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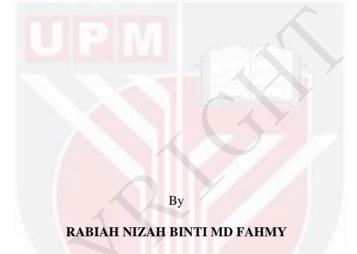
TRANSESTERIFICATION OF JATROPHA CURCAS L. OIL TO BIODIESEL USING Nd2O2 AND Bi2O2 -SUPPORTED CATALYSTS

RABIAH NIZAH BINTI MD FAHMY

FS 2015 26



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Thesis Submitted to the School Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master Science

June 2015

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Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master Science

TRANSESTERIFICATION OF JATROPHA CURCAS L. OIL TO BIODIESEL USING Nd₂O₃ AND Bi₂O₃ -SUPPORTED CATALYSTS

By

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June 2015

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Biodiesel is gaining more attention since it is a renewable source of energy that can be an alternative for petroleum based diesel fuels. Other than being renewable, it is also biodegradable and non-toxic. Biodiesel is even more preferable since it can be produced easily via transesterification reaction. With various resources that can be used to produce biodiesel, Jatropha Curcas oil (JCO) is one of the feasible source since it is a non-edible oil, hence no competition over food resources. One of the major drawback of JCO is that it contains high amount of free fatty acids (FFA). In this study, catalyst with different catalyst (Nd₂O₃ and Bi₂O₃) on La₂O₃ support were compared. Bi_2O_3 catalyst shows higher catalytic activity at lower reaction conditions, hence is used for further study. Different loading of Bi_2O_3 (1.3,5,7) wt.%) using La₂O₃ as a support were prepared using wet impregnation method for simultaneous esterification and transesterification of JCO and its potential as heterogeneous catalyst was assessed. The catalysts were characterized by using Xray Diffractometer (XRD), Brunauer-Emmett-Teller (BET) surface area, Scanning Electron Microscopy (SEM) and Temperature Programmed Desorption (TPD) of CO₂ and NH₃. These catalysts were then used for transesterification reaction under different reaction conditions (methanol to oil molar ratio, amount of catalyst, reaction temperature and reaction time) to investigate the catalytic activities of the catalysts. Under optimum transesterification condition at 150°C with catalyst amount of 2 wt.%, methanol/oil molar ratio of 15:1 and reaction time of 4 h, 5BiLa catalyst gave fatty acid methyl ester (FAME) conversion of 93%. The catalytic activities were found depending on the acidity, basicity and the surface area of the catalyst used. Several tests were conducted to study the physicochemical properties of the product such as pour point, flash point, kinematic viscosity, sulphur content and cloud point of biodiesel produced. Based on the results, the synthesized biodiesel is comparable with conventional diesel in the market since it meets the international standards of biodiesel which are American Standard for testing Materials (ASTM), Europian Standard (EN) and Malaysian Standard (MS) for diesel fuel specifications.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

TRANS-PENGESTERAN BAGI MINYAK JATROPHA CURCAS L. KEPADA BIODIESEL MENGGUNAKAN MANGKIN Nd₂O₃ DAN Bi₂O₃ YANG DISOKONG

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Biodiesel semakin mendapat perhatian kerana ia adalah sumber tenaga yang boleh diperbaharui dan boleh menjadi alternatif kepada bahan api berasaskan petroleum diesel. Selain daripada boleh diperbaharui, ia juga bersifat biodegradasi dan tidak bertoksik. Biodiesel lebih menjadi pilihan kerana iaboleh dihasilkan dengan mudah melalui tindak balas trans-pengesteran. Daripada pelbagai sumber yang boleh digunakan untuk menghasilkan biodiesel, minyak Jatropha Curcas (JCO) adalah salah satu sumber yang boleh dilaksanakan kerana ia adalah minyak yang tidak boleh dimakan, maka tiada persaingan dengan sumber makanan. Salah satu kelemahan utama JCO ialah ia mengandungi jumlah asid lemak bebas (FFA) yang tinggi. Dalam kajian ini, pemangkin yang berbeza (Nd₂O₃ dan Bi₂O₃) kepada sokongan La₂O₃ dibandingkan. Mangkin Bi₂O₃ menunjukkan aktiviti pemangkin lebih tinggi pada keadaan tindak balas yang lebih rendah, oleh itu ia digunakan untuk kajian selanjutnya. Pelbagai muatan Bi₂O₃ (1,3,5,7wt.%) menggunakan La₂O₃ sebagai sokongan disediakan dengan menggunakan kaedah penjerapan untuk pengesteran dan trans-pengesteran serentak JCO dan potensi sebagai pemangkin heterogen dinilai. Pemangkin telah dicirikan dengan menggunakan alat pembelauan sinar-X (XRD), pengukuran luas permukaan Brunauer - Emmett -Teller (BET), pengimbas mikroskopi elektron (SEM), penyahjerapan karbon dioksida pada suhu terkawal (TPD-CO₂) dan penyahjerapan ammonia pada suhu terkawal (TPD-NH₃). Pemangkin-pemangkin ini kemudiannya digunakan untuk tindak balas trans-pengesteran pada beberapa keadaan (nisbah methanol terhadap minyak, jumlah pemangkin, suhu tindak balas dan masa tindak balas) untuk menganalisa aktiviti kesemua mangkin. Di bawah keadaan trans-pengesteran optimum pada suhu 150 °C, jumlah pemangkin 2 wt.%, nisbah methanol kepada minyak 15:1 dan masa tindak balas selama 4 jam, mangkin 5BiLa memberi penukaran asid lemak methil ester (FAME) sebanyak 93%. Aktiviti mangkin didapati bergantung kepada keasidan, kealkalian dan keluasan kawasan permukaan mangkin tersebut. Beberapa ujian telah dijalankan untuk menganalisa sifat-sifat fizikokimia biodiesel yang dihasilkan seperti takat tuang, takat kilat, kelikatan, kandungan sulfur dan takat awan. Berdasarkan keputusan tersebut, biodiesel yang



dihasilkan didapati setanding dengan diesel konvensional yang ada di pasaran memandangkan ianya dapat memenuhi piawaian biodiesel antara bangsa seperti American Standard for testing Materials (ASTM), Europian Standard (EN) dan Malaysian Standard (MS) spesifikasi untuk bahan api diesel di Malaysia.



