UNIVERSITI PUTRA MALAYSIA

ESTERIFICATION OF PALM FATTY ACID DISTILLATE BY USING MANGANESE OXIDE AND NICKEL OXIDE SUPPORTED ON ZIRCONIA FOR BIODIESEL PRODUCTION

SALAM HUSSEIN HAYDER AL-JABERI

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By

SALAM HUSSEIN HAYDER AL-JABERI

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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February 2017

Chairmen : Professor Taufiq Yap Yun Hin, PhD
Faculty : Science

Energy demand is now increasing on daily basis. This is due to increase in population and technical knowhow. Conventional fossil fuel reserves are potentially drying, besides, fossil fuel is associated to many environmental issues such as global warming. Biodiesel is found to be promising alternative fuel to conventional fossil fuel. This is due to its renewability, non-toxic nature, and biodegradability. However, the current biodiesel production using homogeneous catalyst is no longer economical considering the corrosiveness of liquid catalysts and difficulty in separation after use, hence, cannot be reused. Additionally, biodiesel high cost of production is mainly from cost of feedstock which account for more than 80% of total biodiesel production cost. Biodiesel production cost can be reduced by employing non edible feedstock over heterogeneous solid catalyst. Utilizing heterogeneous catalyst for biodiesel production will enable catalyst reusability, reduction in cost of production and proper disposal of used catalyst.

In this research, biodiesel was produced by esterification of palm fatty acid distillate (PFAD) with methanol using heterogeneous manganese-nickel doped on sulfated zirconia catalyst ($MnO\text{-}NiO\text{-}SO_4^{2-}/ZrO_2$). Initially, the catalyst was synthesized using simple wet impregnation method in five different concentrations of manganese 5%-25% and nickel (5%-25%) supported on zirconia. After catalyst screening, two out of five showed significant FFA conversion when concentration of manganese was 10%Mn and the concentration of nickel was 15%NiO after doping manganese and nickel on zirconia under the best concentration and then the catalyst activity was improved by increasing the acidity via treatment with chlorosulfonic acid to form $10\%Mn\text{-}15\%NiO\text{-}4\%SO_4^{2-}/ZrO_2$. The best catalyst was characterized using different characterization techniques in order to study the physic-chemical properties of the catalyst. The optimization of esterification reaction conditions of PFAD using heterogeneous solid catalysts was performed. The TPD-NH_3 result of the synthesized

solid acid catalyst proved the catalytic activity of the catalyst, having achieved 97.7% FFA conversion due to high strength of acid sites. Moreover, the catalyst was reused for at least 5 cycles before complete deactivation of the catalytic active phase.

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

PENGESTERAN ASID LEMAK KELAPA SAWIT TERSULING MENGGUNAKAN MANGAN DAN NIKEL OKSIDA DISOKONG KE ATAS ZIRKONIA UNTUK PENGHASILAN BIODIESEL

Oleh

SALAM HUSSEIN HAYDER AL-JABERI

Februari 2017

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

Permintaan terhadap keperluan tenaga semakin meningkat setiap hari disebabkan oleh peningkatan terhadap populasi dan kepakaran teknikal. Simpanan bahan api konvensional daripada fosil semakin berkurangan, disamping menyumbang kepada isu alam sekitar seperti pemanasan global. Biodiesel berpotensi sebagai bahan bakar alternatif kepada bahan bakar konvensional fosil memandangkan sifatnya yang boleh diperbaharui, tidak toksik, dan biodegradasi. Walau bagaimanapun, penghasilan biodiesel pada masa kini dengan menggunakan mangkin homogen adalah tidak lagi ekonomi dengan mengambil kira sifat kakisan mangkin cecair tersebut dan kesukaran dalam pemisahan mangkin selepas tindak balas, sekali gus menyebabkan ianya tidak boleh digunakan semula. Tambahan pula, kos pengeluaran biodiesel yang tinggi disebabkan oleh kos bahan mentah yang mana ianya adalah lebih daripada 80% jumlah pengeluaran biodiesel secara keseluruhan. Kos pengeluaran biodiesel dapat dikurangkan dengan menggunakan bahan mentah yang tidak boleh dimakan dan mangkin pepejal heterogen. Penggunaan mangkin heterogen untuk pengeluaran biodiesel dapat mengurangkan kos pengeluran, kebolehgunaan semula mangkin dan pengurusan pembuangan sisa mangkin yang lebih baik.

