoza, M. E. (2012). Biodiesel from Jatropha curcas oil using Zn for esterification step and solar radiation as energy source. *Fuel, 97*, 72-79.

Corro, G., Tellez, N., Jimenez, T., Tapia, A., Banuelos, F., & Vazquez-Cuchillo, O. (2011). Biodiesel from waste frying oil. Two step process using acidified SiO2 for esterification step. *Catalysis Today, 166*, 116-122.

Costa, A. A., Braga, P. R. S., de Macedo, J. L., Dias, J. A., & Dias, S. C. L. (2012). Structural effects of WO_3 incorporation on USY zeolite and application to free fatty acids esterification. *Microporous and Mesoporous Materials, 147*, 142-148.

Daniel Bastos de, R., Carlos Augusto, S., Vânya Márcia Duarte, P., & Maria Helena Caño de, A. (2015). Kinetic Modeling of Esterification Reaction of Free Fatty Acids Present in Macauba Oil Using a Cationic Resin as Catalyst. *Journal of Chemistry and Chemical Engineering, 9*, 153-161.

Das, S., Thakur, A. J., & Deka, D. (2014). Two-stage conversion of high free fatty acid Jatropha curcas oil to biodiesel using Bronsted acidic ionic liquid and KOH as catalysts. *Scientific World Journal, 2014*, 1-9.

de Oliveira, P. M., Farias, L. M., Morón-Villarreyes, J. A., & Montes D'Oca, M. G. (2016). Eco-friendly Pretreatment of Oil with High Free Fatty Acid Content Using a Sulfamic Acid/Ethanol System. *Journal of the American Oil Chemists' Society, 93*, 1393-1397.

Delhomme, C., Goh, S. L. M., Kühn, F. E., & Weuster-Botz, D. (2012). Esterification of bio-based succinic acid in biphasic systems: Comparison of chemical and biological catalysts. *Journal of Molecular Catalysis B: Enzymatic, 80*, 39-47.

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*, 2093-2109.

Deshmane, V. G., & Adewuyi, Y. G. (2013). Mesoporous nanocrystalline sulfated zirconia synthesis and its application for FFA esterification in oils. *Applied Catalysis A: General, 462-463*, 196-206.

Devassy, B., & Halligudi, S. (2005). Zirconia-supported heteropoly acids: Characterization and catalytic behavior in liquid-phase veratrole benzoylation. *Journal of Catalysis, 236*, 313-323.

Ding, J., Xia, Z., & Lu, J. (2012). Esterification and Deacidification of a Waste Cooking Oil (TAN 68.81 mg KOH/g) for Biodiesel Production. *Energies, 5*, 2683-2691.

Di Serio, M., Tesser, R., Pengmei, L., & Santacesaria, E. (2008). Heterogeneous catalysts for biodiesel production. *Energy & Fuels, 22*, 207-217.

Encinar, J. M., Sanchez, N., Martinez, G., & Garcia, L. (2011). Study of biodiesel production from animal fats with high free fatty acid content. *Bioresoure Technology, 102*, 10907-10914.

Endalew, A. K., Kiros, Y., & Zanzi, R. (2011). Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. *Biomass and Bioenergy, 35*, 3787-3809.

Eze, V. C., Fisher, J. C., Phan, A. N., & Harvey, A. P. (2017). Intensification of carboxylic acid esterification using a solid catalyst in a mesoscale oscillatory baffled reactor platform. *Chemical Engineering Journal, 322*, 205-214.

Fahed Banihani, F. (2016). Transesterification and Production of Biodiesel from Waste Cooking Oil: Effect of Operation Variables on Fuel Properties. *American Journal of Chemical Engineering, 4*, 154.

Fang, L., Zhang, K., Li, X., Wu, H., & Wu, P. (2012). Preparation of a Carbon-Silica Mesoporous Composite Functionalized with Sulfonic Acid Groups and Its Application to the Production of Biodiesel. *Chinese Journal of Catalysis, 33*, 114-122.

Feng, Y., He, B., Cao, Y., Li, J., Liu, M., Yan, F., & Liang, X. (2010). Biodiesel production using cation-exchange resin as heterogeneous catalyst. *Bioresoure Technology, 101*, 1518-1521.

Feng, Y., Zhang, A., Li, J., & He, B. (2011). A continuous process for biodiesel production in a fixed bed reactor packed with cation-exchange resin as heterogeneous catalyst. *Bioresoure Technology, 102*, 3607-3609.

Fernandes, S. A., Cardoso, A. L., & da Silva, M. J. (2012). A novel kinetic study of H3PW12O40 - catalyzed oleic acid esterification with methanol via 1H NMR spectroscopy. *Fuel Processing Technology, 96*, 98-103.

Figueiredo, K.C.S., Salim, V.M.M., Borges, C.P. 2010. Ethyl Oleate Production By Means of Pervaporation- Assisted Esterification Using Heterogeneous Catalyst. *Brazilian Journal of Chemical Engineering, 27*, 609-617.

Fogler, H. S. (2006). Elements of Chemical Reaction Engineering, 4th Edition: Prentice Hall PTR, 2006.

Fu, J., Chen, L., Lv, P., Yang, L., & Yuan, Z. (2015). Free fatty acids esterification for biodiesel production using self-synthesized macroporous cation exchange resin as solid acid catalyst. *Fuel, 154*, 1-8.

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

Gan, M., Pan, D., Ma, L., Yue, E., & Hong, J. (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*, 83-87.

Gan, S., Ng, H. K., Chan, P. H., & Leong, F. L. (2012). Heterogeneous free fatty acids esterification in waste cooking oil using ion-exchange resins. *Fuel Processing Technology, 102*, 67-72.

Gandi, G. K., Silva, V. M. T. M., & Rodrigues, A. E. (2005). Process development for dimethylacetal synthesis: Thermodynamics and reaction kinetics. *Industrial & Engineering Chemistry Research, 44*, 7287-7297.

Gandhi, N. N. (1995). Studies on the Lipozyme catalyzed synthesis of butyl laureate. *Biotechnology and Bioengineering, 46*, 1-12.

Geankoplis, C. J. (2003). *Transport Processes and Separation Process Principles* (4th ed.). New Jersey: Bernard Goodwin.