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LIST OF ABBREVIATIONS

AES	Atomic Emission Spectroscopy
ASTM	American Society for Testing and Materials
BET	Brunauer Emmett Teller
EN	European Standard
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GC	Gas Chromatography
JCO	Jatropha Curcas Oil
JCPDS	Joint Committee on Powder Diffraction Standards
MS	Malaysian Standard
MPOB	Malaysian Palm Oil Board
SEM	Scanning Electron Microscopy
SV	Saponification Value
TG	Triglyceride
TPD	Temperature Programmed Desorption
WD	Wave Dispersive
XRD	X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Energy and Renewable Energy

The world economy depends on two major energy carriers which are hydrocarbons (natural gas, gasoline, diesel fuel and heating oil) and electrical current. Although the primary energy supply for each country differs greatly, hydrocarbons are still the main source of energy. Lately, energy supply and its security have become a major issue around the world. International Energy Agency (IEA) had estimated 53 % of increase in global energy consumption by 2030, with 70 % of the growth in demand coming from developing countries. Demand for energy expected to increase over the next 24 years both in industrial countries and particularly in the developing countries like Malaysia where rapid economic growth is expected (Rahman Mohamed and Lee, 2006).

Peninsular Malaysia stands at 47 % with an energy reserved margin total of 20,493MW installed capacity. The excessive harnessing of various form of energy that made possible by the advancement of technologies resulted in unwanted by-product such as waste and pollution. For example, fossil fuels consume and pollute water, endanger flora and fauna, generate toxic wastes and cause global warming. Due to the growth in exploration activities, Malaysia's proven oil reserves have declined in recent years and the oil production fell to 693,000 bbl/d in 2008, a 13% decrease from 2006 level. If the production rate is consistent at around 700,000 bbl/d, Malaysia's oil reserves will be exhausted in around 20 years (Mansor, 2008). There is a compelling need for energy variation and containment of the negative environmental impact on extensive use of mineral fuel. By depending mainly on oil and gas for half of a century, Malaysia started to comprehend the importance to adopt renewable energy in the energy mix and continuously reviewed its energy policy to ensure sustainable energy supply and security (Oh *et al.*, 2010).

Renewable energy sources (RESs) is also known as alternative energy. RESs are readily available in nature and they are primary energy resources. It is derived from those natural, mechanical, thermal and growth processes that continuously reproduced predictable quantities of energy when required. RESs use local resources that have potential to provide energy with zero or low emission of air pollutant and greenhouse gases. Renewable energy technologies manufacture marketable energy by converting natural materials into useful form of energy.



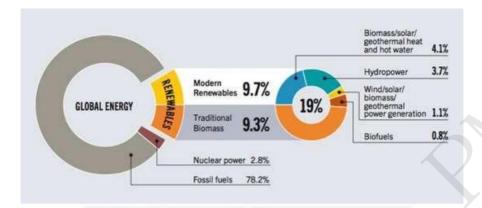


Figure 1.1 Estimated Renewable Energy Share of Global Final Energy Consumption, 2011

(Source: Mcginnet al., 2013)

By the end of 2011 (Figure 1.1), renewable energy supplied an estimated 19 % of global final energy consumption. From this total, approximately 9.3 % came from traditional biomass, geothermal heat about 4.1 %, hydropower made up about 3.7 % and an estimated 1.9 % from wind, solar, biomass, geothermal power generation and biofuels (Mcginn *et al.*, 2013).

1.2 Biofuels

Biofuel refers to liquid or gaseous fuel for transportation that are mostly produced from biomass. Biofuels mainly used in vehicles but also can be used in engine or fuel cells for electricity generation. Fuels that can be produced from biomass resources include liquid fuels such as ethanol, methanol, biodiesel and Fischer-Tropsch diesel and gaseous fuels such as methane and hydrogen. The biggest difference between biofuels and petroleum is the oxygen content. Biofuels have oxygen levels of 10 to 45 % while petroleum has almost none which makes the chemical properties of biofuels very different from petroleum (Demirbas, 2008a). Biofuels usually have very low sulphur and nitrogen levels. Some of the advantages of biofuels are easily derived from common biomass sources, carbon dioxide cycle occurs in combustion, they are environmentally friendly and biodegradable and contribute to sustainability (Kim and Dale, 2005).



With the increasing demands of energy, biofuels economy starts to grow rapidly. In Malaysia, there is biofuels policy of Malaysia which is based on Malaysia's National Biofuel Policy document. The main aim of the policy is to reduce the country's fuel import bill, further promoting the demand for palm oil, which is expected to be the primary commodity for biofuel production in Malaysia, as well as to shore up the price of palm oil especially during periods of low export demand.

1.3 Background and Potential of Biodiesel

Fatty acid methyl ester (FAME) or generally known as "biodiesel", are the best candidate for alternative diesel fuels derived from vegetable oils or animal fats. Biodiesel generally has similar physio-chemical and fuel properties as petroleum based diesel fuel. The major component of vegetable oils and animal fats are triglyceride (TG) where the 3 moles ester of fatty acids (FA) attached to one glycerol backbone. TG from vegetable oils or animal fats contains a few different FA which possesses different physical and chemical properties, making the FA profile the most important factor influencing the properties of vegetable oils or animal fats (Knothe and Gerpen, 2005).

The most common method to obtain biodiesel is through a chemical reaction known as transesterification reaction. In this reaction, TG are converted to FAME in the presence of catalyst with short chain alcohol giving glycerol as a byproduct. Vegetable oils and animal fats have high kinematic viscosity and low volatility making it unsuitable to be used as combustion fuel. Hence, vegetable oils and animal fats must undergo transesterification to reduce the viscosity of the oils (Muniyappa *et al.*, 1996).

1.4 Advantages of Biodiesel as Diesel Fuel Substitutes

Biodiesel have several distinct advantages compared to petroleum-based diesel fuel. Biodiesel is biodegradable, sustainable and environmental friendly given that it is considered to be carbon neutral. Biodiesel feedstock such as Jatropha, rape plant and palm trees absorbs carbon dioxide that released to the atmosphere when used for combustion in diesel engines (Atadashi *et al.*, 2011) as illustrated in Figure 1.2. Biodiesel also gives less exhaust emission with low level of unburned hydrocarbon, carbon monoxide and particulate matter. Compared to mineral diesel, biodiesel have lower sulphur content and no carcinogen, thus it can be called as a clean fuel. Since biodiesel is derived from renewable domestic resource, it would help to reduce the dependency on petroleum as well as preserving petroleum sources (Demirbas, 2008b).



As mentioned earlier, biodiesel possesses similar physico-chemical properties as diesel fuel so it can be used directly without further modification of diesel engine. There are two ways to use biodiesel in engines. It can be used as 100 % biodiesel fuel or it can be blended with diesel fuel since biodiesel is completely miscible with petroleum diesel fuel. A pure (100 %) biodiesel is known as B100 or "neat" fuel. Biodiesel blends are referred as BXX where XX indicates the amount of biodiesel blends in the fuel (i.e. a B10 blend is 10 % biodiesel and 90 % petroleum based diesel). Biodiesel fuels generally have excellent lubricity which helps to prolong engine life and reduce the need for maintenance (Demirbas, 2010). Table 1.1 summarized the advantages of biodiesel as diesel fuel substitute.