Dalam kajian ini, biodiesel dihasilkan melalui proses pengesteran asid lemak kelapa sawit tersuling (PFAD) bersama metanol menggunakan mangkin heterogen mangan-nikel terdop ke atas zirkonia bersulfur ($MnO\text{-}NiO\text{-}SO_4^{2-}/ZrO_2$). Pada mulanya, mangkin telah disintesis menggunakan kaedah pengisitepuan basah dalam lima kepekatan mangan yang berbeza (5%-25%) dan nikel (5%-25%) yang disokong ke atas zirkonia. Selepas penyaringan mangkin, dua daripada lima mangkin menunjukkan penukaran asid lemak bebas (FFA) yang signifikan apabila kepekatan mangan dan nikel masing-masing adalah sebanyak 10 % dan 15 %. Selepas mangan dan nikel didop ke atas zirkonia pada kepekatan yang dipilih dan aktiviti mangkin ditambah baik dengan meningkatkan keasidan mangkin melalui rawatan dengan menggunakan asid

klorosulfonik untuk menghasilkan 10%Mn-15%NiO- 4%SO_4^{2-}/ ZrO_2. Mangkin terbaik yang dipilih dicirikan menggunakan pelbagai teknik pencirian untuk mengkaji sifat fizikokimia bagi mangkin tersebut. Pengoptimuman tindak balas pengesteran PFAD menggunakan mangkin heterogen pepejal telah dilakukan. Keputusan aturcara-suhu-nyahjerapan ammonia (TPD-NH_3) bagi mangkin asid pepejal membuktikan aktivit mangkin mencapai sehingga 97.7% penukaran FFA yang disebabkan oleh kekuatan tapak asid. Tambahan pula, mangkin dapat diguna semula sekurang-kurangnya lima kali kitaran tindak balas sebelum ternyahaktif.

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I certify that a Thesis Examination Committee has met on 23 February 2017 to conduct the final examination of Salam Hussein Hayder on his thesis entitled "Esterification of Palm Fatty Acid Distillate by Using Manganese Oxide and Nickel Oxide Supported on Zirconia for Biodiesel Production" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

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Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mansor bin Hj Ahmad @ Ayob, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Cheng Chin Kui, PhD
Associate Professor
Universiti Malaysia Pahang
Malaysia
(External Examiner)

NOR AINI AB. SHUKOR, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 28 April 2017

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

Taufiq Yap Yun Hin, FASc, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Izham Bin Saiman, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Umer Rashid, PhD
Research Fellow
Institute of Advanced Technology
Universiti Putra Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD
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This is to confirm that:

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Signature: _____
Name of Member of Supervisory Committee: Dr. Mohd Izham Bin Saiman

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

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing And Materials
AAS	Atomic Absorption Spectroscopy
BET	Brunauer-Emmett-Teller
CHSN	CHSN - Elemental Analyser
EDX	Energy-Dispersive X-Ray Spectroscopy
EN	European Standard
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FT-IR	Fourier Transform Infrared
GC	Gas Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
PFAD	Palm Fatty Acid Distillate
SEM	Scanning Electron Microscopy.
TGA	Thermo Gravimetric Analysis
TPD- NH_3	Ammonia-Temperature Programmed Desorption
XRD	X-Ray Power Diffraction
XRF	X-Ray Fluorescence Spectrometry

