UNIVERSITI PUTRA MALAYSIA

PREPARATION OF SOLID HETEROGENEOUS CATALYSTS FOR BIODIESEL PRODUCTION FROM PALM-BASED FEEDSTOCK

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PREPARATION OF SOLID HETEROGENEOUS CATALYSTS FOR BIODIESEL PRODUCTION FROM PALM-BASED FEEDSTOCK

By

THEAM KOK LEONG

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

April 2015

Especially Dedicated To

My Dearest Father & Mother	**Theam Lam Seng** **Wong Yoke Ngoh**
My Beloved Wife	**Lim Ai Sun**
My Cute Daughters	**Theam Yu Xuan** **Theam Yu Tong**

Without whose love and continued support, this thesis would not have been possible

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

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April, 2015

Chairman: **Professor Taufiq Yap Yun Hin, PhD**
Faculty: **Science**

Palm fatty acid distillate (PFAD) and palm stearin (PS) are side products from physical refining of crude palm oil, and it can be a good alternative feedstock for biodiesel production. In this study, PS and PFAD were chemically converted into biodiesel using solid base and acid catalysts. The reaction parameters of the catalytic reaction were thoroughly investigated and optimized via Response Surface Methodology. The optimal values of these factors were found to be related to the chemical and physical properties of the feedstock. Four catalysts were synthesized and used to produce biodiesel and these were (i) nanoscale calcium methoxide (CMS), (ii) zirconia supported calcium methoxide (CMSS), (iii) sulfated zirconia (SZ) and, (iv) ball-milled sucrose-derived carbon acid catalyst (S400M). CMS catalyst possesses a novel morphology due to the sonication treatment during preparation of the catalyst. The nanoscale particles gave a high surface area which may provide more active sites for reactants to anchor and react. The results showed that CMS has excellent basicity and high catalytic ability as a heterogeneous solid base catalyst. This catalyst gave 94.7 % of biodiesel yield within 3 hours at temperature of 70°C, methanol molar ratio and catalyst loading of 6 and 1 wt% of PS, respectively. Besides, CMSS catalyst gave the highest biodiesel yield of 98 % at temperature of 70°C, reaction time of 125 min, using 3 % catalyst loading and methanol to PS molar ratio of 11:1. Furthermore, the recycling experiment results showed it had a longer catalyst lifespan, and the zirconia support had proven to be the good stabilizing agent to the calcium methoxide catalyst. This catalyst appeared to be a promising candidate to replace the existing homogeneous catalysts for biodiesel production as it requires short reaction time with high reusability. Moreover, SZ has been extensively studied and optimized as catalyst for the esterification of free fatty acid in PFAD with methanol. The effect of sonication on the phase structure and its catalytic activity was investigated. TPD-NH_3 coupled with mass spectrometer analysis revealed that the first thermal desorption peak of SZ represented the actual acidity of the catalyst. SZ catalyst exhibited a good catalytic performance as a heterogeneous solid acid catalyst which used to esterify PFAD and 97 % of free fatty acid (FFA) conversion was achieved with 2 hours of reaction time, despite its low surface area. A noticeable deactivation of catalyst has been experimentally detected under the optimized reaction conditions. The characterization results showed that the deactivation is due to the leaching of sulfate groups from the catalyst. Furthermore, the other heterogeneous solid acid catalyst i.e. S400M was prepared in the present study which aims to improve the esterification process and reduce the generation of waste from biodiesel production. The experimental results showed that S400M exhibited good catalytic activity in the esterification of PFAD, providing maximum FFA conversion of 94% at optimum parameters. The good catalytic activity of the aforementioned catalyst in the biodiesel reaction could be attributed to the presence of optimal number of catalytically active acid site density on its surface. The mechanochemical treatment was the good tool to improve the catalytic activity of carbon catalyst by adding extra active sites for esterification of FFA and to intensify the acid strength of the catalyst.

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

PENYEDIAAN PEPEJAL PEMANGKIN HEREROGEN UNTUK PENGHASILAN BIODIESEL DARI BAHAN SUAPAN BERASASKAN SAWIT

Oleh

THEAM KOK LEONG

April, 2015

Pengerusi: **Profesor Taufiq Yap Yun Hin, PhD**
Fakulti: **Sains**

Asid lemak sawit sulingan (PFAD) dan stearin sawit (PS) adalah produk sampingan daripada penapisan fizikal minyak sawit mentah dan ia boleh menjadi bahan mentah alternatif yang baik untuk penghasilan biodiesel. Dalam kajian ini, PS dan PFAD telah ditukar secara kimia kepada biodiesel dengan menggunakan pemangkin pepejal alkali and asid. Faktor-faktor yang berkait dengan tindak balas pemangkinan telah dikaji dengan teliti dan dioptimumkan melalui Kaedah Respon Permukaan. Nilai yang optimum untuk faktor-faktor ini didapati berkaitan dengan sifat-sifat kimia dan fizikal bahan mentah. Empat pemangkin telah dihasilkan dan digunakan untuk menghasilkan biodiesel dan ini adalah (i) kalsium methoxide dalam saiz nanometer (CMS), (ii) kalsium methoxide disokong oleh zirkonia (CMSS), (iii) zirkonia yang bersulfat (SZ) dan, (iv) pemangkin asid karbon yang dikisar (S400M). Pemangkin CMS memiliki morfologi yang khas disebabkan rawatan sonikasi semasa penyediaan pemangkin tersebut. Zarah nano memberikan kawasan luas permukaan yang tinggi dan ia boleh menyediakan tapak-tapak yang aktif untuk bahan mentah bertindak balas. Hasil kajian ini menunjukkan bahawa CMS sangat beralkali ia boleh digunakan sebagai pemangkin pepejal alkali. Pemangkin ini memberikan 94.7% hasil biodiesel dalam tempoh 3 jam pada suhu 70 °C, nisbah mol methanol kepada PS 6:1 dan 1 % mangkin dari berat PS. Selain itu, pemangkin CMSS memberikan hasil biodiesel yang tertinggi iaitu 98% pada suhu 70C, masa tindak balas 125 min dengan menggunakan 3% pemangkin dan nisbah mol metanol kepada PS 11:1. Seterusnya, keputusan eksperimen kitar semula menunjukkan ia mempunyai jangka hayat yang lebih panjang dan sokongan zirkonia telah membuktikan untuk menjadi agen yang baik untuk menstabilkan pemangkin kalsium methoxide. Pemangkin ini muncul sebagai pengganti yang berpotensi kepada pemangkin homogen yang sedia ada dalam penghasilan biodiesel disebabkan ia memerlukan masa tindak balas yang singkat dan penggunaan semula yang tinggi. Selain itu, SZ telah dikaji dan dioptimumkan sebagai pemangkin dalam penukaran asid lemak bebas dalam PFAD kepada biodiesel. Kesan sonikasi pada struktur fasa pemangkin dan aktivitinya yang telah dikaji. Analisis TPD-NH_3 dengan jisim spektrometer mendedahkan bahawa puncak penyaherapan terma pertama untuk SZ mewakili keasidan sebenar pemangkin tersebut. SZ menunjukkan kemampuan pemangkinan yang baik dalam penukaran PFAD kepada biodiesel sebanyak 97%. Pertukaran tersebut dicapai dengan masa tindak balas selama 2 jam, walaupun luas permukaan BET yang rendah. Penyahaktifan pemangkin telah dikesan di bawah keadaan optimum tindak balas. Keputusan analysis menunjukkan bahawa penyahaktifan tersebut disebabkan oleh pelarutan kumpulan sulfat dari pemangkin. Tambahan pula, heterogen asid pemangkin pepejal iaitu S400M telah disediakan dalam kajian ini yang bertujuan untuk meningkatkan hasil pengesteran dan mengurangkan penghasilan sisa-sisa daripada pembuatan biodiesel. Keputusan eksperimen menunjukkan bahawa S400M merupakan pemangkin yang mempunyai aktiviti yang tinggi dalam penukaran PFAD kepada biodiesel sebanyak 94 % pada parameter optimum. Aktiviti yang tinggi pada pemangkin ini dalam tindakbalas penghasilan biodiesel boleh dikaitkan dengan kehadiran tapak aktif asid yang berketumpatan tinggi pada permukaannya. Rawatan pengisaran adalah teknik yang baik untuk meningkatkan aktiviti pemangkin karbon pemangkin dengan menambah tapak aktif untuk penukaran FFA dan meningkatan kekuatan asid pemangkin.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ANOVA	Analysis of variance
BET	Brunauer Emmer Teller
CCD	Central Composite Design
CMS	Calcium methoxide
CMSS	Cacium methoxide with support
FAME	Fatty acid methyl ester
FESEM	Field Emission Scanning Electron Microscopy
FFA	Free fatty acid
FWHM	Full-Width at Half Maximum
GC	Gas Chromatography
JCPDS	Joint Committee on Powder Diffraction Standards
OVAT	One-Variable-At-A-Time
PFAD	Palm fatty acid distillate
PS	Palm stearin
RSM	Response Surface Methodology
SZ	Sulfated Zirconia
T_{max}	Temperature at peak maximum
TCD	Thermal Conductivity Detector
TPD	Temperature Programmed Desorption
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Global Energy Demand