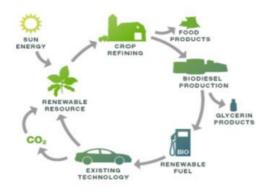


Figure 1.2 Biodiesel Production Cycle (Source:Mann, 2011)

Table 1.1 Auvalitages of Dioulesel as Diesel Fuel Substitutes	
	Sustainability
Economia imposta	Fuel diversity
Economic impacts	Agricultural development
	Reducing the dependency of crude petroleum
	Greenhouse gases reduction
Environmental imposts	Biodegradable
Environmental impacts	Carbon sequestration
	Lower sulphur content
	Domestic targets
Energy accurance	Supply reliability
Energy assurance	Ready availability
	Renewability

Table 1.1 Advantages of Biodiesel as Diesel Fuel Substitutes

1.5 Global Biodiesel Market Demands

The energy demand especially in transportation sector increasing each day due to the rapid urbanization worldwide. This increasing need of energy contributes to the development of the renewable energy making biodiesel as one of the fastest growing industries.



The global biodiesel production from 2000 to 2012 shown inFigure 1.3 and in table 1.2. Global production of biodiesel reached over 22.5 billion litres in 2012. 41 % of the production was from Europe, with major contribution from Germany which produced 2.7 billion liters in 2012. United States held the top spot for world's leading biodiesel producer with 3.6 billion liters followed by Argentina (2.8 billion liters), Brazil and Germany (2.7 billion liters) and France (1.9 billion liters) in 2012 (Mcginn *et al.*, 2013).

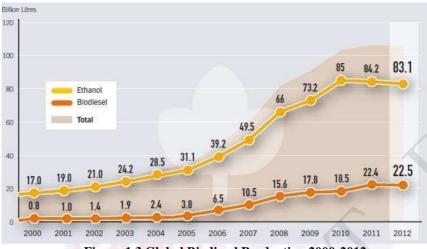


Figure 1.3 Global Biodiesel Production 2000-2012 (Source: Mcginn *et al.*, 2013)

Table 1.2Global Biodiesel Production of Top 14 Countries(Mcginnet al., 2013)

Country	Biodiesel (billion litres)
United States	3.6
Brazil	2.7
Germany	2.7
Argentina	2.8
France	1.9
China	0.2
Canada	0.1
Thailand	0.9
Indonesia	1.5
Spain	0.5
Belgium	0.4
Netherlands	0.5
Colombia	0.3
Austria	0.4



World production and consumption of biodiesel grows rapidly during 2007 to 2012. The high percentages of biodiesel production from European Union (EU) countries mainly comes from the European government supports in terms of production incentives including tax incentives and loan guarantees. Furthermore, the new biofuel policy such as tax exemption, mandates and incentives for biodiesel introduced in countries such as United States, Europe, Brazil and Asia had encouraged the production and consumption of biodiesel to the fullest (Oh *et al.*, 2010).

1.6 Progress of Biodieselin Malaysia

The first biodiesel program in Malaysia was initiated by Malaysian Palm Oil Board (MPOB) in 1982 using palm oil as feedstock. Malaysian government funded the program in order to bring palm biofuel to local and international markets. MPOB collaborated with local oil company Petronas and constructed the first pilot plant two years later. This plant successfully produces 3000 tonnes biodiesel annually. In August 2006, the first commercial biodiesel plant started its operation. Malaysia had announced its national biodiesel policy in 2005 resulting in the government approving around 92 licenses for biodiesel projects to produce 10.2 million tonnes per year (Lopez and Laan, 2008). MPOB reported that Malaysia has exported 47,790 and 95,010 tonnes of biodiesel in 2006 and 2007 (MPOB, 2008).

Since biodiesel production in Malaysia mainly related to palm oil, the government determined to develop palm oil industries by promoting palm biodiesel. In 2011, Petronas, Shell, BHP, ExxonMobil and Chevron have been allocated with a start up fund worth RM 1 million each by MPOB to set up infrastructure for B5 biodiesel blending facilities. By June 2011, B5 biodiesel sold at six petrol stations located in Putrajaya (Times, 2011). Due to the unstable price of palm oil, Jatropha has become another alternative as biodiesel feedstock. MPOB carried out some performance test on Jatropha biodiesel alongside with Malaysian Rubber Board and The National Tobacco Board. Malaysian Rubber Board engaged in the seed breeding of Jatropha while The National Tobacco Board is responsible to gauge the suitability of cultivating Jatropha on bris soils in the northern part of Malaysia (Cottrell and Hoh, 2011).

1.7 Problem Statements

Biodiesel production industry grown exponentially in many countries as alternative fuels. A lot of studies had been done with growing interest in biodiesel production. Despite the fact that biodiesel offers several advantages over fossil fuels, the major concern about biodiesel are the cost and economic issues. Homogeneous catalysts are typically used for transesterification reaction. Although homogeneous catalyst produces high yield of biodiesel at lower reaction conditions, it is difficult to separate the catalyst from the product and needs purification of the product that leads to environmental pollution. Hence, heterogeneous catalysts are used in this research to overcome the weakness of homogeneous catalyst since it is more efficient and environmental friendly.

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Conventionally, vegetable oils such as canola, soybean and corn are normally used as feedstocks for biodiesel production. However, nowadays, we are facing "food vs. fuel" dilemma regarding the risk of diverting corps for biofuel production which harms the food supply on global scale. Non-edible oils meet these requirements because they are inedible and can be grown in waste land with low fertilizer. In this research, *Jatropha Curcas* oil (JCO) which is a non-edible oil are selected as a feedstock to replace the food corpses. Jatropha is reported as one of the best candidate for future biodiesel production (Lim and Teong, 2010).

Unfortunately, crude JCO contains high amount of free fatty acid (FFA). An acid and base catalyzed two step method usually used for oils with high FFA's. In this method, the oil is pretreated with an acidic catalyst before transesterification performed by using a basic catalyst. This reaction requires several reactions, washing and separation stages which is not economic. To overcome the disadvantageous of the two step process for biodiesel from oils containing high FFA, a new class of heterogeneous catalysts with both acid-base properties is developed. To improve these catalysts, a bi-functional acid-base heterogeneous catalyst is developed. Lanthanum oxide (La₂O₃)found to contain moderate Lewis acid sites (La^{3+}) and base sites (O^{2-}, OH) . The role of metal dopant in lanthanum oxide catalyst was extendedly revised. In this research, the influence of two different metal substitutions and influence of different weight percent of Bi³⁺ substituted on lanthanum oxide catalyst were investigated towards Jatropha conversion. Furthermore, the parameter biodiesel optimization for transesterification reaction such as methanol/oil molar ratio, catalyst loading, reaction time and reaction temperature were studied to get high biodiesel conversion.