CHAPTER 1

INTRODUCTION

1.1 Background

Science and technological revolution that started over a century ago was meant to modified and improved human activities such as industrialization for the production of goods and services, modern transport system, mechanized agriculture and modern telecommunication. The aforementioned human activities are solely depending on energy which could be solar, hydro, coal or petrochemical based sources. Nowadays, the most used source of energy is petrochemical based which is fossil in nature. Fossil fuel is now considered as conventional source of energy for the production of goods and services in the industries as well as modern transportation. However, as a result of global rapid growth of human population from developing nations, possible future depletion of the fossil fuel reserved and concern over environmental issues such as global warming, fossil fuel is generally no longer considered as reliable sustainable source of energy in the future. These and other factors led to the search in renewable alternative sources of energy such as biofuels that could replace the diminishing fossil fuel. Biodiesel was found one of the most promising alternatives to conventional diesel due to its biodegradability, less poisonous exhaust, availability of feedstocks, low cost of production when compared to crude oil exploration and refining. Apart from the aforementioned advantages, biodiesel possesses similar chemical properties to that of conventional fossil fuel such as high flash point, enhanced cetane number and density. The production of biodiesel or fatty acid methyl ester (FAME) involve the reversible chemical reaction of triglycerides (TGs) a major component of vegetable oil or free fatty acid (FFA) a major component of Palm Fatty Acid Distillate (PFAD) with lower chain methyl alcohol (methanol) facilitated by good catalytic system under temperature and pressure over a period of time. Traditionally, biodiesel or FAME is produced using homogeneous catalyst such as NaOH, H_2SO_4, KOH, in which the catalyst and the feedstock are in the same phase. These catalysts are very active as they can convert vegetable oil to biodiesel at low reaction conditions. However, homogeneous catalysts are only fit to high grade vegetable oil (containing <1% FFA) which would make biodiesel production very expensive considering the high cost of fresh vegetable oil. A part from that, homogeneous catalysts are associated with difficulty in separation after the reaction which involves regular water washing that could pollute the environment and make biodiesel production difficult. Continual usage of high grade vegetable oil suitable for homogeneous catalysts for the production of biodiesel is no longer sustainable considering the consequences of food versus fuel competition which would pose hunger threats and environmental degradation through agricultural practices. Besides, homogeneous catalysts require considerable amount of energy for the purification of products and catalyst separation, additionally the catalysts are not reusable. In order to overcome such challenges, low grade feedstocks such as waste cooking oil (WCO), PFAD would be adopted as feedstock for the production of biodiesel considering their low cost. About 70% of total cost of biodiesel production goes to feedstock, hence using low cost feedstock like PFAD would make the production cost low and sustainable. However, low grades feedstock like PFAD and waste cooking oil have high FFA content usually >1. PFAD contain more than 85% FFA which cannot be handled by homogeneous catalyst for

biodiesel. Heterogeneous acid or base catalysts have revealed less marked operational difficulty when compared to conventional homogeneous catalysts for biodiesel production considering their easy separation which has minimum environmental effect compared to their counterpart. One of the most important aspects about biodiesel is that it possessed all the chemical and physical properties as contained to conventional fossil fuel.

1.2 Catalyst

Generally, a catalyst is defined as a material or substance which accelerates the rate of a chemical reaction by reducing the activation energy. Activation energy is the energy needed for a chemical reaction to occur. Very minute quantity of a catalyst is needed for a reaction compared to the quantities of the reactants. Catalyst speeds up the chemical reaction without affecting the reactants during the chemical transformation. Hence, called initiator. Nevertheless, in few cases the catalyst affects the reaction by being consumed and regenerated while in some cases it seems not to take part in the process and functions by high calibre of surface characteristics (Ertl *et al*., 2008). Similarly, Ostwald (1895) defined the catalyst as a material that speeds up a chemical transformation without shifting the position of the equilibrium (Ertl *et al.,* 2008).