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

Gerpen, J.V. 2014. Animal Fats for Biodiesel Production. Retrived from http://articles.extension.org/pages/30256/animal-fats-for-biodiesel-production

Ghadge, S. V., & Raheman, H. (2005). Biodiesel production from mahua (Madhuca indica) oil having high free fatty acids. *Biomass and Bioenergy, 28*, 601-605.

Haigh, K. F., Abidin, S. Z., Vladisavljević, G. T., & Saha, B. (2013). Comparison of Novozyme 435 and Purolite D5081 as heterogeneous catalysts for the pretreatment of used cooking oil for biodiesel production. *Fuel, 111*, 186-193.

Haigh, K. F., Vladisavljević, G. T., Reynolds, J. C., Nagy, Z., & Saha, B. (2014). Kinetics of the pre-treatment of used cooking oil using Novozyme 435 for biodiesel production. *Chemical Engineering Research and Design, 92*, 713-719.

Hameed, B. H., Lai, L. F., & Chin, L. H. (2009). Production of biodiesel from palm oil (Elaeis guineensis) using heterogeneous catalyst: An optimized process. *Fuel Processing Technology, 90*, 606-610.

Han, Y., Lv, E., Ma, L., Lu, J., Chen, K., & Ding, J. (2015). Coupling membrane pervaporation with a fixed-bed reactor for enhanced esterification of oleic acid with ethanol. *Energy Conversion and Management, 106*, 1379-1386.

He, B. B., Van Gerpen, J. H., & Thompson, J. C. (2009). Sulfur content in selected oils and fats and their corresponding methyl esters. *Applied Engineering in Agriculture, 25*, 223-226.

Heydarzadeh, J.K., Amini, G., Khalizadeh, M.A., Pazouki, M., Ghoreyshi, A.A., Rabeai, M., and Najafpour, G.D. 2010. Esterification of Free Fatty Acids by Heterogeneous γ- Alumina- Zirconia Catalyst for Biodiesel Synthesis. *World Applied Science Journal, 9*, 1306-1312.

Hidayat, A., Rochmadi, Wijaya, K., & Budiman, A. (2016). Removal of free fatty acid in Palm Fatty Acid Distillate using sulfonated carbon catalyst derived from biomass wastefor biodiesel production. *IOP Conference Series: Materials Science and Engineering, 105*, 012026.

Hidayat, A., Rochmadi, Wijaya, K., Nurdiawati, A., Kurniawan, W., Hinode, H., Yoshikawa, K., & Budiman, A. (2015). Esterification of Palm Fatty Acid Distillate with High Amount of Free Fatty Acids Using Coconut Shell Char Based Catalyst. *Energy Procedia, 75*, 969-974.

Hincapié, G., Mondragón, F., & López, D. (2011). Conventional and in situ transesterification of castor seed oil for biodiesel production. *Fuel, 90*, 1618-1623.

Hossain, A. B. M. S., Boyce, A. N., Salleh, A., & Chandran, S. (2010a). Biodiesel production from waste soybean oil biomass as renewable energy and environmental recycled process. *African Journal of Biotechnology, 9*, 4233-4240.

Hossain, A. B. M. S., Boyce, A. N., Salleh, A., & Chandran, S. (2010b). Impacts of alcohol type, ratio and stirring time on the biodiesel production from waste canola oil. *African Journal of Agricultural Research, 5*, 1851-1859.

Hosseini, S., Janaun, J., & Choong, T. S. Y. (2015). Feasibility of honeycomb monolith supported sugar catalyst to produce biodiesel from palm fatty acid distillate (PFAD). *Process Safety and Environmental Protection, 98*, 285-295.

Hu, X., Wei, T., Liao, A., & Tong, Z. (2016). Use of acid cation-exchange resin for catalytic conversion of soybean acid oil to biodiesel. *Journal of Material Cycles and Waste Management, 18*, 123-131.

Ilgen, O. (2014). Investigation of reaction parameters, kinetics and mechanism of oleic acid esterification with methanol by using Amberlyst 46 as a catalyst. *Fuel Processing Technology, 124*, 134-139.

International Energy Outlook 2016. (2016). Retrieved from www.eia.gov/forecasts/ieo/ pdf/ 0484(2016).pdf.

Jaichandar, S., & Annamalai, K. (2011). The status of biodiesel as an alternative fuel for diesel engine- An overview. *Journal of Sustainable Energy & Environment, 2*, 71-75.

Jena, P. C., Raheman, H., Prasanna Kumar, G. V., & Machavaram, R. (2010). Biodiesel production from mixture of mahua and simarouba oils with high free fatty acids. *Biomass and Bioenergy, 34*, 1108-1116.

Jeřábek, K., Hanková, L., & Holub, L. (2010). Working-state morphologies of ion exchange catalysts and their influence on reaction kinetics. *Journal of Molecular Catalysis A: Chemical, 333*, 109-113.

Jin, T. W., Wang, B., Zeng, J. H., Yang, C., Wang, Y. Q., & Fang, T. (2015). Esterification of free fatty acids with supercritical methanol for biodiesel production and related kinetic study. *RSC Advances, 5*, 52072-52078.

Ju, I. B., Lim, H-W., Jeon, W., Suh, D. J., Park, M-J., & Suh, Y-W. (2011). Kinetic study of catalytic esterification of butyric acid and n-butanol over Dowex 50Wx8-400. *Chemical Engineering Journal, 168*, 293-302.

Kaul, S., Kumar, A., Bhatnagar, A.K., Goyal, H.B., and Gupta, A.K. 2003. Biodiesel: A Clean and Sustainable Fuel for Future. Scientific Strategies for Production of Non-edible Vegetable Oils for Use as Biofuels. All India seminar on national policy on non-edible oils as biofuels. SUTRA, IISc Bangalore.

Kaur, N., & Ali, A. (2015). Preparation and application of as solid catalyst for the esterification of fatty acids. *Renewable Energy, 81*, 421-431.

Khder, A. S., El-Sharkawy, E. A., El-Hakam, S. A., & Ahmed, A. I. (2008). Surface characterization and catalytic activity of sulfated tin oxide catalyst. *Catalysis Communications, 9*, 769-777.