1.8 Objectives

The objectives of this research are:

- 1. To synthesize Nd₂O₃-La₂O₃ and Bi₂O₃-La₂O₃catalysts via impregnation method.
- 2. To characterize the catalysts using several methods:
 - (a) X-Ray diffraction (XRD) Analysis
 - (b) Brunauer-Emmett-Teller (BET) surface area analysis
 - (c) Temperature programmed desorption of ammonia (TPD-NH₃)
 - (d) Temperature programmed desorption of carbon dioxide (TPD- CO_2)
 - (e) Scanning electron microscopy (SEM) and energy dispersive X-Ray (EDX)
 - (f) Inductively coupled plasma-atomic emission spectrometer (ICP-AES)
- 3. To produce biodiesel from crude JCO in the presence of Nd_2O_3 -La₂O₃ and Bi_2O_3 -La₂O₃ catalysts and investigate the catalytic performance of the catalysts towards biodiesel production.

REFERENCES

Abdullah, A. Z., Razali, N., Mootabadi, H., & Salamatinia, B. (2007). Critical technical areas for future improvement in biodiesel technologies. *Environmental Research Letters*, 2(3), 034001.

Abdullah, A. Z., Salamatinia, B., Mootabadi, H., & Bhatia, S. (2009). Current status and policies on biodiesel industry in Malaysia as the world's leading producer of palm oil. *Energy Policy*, *37*(12), 5440–5448.

Alsalme, A., Kozhevnikova, E. F., & Kozhevnikov, I. V. (2008). Heteropoly acids as catalysts for liquid-phase esterification and transesterification. *Applied Catalysis A: General*, *349*(1-2), 170–176.

Antolin, G., Tinaut, F. V, Briceno, Y., Ramirez, A. I., Castano, V., & Perez, C. (2002). Optimisation of biodiesel production by sunflower oil transesterification, *83*, 111–114.

Atadashi, I. M., Aroua, M. K., & Aziz, A. A. (2011). Biodiesel separation and purification: A review. *Renewable Energy*, *36*(2), 437–443.

Barakos, N., Pasias, S., & Papayannakos, N. (2008). Transesterification of triglycerides in high and low quality oil feeds over an HT2 hydrotalcite catalyst. *Bioresource Technology*, *99*(11), 5037–42.

Bart, J. C. J., Palmeri, N., & Cavallaro, S. (2010). *Biodiesel Science and Technology* (p. 137). Woodheart Publishing Limited.

Berchmans, H. J., & Hirata, S. (2008). Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. *Bioresource Technology*, *99*(6), 1716–21.

Bhatti, H., Hanif, M., & Qasim, M. (2008). Biodiesel production from waste tallow. *Fuel*, 87(13-14), 2961–2966.

Cantrell, D. G., Gillie, L. J., Lee, A. F., & Wilson, K. (2005). Structure-reactivity correlations in MgAl hydrotalcite catalysts for biodiesel synthesis. *Applied Catalysis A: General*, 287(2), 183–190.

Chen, S.-Y., Lao-Ubol, S., Mochizuki, T., Abe, Y., Toba, M., & Yoshimura, Y. (2014). Production of Jatropha biodiesel fuel over sulfonic acid-based solid acids. *Bioresource Technology*, *157*, 346–50.



Cheng, B. L., Wang, S. Y., Lu, H. B., Zhou, Y. L., Chen, Z. H., & Yang, G. Z. (2005). Effects of oxygen pressure on lattice parameter, orientation, surface morphology and deposition rate of $(Ba_{0.02}Sr_{0.98})TiO_3$ thin films grown on MgO substrate by pulsed laser deposition. *Thin Solid Films*, 485(1-2), 82–89.

Cottrell, D. W., & Hoh, R. (2011). Malaysia Biofuels Annual Annual Report 2010. USD Foreign Agricultural Service. Kuala Lumpur.

Demirbas, A. (2007). Biodiesel from sunflower oil in supercritical methanol with calcium oxide. *Energy Conversion and Management*, 48(3), 937–941.

Demirbas, A. (2008a). Biofuels. In *Biodiesel: A realistic fuel alternative for diesel* engines. (pp. 39–64). Springer.

Demirbas, A. (2008b). Biodiesel. In *Biodiesel: A realistic fuel alternative for diesel* engines. (pp. 115–116). Springer.

Demirbas, A. (2008c). Biodiesel from Triglycerides via Transesterification. In *Biodiesel: A realistic fuel alternative for diesel engines* (pp. 121–140). Springer.

Demirbas, A. (2009). Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*, 50(1), 14–34.

Demirbas, A. (2010). Biodiesel for Future Transportation Energy Needs. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 32*(16), 1490–1508.

Demirbas, A. (2011). Competitive liquid biofuels from biomass. *Applied Energy*, 88(1), 17–28.

Deng, X., Fang, Z., & Liu, Y. (2010). Ultrasonic transesterification of Jatropha curcas L. oil to biodiesel by a two-step process. *Energy Conversion and Management*, 51(12), 2802–2807.

Deng, X., Fang, Z., Liu, Y., & Yu, C.-L. (2011). Production of biodiesel from Jatropha oil catalyzed by nanosized solid basic catalyst. *Energy*, *36*(2), 777–784.

El Bassam, N. (2010). *Handbook of Bioenergy Crops A Complete Reference to Species, Development* (p. 206). Earthscan.

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

Freedman, B., Butterfield, R. O., & Pryde, E. H. (1986). Transesterification Kinetics of Soy bean Oil, 63(10).



García, J., López, T., Álvarez, M., Aguilar, D. H., & Quintana, P. (2008). Spectroscopic, structural and textural properties of CaO and CaO–SiO₂ materials synthesized by sol–gel with different acid catalysts. *Journal of Non-Crystalline Solids*, *354*(2-9), 729–732.

Gayko, G., Wolf, D., Kondratenko, E. V, & Baerns, M. (1998). Interaction of Oxygen with Pure and SrO-Doped Nd_2O_3 Catalysts for the Oxidative Coupling of Methane: Study of Work Function Changes, *449*, 441–449.

Giibitz, M., Mittelbach, M., & Trabi, M. (1999). Exploitation of the tropical oil seed plant Jatropha Curcus L., *67*, 73–82.

Granados, M. L., Alonso, D. M., Sádaba, I., Mariscal, R., & Ocón, P. (2009). Leaching and homogeneous contribution in liquid phase reaction catalysed by solids: The case of triglycerides methanolysis using CaO. *Applied Catalysis B: Environmental*, 89(1-2), 265–272.