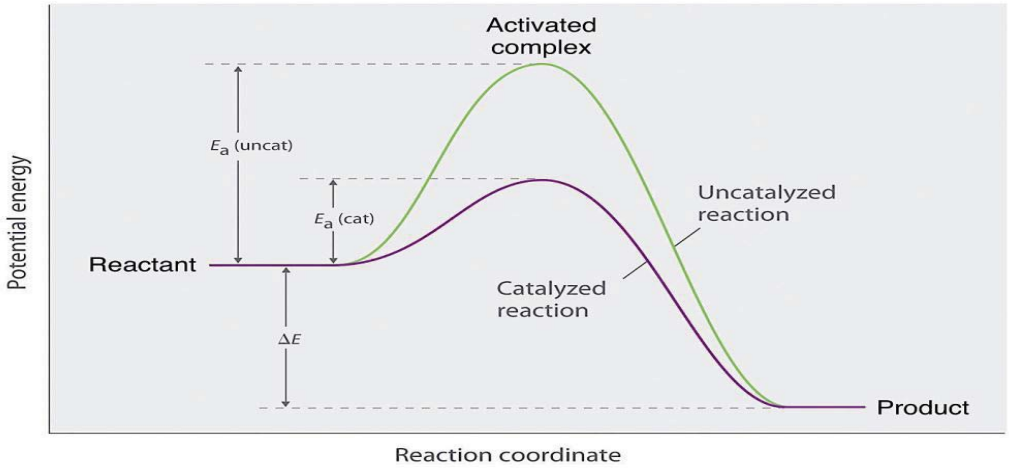

Figure 1.1 : The effect of catalyst on the activation energy of the reaction

1.3 Problem Statement and Hypothesis

The current sources of energy are petroleum based fuels which have greater environmental effects such as global warming and toxic exhaust as a result of release of Green House Gases (GHG) through internal combustion of hydrocarbons by motorist and industries to the planet earth. Renewable alternative sources of energy such as biofuels are the only option that can mitigate the aforementioned problems associated to fossil fuels. Biodiesel was found promising considering its biodegradability, less toxic exhaust, availability of feedstock. However, the conventional method of biodiesel production employs the use of homogeneous catalysts over a high-grade vegetable oil. Besides high cost price of fresh vegetable oil, homogeneous

catalysts are corrosive and are difficult to be separated after the reaction, therefore, it can only be used once. The use of heterogeneous solid catalyst and non-edible feedstock would make biodiesel production low cost and sustainable.

In this study, biodiesel was produced from low cost PFAD using heterogeneous acid catalyst ($MnO\text{-}NiO\text{-}SO_4^{2-}/ZrO_2$), which is believed to reduce biodiesel production cost and make significant contribution towards its commercialization in the near future. The heterogeneous solid catalyst could be separated easily and reused severally before total loss of activity. Solid catalysts are less corrosive and more environmentally benign in terms of disposal after use.

1.4 Objectives of the Research

The purpose of this research is to synthesize a heterogeneous solid acid catalyst and apply it for the production of biodiesel from PFAD. There four main objectives that have been highlighted and concentrated are;

1- To synthesize and characterize the heterogeneous solid acid catalyst ($MnO\text{-}NiO/ZrO_2$)
2- To evaluate sulfate group in to the $MnO\text{-}NiO/ZrO_2$ catalyst to increase the acidity of the catalyst.
3- To examine the synthesized solid acid catalyst on PFAD to produce biodiesel via esterification reaction and optimize the reaction parameters.
4- To determine the catalyst reusability and biodiesel properties.

1.5 Scope of the Research

This research covers the production of the low-cost biodiesel from the low-quality feedstock over a synthesized solid acid catalyst.

1- The solid acid catalyst ($MnO\text{-}NiO\text{-}SO_4^{2-}/ZrO_2$) would be synthesized using simple wet impregnation method from the oxides of nickel and manganese as dopants on surface of sulphated zirconia, in array to develop their catalytic activity towards the synthesis of biodiesel from high FFA feedstock.
2- The catalytic activity of the synthesized catalyst would be tested through biodiesel production using direct esterification reaction of PFAD with short chain alcohol (methanol), catalyst and temperature as reaction conditions.
3- Physico-chemical properties of the synthesized solid acid catalyst would be explored and evaluated using different characterization techniques to understand the features that control their catalytic activity as well as recyclability, regeneration and the leaching problems of active sites.
4- Optimization of biodiesel production parameters would be assessed over the most active catalyst within the screened synthesized solid catalysts under the reaction conditions (catalyst loading, methanol oil ratio, temperature and reaction time).

REFERENCES

Ahmad, A. L., Yasin, N. M., Derek, C. J. C., & Lim, J. K. (2011). Microalgae as a sustainable energy source for biodiesel production: a review. *Renewable and Sustainable Energy Reviews*, *15*(1), 584-593.

Ahmad, A. L., Yasin, N. M., Derek, C. J. C., & Lim, J. K. (2016). Microalgae as a sustainable energy source for biodiesel production: a review. *Renewable and Sustainable Energy Reviews*, 15(1), 584-593.

Alhassan, F. H., Rashid, U., & Taufiq-Yap, Y. H. (2015). Synthesis of waste cooking oil-based biodiesel via effectual recyclable bi-functional Fe 2 O 3 MnO SO 4 2−/ZrO 2 nanoparticle solid catalyst. *Fuel*, 142, 38-45.

Alsultan, A., Mijan, A., & Taufiq-Yap, Y. H. (2016). Preparation of Activated Carbon from Walnut Shell Doped La and Ca Catalyst for Biodiesel Production from Waste Cooking Oil. *In Materials Science Forum* (Vol. 840, pp. 348-352). Trans Tech Publications.