Fossil fuels play an important role on worldwide energy production. As the population growth and industrialization increases, the demand for utilization of energy increases speedily. It causes fossil fuel's resources decreasing and consequent in increasing the price of fossil fuels. Hence, The World Energy Forum predicted that fossil oil will be exhausted in less than 10 decades, if new oil wells are not found (Sharma & Singh, 2009). Besides that, environmental pollution problems have become alarming rate due to the extensive usage of fossil fuels. Therefore, the development of alternative sources to fossil fuels, specifically petroleum-based is required to fulfill the energy demand throughout the world. Renewable energy has gained most focus recently due to its potential to replace fossil fuel, particularly for transportation. Renewable energy from biomass has been successfully developed and used worldwide to reduce the use of fossil fuels. Furthermore, based on the study of International Energy Agency (IEA), only energy produced from renewable sources and waste has the highest potential to replace fossil-fuel energy among other renewable resources as shown in Figure 1.1 (International Energy Agency, 2013)

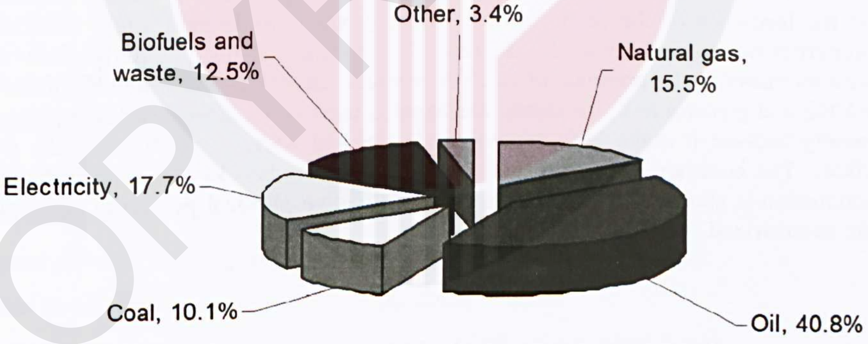


Figure 1.1. **World total energy comsumption by fuel (Mtoe) in Year 2013. Total: 8,918 million tonnes of oil equivalent (Mtoe). (International Energy Agency, 2013)**

The increasing awareness of the depletion of fossil-fuel resources and greenhouse-gas emissions from the fuel combustion has become the main concern to many countries all around the world (Zabeti *et al.,* 2009). Many researchers have started to utilize lipids from biomass to supply power usage because of the gradual increases in the price of petroleum, limited resources of fossil oils and environmental concerns (Laksmono *et al.*, 2013; Sharma *et al.*, 2010; Taufiq-Yap *et al.*, 2011). The environmental benefits of biodiesel have made it more and more attractive in this recent moment. Biodiesel is defined as non-petroleum-based diesel fuel, which is derived from the fats and oils of biomass and used as combusting fuel to generate power in ordinary diesel engines (Agarwal, 2007). The animal fats and vegetable oils belong to lipids, which are the essential products of metabolism of living things, functioning as energy storage. Yet, there are many problems dealt with using the oil and fat from living organism in diesel engines, such as the large molecular size of triglycerides, high viscosity and low combustion efficiency. All of these can be solved if the oils and fats are chemically modified to biodiesel, which has the similar properties with petroleum-based diesel (Murugesan *et al.*, 2009; Wang *et al.*, 2006).

1.2 Biodiesel

The term biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from oils or fats of living organism, recognized as B100 in biodiesel standard ASTM D6751, and referring to fatty acid methyl esters (FAME) in European biodiesel standard EN 14214. Furthermore, the prefix "bio" can be related to the biodegradable characteristic of the biodiesel fuel (Gerhard, 2009). Biodiesel is a clear amber yellow liquid with a viscosity similar to that of petroleum diesel. Biodiesel is non-flammable and, in contrast to petroleum diesel, is non-explosive, with a flash point at 150 °C for biodiesel as compared to 187 °C for petroleum diesel (Ma *et al.*, 1998). The fatty acid composition of the triglyceride used in biodiesel production has a significant influence on the physical and chemical properties of biodiesel. Depending on the feedstock of the production, the final product would have slight variation in properties due to the fatty acids' identities. In the transesterification, triglycerides react with methanol in the presence of catalyst in which ultimately leads to the formation of FAME and glycerol as by-products. Methanol is used as the alcohol for the production, mainly because it is the least-expensive alcohol and widely available (Knothe *et al.*, 2004). The common fatty acid that found in some feedstocks that used in biodiesel production is shown in Table 1.1. In Table 1.2, some physical properties of biodiesel are summarized.

Table 1.1 : The chemical structures of common fatty acids (Lin *et al.*, 2010)

Fatty acid	Chemical structure
Lauric (12 : 0)	$CH_3(CH_2)_{10}COOH$
Myristic (14 : 0)	$CH_3(CH_2)_{12}COOH$
Palmitic (16 : 0)	$CH_3(CH_2)_{14}COOH$
Stearic (18 : 0)	$CH_3(CH_2)_{16}COOH$
Oleic (18 : 1)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Linoleic (18 : 2)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Linolenic (18 : 3)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Arachidic (20 : 0)	$CH_3(CH_2)_{18}COOH$
Behenic (22 : 0)	$CH_3(CH_2)_{20}COOH$
Erucic (22 : 1)	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$

Table 1.2 : Physical properties of biodiesel (Demirbas, 2009)

Common name	Biodiesel
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C_{14}-C_{24} methyl esters or $C_{15-25}H_{28-48}O_2$
Kinematic viscosity range (mm^2/s, at 40°C)	3.3 - 5.2
Density range (kg/m^3, at 15 °C)	860 - 894
Boiling point range (°C)	> 184
Flash point range (°C)	147 - 177
Distillation range (°C)	197 - 327
Vapour pressure (mm Hg, at 22°C)	< 5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odour	Light musty or soapy odour
Biodegradability	More degradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidising agents

1.3 Sources of Biodiesel

Triglyceride which is basically a triester is the major lipid form of energy storage in most living creatures, consisting of a glycerol molecule (triol) esterified with three fatty acid molecules (carboxylic acids with a long hydrocarbon chain). The different types of triglycerides arise from various types of the esterified fatty acids. Fatty acids are generally categorized into two main classes, which are saturated (no C = C) and unsaturated (C = C). Different fatty acids contain distinct numbers of C = C double bonds and number of carbon atoms in their hydrocarbon chain. Therefore, after transesterification in biodiesel production, the biodiesel contains a variety of fatty acid alkyl esters with different hydrocarbon chains, depending on the source of triglycerides used. Other than triglycerides, other compounds contained in natural oils and fats include pigments, waxes, sterols, glycolipids, lipoproteins, hydrocarbons, long chain alcohols, carbohydrates, vitamins (A, D, E and K) in minor concentrations and free fatty acids (Lotero *et al.*, 2005).

Renewable in nature and in environmental friendly ways leads to virgin vegetable oils become most popular as feedstock for the biodiesel synthesis. There are two main categories of vegetable oils, which are edible and non-edible. Edible vegetable oils like canola, soybean, rapeseed, sunflower and corn have been used for biodiesel production and found to be good as a diesel substitute. The non-edible vegetables such as madhuca indica, Jatropha curcas and Pongamia pinnata have also found to be suitable (Tapanes, Gomes, Mesquita & Ceva, 2008).

In order to prevent competition between food and fuel, palm fatty acid distillate is an inedible side product from physical refining of crude palm oil, and it will be a good alternative feedstock for biodiesel production. It exists in solid form at room temperature and it contains high levels of free fatty acid (>82%) compared to its counter parts. However, only 4% of palm fatty acid distillate was estimated for each production of crude palm oil (Top, 2010). The main fatty acid components in palm fatty acid distillate (PFAD) included palmitic acid (C16:0), oleic acid (C18:1), linoleic acid (C18:2), lauric acid (C12:0), and myristic acid (C14:0) (Chongkhong *et al.*, 2007; Mongkolbovornkij *et al.*, 2010). Figure 1.2 shows the fatty composition of PFAD.

Due to the high cost of feedstock, palm stearin (PS) may become a promising alternative of biodiesel production feedstock. Palm stearin is the solid fraction obtained by fractionation of palm oil after crystallization at a controlled temperature. It is not used directly for edible purposes due to its high melting point ranging from 44 to 56 °C (De Martini Soares *et al.*, 2009; Norizzah *et al.*, 2004; Pantzaris, 2000). The liquid fraction is known as palm olein and more expensive as compared to solid fraction due to its wider usage. The physical characteristics of palm stearin differ significantly from those of palm olein. It contains mainly palmitic acid and other fatty acids (Lai *et al.*, 2000). The high degree of saturation of palm stearin poses problems in the manufacture of edible fats such as margarine and shortening as it confers low plasticity to the end product, thus limiting the commercial exploitation of the material (Lai *et al.*, 2000; Laia *et al.*, 2000). Figure 1.3 shows the fatty acid composition of PS.