Kim, M., DiMaggio, C., Salley, S. O., & Simon Ng, K. Y. (2012). A new generation of zirconia supported metal oxide catalysts for converting low grade renewable feedstocks to biodiesel. *Bioresoure Technology, 118*, 37-42.

Kim, M., DiMaggio, C., Yan, S., Wang, H., Salley, S. O., & Ng, K. Y. (2011). Performance of heterogeneous ZrO2 supported metaloxide catalysts for brown grease esterification and sulfur removal. *Bioresoure Technology, 102*, 2380-2386.

Kiss, A. A., Dimian, A. C., & Rothenberg, G. (2006). Solid acid catalysts for biodiesel production - Towards sustainable energy. *Advanced Synthesis & Catalysis, 348*, 75-81.

Klaewkla, R., Arend, M., and Hoelderich, W.F. 2011. A Review of Mass Transfer Controlling the Reaction Rate in Heterogeneous Catalyst Systems, Mass Transfer-Advanced Aspects, Dr. Hironori Nakajima, ISBN: 978-953-307-636-2 In Tech, Available from: http://cdn.intechopen.com/pdfs-wm/23539.pdf

Kolyaei, M., Zahedi, G., Nasef, M. M., & Azarpour, A. (2015). Optimization of biodiesel production from waste cooking oil using ion-exchange resins. *International Journal of Green Energy, 13*, 28-33.

Konwar, L. J., Wärnå, J., Mäki-Arvela, P., Kumar, N., & Mikkola, J.-P. (2016). Reaction kinetics with catalyst deactivation in simultaneous esterification and transesterification of acid oils to biodiesel (FAME) over a mesoporous sulphonated carbon catalyst. *Fuel, 166*, 1-11.

Kostic, M. D., Velickovic, A. V., Jokovic, N. M., Stamenkovic, O. S., & Veljkovic, V. B. (2016). Optimization and kinetic modeling of esterification of the oil obtained from waste plum stones as a pretreatment step in biodiesel production. *Waste Management, 48*, 619-629.

Kouzu, M., Nakagaito, A., & Hidaka, J-s. (2011). Pre-esterification of FFA in plant oil transesterified into biodiesel with the help of solid acid catalysis of sulfonated cation-exchange resin. *Applied Catalysis A: General, 405*, 36-44.

Kumar, G., Kumar, D., Singh, S., Kothari, S., Bhatt, S., & Singh, C. P. (2010). Continuous Low Cost Transesterification Process for the Production of Coconut Biodiesel. *Energies, 3*, 43-56.

Kumar, S., & Pal, A. (2014). A review of Bio-diesel as an alternative fuel for vehicles. *International Journal of Engineering Technology, 2*, 2349-4476.

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

Kuzminska, M., Backov, R., & Gaigneaux, E. M. (2015). Behavior of cation-exchange resins employed as heterogeneous catalysts for esterification of oleic acid with trimethylolpropane. *Applied Catalysis A: General, 504*, 11-16.

Lam, M. K., Lee, K. T., & Mohamed, A. R. (2009). Sulfated tin oxide as solid superacid catalyst for transesterification of waste cooking oil: An optimization study. *Applied Catalysis B: Environmental, 93*, 134-139.

Langpape, M., Millet, J. M. M., Ozkan, U. S., & Boudeulle, M. (1999). Study of cesium or cesium-transition metal-substitued keggin-type phosphomolybdic acid as isobutane oxidation catalysts. *Journal of Catalysis, 181*, 80-90.

Lee, D-W., & Lee, K-Y. (2014). Heterogeneous Solid Acid Catalysts for Esterification of Free Fatty Acids. *Catalysis Surveys from Asia, 18*, 55-74.

Leevijit, T., Wisutmethangoon, W., Prateepchaikul, G., Tongurai, C., and Allen, M. 2006. Trans-esterification of Palm Oil in Series of Continuous Stirred Tank Reactors. *Asian Journal on Energy and Environment, 7*, 336-346.

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

Li, M., Zheng, Y., Chen, Y., & Zhu, X. (2014). Biodiesel production from waste cooking oil using a heterogeneous catalyst from pyrolyzed rice husk. *Bioresoure Technology, 154*, 345-348.

Li, Z.-H., Lin, P.-H., Wu, J. C. S., Huang, Y.-T., Lin, K.-S., & Wu, K. C. W. (2013). A stirring packed-bed reactor to enhance the esterification–transesterification in biodiesel production by lowering mass-transfer resistance. *Chemical Engineering Journal, 234*, 9-15.

Lianhua, L., Pengmei, L., Wen, L., Zhongming, W., & Zhenhong, Y. (2010). Esterification of high FFA tung oil with solid acid catalyst in fixed bed reactor. *Biomass and Bioenergy, 34*, 496-499.

Liu, C-H., Huang, C-C., Wang, Y-W., Lee, D-J., & Chang, J-S. (2012). Biodiesel production by enzymatic transesterification catalyzed by Burkholderia lipase immobilized on hydrophobic magnetic particles. *Applied Energy, 100*, 41-46.

Liu, Y., Wang, L., & Yan, Y. (2009). Biodiesel synthesis combining pre-esterification with alkali catalyzed process from rapeseed oil deodorizer distillate. *Fuel Processing Technology, 90*, 857-862.

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

Lopez, D., Goodwinjr, J., & Bruce, D. (2007). Transesterification of triacetin with methanol on Nafion® acid resins. *Journal of Catalysis, 245*, 381-391.

López, D. E., Goodwin, J. G., Bruce, D. A., & Furuta, S. (2008). Esterification and transesterification using modified-zirconia catalysts. *Applied Catalysis A: General, 339*, 76-83.

Lotero, E., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D. A., & Goodwin, J. G. (2005). Synthesis of biodiesel via acid catalysis. *Industrial & Engineering Chemistry Research, 4*, 5353-5363.

Lu, X., Zhang, Y., Yu, Y., & JI, J. (2010). Deacification and esterification of waste cooking oil: Comparison of the coupled process with stand alone catalytic esterification and extraction processes. *Bioresources, 5*, 147-158.