Granados, M. L., Poves, M. D. Z., Alonso, D. M., Mariscal, R., Galisteo, F. C., Moreno-Tost, R., Santamaría, J., Fierro, J. L. G. (2007). Biodiesel from sunflower oil by using activated calcium oxide. *Applied Catalysis B: Environmental*, 73(3-4), 317–326.

Gressel, J. (2008). Transgenics are imperative for biofuel crops. *Plant Science*, 174(3), 246–263.

Hayyan, A., Alam, M. Z., Mirghani, M. E. S., Kabbashi, N. a, Hakimi, N. I. N. M., Siran, Y. M., & Tahiruddin, S. (2010). Sludge palm oil as a renewable raw material for biodiesel production by two-step processes. *Bioresource Technology*, *101*(20), 7804–11.

Helwani, Z., Othman, M. R., Aziz, N., Fernando, W. J. N., & Kim, J. (2009a). Technologies for production of biodiesel focusing on green catalytic techniques: A review. *Fuel Processing Technology*, *90*(12), 1502–1514.

Helwani, Z., Othman, M. R., Aziz, N., Kim, J., & Fernando, W. J. N. (2009b). Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. *Applied Catalysis A: General*, *363*(1-2), 1–10.

Hingu, S. M., Gogate, P. R., & Rathod, V. K. (2010). Synthesis of biodiesel from waste cooking oil using sonochemical reactors. *Ultrasonics Sonochemistry*, *17*(5), 827–32.

Jain, S., & Sharma, M. P. (2010). Biodiesel production from Jatropha curcas oil. *Renewable and Sustainable Energy Reviews*, *14*(9), 3140–3147.



Jitputti, J., Kitiyanan, B., Rangsunvigit, P., Bunyakiat, K., Attanatho, L., & Jenvanitpanjakul, P. (2006). Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. *Chemical Engineering Journal*, *116*(1), 61–66.

Jordanov, D. I., Petkov, P. S., Kirov, Y., & Ivanov, S. K. (2007). Methanol Transesterification of Different Vegetable Oils. *Petroleum and Coal*, 49(2), 21–23.

Juan, J. C., Kartika, D. A., Wu, T. Y., & Hin, T.-Y. Y. (2011). Biodiesel production from Jatropha oil by catalytic and non-catalytic approaches: an overview. *Bioresource Technology*, *102*(2), 452–60.

Kabashima, H., Tsuji, H., & Hatton, H. (1997). Michael addition of methyl crotonate over solid base catalysts, *165*, 319–325.

Kaur, N., & Ali, A. (2014). Kinetics and reusability of Zr/CaO as heterogeneous catalyst for the ethanolysis and methanolysis of Jatropha crucas oil. *Fuel Processing Technology*, *119*, 173–184.

Kim, H.-J., Kang, B.-S., Kim, M.-J., Park, Y. M., Kim, D.-K., Lee, J.-S., & Lee, K.-Y. (2004). Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis Today*, *93-95*, 315–320.

Kim, S., & Dale, B. E. (2005). Life cycle assessment of various cropping systems utilized for producing biofuels: Bioethanol and biodiesel. *Biomass and Bioenergy*, 29(6), 426–439.

Knothe, G., & Gerpen, J. Van. (2005). *The Biodiesel Handbook Editors*. Champaign, Illinois: AOCS PRESS.

Kondamudi, N., Mohapatra, S. K., & Misra, M. (2011). Quintinite as a bifunctional heterogeneous catalyst for biodiesel synthesis. *Applied Catalysis A: General*, 393(1-2), 36–43.

Kozlowski, J. T., Aronson, M. T., & Davis, R. J. (2010). Transesterification of tributyrin with methanol over basic Mg:Zr mixed oxide catalysts. *Applied Catalysis B: Environmental*, 96(3-4), 508–515.

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

Kumar, D., Kumar, G., Poonam, & Singh, C. P. (2010). Ultrasonic-assisted transesterification of Jatropha curcus oil using solid catalyst, Na/SiO₂. *Ultrasonics Sonochemistry*, *17*(5), 839–44.



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(1-2), 134–139.

Lee, D.-W., Park, Y.-M., & Lee, K.-Y. (2009). Heterogeneous Base Catalysts for Transesterification in Biodiesel Synthesis. *Catalysis Surveys from Asia*, *13*(2), 63–77.

Leofanti, G., Padovan, M., Tozzola, G., & Venturelli, B. (1998) Surface area and pore texture of catalysts. *Catalysis Today*, *41*, 207-219.

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

Li, E., Xu, Z. P., & Rudolph, V. (2009). MgCoAl–LDH derived heterogeneous catalysts for the ethanol transesterification of canola oil to biodiesel. *Applied Catalysis B: Environmental*, 88(1-2), 42–49.

Li, H., & Xie, W. (2008). Fatty Acid Methyl Ester Synthesis over Fe³⁺-Vanadyl Phosphate Catalysts. *Journal of the American Oil Chemists' Society*, 85(7), 655–662.

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

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

Liu, X., He, H., Wang, Y., & Zhu, S. (2007). Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. *Catalysis Communications*, 8(7), 1107–1111.

Liu, X., Piao, X., Wang, Y., Zhu, S., & He, H. (2008). Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. *Fuel*, *87*(7), 1076–1082.

Lokman, I. M., Rashid, U., Yunus, R., Taufiq-Yap, Y. H. (2014) Carbohydratederived solid acid catalysts for biodiesel production from low-cost feedstocks : A review. *Catalysis Reviews: Science and Engineering*, *56*(2), 187-219.

Lopez, G. P., & Laan, T. (2008). BIOFUELS - AT WHAT COST? Government support for biodiesel in Malaysia.



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*, 44(14), 5353–5363.

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

Lu, H., Liu, Y., Zhou, H., Yang, Y., Chen, M., & Liang, B. (2009). Production of biodiesel from Jatropha curcas L. oil. *Computers & Chemical Engineering*, 33(5), 1091–1096.

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

Macario, A., Giordano, G., Onida, B., Cocina, D., Tagarelli, A., & Giuffrè, A. M. (2010). Biodiesel production process by homogeneous/heterogeneous catalytic system using an acid–base catalyst. *Applied Catalysis A: General*, *378*(2), 160–168.

Makkar, H. P. S., Becker, K., Sporer, F., & Wink, M. (1997). Studies on Nutritive Potential and Toxic Constituents of Different Provenances of Jatropha curcas, *Journal of Agriculture and Food Chemistry*, 45(8), 3152–3157.