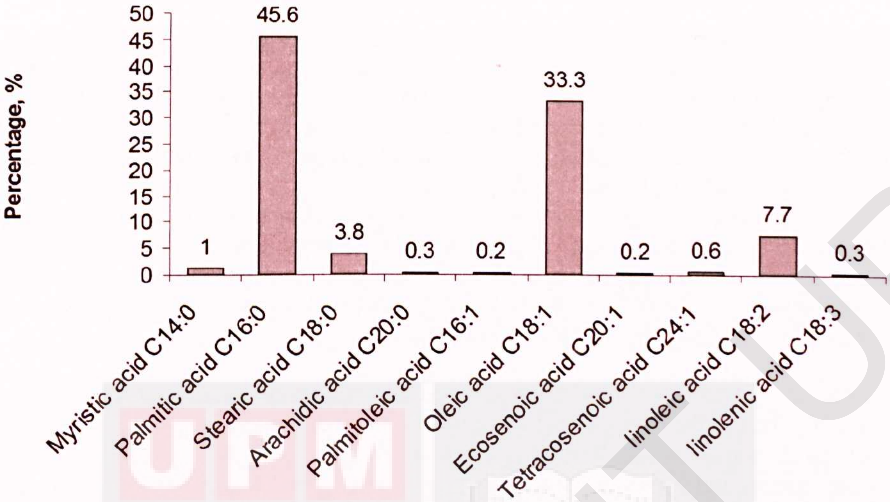


Figure 1.2. **Fatty acid composition of palm fatty acid distillate. (Chongkhong *et al.*, 2009)**

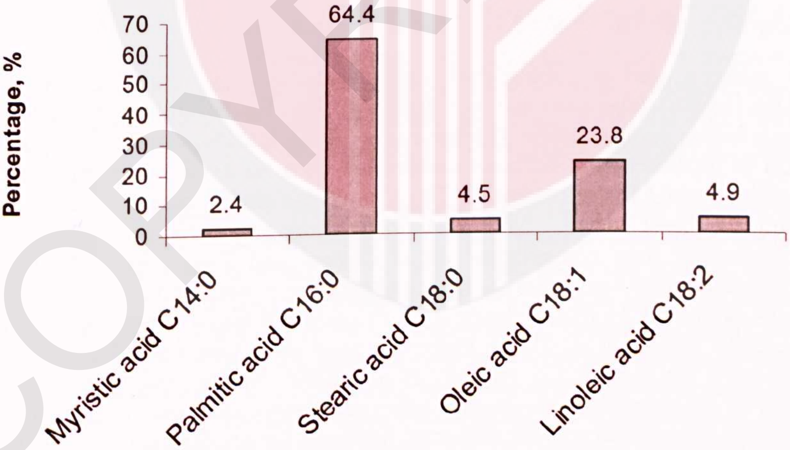


Figure 1.3. Fatty acid composition of palm stearin. (Soares et al., 2009)

1.4 Advantages of Biodiesel Production

The use of biodiesel has attracted huge attention from worldwide countries due to its availability, renewability, non-toxicity, harmless gas emission as well as its biodegradability (Demirbas *et al.,* 2009). The biodiesel synthesized from biomass is biodegradable and has unlimited sources used for synthesis, comparing to the petroleum which is a limited resource. Biodiesel is reported to be highly biodegradable in fresh water and soil medium. About 90-98% of biodiesel is mineralized in 21-28 days under aerobic as well as anaerobic conditions (Leung *et al.*, 2010; Mudge and Pereira, 1999; Sharma *et al.*, 2008). Some authors reported biodiesel-nature fuel blend enhanced the biodegradation rate of diesel fuel and gasoline through cometabolism (Pasqualino *et al.*, 2006; Sharma *et al.*, 2008). This fuel is nontoxic as the raw materials are mainly the vegetable oils and the animal fat.

Moreover, the emission resulted from biodiesel combustion contributes to nearly no harmful effect to the environment since the emission of hazardous gases is significantly reduced (Demirbas *et al.,* 2008). In particular, biodiesel provides significant reductions in particulates and carbon monoxide over petroleum diesel fuel. Furthermore, biodiesel contains virtually trace amount of sulphur, so SO_2 emissions are reduced in direct proportion to the petrol-diesel replacement (Canakci *et al.*, 2009). The oxygen content of biodiesel is 10 – 11% by weight, offering a pathway to recycle carbon dioxide through emission (Lotero *et al.,* 2006). Therefore, air pollution, green house effect and global warming are no longer the problems taken into account power generation by combusting diesel fuel. Instead of using the refined virgin oils, manufacturers also use the waste oils collected from food industries as the lipid feedstock of biodiesel production. Reusing of the waste oils has the benefits of producing environmental-friendly diesel fuel and reducing the amount of waste oil disposal, which leads to water pollution. This is a proper utilization and management of waste oils as combusting fuel (Krawczyk, 1996; Talebian-Kiakalaieh *et al.*, 2013).

The most common used as a diesel-fuel quality factor is cetane number (CN). It is related to the ignition-delay time and combustion quality. Better ignition properties are come from a higher cetane number (Meher *et al.*, 2006). Ramos *et al.* (2009) reported that the CN of biodiesel from different sources has been assumed to ranging from 48 (grape biodiesel) to 61 (palm biodiesel). The CN of biodiesel is generally higher than for conventional diesel due to biodiesel has longer fatty acid carbon chain and more saturated molecules than conventional diesel (Bajpai and Tyagi, 2006; Dermibas, 2005). Some researchers found that the higher percentage of saturated fatty acid methyl ester such as palmitic (C16:0) and stearic (C18:0) acids will lead to a better CN (Bajpai and Tyagi, 2006; Knothe *et al.*, 2003). Therefore, palm methyl ester which rich in these fatty acids gave the highest CN (Ramos *et al.*, 2009). Smoke-opacity percentages during each of the vegetable oils methyl ester were lower than that with petroleum diesel. Besides, it was observed that with pure biodiesel the acceleration time increased by approximately 8 % compared to the normal diesel fuel. (Fontaras *et al.*, 2009). The oxygen content in biodiesel accelerates the combustion process due to the increase of the homogeneity of oxygen with the fuel during combustion and retarded its oxidation potential. Consequently, the combustion efficiency of biodiesel is higher than petroleum diesel (Demirbas, 2007).

1.5 Problem Statement on Biodiesel Production

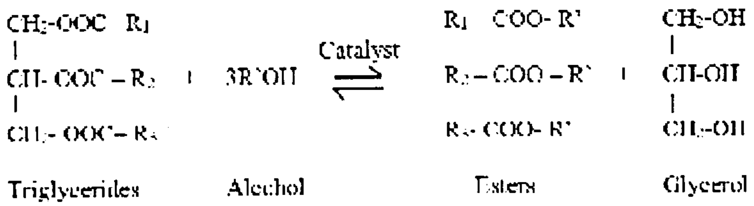
In spite of the advantages of biodiesel stated above, biodiesel has higher cloud point and pour point compared to conventional diesel (Prakash, 1998). Besides that, other disadvantages of biodiesel include its higher viscosity, low energy content, low volatility and injector coking. Furthermore, the biodiesel still has to improve in the future to lower the calorific value, the horsepower output, and its comparatively higher emission of nitrogen oxides (Buyukkaya, 2010). The cost of biodiesel, however, is the main obstacle to commercialization which usually more expensive than petroleum-based diesel fuel from 10 – 50 % (Leung and Guo, 2006). Feedstock costs usually account for 80% of the total cost of the biodiesel production (Demirbas *et al.*, 2008). In order to reduce the cost of raw materials used in biodiesel production, waste oils used for frying food are recycled to be the biodiesel lipid feedstock instead of neat oils. However, the waste oils collected from different restaurants and food industries possess wide ranges of properties, compositions and qualities. Thus, the pre-treatments of waste oils are required to get rid of the impurities and undesired substances which lessen the efficiency of biodiesel production (Yaakob *et al.*, 2013). Furthermore, the line between food and fuel economies is blurred as both fields competing for the same oil resources. In other words, biodiesel is competing with the food industry for limited land availability for the plantation of oil crops (Demirbas, 2008).

Solid heterogeneous catalyst although it can reuse and separate from the reaction mixture, however it has a lower catalytic activity as compared with homogeneous catalyst. Furthermore, solid catalyst also has mass transfer limitation during the catalytic reaction.

1.6 Synthesis of Biodiesel

Biodiesel can be produced through several pathways, such as pyrolysis, micro emulsion, supercritical methanol method and transesterification of triglycerides and esterification of free fatty acids with alcohols of low molecular weight (Fukuda *et al.*, 2001; Ghoreishi and Moein, 2013; Kusdiana and Saka, 2001; Ma and Hanna, 1999; Schwab *et al.*, 1988; Singh & Singh, 2010; Tan *et al.*, 2010; Warabi *et al.*, 2004).

Transesterification is one of the most commercially compatible methods employed universally to produce biodiesel. Transesterification process is necessary to convert the lipid sources which are oils and fats to much lower molecular species, such as fatty acid methyl esters. A stoichiometry ratio of 3:1 of alcohol to vegetable oils or animal fats is needed for a completion of the transesterification process. Normally, to have an optimum yield of ester from transesterification process, excess alcohol is needed. The present of catalyst usually can enhance the reaction rate and biodiesel yield. Due to the transesterification is a reversible process, excess alcohol is used to shift the equilibrium process to the product side (Ma and Hanna, 1999). Transesterification of triglyceride by using alcohol is shown in the following figure:



$$\begin{array}{l}CH_2\text{-}OOC\ R_1\\ |\\ CH\text{-}OOC-R_2\\ |\\ CH_2\text{-}OOC-R_3\end{array} + 3R'OH \overset{\text{Catalyst}}{\rightleftharpoons} \begin{array}{l}R_1\ COO\text{-}R'\\ R_2-COO-R'\\ R_3\text{-}COO\text{-}R'\end{array} + \begin{array}{l}CH_2\text{-}OH\\ |\\ CH\text{-}OH\\ |\\ CH_2\text{-}OH\end{array}$$

(Equation. 1.1)

Esterification is a chemical reaction involved free fatty acid (FFA) and alcohol as reactants to produce fatty acid alkyl ester and water with the present of acid catalyst (Zhang *et al.*, 2003). The one-step reaction of esterification of FFA is reported to be faster than transesterification of triglycerides as the latter reaction involved multi-steps reaction to form ester (Warabi *et al.*, 2004). The esterification reaction is shown in the following equation:

$$\underset{\text{Fatty Acid}}{R_1\text{-}COOH} + \underset{\text{Alcohol}}{ROH} \overset{\text{Catalyst}}{\rightleftharpoons} \underset{\text{Ester}}{R_1\text{-}COOR} + \underset{\text{Water}}{H_2O} \qquad \text{(Equation. 1.2)}$$

Among all the alcohol used in synthesizing the biodiesel; methanol and ethanol are the most commonly, especially the methanol. This is because methanol consists of suitable physico-chemical properties, low cost, mild reaction conditions and easy phase separation. Apart from that, higher and secondary alcohols is a good pouring characteristics of their fatty esters at low temperature, however, high price and expensive reaction conditions make these reactants unsuitable for biodiesel production (Leung *et al.*, 2010; Stamenković *et al.*, 2011).