Lucena, I. L., Silva, G. F., & Fernandes, F. A. N. (2008). Biodiesel production by esterification of oleic acid with methanol using a water adsorption apparatus. *Industrial & Engineering Chemistry Research, 47*, 6885-6889.

Luu, P. D., Truong, H. T., Van Luu, B., Pham, L. N., Imamura, K., Takenaka, N., & Maeda, Y. (2014). Production of biodiesel from Vietnamese Jatropha curcas oil by a co-solvent method. *Bioresour Technol, 173*, 309-316.

Ma, F., & Hanna, M. A. (1999). Biodiesel production: a review. *Bioresoure Technology, 70*, 1-15.

Ma, L., Han, Y., Sun, K., Lu, J., & Ding, J. (2015a). Kinetic and thermodynamic studies of the esterification of acidified oil catalyzed by sulfonated cation exchange resin. *Journal of Energy Chemistry, 24*, 456-462.

Ma, L., Han, Y., Sun, K., Lu, J., & Ding, J. (2015b). Optimization of acidified oil esterification catalyzed by sulfonated cation exchange resin using response surface methodology. *Energy Conversion and Management, 98*, 46-53.

Maceiras, R., Vega, M., Costa, C., Ramos, P., & Márquez, M. C. (2009). Effect of methanol content on enzymatic production of biodiesel from waste frying oil. *Fuel, 88*, 2130-2134.

Madankar, C. S., Pradhan, S., & Naik, S. N. (2013). Parametric study of reactive extraction of castor seed (Ricinus communis L.) for methyl ester production and its potential use as bio lubricant. *Industrial Crops and Products, 43*, 283-290.

Mahajani, S. M. (2000). Reactions of glyoxylic acid with aliphatic alcohols using cationic exchange resins as catalysts. *Reactive & Functional Polymers, 43*, 253-268.

Malaysia Energy Statistics Handbook 2016. (2016). Retrieved from http://meih.st.gov.my/documents/10620/57af5e2a-7695-4618-a111-4ba0a49ba992

Man, Z., Elsheikh, Y. A., Bustam, M. A., Yusup, S., Mutalib, M. I. A., & Muhammad, N. (2013). A Brønsted ammonium ionic liquid-KOH two-stage catalyst for biodiesel synthesis from crude palm oil. *Industrial Crops and Products, 41*, 144-149.

Mandake, M. B., Anekar, S. V., & Walke, S. M. (2013). Kinetic study of catalyzed and uncatalyzed esterification reaction of acetic acid with methanol. *American International Journal of Research in Science, Techonogy, Engineering & Mathematics, 3*, 114-121.

Manjunath, H., Hebbal, O., & Hemachandra Reddy, K. (2015). Process Optimization for Biodiesel Production from Simarouba, Mahua, and Waste Cooking Oils. *International Journal of Green Energy, 12*, 424-430.

Matsuhashi, H., Miyazaki, H., Kawamura, Y., Nakamura, H., & Arata, K. (2001). Preparation of a solid superacid of sulfated tin oxide with acidity higher than that of sulfated zirconia and its applications to aldol condensation and benzoylation. *Chemistry of Materials, 13*, 3038-3042.

Meher, L., Vidyasagar, D., & Naik, S. (2006). Technical aspects of biodiesel production by transesterification—a review. *Renewable and Sustainable Energy Reviews, 10*, 248-268.

Melero, J. A., Bautista, L. F., Iglesias, J., Morales, G., & Sánchez-Vazquez, R. (2014). Production of biodiesel from waste cooking oil in a continuous packed bed reactor with an agglomerated Zr-SBA-15/bentonite catalyst. *Applied Catalysis B: Environmental, 145*, 197-204.

Meneghetti, S. M. P., Meneghetti, M. R., Wolf, C. R., Silva, E.C., Lima, G.E.S., L, et al. 2006. Ethanolysis of Castor and Cottonseed Oil: A systematic Study Using Classical Catalysts. *Journal of the American Oil Chemists' Society*, 83, 819-822.

Miao, S., & Shanks, B. H. (2011). Mechanism of acetic acid esterification over sulfonic acid-functionalized mesoporous silica. *Journal of Catalysis, 279*, 136-143.

Miao, X., Li, R., & Yao, H. (2009). Effective acid-catalyzed transesterification for biodiesel production. *Energy Conversion and Management, 50*, 2680-2684.

Mohammad Fauzi, A. H., & Amin, N. A. S. (2012). An overview of ionic liquids as solvents in biodiesel synthesis. *Renewable and Sustainable Energy Reviews, 16*, 5770-5786.

Montes D'Oca, M. G., Soares, R. M., de Moura, R. R., & de Freitas Granjão, V. (2012). Sulfamic acid: An efficient acid catalyst for esterification of FFA. *Fuel, 97*, 884-886.

Moreno, J. I., Jaimes, R., Gómez, R., & Niño-Gómez, M. E. (2011). Evaluation of sulfated tin oxides in the esterification reaction of free fatty acids. *Catalysis Today, 172*, 34-40.

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

Mulalee, S., Srisuwan, P., & Phisalaphong, M. (2015). Influences of operating conditions on biocatalytic activity and reusability of Novozym 435 for esterification of free fatty acids with short-chain alcohols: A case study of palm fatty acid distillate. *Chinese Journal of Chemical Engineering, 23*, 1851-1856.

Musa, I. A. (2016). The effects of alcohol to oil molar ratios and the type of alcohol on biodiesel production using transesterification process. *Egyptian Journal of Petroleum, 25*, 21-31.

Mushtaq, M., Tan, I. M., Sagir, M., Tahir, M. S., & Pervaiz, M. (2016). A novel hybrid catalyst for the esterification of high FFA in Jatropha oil for biodiesel production. *Grasas Y Aceites, 67*, e150.

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

Nandiwale, K. Y., & Bokade, V. V. (2014). Process Optimization by Response Surface Methodology and Kinetic Modeling for Synthesis of Methyl Oleate Biodiesel over H3PW12O40Anchored Montmorillonite K10. *Industrial & Engineering Chemistry Research, 53,* 18690-18698.

Narasimharao, K., Brown, D., Lee, A., Newman, A., Siril, P., Tavener, S., & Wilson, K. (2007). Structure–activity relations in Cs-doped heteropolyacid catalysts for biodiesel production. *Journal of Catalysis, 248,* 226-234.