Mann, S. (2011). Sustainable Lense: A Visual Guide. NewSplash

Manoilova, O. V, Podkolzin, S. G., Tope, B., Lercher, J., Stangland, E. E., Goupil, J., & Weckhuysen, B. M. (2004). Surface Acidity and Basicity of La_2O_3 , LaOCl, and LaCl₃ Characterized by IR Spectroscopy, TPD, and DFT Calculations, *The Journal of Physical Chemistry B*. 108(40), 15770–15781.

Mansor, S.A., (2008). Keynote address: International Energy Security Forum, Kuala Lumpur; November 2008.

Martyanov, I. N., & 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(1), 45–52.

Mcginn, D., Green, D., Hinrichs-rahlwes, R., Sawyer, S., Sander, M., Taylor, R., Giner-reichl, I., Teske, S., Lehmann, H., Hales, D. (2013). *RenewableS 2013* GLOBAL STATUS REPORT 2013. Paris

Meher, L., Vidyasagar, D., & Naik, S. (2006). Technical aspects of biodiesel production by transesterification—a review. *Renewable and Sustainable Energy Reviews*, 10(3), 248–268.



Melero, J. A., Bautista, L. F., Morales, G., Iglesias, J., & Briones, D. (2009). Biodiesel production with heterogeneous sulfonic acid-functionalized mesostructured catalysts. *Energy Fuels*, *23*(1), 539-547.

Meng, X., Chen, G., & Wang, Y. (2008). Biodiesel production from waste cooking oil via alkali catalyst and its engine test. *Fuel Processing Technology*, 89(9), 851–857.

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

MPOB. (2008). A summary on the performance of the Malaysian oil palm industry. Retrieved from http://econ.mpob.gov.my/economy/performance 2007.htm

Muniyappa, P. R., Brammer, S. C., & Noureddini, H. (1996). Improved conversion of plant oils and animal fats into biodiesel and co-product. *Bioresource Technology*, *56*(1), 19–24.

Naik, S. N., Goud, V. V, Rout, P. K., & Dalai, A. K. (2010). Production of first and second generation biofuels: A comprehensive review, *14*, 578–597.

Nakagaki, S., Bail, A., Santos, V. C. Dos, Souza, V. H. R. De, Vrubel, H., Nunes, F. S., & Ramos, L. P. (2008). Use of anhydrous sodium molybdate as an efficient heterogeneous catalyst for soybean oil methanolysis. *Applied Catalysis A: General*, *351*(2), 267–274.

Ngamcharussrivichai, C., Totarat, P., & Bunyakiat, K. (2008). Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil. *Applied Catalysis A: General*, *341*(1-2), 77–85.

Ofari-Boateng, C., Lee, K. T., & Lim, J. K. (2012). Comparative exergy analyses of Jatropha curcus oil extraction methods; solvent and mechanical extraction processes. *Energy Conversion Management*, *55*, 164–71.

Oh, T. H., Pang, S. Y., & Chua, S. C. (2010). Energy policy and alternative energy in Malaysia: Issues and challenges for sustainable growth. *Renewable and Sustainable Energy Reviews*, 14(4), 1241–1252.

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). *Bioresource Technology*, *101*(17), 6589–93.

Patel, V., & Singh, K. (1991). Oil gloom to oil boom (Jatropha curcas). In Agro-Forestry Federation Maharastra. Shree press.



Patil, P. D., & Deng, S. (2009). Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel*, 88(7), 1302–1306.

Peng, B.-X., Shu, Q., Wang, J.-F., Wang, G.-R., Wang, D.-Z., & Han, M.-H. (2008). Biodiesel production from waste oil feedstocks by solid acid catalysis. *Process Safety and Environmental Protection*, 86(6), 441–447.

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

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

Rahman Mohamed, A., & Lee, K. T. (2006). Energy for sustainable development in Malaysia: Energy policy and alternative energy. *Energy Policy*, *34*(15), 2388–2397.

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

Ramos, M. J., Casas, A., Rodríguez, L., Romero, R., & Pérez, Á. (2008). Transesterification of sunflower oil over zeolites using different metal loading: A case of leaching and agglomeration studies. *Applied Catalysis A: General*, 346(1-2), 79–85.

Refaat, A. A. (2009). Different techniques for the production of biodiesel from waste vegetable oil. *International Journal of Environmental Science & Technology*, 7(1), 183–213.

Romero, R., Martínez, S. L., & Natividad, R. (2007). Biodiesel Production by Using Heterogeneous Catalysts.

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

Sastry, G. R. K. (2008). *Bio-diesel Biodegradable Alternative Fuel for Diesel Engines - Gadepalli Ravi Kiran Sastry - Google Books* (pp. 52–55). Readworthy.



Serio, M. Di, Ledda, M., Cozzolino, M., Minutillo, G., Tesser, R., & Santacesaria, E. (2006). Transesterification of Soybean Oil to Biodiesel by Using Heterogeneous Basic Catalysts, *Industrial & Engineering Chemistry Research.* 45, 3009–3014.

Shamshuddin, S. Z. M., & Nagaraju, N. (2006). Transesterification: Salol synthesis over solid acids. *Catalysis Communications*, 7(8), 593–599.

Shibasaki-Kitakawa, N., Honda, H., Kuribayashi, H., Toda, T., Fukumura, T., & Yonemoto, T. (2007). Biodiesel production using anionic ion-exchange resin as heterogeneous catalyst. *Bioresource Technology*, *98*(2), 416–21.

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

Singh, A. K., & Fernando, S. D. (2008). Transesterification of Soybean Oil Using Heterogeneous Catalysts. *Energy Fuels*, 22 (3), 2067–2069.

Soriano, N. U., Migo, V. P., Sato, K., & Matsumura, M. (2005). Crystallization behavior of neat biodiesel and biodiesel treated with ozonized vegetable oil. *European Journal of Lipid Science and Technology*, *107*(9), 689–696.

Sunita, G., Devassy, B. M., Vinu, A., Sawant, D. P., Balasubramanian, V. V., & Halligudi, S. B. (2008). Synthesis of biodiesel over zirconia-supported isopoly and heteropoly tungstate catalysts. *Catalysis Communications*, *9*(5), 696–702.

Suppes, G. J., Bockwinkel, K., Lucas, S., Botts, J. B., Mason, M. H., & Heppert, J. a. (2001). Calcium carbonate catalyzed alcoholysis of fats and oils. *Journal of the American Oil Chemists' Society*, 78(2), 139–146.

Suwannakarn, K., Lotero, E., Goodwinjr, J., & Lu, C. (2008). Stability of sulfated zirconia and the nature of the catalytically active species in the transesterification of triglycerides. *Journal of Catalysis*, 255(2), 279–286.