1.7 Objectives

The major objectives of this research study are as followings:

i. To prepare four solid heterogeneous catalysts and characterize these catalysts using X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area measurement, Field Emission Scanning Electron Microscopy (FESEM) and Temperature Programmed Desorption coupled with mass spectrometer.

ii. To determine the effect of various parameters to the production of biodiesel through transesterification and esterification reaction from palm stearin and palm fatty acid distillate via solid acid and base catalysts..

iii. To determine the optimum conditions of biodiesel production via Response Surface Methodology (RSM).

iv. To characterize the optimized biodiesel using acid value test, Atomic Absorption Spectroscopy, CHNS analysis and Gas Chromatography (GC).

REFERENCES

Agarwal, A.K. (2007). Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science* 33: 233–271.

Akoh, C.C., Chang, S-W., Lee, G-C. and Shaw, J-F. (2007). Enzymatic Approach to Biodiesel Production. *Journal of Agricultural and Food Chemistry* 55: 8995–9005.

Atadashi, I.M., Aroua, M.K., Abdul Aziz, A.R. and Sulaiman, N.M.N. (2012). The effects of water on biodiesel production and refining technologies: A review. *Renewable and Sustainable Energy Reviews* 16: 3456– 3470.

Avramović, J.M., Stamenković, O.S., Todorović, Z.B., Lazić, M.L. and Veljković, V.B. (2010). The optimization of the ultrasound-assisted base-catalyzed sunflower oil methanolysis by a full factorial design. *Fuel Processing Technology* 91: 1551–1557.

Bala, B.K. (2005). Studies on biodiesels from transformation of vegetable oils for diesel engines. *Energy Education Science Technology* 15: 1–43.

Balasubramanian, R.K. and Obbard, J.P. (2011). Heterogeneous catalytic transesterification of phosphatidylcholine. *Bioresource Technology* 102: 1942-1946.

Bajpai, D. and Tyagi, V.K. (2006). Biodiesel: source, production, composition properties and its benefits. *Journal of Oleo Science* 55: 487–502.

Bancquart, S., Vanhove, C., Pouilloux,Y. and Barrault, J. (2001). Glycerol transesterification with methyl stearate over solid basic catalysts: I. Relationship between activity and basicity. *Applied Catalysis A: General* 218: 1–11.

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

Barnwal, B. K. and Sharma, M. P. (2005). Prospects of biodiesel production from vegetable oils in India. *Renewable and Sustainable Energy Reviews* 9: 363-378.

Bart, J.C.J., Palmeri, N. and Cavallaro, S. 2010. *Biodiesel science and technology from soil to oil.* Boca, Raton, Boston, New York, Washington DC: CRC Press.

Benjaram, M. R., Sreekanth, P.M., Reddy, V.R. (2005). Modified zirconia solid acid catalysts for organic synthesis and transformations. *Journal of Molecular Catalysis A: Chemical* 225: 71–78.

Berrios, M., Gutiérrez, M.C., Martín, M.A. and Martín, A. (2009). Application of the factorial design of experiments to biodiesel production from lard. *Fuel Processing Technology* 90: 1447–1451.

Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S. and Escaleira, L.A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta* 76: 965–977.

Boey, P.-L., Maniam, G. P. and Hamid, S. A. (2011). Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review. *Chemical Engineering Journal* 168: 15-22.

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.

Boffito, D.C., Pirola, C., Galli, F., Michele, A.D. and Bianchi, C.L. (2013). Free fatty acids esterification of waste cooking oil and its mixtures with rapeseed oil and diesel. *Fuel* 108: 612–619.

Boro, J., Thakur, A. J. and Deka, D. (2011). Solid oxide derived from waste shells of Turbonilla striatula as a renewable catalyst for biodiesel production. *Fuel Processing Technology* 92: 2061-2067.

Bournay, L., Casanave, D., Delfort, B., Hillion, G. and Chodorge, J. A. (2005). New heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerin produced by biodiesel plants. *Catalysis Today* 106: 190–192.

Box, G. E. P. and Wilson, K. B. (1951). On the Experimental Attainment of Optimum Conditions. *Journal of the Royal Statistical Society. Series B (Methodological)* 13: 1–45

Box, G. E. P. and Wilson, K. B. 1992. On the Experimental Attainment of Optimum Conditions. In *Breakthroughs in Statistics: Volume II: Methodology and Distribution*, ed. S. Kotz, and N.L. Johnson, pp. 270–310. New York: Springer.

Buyukkaya, E. (2010). Effetcs of Biodiesel on a DI Diesel Engine Performance, Emission and Combustion Characteristics. *Fuel* 89: 3099–3105.

Canakci, M. and Gerpen, J.V. (1999). Biodiesel production via acid catalysis. *Journal of Transactions of the ASAE* 42: 1203–1210.

Canakci, M. and Gerpen, J. V. (2003). A pilot plant to produce biodiesel from high free fatty acid feedstocks. *Transactions of the ASAE* 46: 945–955.

Canakci, M., Ozsezen, A.N., Arcaklioglu, E. and Erdil, A. (2009). Prediction of performance and exhaust emissions of a diesel engine fuelled with biodiesel produced from waste frying palm oil. *Expert System Application* 36: 9268–9280.

Chabukswar, D.D., Heer, Parminder Kaur, K.S. and Gaikar, V.G. (2013). Esterification of Palm Fatty Acid Distillate Using Heterogeneous Sulfonated Microcrystalline Cellulose Catalyst and Its Comparison with H_2SO_4 Catalyzed Reaction. *Industrial & Engineering Chemistry Research* 52: 7316–7326.

Chang, T-S., Masood, H., Yunus, R., Rashid, U., Thomas Choong, S.Y., and Biak, D.R.A. (2012). Activity of Calcium Methoxide Catalyst for Synthesis of High Oleic Palm Oil Based Trimethylolpropane Triesters as Lubricant Base Stock. *Industrial Engineering Chemistry Research* 51: 5438–5442.

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

Chen, G., Shan, R., Shi, J. and Yan, B. (2014). Ultrasonic-assisted production of biodiesel from transesterification of palm oil over ostrich eggshell-derived CaO catalysts. *Bioresource Technology* 171: 428-432.

Chin, L.H., Abdullah, A.Z. and 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.

Chongkhong, S., Tongurai, C., Vhetpattananondh, P. and Bunyakan, C. (2007). Biodiesel Production by Esterification of Palm Fatty Acid Distillate. *Biomass and Bioenergy* 31: 563–568.

Chongkhong, S., Tongurai, C. and Chetpattananondh, P. (2009). Continuous Esterification for Biodiesel Production from Palm Fatty Acid Distillate using Economical Process. *Renewable Energy* 34 : 1059–1063.

Chorkendorff, I.. and Niemantsverdriet, J.W. 2003. *Concepts of Modern Catalysis and Kinetics*. Germany: Wiley-VCH.

Chuah, G.K., Jaenicke, S., Cheong, S.A. and Chan, K.S. The influence of preparation conditions on the surface area of zirconia. *Applied Catalysis A: General* 145 : 267-284.

Cravotto, G. and Cintas, P. (2006). Power ultrasound in organic synthesis: Moving cavitational chemistry from academia to innovative and large-scale applications. *Chemical Society Reviews* 35: 180-196.

Dermibas, A. (2005). Biodiesel production from vegetable oils via catalytic and noncatalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science* 31: 466–487.

Deshmane, V.G., Gogate, P.R. and Pandit, A.B. (2009). Ultrasound-Assisted Synthesis of Biodiesel from Palm Fatty Acid Distillate. *Industrial & Engineering Chemistry Research* 48: 7923–7927.

Devulapelli, V.G. and Weng, H-S. (2009). Esterification of 4-methoxyphenylacetic acid with dimethyl carbonate over mesoporous sulfated zirconia. *Catalysis Communications* 10: 1711–1717.

Demirbas, A. (2008). Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy Conversion and Management* 49: 125–130.

Demirbas, A. (2009). Progress and Recent Trends in Biodiesel Fuels. *Energy Conversion and Management* 50: 14–34.

De Martini Soares, F.A.S., da Silva, R.C., da Silva, K.C.G., Lourenco, M.B., Soares, D.F. and Gioielli, L.A. (2009). Effects of chemical interesterification on physicochemical properties of blends of palm stearin and palm olein. *Food Research International* 42: 1287–1294.

Di Serio, M., Cozzolino, M., Tesser R., Patrono, P., Pinzari, F., Bonelli, B. and Santacesaria, E. (2007). Vanadyl phosphate catalysts in biodiesel production. *Applied Catalysis A: General* 320: 1–7.