Narkhede, N., & Patel, A. (2013). Biodiesel Production by Esterification of Oleic Acid and Transesterification of Soybean Oil Using a New Solid Acid Catalyst Comprising 12-Tungstosilicic Acid and Zeolite Hβ. *Industrial & Engineering Chemistry Research, 52,* 13637-13644.

National Energy Balance 2015. (2015). Putrajaya, Malaysia: Suruhanjaya Tenaga Energy Commission.

Niju, S., Begum, K. M. M. S., & Anantharaman, N. (2016). Clam shell catalyst for continuous production of biodiesel. *International Journal of Green Energy, 13,* 1314-1319.

Nizah, M. F. R., Taufiq-Yap, Y. H., Rashid, U., Teo, S. H., Nur, Z. A. S., & Islam, A. (2014). Production of biodiesel from non-edible Jatropha curcas oil via transesterification using Bi2O3–La2O3 catalyst. *Energy Conversion and Management, 88,* 1257-1262.

No, S.-Y. (2011). Inedible vegetable oils and their derivatives for alternative diesel fuels in CI engines: A review. *Renewable and Sustainable Energy Reviews, 15,* 131-149.

Noda, L. K., de Almeida, R. M., Probst, L. F. D., & Gonçalves, N. S. (2005). Characterization of sulfated TiO2 prepared by the sol–gel method and its catalytic activity in the n-hexane isomerization reaction. *Journal of Molecular Catalysis A: Chemical, 225,* 39-46.

Noureddini, H., & Zhu, D. (1997). Kinetics of transeterification of soybean oil. *Journal of the American Oil Chemist's Society, 74,* 1458-1463.

Nuithitikul, K., & Prasitturattanachai, W. (2014). Activity of Sulfated Aluminium-Tin Mixed Oxides for the Esterification of Free Fatty Acids in Crude Palm Oil. *International Journal of Green Energy, 11,* 1097-1106.

Okuhara, T., Mizuno, N., & Misono, M. (1996). Catalytic chemistry of heteropoly compounds. *Advances in Catalysis, 41*, 113-252.

Okuhara, T., Watanabe, H., Nishimura, T., Inumaru, K., & Misono, M. (2000). Microstructure of cesium hydrogen salts of 12-tungstophosphoric acid relevant to novel acid catalysis. *Chemistry of Materials, 12*, 2230-2238.

Oliveira, C. F., Dezaneti, L. M., Garcia, F. A. C., de Macedo, J. L., Dias, J. A., Dias, S. C. L., & Alvim, K. S. P. (2010). Esterification of oleic acid with ethanol by 12-tungstophosphoric acid supported on zirconia☆. *Applied Catalysis A: General, 372*, 153-161.

Owusu, P. A., Asumadu-Sarkodie, S., & Dubey, S. (2016). A review of renewable energy sources, sustainability issues and climate change mitigation. *Cogent Engineering, 3*, 1-14

Özbay, N., Oktar, N., & Tapan, N. A. (2008). Esterification of free fatty acids in waste cooking oils (WCO): Role of ion-exchange resins. *Fuel, 87*, 1789-1798.

Park, Y-M., Lee, D-W., Kim, D-K., Lee, J-S., & 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*, 238-243.

Park, J.-Y., Kim, D-K., & Lee, J-S. (2010). Esterification of free fatty acids using water-tolerable Amberlyst as a heterogeneous catalyst. *Bioresoure Technology, 101*, S62-65.

Park, Y-M., Chung, S. H., Eom, H. J., Lee, J-S., & Lee, K-Y. (2010). Tungsten oxide zirconia as solid superacid catalyst for esterification of waste acid oil (dark oil). *Bioresoure Technology, 101*, 6589-6593.

Park, Y-M., Lee, J. Y., Chung, S-H., Park, I. S., Lee, S. Y., Kim, D. K., Lee, J-S., & Lee, K-Y. (2010). Esterification of used vegetable oils using the heterogeneous WO_3/ZrO_2 catalyst for production of biodiesel. *Bioresoure Technology, 101*, S59-S61.

Patel, A., & Brahmkhatri, V. (2013). Kinetic study of oleic acid esterification over 12-tungstophosphoric acid catalyst anchored to different mesoporous silica supports. *Fuel Processing Technology, 113*, 141-149.

Patel, A., & Narkhede, N. (2012). 12-Tungstophosphoric Acid Anchored to Zeolite Hβ: Synthesis, Characterization, and Biodiesel Production by Esterification of Oleic Acid with Methanol. *Energy & Fuels, 26*, 6025-6032.

Pereira, A. L. C., Marchetti, S. G., Albornoz, A., Reyes, P., Oportus, M., & Rangel, M. d. C. (2008). Effect of iron on the properties of sulfated zirconia. *Applied Catalysis A: General, 334*, 187-198.

Peres, A., Lunelli, B., and Maciel, F. 2013. Application of Biomass to Hydrogen and Syngas Production, *Chemical Engineering Transactions, 32*, 589-594.

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

Pina, C. G., & Meirelles, A. J. A. (2000). Deacification of corn oil by solvent extraction in a perforated rotating disc column. *Journal of the American Oil Chemists' Society, 77*, 553-559.

Pinmai, K., & Laosiripojana, N. (2014). *Modelling of continuous operation esterification of fatty acid catalyzed by Amberlyst 15 in the presence of molecular sieve*. 5th International Conference on Sustainable Energy and Environment (SEE2014): Science, Technology and Innovation for ASEAN Green Growth, 19-21 November 2014, Bangkok, Thailand.

Pires, L. H. O., de Oliveira, A. N., Jr, O. V. M., Angélica, R. S., Costa, C. E. F. d., Zamian, J. R., do Nascimento, L. A. S., & Filho, G. N. R. (2014). Esterification of a waste produced from the palm oil industry over 12-tungstophosforic acid supported on kaolin waste and mesoporous materials. *Applied Catalysis B: Environmental, 160-161*, 122-128.