Taufiq-Yap, Y. H., Lee, H. V., Hussein, M. Z., & Yunus, R. (2011). Calciumbased mixed oxide catalysts for methanolysis of Jatropha curcas oil to biodiesel. *Biomass and Bioenergy*, *35*(2), 827–834.

Teo, S. H., Rashid, U., & Taufiq-Yap, Y. H. (2014). Biodiesel production from crude Jatropha Curcas oil using calcium based mixed oxide catalysts. *Fuel*, *136*, 244–252.

Times, B. (2011). B5 biodiesel in stages, starting with Putrajaya. *Business Times*. Retrieved from

http://www.btimes.com.my/Current_News/BTIMES/articles/biod19/Article/#ixzz1 MrO1G6Dq

Tiwari, A. K., 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.

Tomasevic, a. V., & Siler-Marinkovic, S. S. (2003). Methanolysis of used frying oil. *Fuel Processing Technology*, 81(1), 1–6.



Valange, S., Beauchaud, a, Barrault, J., Gabelica, Z., Daturi, M., & Can, F. (2007). Lanthanum oxides for the selective synthesis of phytosterol esters: Correlation between catalytic and acid–base properties. *Journal of Catalysis*, 251(1), 113–122.

Voon, L. H., Juan, J. C., Abdullah, N. F., Rabiah Nizah, M. F., Taufiq-Yap, Y. H. (2014). Heterogeneous base catalysts for edible palm and non-edible Jatrophabased biodiesel production. *Chemistry Central Journal*, 8(30).

Vyas, A. P., Subrahmanyam, N., & Patel, P. a. (2009). Production of biodiesel through transesterification of Jatropha oil using KNO_3/Al_2O_3 solid catalyst. *Fuel*, 88(4), 625–628.

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

Wen, Z., Yu, X., Tu, S.-T., Yan, J., & Dahlquist, E. (2010). Biodiesel production from waste cooking oil catalyzed by TiO2-MgO mixed oxides. *Bioresource Technology*, *101*(24), 9570–6.

Yan, S., DiMaggio, C., Mohan, S., Kim, M., Salley, S. O., & Ng, K. Y. S. (2010a). Advancements in Heterogeneous Catalysis for Biodiesel Synthesis. *Topics in Catalysis*, 53(11-12), 721–736.

Yan, S., Kim, M., Mohan, S., Salley, S. O., & Ng, K. Y. S. (2010b). Effects of preparative parameters on the structure and performance of Ca–La metal oxide catalysts for oil transesterification. *Applied Catalysis A: General*, 373(1-2), 104–111.

Yan, S., Lu, H., & Liang, B. (2008). Supported CaO Catalysts Used in the Transesterification of Rapeseed Oil for the Purpose of Biodiesel Production, 22(1), 646–651.

Yan, S., Salley, S. O., & Simon Ng, K. Y. (2009). Simultaneous transesterification and esterification of unrefined or waste oils over ZnO-La₂O₃ catalysts. *Applied Catalysis A: General*, *353*(2), 203–212.

Yee, K. F., Lee, K. T., Ceccato, R., & Abdullah, A. Z. (2011a). Production of biodiesel from Jatropha curcas L. oil catalyzed by $SO_4^{2^-}/ZrO_2$ catalyst: effect of interaction between process variables. *Bioresource Technology*, *102*(5), 4285–9.

Yee, K. F., Wu, J. C. S., & Lee, K. T. (2011b). A green catalyst for biodiesel production from jatropha oil: Optimization study. *Biomass and Bioenergy*, *35*(5), 1739–1746.



Zagonel, G. F., Peralta-Zamora, P. G., & Ramos, L. P. (2002). Production of ethyl esters from crude soybean oil: Optimization of reaction yields using a 2³ experimental design and development of a new analytical strategy for reaction control . *ACS Division of Fuel Chemistry, Preprints*, 47(1), 363–364.

Zanette, A. F., Barella, R. A., Pergher, S. B. C., Treichel, H., Oliveira, D., Mazutti, M. A., Silva, E. A., Oliveira, J. V. (2011). Screening, optimization and kinetics of Jatropha curcas oil transesterification with heterogeneous catalysts. *Renewable Energy*, *36*(2), 726–731.

Zhang, J., Chen, S., Yang, R., & Yan, Y. (2010). Biodiesel production from vegetable oil using heterogenous acid and alkali catalyst. *Fuel*, 89(10), 2939–2944.



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APPENDIX

A. BET Surface Area Analysis

Data collected was evaluated by using BET adsorption isotherm Equation 3:

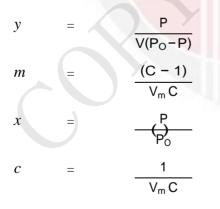
$$\frac{P}{V(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \left(\frac{P}{P_0}\right)$$
(3)

Where:

Р	=	equilibrium partial pressure of adsorbate gas in equilibrium with the surface at -196 °C
P_o	=	saturated pressure of adsorbates at corresponding temperature
V	=	volume of gas adsorbed at STP
V_m	=	volume of monolayer gas adsorbed at STP on the catalyst surface
С	=	BET constant related to the enthalpy of adsorption

BET equation can be rearranged into linear form to: y = mx + c

Where:



Hence, a graph of $\frac{P}{V(P_0-P)}$ versus $\left(\frac{P}{P_0}\right)$ be plotted and the surface area of the catalyst can be calculated by using $\frac{P_0}{V_mC}$ as the value of m and $\frac{1}{V_mC}$ as the value of c (y-intercept)

B. Determination of Saponification Value& Molecular weight

The saponification value was determined by Equation 4 :

$$SV = \frac{56.1 \text{ N} (V_{b} - V_{c})}{W} (4)$$

Where :

SV	is the saponification value in mg/g
Vb	is the volume (mL) of HCl solution used for blank;
Vs	is the volume (mL) of the solution used for determination of the sample;
Ν	is the normality of HCl;
W	is the weight (g) of the test portion;
56.1	is the molecular weight of KOH

Average molecular weight (MW) of triglyceride (TG) of oil can be estimated by Equation 5 :

AverageMWofTG =
$$\frac{56.1 \times 1000 \text{ mg} \times 3}{\text{SV}}$$
 (5)

Where :

0

56.1 is molecular weight of KOH

The saponification value for crude JCO used in this study :

Saponification Value =
$$\frac{56.1 (0.5 \text{ N}) (21.70 - 7.65 \text{ mL})}{2.004 \text{ g}}$$

$$= 188.64 \text{ mg/g}$$

Average molecular weight of crude JCO :

Average MW of TG = $\frac{56.1 \times 1000 \text{mg} \times 3}{188.64 \text{ mg/g}}$