Di Serio, M., Tesser, R., Pengmei, L. and Santacesaria, E. (2008). Heterogeneous Catalysts for Biodiesel Production. *Energy & Fuels* 22: 207–217.

Dossin, T.F., Reyniers, M.F., Berger, R.J. and Marin, G.B. (2006). Simulation of heterogeneously MgO-catalysed transesterification for fine-chemical and biodiesel industrial production. *Applied Catalysis B* 67: 136–148.

Duangkamol, Y., 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: 2011–2016.

Eckey, E.W. (1956). Esterification and interesterification. *Journal of the American Oil Chemists' Society* 33: 575–579.

Encinar, J.M., González, J.F. and Rodríguez-Reinares, A. (2005). Biodiesel from Used Frying Oil. Variables Affecting the Yields and Characteristics of the Biodiesel. *Industrial & Engineering Chemistry Research* 44: 5491–5499.

Encinar, J. M., González. J. F., Rodríguez, J. J. and Tejedor, A. (2002) Biodiesel Fuels from Vegetable Oils: Transesterification of Cynara cardunculus L. Oils with Ethanol. *Energy & Fuels* 16: 443–450.

Farag, H.A., El-Maghraby, A. and Taha, N.A. (2011). Optimization of factors affecting esterification of mixed oil with high percentage of free fatty acid. *Fuel Processing Technology* 92: 507–510.

Ferrari, A.C. and Robertson, J. (2000). Interpretation of Raman spectra of disordered and amorphous carbon. *Physical Review B* 61: 14095–14107.

Ferreira, S.L.C., Bruns, R.E., Ferreira, H.S., Matos, G.D., David, J.M., Brandão, G.C., da Silva, E.G.P., Portugal, L.A., dos Reis, P.S., Souza, A.S., dos Santos, W.N.L. (2007). Box-Behnken design: An alternative for the optimization of analytical methods. *Analytica Chimica Acta* 597: 179–186.

Fontaras, G., Karavalakis, G., Kousoulidou, M., Tzamkiozis, T., Ntziachristos, L., Bakeas, E., Stournas, St. and Samaras, Z. (2009). Effect of biodiesel on passenger car fuel consumption, regulated and non-regulated pollutant emissions over legislated and real-world driving cycles. *Fuel* 88: 1608–1617.

Franceschini, G. and Macchietto, S. (2008). Model-based design of experiments for parameter precision: State of the art. *Chemical Engineering Science* 63: 4846–4872.

Fu, X., Li, D., Chen, J., Zhang, Y., Huang, W., Zhu, Y., Yang, J. and Zhang, C. (2013). A microalgae residue based carbon solid acid catalyst for biodiesel production. *Bioresource Technology* 146: 767-770.

Fukuda, H., Kondo, A., and Noda, H. (2001). Biodiesel fuel production by transesterification of oils. *Journal of Bioscience and Bioengineering*, 92: 405–416.

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

Gao, S., Chen, X., Wang, H., Mo, J., Wu, Z., Liu, Y. and Weng, X. (2013). Ceria supported on sulfated zirconia as a superacid catalyst for selective catalytic reduction of NO with NH_3. *Journal of Colloid and Interface Science* 394, 515–521.

Granados, M. L., Poves, M. D. Z., Alonso, D. M., Mariscal, R., Galisteo, F. C., Moreno-Tost, R., Santamaria, J. and Fierro, J. L. G. (2007). Biodiesel from sunflower oil by using activated calcium oxide. *Applied Catalysis B: Environmental* 73: 317– 326.

Georgogianni, K.G., Katsoulidis, A.P., Pomonis, P.J. and Kontominas, M.G. (2009). Transesterification of soybean frying oil to biodiesel using heterogeneous catalyst. *Fuel Processing Technology* 90: 671–676.

Gerhard, K. (2009). Biodiesel and renewable diesel: A comparison. *Progress in Energy and Combustion Science* 36: 364–373.

Ghoreishi, S.M. and Moein, P. (2013). Biodiesel synthesis from waste vegetable oil via transesterification reaction in supercritical methanol. *The Journal of Supercritical Fluids* 76: 24–31.

Gryglewicz S. (1999). Rapeseed oil methyl esters preparation using heterogeneous catalysts. *Bioresource Technology* 70:249–253.

Gryglewicz S. (2000). Alkaline-earth metal compounds as alcoholysis catalysts for ester oils synthesis. *Applied Catalysis A: General* 192: 23–28.

Hanrahana, G. and Lu, K. (2006). Application of Factorial and Response Surface Methodology in Modern Experimental Design and Optimization. *Critical Reviews in Analytical Chemistry* 36: 141–151.

Helwani, Z., Othman, M.R., Aziz, N., Fernando, W.J.N, Kim, J. (2009). Technologies for production of biodiesel focusing on green catalytic techniques: a review. *Fuel Processing Technology* 90: 1502–1514.

Ho, W. W. S., Ng, H. K., Gan, S. and Tan, S. H. (2014). Evaluation of palm oil mill fly ash supported calcium oxide as a heterogeneous base catalyst in biodiesel synthesis from crude palm oil. *Energy Conversion and Management* 88: 1167-1178.

Hoque, M. E., Singh, A. and Chuan, Y. L. (2011). Biodiesel from low cost feedstocks: The effects of process parameters on the biodiesel yield. *Biomass and Bioenergy* 35: 1582-1587.

Hui, Y. H. (1996). Bailey's Industrial Oil and Fat Products, Industrial and Consumer Nonedible Products from Oils and Fats: Wiley.

International Energy Agency. Key world energy statistic; 2013. Retrieved 17 December 2013 from http://www.iea.org/publications/freepublications/publication/KeyWorld2013_FINAL_WEB.pdf

Jacobson K, Gopinath R, Meher LC, Dalai AK. (2008). Solid acid catalyzed biodiesel production from waste cooking oil. *Applied Catalysis B: Environmental* 85: 86–91.

Ji, W., Xu, L., Wang, X., Hu, Z., Yan, Q. and Chen, Y. 2002. Effects of ball milling on the doped vanadium phosphorus oxide catalysts. *Catalysis Today* 74: 101–110.

Kafuku, G., Mbarawa, M. (2010). Biodiesel production from Croton megalocarpus oil and its process optimization. *Fuel* 89: 2556–2560.

Karabas, H. (2013). Biodiesel production from crude acorn (*Quercus frainetto L.*) kernel oil: An optimisation process using the Taguchi method. *Renewable Energy* 53: 384–388.

Katada, N., Hatanaka, T., Ota, M., Yamada, K., Okumura, K. and Niwa, M. (2009). Biodiesel production using heteropoly acid-derived solid acid catalyst $H_4PNbW_{11}O_{40}/WO_3–Nb_2O_5$. *Applied Catalysis A: General* 363: 164–168.

Kawashima, A., Matsubara, K. and Honda, K. (2008). Development of heterogeneous base catalysts for biodiesel production. *Bioresource Technology* 99: 3439–3443.

Khatri, C., Mishra, M.K. and Rani, A. (2010). Synthesis and characterization of fly ash supported sulfated zirconia catalyst for benzylation reactions. *Fuel Processing Technology* 91: 1288–1295.

Kim, S.T., Yim, B. and Park, Y. (2010). Application of Taguchi Experimental Design for the Optimization of Effective Parameters on the Rapeseed Methyl Ester Production. *Environmental Engineering Research* 15: 129–134.

Kiss, A.A., Alexandre, C.D. and Gadi, R. (2006). Solid Acid Catalysts for Biodiesel Production – Towards Sustainable Energy. *Advanced Synthesis & Catalysis* 348: 75–81

Klug, P.H. and Alexander, L.E. 1974. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. New York: John Wiley and Sons.

Knothe, G., Matheaus, A.C. and Ryan III, T.W. (2003). Cetane numbers of branched and straight chain fatty esters determined in an ignition quality tester. *Fuel* 82: 971–975.

Knothe G., Gerpen J.V., and Krahl J. 2004.*The Biodiesel Handbook*. AOCS Press: Urbana Illinois.

Koh, M. Y. and Mohd. Ghazi, T. I. (2011). A review of biodiesel production from Jatropha curcas L. oil. *Renewable and Sustainable Energy Reviews* 15: 2240-2251.

Kouzu, M., Kasuno, T., Tajika, M., Yamanaka, S., Hidaka, J. (2008). Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol. *Applied Catalysis A: General* 334: 357–365.

Krawczyk, T. (1996). Biodiesel – Alternative fuel makes inroads but hurdles remain. *Inform* 7: 801–829.

Kulkarni, M.G., Gopinath, R., Meher, L.C. and Dalai, A.K. (2006). Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification. *Green Chemistry* 8: 1056–1062.

Kumar, R., Kumar, G.R. and Chandrashekar, N. (2011). Microwave assisted alkali-catalyzed transesterification of Pongamia pinnata seed oil for biodiesel production. *Bioresource Technology* 102: 6617–6620.

Kusdiana, D. and Saka, K. (2001). Kinetics of transesterification in rapeseed oil to biodiesel fuels as treated in supercritical methanol. *Fuel* 80: 693–698.

Kusdiana, D. and Saka, S. (2004). Effects of water on biodiesel fuel production by supercritical methanol treatment. *Bioresource Technology* 91: 289–295.