Pirola, C., Galli, F., Bianchi, C.L., Boffito, D.C., Comazzi, A., and Manenti, F. 2014. Vegetable Oil Deacidification by Methanol Heterogeneously Catalyzed Esterification in (Monophasic Liquid)/Solid Batch and Continuous Reactors. *Energy and Fuels*, 28, 5236-5240.

Prateepchaikul, G., Somnuk, K., & Allen, M. (2009). Design and testing of continuous acid-catalyzed esterification reactor for high free fatty acid mixed crude palm oil. *Fuel Processing Technology, 90*, 784-789.

Punsuvon, V., Nokkaew, R., Somkliang, P., Tapanwong, M., & Karnasuta, S. (2015). The Optimization of Esterification Reaction for Biodiesel Production from

Animal Fat. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 37*, 846-853.

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

Said, N. H., Ani, F. N., & Said, M. F. M. (2015). Review of the Production of Biodiesel from Waste Cooking Oil Using Solid Catalysts. *Journal of Mechanical Engineering and Sciences, 8*, 1302-1311.

Santacesaria, E., Tesser, R. Di Serio, M., Gaetano, D., & Garcia Agreda, A. 2007. Kinetics and Mass Transfer of Free Fatty Acids Esterification with Methanol in a Tubular Packed Bed Reactor: A Key Pretreatment in Biodiesel Production. *Industrial and Engineering Chemistry Research, 46*, 5113-5121.

Saravanan, K., Tyagi, B., & Bajaj, H. C. (2012). Sulfated zirconia: an efficient solid acid catalyst for esterification of myristic acid with short chain alcohols. *Catalysis Science & Technology, 2*, 2512.

Saravanan, K., Tyagi, B., & Bajaj, H. C. (2016). Nano-crystalline, mesoporous aerogel sulfated zirconia as an efficient catalyst for esterification of stearic acid with methanol. *Applied Catalysis B: Environmental, 192*, 161-170.

Saravanan, K., Tyagi, B., Shukla, R. S., & Bajaj, H. C. (2015). Esterification of palmitic acid with methanol over template-assisted mesoporous sulfated zirconia solid acid catalyst. *Applied Catalysis B: Environmental, 172-173*, 108-115.

Sarkar, A., Ghosh, S. K., & Pramanik, P. (2010). Investigation of the catalytic efficiency of a new mesoporous catalyst SnO2/WO3 towards oleic acid esterification. *Journal of Molecular Catalysis A: Chemical, 327*, 73-79.

Satheesh, K., JagadeeshBabu, P. E., & Saidutta, M. B. (2015). Two-step Biodiesel Production and its Kinetics Studies Using Indion-190/AmberliteIRA-900 from Waste Cooking Oil. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 37*, 92-100.

Sert, E., Buluklu, A. D., Karakuş, S., & Atalay, F. S. (2013). Kinetic study of catalytic esterification of acrylic acid with butanol catalyzed by different ion exchange resins. *Chemical Engineering and Processing: Process Intensification, 73*, 23-28.

Sepulveda, J. H., Vera, C. R., Yori, J. C., & Badano, J. M. (2011). $H_3PW_{13}O_{40}$ (HPA), An efficient and reusable catalyst for biodiesel production related reactions esterification of oleic acid and etherification of glycerol. *Quimica Nova, 34*, 601-606.

Shambhu, V. B., & Bhattacharya, T. K. (2015). Production of Biodiesel from Jatropha Curcas L. Oil Having High Free Fatty Acids Content. *Ama-Agricultural Mechanization in Asia Africa and Latin America, 46*, 63-66.

Sharma, Y.C., Singh, B., and Upadhyay, S.N. 2008. Advancements in Development and Characterization of Biodiesel: A Review. *Fuel*, **87**: 2355-2373.

Sharma, Y. C., & Singh, B. (2009). Development of biodiesel: Current scenario. *Renewable and Sustainable Energy Reviews, 13*, 1646-1651.

Sharma, Y. C., & Singh, B. (2010). A hybrid feedstock for a very efficient preparation of biodiesel. *Fuel Processing Technology, 91*, 1267-1273.

Sharma, Y. C., Singh, B., & Korstad, J. (2010). High yield and conversion of biodiesel from a nonedible feedstock (Pongamia pinnata). *Journal of Agricultural and Food Chemistry, 58*, 242-247.

Singh, S. P., & 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*, 200-216.

Shibasaki-Kitakawa, N., Tsuji, T., Chida, K., Kubo, M., & Yonemoto, T. 2010. Simple Continuous Production Process of Biodiesel Fuel from Oil with High Content of Free Fatty Acid Using Ion-Exchange Resin Catalysts. *Energy Fuels, 24*, 3634-3638.

Shibasaki-Kitakawa, N., Honda, H., Kuribayashi, H., Toda, T., Fukumura, T., & Yonemoto, T. (2007). Biodiesel production using anionic ion-exchange resin as heterogeneous catalyst. *Bioresoure Technology, 98*, 416-421.

Shu, Q., Yang, B., Yuan, H., Qing, S., & Zhu, G. (2007). Synthesis of biodiesel from soybean oil and methanol catalyzed by zeolite beta modified with La3+. *Catalysis Communications, 8*, 2159-2165.

Singh, S., & Patel, A. (2014). 12-Tungstophosphoric acid supported on mesoporous molecular material: synthesis, characterization and performance in biodiesel production. *Journal of Cleaner Production, 72,* 46-56.

Sivaramakrishnan, R., & Muthukumar, K. (2012). Isolation of thermo-stable and solvent-tolerant Bacillus sp. lipase for the production of biodiesel. *Applied Biochemistry and Biotechnology, 166,* 1095-1111.

Srilatha, K., Lingaiah, N., Sai Prasad, P.S., Prabhavathi Devi, B.L.A., & Prasad, R.B.N. 2011. Kinetics of the Esterification of Palmitic Acid with Methanol Catalyzed by 12-tungstophosphoric Acid Supported on ZrO_2. *Reaction Kinetics Mechanisms and Catalysis*, 104, 211-226.

Srilatha, K., Sree, R., Prabhavathi Devi, B. L., Sai Prasad, P. S., Prasad, R. B., & Lingaiah, N. (2012). Preparation of biodiesel from rice bran fatty acids catalyzed by heterogeneous cesium-exchanged 12-tungstophosphoric acids. *Bioresour Technol, 116*, 53-57.