= 892.19 g/mol

C. Determination of Acid Value& %FFA

The acid value was determined by Equation 6 :

$$AV = \frac{(V_{b} - V_{c}) N 56.1}{W} (6)$$

Where :AVis the acid value in mg/gVbis the volume (mL) of KOH solution used for blank;Vsis the volume (mL) of the solution used for determination of the sample;Nis the normality of KOH;Wis the weight (g) of the test portion;56.1is the molecular weight of KOH

FFA content can be estimated by Equation 7:

$$\frac{\% \text{FFA}}{28.2} = \frac{(\text{V}_{\text{b}} - \text{V}_{\text{c}}) \text{ N}}{\text{W}} (7)$$

Where :

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- Vb is the volume (mL) of KOH solution used for blank;
- Vs is the volume (mL) of the solution used for determination of the sample;
- N is the normality of KOH;
- W is the weight (g) of the test portion
- 28.2 is molecular weight of oleic acid divided by 10

By combining Equation 6 and 7, % FFA can be calculated as in Equation 8:

$$\%$$
FFA = $\frac{70}{1.99}(8)$

The acid value for crude JCO used in this study :

Acid Value =
$$\frac{(8.10 - 7.50 \text{ mL})(0.1 \text{ N})56.1}{0.2011 \text{ g}}$$

= 16.73 mg/g

The %FFA for crude JCO used in this study :

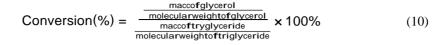
%FFA =
$$\frac{16.73}{1.99}$$

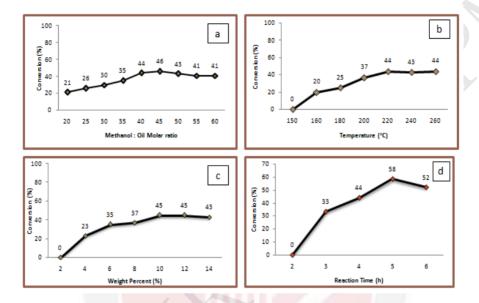
= **8.40%**

D. Determination of FAME conversion

The conversions of the jatropha oil into biodiesel were calculated from the weight of the glycerol obtained using these equations Equation 9 and 10as in below:

$$Conversion(\%) = \frac{\text{moseofesperimentalsglyceros}}{\text{moseoftheoreticalsglyceros}} \times 100\%$$
(9)





E. Optimization conditions for La₂O₃ support (page31)

Figure A1. (a) Effect of Me:Oil molar ratio, (b) Effect of reaction temperature, (c) Effect of catalyst amount and (d) Effect of reaction time

F. TPD- CO₂ and TPD-NH₃graphs for preliminary study (pg32)

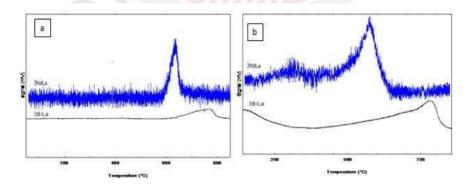


Figure A2 (a) TPD-CO₂ profiles for 3Bila and 3NdLa catalysts, (b) TPD-NH₃ profiles for 3BiLa and 3NdLa catalysts

BIODATA OF STUDENT

Born in Port Dickson, Negeri Sembilan on 18th August 1988, Rabiah Nizah attended her primary school at Sekolah Kebangsaan Port Dickson from 1995 to 2000. From year 2001-2003, she went to secondary school at Sekolah Menengah Kebangsaan Tinggi Port Dickson and had her PMR. Then in 2004-2005, she went to Sekolah Menengah Sains Muar located Muar, Johor and did her SPM there. After that, she continues her study at Johor Matriculation College, Tangkak, Johor in Physical Science for two semesters. In 2007, she was accepted to further her study in Universiti Putra Malavsia (UPM) and she managed to complete her Bachelors degree majoring in Petroleum Chemistry in 2010. Next, she pursued her second degree in Master of Science, majoring in Catalysis at Catalysis Science and Technology Research Centre, Faculty of Science, UPM under Professor Taufig Yap Yun Hin's supervision. During her research period, she gained experiences in operating various instruments such as x-ray diffraction (XRD), BET surface area, temperature desorption programmed of carbon dioxide (TPD-CO₂), gas chromatography (GC), scanning electron microscopy (SEM) and so on. Her research was supported financially by Ministry of Education.

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LIST OF PUBLICATIONS

Published papers:

- Rabiah Nizah, M.F., Taufiq-Yap, Y.H. and Hussein, M.Z. (2013) Production of Biodiesel From Non-edible *Jatropha Curcas* Oil via Transesterification Using Nd₂O₃-La₂O₃ catalyst. *Advance Materials Research* 620: 335-339.
- Rabiah Nizah, M.F., Taufiq-Yap, Y.H., Umer Rashid, Teo, S.H., Shajaratun Nur, Z.A. and Aminul, I. (2014). Production of biodiesel from non-edible *Jatropha Curcas* oil via Bi₂O₃-La₂O₃ catalyst. *Energy Conversion and Management*. 88: 1257-1262.

List of seminars/ conferences/ workshops attended:

- 1. The 7th International Conference of Chemical Engineering on Science and Applications (ChESA), Banda Aceh, Indonesia. (Oral presenter).
- 2. International Conference on X-Rays And Related Techniques in Research & Industry, Universiti Sains Malaysia, 2012. (Oral Presenter).
- 3. 19th IUPAC International Conference on Chemical Research Applied to World Needs (CHEMRAWN XIX), Putra World Trade Center (PWTC), 2011. (Participant).
- 4. Response Surface Methodolgy (RSM) Workshop, Institute of Bioscience, Universiti Putra Malaysia, 2011. (Participant).
- 5. X-Ray Fluorescence Workshop, Universiti Kebangsaan Malaysia, 2011. (Participant).
- 6. 2nd Seminar on Catalysis Science and Technology (2nd CAST), Universiti Putra Malaysia. (Participant)
- 7. Public Lecture: Energy Issues and Renewable Energy from Biomass/Wastes by Professor Dr. Kuniyuki Kitagawa, Universiti Putra Malaysia, 2010. (Participant)
- 8. PutraCAT Public Lectures: Hydrogen for Sustainable Energy by Professor Dr. Ichiro Naruse and Professor Dr. Yukihiko Matsumura, Universiti Putra Malaysia, 2013. (Participant).



- 9. PutraCAT Public Lecture: Rational Catalyst Design A case study of thermo neutral reforming catalyst development by Dr. Shakeel Ahmed, Universiti Putra Malaysia, 2012. (Participant)
- 10. PutraCAT Public Lecture: Renewable Energy from Waste Biomass by Assoc. Prof. Dr. Larence M. Pratt, Universiti Putra Malaysia, 2012. (Participant)



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