Kuwahara, Y., Tsuji, K., Ohmichi, T., Kamegawa, T., Mori, K. and Yamashita, H. (2012). Transesterifications using a hydrocalumite synthesized from waste slag: an economical and ecological route for biofuel production. *Catalysis Science & Technology* 2: 1842-1851.

Lai, O.M., Ghazali, H.M., Cho, F., Chong, C.L. (2000). Enzymatic transesterification of palm stearin: anhydrous milk fat mixtures using 1,3-specific and non-specific lipases. *Food Chemistry* 70: 221–225.

Laia, O.M, Ghazalia, H.M., Cho, F. and Chong, C.L. (2000). Physical and textural properties of an experimental table margarine prepared from lipase-catalysed transesterified palm stearin: palm kernel olein mixture during storage. *Food Chemistry* 71: 173–179.

Laksmono, N., Paraschiv, M., Loubar, K. and Tazerout, M.. (2013). Biodiesel production from biomass gasification tar via thermal/catalytic cracking. *Fuel Processing Technology* 106: 776–783.

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: 500–518.

Lee, H.V., Taufiq-Yap, Y.H., Hussein, M.Z., Yunus, R. (2013). Transesterification of jatropha oil with methanol over Mg-Zn mixed metal oxide catalysts. *Energy* 49: 12–18.

Lee, H. V. and Taufiq-Yap, Y. H. Optimization study of binary metal oxides catalyzed transesterification system for biodiesel production. *Process Safety and Environmental Protection*. doi: http://dx.doi.org/10.1016/j.psep.2014.10.001

Lee, J-S. and Saka, S. (2010). Biodiesel Production by Heterogeneous Catalyst Technologies. *Bioresource Technology* 101: 7191-7200.

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

Leung, D.Y.C., Wu, X. and Leung, M.K.H. (2010). A review on biodiesel production using catalysed transesterification. *Applied Energy* 87: 1083 – 1095.

Li, Y., Zhang, X-D., Sun, L., Zhang, J. and Xu, H-P. (2010). Fatty acid methyl ester synthesis catalyzed by solid superacid catalyst $SO_4^{2-}/ZrO_2–TiO_2/La^{3+}$. *Applied Energy* 87: 156–159.

Lin L., Cunshan, Z., Vittayapadung, S., Xiangqian, S. and Mingdong, D. (2010). Opportunities and challenges for biodiesel fuel. *Applied Energy* 88: 1020–1031.

Liu, W., Yin, P., Zhang, J., Tang, Q., and Qu, R. (2014). Biodiesel production from esterification of free fatty acid over PA/NaY solid catalyst. *Energy Conversion and Management* 82: 83-91.

Liu, X., Piao, X., Wang, Y., Zhu, S. and He, H. (2008). Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. *Fuel* 87: 1076–1082.

Lin, Y-C., Hsu, K-H. and Lin, J-F. (2014). Rapid palm-biodiesel production assisted by a microwave system and sodium methoxide catalyst. *Fuel* 115: 306–311.

Lopez, D.E., James, G.G.J., David, A.B. and Satoshi, F. (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. and Goodwin J.G.J. (2005). Synthesis of biodiesel via acid catalysis. *Industrial & Engineering Chemistry Research* 44: 5353–5363.

Lotero, E., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D. A. and Goodwin, J.G.J. (2006). The Catalysis of Biodiesel Synthesis. *Catalysis* 19: 41–83.

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: 8752–8758.

Lü, L. and Lai, M.O. 1998. *Mechanical Alloying.* U.S.A.: Kluwer Academic Publishers.

Lundstedt, T., Seifert, E., Abramo, L., Thelin, B., Nyström, A., Pettersen, J. and Bergman, R. (1998). Experimental design and optimization. *Chemometrics and Intelligent Laboratory Systems* 42: 3–40.

Nakajima, K., Okamura, M., Kondo, J. N., Tatsumi, T., Domen, K., Hayashi, S. and Hara, M. (2009). Amorphous Carbon Bearing Sulfonic Acid Groups in Mesoporous Silica as a Selective Catalyst. *Chemistry of Materials* 21: 186–193.

Ma, F., Clements, L.D. and Hanna, M.A. (1998). Biodiesel fuel from animal fat. Ancillary studies on transesterification of beef tallow. *Industrial and Engineering Chemistry Research* 37: 3768–3771.

Ma, F. and Hanna M.A. (1999). Biodiesel Production: A review. *Bioresource Technology* 70: 1–15.

Martyanov, I.N. and Sayari, A. (2008). Comparative study of triglyceride transesterification in the presence of catalytic amounts of sodium, magnesium, and calcium methoxides. *Applied Catalysis A: General* 339: 45–52.

Mason, T.J., Paniwnyk, L., Lorimer, J.P. (1996). The uses of ultrasound in food technology. Ultrasonics Sonochemistry 3: S253-S260.

Mason, T.J. (2003). Sonochemistry and sonoprocessing: the link, the trends and (probably) the future. Ultrasonics Sonochemistry 10: 175-179.

Masood, H., Yunus, R., Choong, T.S.Y., Rashid, U. and Taufiq Yap, Y.H. (2012). Synthesis and characterization of calcium methoxide as heterogeneous catalyst for trimethylolpropane esters conversion reaction. *Applied Catalysis A: General* 425–426: 184–190.

Mbaraka, I.K. and Shanks, B.H. (2006). Conversion of oils and fats using advanced mesoporous heterogeneous catalysts. *Journal of the American Oil Chemists' Society* 83: 79–91.

McIntosh D. J. and Kydd R.A. (2000). Tailoring the pore size of mesoporous sulfated zirconia. *Microporous and Mesoporous Materials* 37: 281–289.

Meher, L.C., Sagar, D.V. and Naik, S.N. (2006). Technical aspects of biodiesel production by transesterification – a review. *Renewable and Sustainable Energy Reviews* 10: 248–268.

Melero, J.A., Iglesias, J. and Morales, G. (2009). Heterogeneous acid catalysts for biodiesel production: current status and future challenges. *Green Chemistry* 11: 1285–1308.

Meng, Y.-L., Wang, B.-Y., Li, S.-F., Tian, S.-J., and Zhang, M.-H. (2013). Effect of calcination temperature on the activity of solid Ca/Al composite oxide-based alkaline catalyst for biodiesel production. *Bioresource Technology* 128: 305-309.

Mishra, M.K., Tyagi, B. and Jasra, R.V. (2004). Synthesis and characterization of nano-crystalline sulfated zirconia by sol–gel method. *Journal of Molecular Catalysis A: Chemical* 223: 61–65.

Mo, X., Lotero, E., Lu, C., Liu, Y. and Goodwin, J.G.J. (2008). A Novel Sulfonated Carbon Composite Solid Acid Catalyst for Biodiesel Synthesis. *Catalysis Letters* 123: 1–6.

Molaei Dehkordi, A., 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.

Mongkolbovornkij, P., Champreda, V., Sutthisripok, W. and Laosiripojana, N. (2010). Esterification of industrial-grade palm fatty acid distillate over modified ZrO_2 (with WO_3^-, SO_4^- and TiO_2) : Effects of co-solvent adding and water removal. *Fuel Processing Technology* 91: 1510–1516.

Mudge, S.M. and Pereira, G. (1999). Stimulating the biodegradation of crude oil with biodiesel preliminary results. *Spill Science & Technology Bulletin* 5: 353–355.

Muniyappa, P.R., Brammer, S.C. and Noureddini, H. (1996). Improved conversion of plant oils and animal fats into biodiesel and co-product. *Bioresource Technology*, 56: 19–24.

Nakajima, K., Okamura, M., Kondo, J. N., Tatsumi, T., Domen, K., Hayashi, S. and Hara, M. (2009). Amorphous Carbon Bearing Sulfonic Acid Groups in Mesoporous Silica as a Selective Catalyst. *Chemistry of Materials* 21: 186–193.

Norizzah, A.R., Chong, C.L., Cheow, C.S. and Zaliha, O. (2004). Effects of chemical interesterification on physicochemical properties of palm stearin and palm kernel olein blends. *Food Chemistry* 86: 229–235.

Oliveira, C.F., Dezaneti, L.M., Garcia, F.A.C., de Macedo, J.L., Dias, J.A., Dias, S.C.L. and 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.

Pantzaris, T. P. 2000. *Pocketbook of palm oil uses.* Kuala Lumpur: Malaysian Palm Oil Board. ISBN 967-961-015-2. 5th Edition.

Park, Y-M., Lee, J.Y., Chung, S-H, In Seon Park, Seung-Yeon Lee, Kim, D-K., Lee, J-S. and Lee, K-Y. (2010). Esterification of used vegetable oils using the heterogeneous WO_3/ZrO_2 catalyst for production of biodiesel. *Bioresource Technology* 101: S59–S61.

Pasqualino, J.C., Montane, D. and Salvado, J. (2006) Synergic effects of biodiesel in the biodegradability of fossil-derived fuels. *Biomass Bioenergy* 30: 874–879.

Patel, A. and 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.

Peng, B-X., Shu, Q., Wang, J-F., Wang, G-R., Wang, D-Z. and Han, M-H. (2008). Biodiesel production from waste oil feedstocks by solid acid catalysis. *Process safety and environment protection* 86: 441–447.

Peng, F., Zhang, L., Wang, H., Lv, P. and Yu, H. (2005). Sulfonated carbon nanotubes as a strong protonic acid catalyst. *Carbon* 43: 2405–2408.