Soares, D., Pinto, A.F., Goncalves, A.G., Mitchell, D.A., & Krieger, N. 2013. Biodiesel Production from Soybean Soapstock Acid Oil by Hydrolysis in Subcritical Water Followed by Lipase-catalyzed Esterification Using a Fermented Solid in a Packed-bed Reactor. *Biochemical Engineering Journal*, *81*, 15-23.

Son, S. M., Kimura, H., & Kusakabe, K. (2011). Esterification of oleic acid in a three-phase, fixed-bed reactor packed with a cation exchange resin catalyst. *Bioresoure Technology, 102,* 2130-2132.

Southeast Asia Energy Outlook 2015. Retrieved from https://www.iea.org/publications /freepublications/publication/WEO2015_SouthEastAsia.pdf

Srilatha, K., Sree, R., Prabhavathi Devi, B. L., Sai Prasad, P. S., Prasad, R. B., & Lingaiah, N. (2012). Preparation of biodiesel from rice bran fatty acids catalyzed by heterogeneous cesium-exchanged 12-tungstophosphoric acids. *Bioresoure Technology, 116*, 53-57.

Strategy Paper 17: Sustainable usage of energy to support growth. (2015). Retrieved from http://www.epu.gov.my/sites/default/files/Strategy%20Paper%2017.pdf

Sudarsanam, P., Mallesham, B., Reddy, P.S., and Reddy, B.M. 2013. Highly Promising Sulfate Ion Promoted M-ZrO2 (M=Al2O3 and CeO2) Heterogeneous Solid Acids

for Biodiesel-derived Glycerol Esterification. *Journal of Chemical Science and Technology, 2*, 161-168.

Sun, K., Lu, J., Ma, L., Han, Y., Fu, Z., & Ding, J. (2015). A comparative study on the catalytic performance of different types of zeolites for biodiesel production. *Fuel, 158*, 848-854.

Supple, B., Howard-Hildige, R., Gonzalez-Gomez, E., & Leahy, J. J. (2002). The effect of steam treating waste cooking oil on the yield of methyl ester. *Journal of the American Oil Chemists' Society, 79*, 175-178.

Suprarukmi, D. D., Sudrajat, B. A., & Widayat. (2015). Kinetic Study on Esterification of Oleic Acid with Ultrasound Assisted. *Procedia Environmental Sciences, 23*, 78-85.

Suresh, R., Antony, J. V., Vengalil, R., Kochimoolayil, G. E., & Joseph, R. (2017). Esterification of free fatty acids in non- edible oils using partially sulfonated polystyrene for biodiesel feedstock. *Industrial Crops and Products, 95*, 66-74.

Tan, T., Lu, J., Nie, K., Deng, L., & Wang, F. (2010). Biodiesel production with immobilized lipase: A review. *Biotechnology Advances, 28*, 628-634.

Tanabe, K., & Holderich, W. F. (1999). Industrial application of solid acid-base catalysts. *Applied Catalysis A: General, 181*, 399-434.

Tariq, M., Ali, S., & Khalid, N. (2012). Activity of homogeneous and heterogeneous catalysts, spectroscopic and chromatographic characterization of biodiesel: A review. *Renewable and Sustainable Energy Reviews, 16*, 6303–6316.

Tashtoush, G. M., Al-Widyan, M. I., & Al-Jarrah, M. M. (2004). Experimental study on evaluation and optimization of conversion of waste animal fat into biodiesel. *Energy Conversion and Management, 45*, 2697-2711.

Teixeira, D. A., da Motta, C. R., Ribeiro, C. M. S., & de Castro, A. M. (2017). A rapid enzyme-catalyzed pretreatment of the acidic oil of macauba (Acrocomia aculeata) for chemoenzymatic biodiesel production. *Process Biochemistry, 53*, 188-193.

Tesser, R., Casale, L., Verde, D., Di Serio, M., & Santacesaria, E. (2009). Kinetics of free fatty acids esterification: Batch and loop reactor modeling. *Chemical Engineering Journal, 154*, 25-33.

Tesser, R., Casale, L., Verde, D., Di Serio, M., & Santacesaria, E. (2010). Kinetics and modeling of fatty acids esterification on acid exchange resins. *Chemical Engineering Journal, 157*, 539-550.

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

Thiruvengadaravi, K. V., Nandagopal, J., Baskaralingam, P., Sathya Selva Bala, V., Vijayalakshmi, P., Dinesh Kirupha, S., & Sivanesan, S. (2012). The Esterification of Free Fatty Acids in Karanja (Pongamia Pinnata) Oil Using Phosphoric Acid Modified Zeolite. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 34*, 2234-2241.

Tian, K., & Li, Z. (2016). High-yielding, one-pot, and green production of biodiesel from waste grease using wet cells of a recombinant Escherichia coli strain as catalyst. *Biochemical Engineering Journal, 115*, 30-37.

Tropecêlo, A. I., Casimiro, M. H., Fonseca, I. M., Ramos, A. M., Vital, J., & Castanheiro, J. E. (2010). Esterification of free fatty acids to biodiesel over heteropolyacids immobilized on mesoporous silica. *Applied Catalysis A: General, 390*, 183-189.

Turapan, S., Yotkamchornkun, C., and Nuithikul, K. 2010. Esterification of Free Fatty Acids in Crude Palm Oil with Sulfated Zirconia: Effect of Calcination Temperature. *World Academy of Science, Engineering and Technology, 41*, 310-314.

Turkay, S., & Civelekoglu, H. (1991). Deacification of sulfur olive oil. I. Single-stage liquid-liquid extraction of miscella with ethyl alcohol. *Journal of the American Oil Chemists' Society, 68*, 83-86.

Ullah, Z., Bustam, M. A., & Man, Z. (2015). Biodiesel production from waste cooking oil by acidic ionic liquid as a catalyst. *Renewable Energy, 77*, 521-526.