Petchmala, A., Laosiripojana, N., Jongsomjit, B., Goto, M., Panpranot, J., Mekasuwandumrong, O. and Shotipruk, A. (2010). Transesterification of palm oil and esterification of palm fatty acid in near- and super-critical methanol with SO_4–ZrO_2 catalysts. *Fuel.* 89: 2387–2392.

Prakash, C.B. 1998. *A critical review of biodiesel as a transportation fuel in Canada*; GCSI-Global Change Strategies International Inc.: Canada.

Qiu, F., Li, Y., Yang, D., Li, X. and Sun, P. (2011). Biodiesel production from mixed soybean oil and rapeseed oil. *Applied Energy* 88: 2050-2055.

Ramos, M.R., Fernandez, C.M., Casas, A., Rodriguez, L. and Perez, A. (2009). Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology* 100: 261–268.

Reddy, B.M., Sreekanth, P.M. and Reddy, V.R. (2005). Modified zirconia solid acid catalysts for organic synthesis and transformations. *Journal of Molecular Catalysis A: Chemical* 225: 71–78.

Richardson, J.T. 1989. *Principles of Catalyst Development.* New York: Plenum.

Rived, F., Canals, I., Bosch, E and Roses, M. (2001). Acidity in methanol-water. *Analytica Chimica Acta* 439: 315–333.

Ropkins, K., Quinn, R., Beebe, J., Li, H., Daham, B., Tate, J., Bell, M. and Andrews, G. (2007). Real-world comparison of probe vehicle emissions and fuel consumption using diesel and 5% biodiesel (B5) blend. *Science of the Total Environment* 376: 267–284.

Ross, P.J. 1996. *Taguchi Techniques for Quality Engineering: Loss Function, Orthogonal Experiments, Parameter and Tolerance Design.* New York: McGraw-Hill, 2nd Edition.

Roy, R.K. 2001. *Design of experiments using the Taguchi approach: 16 steps to product and process improvement.* New York: Wiley.

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

Sayari, A. (1996). Catalysis by Crystalline Mesoporous Molecular Sieves. *Chemistry of Materials* 8: 1840-1852.

Schiøtt, B. and Jørgensen, K.A. (1993). The Oxidative Species on a Vanadyl Pyrophosphate Surface.A Model for Some Steps in the Maleic Anhydride Synthesis. *Catalysis Today* 16: 79–90.

Schuchardta, U., Serchelia, R. and Vargas, R.M. (1998). Transesterification of vegetable oils: A review. *Journal of the Brazilian Chemical Society* 9: 199 – 210.

Schwab, A. W., Bagby, M. O. and Freedman, B. (1987). Preparation and properties of diesel fuels from vegetable oils. *Fuel* 66: 1372–1380.

Schwab, A.W., Dykstra, G. J., Selke, E., Sorenson, S.C. and Pryde, E.H. (1988). Diesel fuel from thermal decomposition of soybean oil. *Journal of the American Oil Chemists' Society* 65: 1781–1786.

Scurrell, M.S. (1987). Conversion of methane-ethylene mixtures over sulphate-treated zirconia catalysts. *Applied Catalysis* 34: 109–117.

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. and Singh, B. (2009). Development of Biodiesel: Current Scenario. *Renewable and Sustainable Energy Reviews* 13: 1646–1651.

Sharma, Y.C., Singh, B. and Korstad, J. (2010). High Yield and Conversion of Biodiesel from a Nonedible Feedstock (Pongamia pinnata). *Journal of Agricultural and Food Chemistry* 58: 242–247.

Sharma, Y.C., Singh, B. and Korstad, J. (2011). Latest developments on application of heterogenous basic catalysts for an efficient and eco friendly synthesis of biodiesel: A review. *Fuel* 90: 1309–1324.

Singh, S.P. 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* 17: 200–216.

Soares, F.A.S.D.M., Silva, R.C.d, Silva, K.C.G.d., Lourenco, M.B., Soares, D.F. and Gioielli, L.A. (2009). Effects of chemical interesterification on physicochemical properties of blends of palm stearin and palm olein. *Food Research International* 42: 1287–1294.

Sohn, J. R. and Kim, H.W. (1989). Catalytic and surface properties of ZrO_2 modified with sulfur compounds. *Journal of Molecular Catalysis* 52: 361–374.

Song, X.-L., Fu, X.-B., Zhang, C.-W., Huang, W.-Y., Zhu, Y., Yang, J. and Zhang, Y.-M. (2012). Preparation of a Novel Carbon Based Solid Acid Catalyst for Biodiesel Production via a Sustainable Route. *Catalysis Letters* 142: 869–874.

Sreeprasanth, P.S., Srivastava, R., Srinivas, D.and Ratnasamy, P. (2006). Hydrophobic, solid acid catalysts for production of biofuels and lubricants. *Applied Catalysis A: General* 314: 148–159.

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

Stamenković, O.S., Veličković, A.V. and Veljković, V.B. (2011). The production of biodiesel from vegetable oils by ethanolysis: Current state and perspectives. *Fuel* 90: 3141–3155.

Su, D.S., Roddatis, V., Willinger, M., Weinberg, Kitzelmann, G., Schlögl, E. R. and Knözinger, H. 2001. Tribochemical modification of the microstructure of V_2O_5. *Catalysis Letters* 74: 169–175.

Suganuma, S., Nakajima, K., Kitano, M., Yamaguchi, D., Kato, H., Hayashi, S. and Hara, M. (2008). Hydrolysis of Cellulose by Amorphous Carbon Bearing SO_3H, COOH, and OH Groups. *Journal of the American Chemical Society* 130: 12787–12793.

Sunita, G., Devassy, B.M., Vinu, A., Sawant, D.P., Balasubramanian, V.V. and Halligudi, S.B. (2008). Synthesis of biodiesel over zirconia-supported isopoly and heteropoly tungstate catalysts. *Catalysis Communications* 9: 696–702.

Suppes, G.J., Dasari, M.A., Doskocil, E.J., Mankidy, P.J. and Goff, M.J. (2004). Transesterification of soybean oil with zeolite and metal catalysts. *Applied Catalysis A: General* 257: 213–223.

Suwannakarn, K., Lotero, E., Goodwin J.J.G. and Lu, C. (2008). Stability of sulfated zirconia and the nature of the catalytically active species in the transesterification of triglycerides. *Journal of Catalysis* 255: 279–286.

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: 157–161.

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

Talukder, M.M.R., Wu, J. C., Lau, S.K., Cui, L.C., Shimin, G. and Lim, A. (2009) Comparison of Novozym 435 and Amberlyst 15 as Heterogeneous Catalyst for Production of Biodiesel from Palm Fatty Acid Distillate. *Energy & Fuels* 23: 1–4.

Tan, K.T., Gui, M.M., Lee, K.T. and Mohamed, A.R. (2010). An optimized study of methanol and ethanol in supercritical alcohol technology for biodiesel production. *Journal of Supercritical Fluids* 53: 82–87.

Tan, K.T., Lee, K.T. and Mohamed, A.R. (2010a). Effects of free fatty acids, water content and co-solvent on biodiesel production by supercritical methanol reaction. *Journal of Supercritical Fluids* 53: 88–91.

Tang, C-Y., Wu, Y-L. and Peng, C-C. (2012). Fundamental matrix estimation by multiobjective genetic algorithm with Taguchi's method. *Applied Soft Computing* 12: 553–558.

Tapanes, N.C.O., Aranda D.A.G., Carneiro, J.W.M. and Antunes, O.A.C. (2008). Transesterification of Jatropha curcas oil glycerides: theoretical and experimental studies of biodiesel reaction. *Fuel* 87: 2286–2295.

Taufiq-Yap, Y.H., Goh, C.K., Hutchings, G.J., Dummer, N. and Bartley, J.K. (2006). Effects of mechanochemical treatment to the vanadium phosphate catalysts derived from $VOPO_4 \cdot 2H_2O$. *Journal of Molecular Catalysis A: Chemical* 260: 24–31.

Taufiq-Yap, Y.H., Lee, H.V., Hussein, M.Z. and Yunus, R. (2011). Calcium-based mixed oxide catalysts for methanolysis of Jatropha curcas oil to biodiesel. *Biomass and Bioenergy* 35: 827–834.

Taufiq-Yap, Y. H., Teo, S. H., Rashid, U., Islam, A., Hussien, M. Z., and Lee, K. T. (2014). Transesterification of Jatropha curcas crude oil to biodiesel on calcium lanthanum mixed oxide catalyst: Effect of stoichiometric composition. *Energy Conversion and Management* 88: 1290-1296.

Teo, S. H., Islam, A., Yusaf, T., and Taufiq-Yap, Y. H. (2014). Transesterification of Nannochloropsis oculata microalga's oil to biodiesel using calcium methoxide catalyst. Energy(0). doi: http://dx.doi.org/10.1016/j.energy.2014.07.045

Thiruvengadaravi, K.V., Nandagopal, J., Baskaralingam, P., Bala, V. S.S. and Sivanesan, S. (2012). Acid-catalyzed esterification of karanja (*Pongamia pinnata*) oil with high free fatty acids for biodiesel production. *Fuel* 98: 1–4.

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: 178.

Top, A.G.M. (2010). Production and utilization of palm fatty acid distillate (PFAD). *Lipid Technology* 22: 11–13.

Tsubouchi, N., Xu, C. and Ohtsuka, Y. (2003). Carbon Crystallization during High-Temperature Pyrolysis of Coals and the Enhancement by Calcium. *Energy Fuels* 17: 1119–1125.

Tyagi, B., Mishra, M.K. and Jasra, R.V. (2009). Solvent free synthesis of 7-isopropyl-1,1-dimethyltetralin by the rearrangement of longifolene using nano-crystalline sulfated zirconia catalyst. *Journal of Molecular Catalysis A: Chemical* 301: 67–78.

Tyagi, B., Mishra, M.K. and Jasra, R.V. (2010). Solvent free synthesis of acetyl salicylic acid over nano-crystalline sulfated zirconia solid acid catalyst. *Journal of Molecular Catalysis A: Chemical* 317: 41–45.

Viriya-empikul, N., Krasae, P., Nualpaeng, W., Yoosuk, B. and Faungnawakij, K. (2012). Biodiesel production over Ca-based solid catalysts derived from industrial wastes. *Fuel* 92: 239-244.

Wan Omar, W.N.N. and Amin, N.A.S. (2011). Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. *Biomass and Bioenergy* 35: 1329–1338.

Wang, L. and Yang, J. (2007). Transesterification of soybean oil with nano-MgO or not in supercritical and subcritical methanol. *Fuel* 86: 328 – 333.

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: 107–112.

Wang, Y.D., Al-Shemmeri, T., Eames, P., McMullan, J., Hewitt, N., Huang, Y. and Rezvani, S. (2006). An experimental investigation of the performance and gaseous exhaust emissions of a diesel engine using blends of a vegetable oil. *Applied Thermal Engineering* 26: 1684–1691.

Warabi, Y., Kusdiana, D. and Saka, S. (2004).Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols.*BioresourceTechnology* 91: 283–287.

Wu, H., Liu, Y., Zhang, J., and Li, G. (2014). In situ reactive extraction of cottonseeds with methyl acetate for biodiesel production using magnetic solid acid catalysts. *Bioresource Technology* 174: 182-189.

Xie, W. and Zhao, L. (2013). Production of biodiesel by transesterification of soybean oil using calcium supported tin oxides as heterogeneous catalysts. *Energy Conversion and Management* 76: 55-62.

Xie, W., and Zhao, L. (2014). Heterogeneous CaO–MoO_3–SBA-15 catalysts for biodiesel production from soybean oil. *Energy Conversion and Management* 79: 34–42.

Yaakob, Z., Mohammad, M., Alherbawi, M., Alam, Z. and Sopian, Kamaruzaman. (2013). Overview of the production of biodiesel from Waste cooking oil. *Renewable and Sustainable Energy Reviews* 18: 184–193.

Yadav, G.D. and Ambareesh, D.M. (2004). Preparation of a novel catalyst UDCaT- 5: enhancement in activity of acid-treated zirconia – effect of treatment with chlorosulfonic acid vis-à-vis sulfuric acid. *Journal of catalysis* 224: 218 – 223.

Yadav, G.D., Ajgaonkar, N.P. and Varma, A. (2012). Preparation of highly superacidic sulfated zirconia via combustion synthesis and its application in Pechmann condensation of resorcinol with ethyl acetoacetate. *Journal of Catalysis* 292: 99–110.

Yang, Z. and Xie, W. (2007). Soybean oil transesterification over zinc oxide modified with alkali earth metals. *Fuel Process Technology* 88: 631 – 638.

Yin, P., Chen, L., Wang, Z., Qu, R., Liu, X., Xu, Q., Ren, S. (2012). Biodiesel production from esterification of oleic acid over aminophosphonic acid resin D418. *Fuel* 102: 499–505.

Yusup, S. and Khan, M.A. 2010. Base catalyzed transesterification of acid treated vegetable oil blend for biodiesel production. *Biomass and Bioenergy* 34: 1500–1504.

Zabeti, M., Wan Daud, W. M. A. and Aroua, M. K. (2009). Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology* 90: 770–777.

Zabeti, M., Wan Daud, W. M. A. and Aroua, M.K. (2010). Biodiesel production using alumina-supported calcium oxide: An optimization study. *Fuel Processing Technology* 91: 243–248.

Zazhigalov, V.A., Haber, J., Stoch, J., Kharlamov, A.I., Bogutskaya, L.V., Bacherikova, I.V. and Kowal. A. (1997). Influence of the mechanochemical treatment on the reactivity of V-containing oxide systems. *Solid State Ionics* 101-103: 1257–1262.

Zhang, J. and Jiang, L. (2008). Acid-catalyzed esterification of Zanthoxylum bungeanum seed oil with high free fatty acids for biodiesel production. *Bioresource Technology* 99: 8995–8998.

Zhang, J.H., Chen, S.X., Yang, R. and Yan, Y.Y. (2010). Biodiesel production from vegetable oil using heterogeneous acid and alkali catalyst. *Fuel* 89: 2939 – 2944.

Zhang, X., Peterson, C., Reece, D., Haws, R. and Moller, G. (1998). Biodegradability of biodiesel in the aquatic environment. *Journal of Transactions of the ASAE* 41: 1423–1430.

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

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

Ziarati, A., Safaei-Ghomi, J. and Rohani, S. (2013). Sonochemically synthesis of pyrazolones using reusable catalyst CuI nanoparticles that was prepared by sonication. *Ultrasonics Sonochemistry* 20: 1069–1075.

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: 434–437.

Zubir, M.I. and Chin, S.Y. (2010). Kinetics of Modified Zirconia-Catalyzed Heterogeneous Esterification Reaction for Biodiesel Production. *Journal of Applied Sciences* 10: 2584–2589.

BIODATA OF THE STUDENT

Mr. Theam Kok Leong was born on 4th April 1982 in Kuala Lumpur. He completed his primary and secondary school in SRJK (C) Jinjang Utara and SMK Menjalara, Kepong, Kuala Lumpur. He further completed his form six studies in SMK Maxwell, Kuala Lumpur. He obtained his first degree in Bachelor of Science (Hons.), majoring in Chemistry from Universiti Putra Malaysia, Serdang in the year 2006. He has completed his Master of Science in the field of Catalysis in the same university in 2008. In addition, his PhD course fee was supported by *MyBrain 15* scholarship from Ministry of Education, Malaysia. He is working as a chemistry lecturer since year 2009.

LIST OF PUBLICATIONS

1. **Kok Leong Theam**, Aminul Islam, Yun Hin Taufiq-Yap and Yuen May Choo. Binary metal-doped methoxide catalyst for biodiesel production from palm stearin, *Research on Chemical Intermediates (2015), DOI 10.1007/s11164-015-2127-x.*

2. **Kok Leong Theam**, Aminul Islam, Hwei Voon Lee and Yun Hin Taufiq-Yap. Sucrose-derived catalytic biodiesel synthesis fromlow cost palm fatty acid distillate, *Process Safety and Environmental Protection (2015), volume: 95, Page: 126-135.*

3. Yun Hin Taufiq-Yap, Hwei Voon Lee, Yin Chang Wong, **Kok Leong Theam** and Wen Jiunn Tang, Effect of different calcination duration on physicochemical properties of vanadium phosphate catalysts, *E-Journal of Chemistry (2012), volume: 9, Issue: 3, Page: 1440-1448.*

4. Y. H. Taufiq-Yap, **K. L. Theam**, G.J. Hutchings, N. Dummer and J. K. Bartley, Effect of Cr, Ni, Fe and Mn dopants on the performance of hydrothermal synthesized vanadium phosphate catalysts for *n*-butane oxidation, *Petroleum Science and Technology (2010), volume: 28, Issue: 10, Page: 997-1012.*

5. Yun Hin Taufiq-Yap and **Kok Leong Theam**, Modification and microstructure study of vanadyl pyrophosphate catalysts synthesized via hydrothermal method, *Proceedings of the Seminar on Science and Technology (2008), Page: 40-46 (ISBN 978-983-2641-30-8).*

List of the seminars/conferences/workshops attended:

1. Seminar on "Small Molecule Single Crystal Diffraction" by Dr. Martin Adam, 17th April 2007, Lecture Hall 207, 2nd Floor, Faculty Science (Participant).

2. Seminar on "Laser Raman Spectroscopy" by Dr. Joel Oswalt, 27th April 2007, Bilik Saintis Gemilang, Faculty Science (Participant).

3. Workshop on "Publishing for Postgraduates", 4-5th June 2007, organised by School of Graduate Studies, Universiti Putra Malaysia, Dewan Persidangan, Center for External Education (Participant).

4. Seminar on "Seminar Sains 2007", 4th August 2007, Dewan Kuliah Akademik Pusat, Universiti Putra Malaysia (Oral presenter).

5. Nobel Laureate Public Lecture-'Investing in the Future' by Nobel Laureate Professor Dr. Ahmed Zewail, 8th August 2007, Exhibition Hall 1, Ground Floor, Kuala Lumpur Convention Centre (KLCC) (Participant).

6. Seminar on "Half-Day Seminar on Oxidation Catalysis", 22th August 2007, Bilik Saintis Gemilang, Faculty of Science (Participant).

7. 12th Asian Chemical Congress (12ACC), 23-25th August 2007, Putra World Trade Centre, Kuala Lumpur, Malaysia (Oral presenter).

8. Seminar on "Short Course in Catalysis", 4-5th December 2007, School of Chemical Sciences, Universiti Sains Malaysia (Participant).

9. Pameran Reka Cipta, Penyelidikan dan Inovasi (PRPI), 27-29th November 2007, Dewan Besar, PKKSSAAS, Universiti Putra Malaysia (Poster presenter).

10. The 6th Asia-Pacific Congress on Catalysis (APCAT-6), 13-17th October 2013, Taipei International Convention Center (TICC), Taiwan (Poster presenter)