United States of Departmnet of Agriculture (2017). Global Palm Oil Production 2017/2018. Retrieved from http://www.globalpalmoilproduction.com/

Van Gerpen, J., Shanks, J., Pruszko, R., Clements, D., & Knothe, G. (2004). *Biodiesel Production Technology, August 2002-January 2004*. Retrieved from Colorado, United State: https://www.nrel.gov/docs/fy04osti/36244.pdf

Veljkovic, V., Lakicevic, S., Stamenkovic, O., Todorovic, Z., & Lazic, M. (2006). Biodiesel production from tobacco (Nicotiana tabacum L.) seed oil with a high content of free fatty acids. *Fuel, 85*, 2671-2675.

Venkatesh, Mohamed Shamshuddin, S.Z., Shyamsundar, M., and Vasanth, V.T. 2014. Biodiesel Synthesis from Pongamia pinnata Oil over Modified CeO_2 Catalysts. *Journal of the Mexican Chemical Society, 58*, 378-385.

Vieira, S. S., Magriotis, Z. M., Graça, I., Fernandes, A., Ribeiro, M. F., Lopes, J. M. F. M., . . . Saczk, A. A. (2017). Production of biodiesel using HZSM-5 zeolites modified with citric acid and SO 4 2− /La 2 O 3. *Catalysis Today, 279*, 267-273.

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

von Harbou, E., Yazdani, A., Schmitt, M., Großmann, C., & Hasse, H. (2013). Reaction Kinetics for Reactive Distillation Using Different Laboratory Reactors. *Industrial & Engineering Chemistry Research, 52*, 624-637.

Wan, Z., Lim, J. K., & Hameed, B. H. (2015). Chromium–tungsten heterogeneous catalyst for esterification of palm fatty acid distillate to fatty acid methyl ester. *Journal of the Taiwan Institute of Chemical Engineers, 54*, 64-70.

Wang, K., Zhang, X., Zhang, J., Zhang, Z., Fan, C., & Han, P. (2016). Theoretical Study on Free Fatty Acid Elimination Mechanism for Waste Cooking Oils to Biodiesel over Acid Catalyst. *Journal of Molecular Graphics and Modelling, 66*, 41-46.

Wang, L., Dong, X., Jiang, H., Li, G., & Zhang, M. (2014). Ordered mesoporous carbon supported ferric sulfate: A novel catalyst for the esterification of free fatty acids in waste cooking oil. *Fuel Processing Technology, 128*, 10-16.

Wang, R., Zhou, W-W., Hanna, M. A., Zhang, Y-P., Bhadury, P. S., Wang, Y., Song, B-A., & Yang, S. (2012). Biodiesel preparation, optimization, and fuel properties from non-edible feedstock, Datura stramonium L. *Fuel, 91*, 182-186.

Warabi, Y., Kusdiana, D., & Saka, S. 2004. Reactivity of Triglycerides and Fatty Acids of Rapeseed Oil in Supercritical Alcohols. *Bioresource Technology, 91*, 283-287.

Wilson, K., & Clark, J. H. (2000). Solid acids and their use as environmentally friendly catalysts in organic synthesis. *Pure and Applied Chemistry, 72*, 1313-1319.

Xiao, Y., Gao, L. J., Xiao, G. M., Fu, B. S., & Niu, L. (2012). Experimental and Modeling Study of Continuous Catalytic Transesterification to Biodiesel in a Bench-Scale Fixed-Bed Reactor. *Industrial & Engineering Chemistry Research, 51*, 11860-11865.

Xue, J., Grift, T. E., & Hansen, A. C. (2011). Effect of biodiesel on engine performances and emissions. *Renewable and Sustainable Energy Reviews, 15*, 1098-1116.

Yan, J., Li, A., Xu, Y., Ngo, T. P., Phua, S., & Li, Z. (2012). Efficient production of biodiesel from waste grease: one-pot esterification and transesterification with tandem lipases. *Bioresoure Technology, 123*, 332-337.

Yan, S., DiMaggio, C., Mohan, S., Kim, M., Salley, S. O., & Ng, K. Y. S. (2010). Advancements in Heterogeneous Catalysis for Biodiesel Synthesis. *Topics in Catalysis, 53*, 721-736.

Yang, Z., Zhou, C., Zhang, W., Li, H., & Chen, M. (2010). β-MnO2 nanorods: A new and efficient catalyst for isoamyl acetate synthesis. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 356*, 134-139.

Yao, L., & Hammond, E. G. (2006). Isolation and Melting Properties of Branched-chain Esters from Lanolin. *Journal of the American Oil Chemists' Society, 83*, 547-552.

Yunus, N. B. M., Roslan, N. A. B., Yee, C. S., & Abidin, S. Z. (2016). Esterification of Free Fatty Acid in Used Cooking Oil Using Gelular Exchange Resin as Catalysts. *Procedia Engineering, 148*, 1274-1281.

Yusuf, N. N. A. N., Kamarudin, S. K., & Yaakub, Z. (2011). Overview on the current trends in biodiesel production. *Energy Conversion and Management, 52*, 2741-2751.

Zhang, H., Ding, J., Qiu, Y., & Zhao, Z. (2012). Kinetics of esterification of acidified oil with different alcohols by a cation ion-exchange resin/polyethersulfone hybrid catalytic membrane. *Bioresoure Technology, 112*, 28-33.

Zhang, Y., Dube, M. A., McLean, D. D., & Kates, M. (2003). Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technology, 89*, 1-16.

Zhang, Y., Dubé, M. A., McLean, D. D., & Kates, M. (2003). Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. *Bioresource Technology, 90*, 229-240.

Zhang, M., Sun, A., Meng, Y., Wang, L., Jiang, H., & Li, G. (2015). Catalytic Performance of Biomass Carbon-Based Solid Acid Catalyst for Esterification of Free Fatty Acids in Waste Cooking Oil. *Catalysis Surveys from Asia, 19*, 61-67.

Zhang, Z.Y., Hidajat, K., & Ray, A.K. 2001. Determination of Adsorption and Kinetic Parameters for Methyl *tert*-butyl Ether Synthesis from *tert*-butyl Alcohol and Methanol. *Journal of Catalysis, 200*, 209-221.

Zhou, W., Konar, S. M., & Boocock, D. G. B. (2003). Ethyl esters from the single-phase base-catalyzed ethanolysis of vegetable oils. *Journal of the American Oil Chemists' Society, 80*, 367-371.