Abdulkareem-Alsultan, G., Asikin-Mijan, N., Lee, H. V., & Taufiq-Yap, Y. H. (2016). A new route for the synthesis of La-Ca oxide supported on nano activated carbon via vacuum impregnation method for one pot esterification-transesterification reaction. *Chemical Engineering Journal*, *304*, 61-71.

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

American Oil Chemists' Society, & Firestone, D. (1989). *Official methods and recommended practices of the American Oil Chemists' Society* (Vol. 5). Champaign, IL, USA: AOCS.

Atabani, A. E., Silitonga, A. S., Badruddin, I. A., Mahlia, T. M. I., Masjuki, H. H., & Mekhilef, S. (2012). A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews*, 16(4), 2070-2093.

Atadashi, I. M., Aroua, M. K., Aziz, A. A., & Sulaiman, N. M. N. (2012). Production of biodiesel using high free fatty acid feedstocks. *Renewable and Sustainable Energy Reviews*, 16(5), 3275-3285.

Avinash, A., Subramaniam, D., & Murugesan, A. (2014). Bio-diesel—A global scenario. Renewable and Sustainable Energy Reviews, 29, 517-527.

Balat, M. (2011). Potential alternatives to edible oils for biodiesel production–A review of current work. *Energy Conversion and Management*, 52(2), 1479-1492.

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

Basiron, Y. (2007). Palm oil production through sustainable plantations. *European Journal of Lipid Science and Technology*, 109(4), 289-295.

Bendz, K. (2005). EU-25-Oilseeds and Products: Biofuel Situation in the European Union 2005.USDA Foreign Agricultural Service, Gain Report E35058, *Global Agriculture Information Network* 1-11.

Berrios, M., & Skelton, R. L. (2008). Comparison of purification methods for biodiesel. *Chemical Engineering Journal*, *144*(3), 459-465.

Borugadda, V. B., & Goud, V. V. (2012). Biodiesel production from renewable feedstocks: Status and opportunities. *Renewable and Sustainable Energy Reviews,* 16(7), 4763-4784.

Bouaid, A., Hahati, K., Martinez, M., & Aracil, J. (2014). Biodiesel production from biobutanol. Improvement of cold flow properties. *Chemical Engineering Journal*, *238*, 234-241.

Brito, A., Borges, M., & Otero, N. (2007). Zeolite Y as a heterogeneous catalyst in biodiesel fuel production from used vegetable oil. *Energy & Fuels*, 21(6), 3280-3283.

Cheah, K. Y., Toh, T. S., & Koh, P. M. (2010). Palm fatty acid distillate biodiesel. *Inform*, *21*(5), 264-266.

Cheikh, K., Sary, A., Khaled, L., Abdelkrim, L., & Mohand, T. (2016). Experimental assessment of performance and emissions maps for biodiesel fueled compression ignition engine. *Applied Energy*, *161*, 320-329.

Clauss, Francis J., ed. *Solid lubricants and self-lubricating solids*. Elsevier, 2012.

Chen, G., & Fang, B. (2011). Preparation of solid acid catalyst from glucose–starch mixture for biodiesel production. *Bioresource technology*, 102(3), 2635-2640.

Chen, H., Peng, B., Wang, D., & Wang, J. (2007). Biodiesel production by the transesterification of cottonseed oil by solid acid catalysts. *Frontiers of Chemical Engineering in China*, 1(1), 11-15.

Cho, H. J., Kim, S. H., Hong, S. W., & Yeo, Y. K. (2012). A single step non-catalytic esterification of palm fatty acid distillate (PFAD) for biodiesel production. *Fuel,* 93, 373-380.

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

Choedkiatsakul, I., Ngaosuwan, K., Cravotto, G., & Assabumrungrat, S. (2014). Biodiesel production from palm oil using combined mechanical stirred and ultrasonic reactor. *Ultrasonics sonochemistry,* 21(4), 1585–1591.

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

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

Chung, K.-H., Kim, J., & Lee, K.-Y. (2009). Biodiesel production by transesterification of duck tallow with methanol on alkali catalysts. *Biomass and Bioenergy*, 33(1), 155-158.

Clarens, A. F., Resurreccion, E. P., White, M. A., & Colosi, L. M. (2010). Environmental life cycle comparison of algae to other bioenergy feedstocks. *Environmental Science & Technology,* 44(5), 1813-1819.

Clark, C. (2012). Principles of General Chemistry. Chapter 14: Chemical

Costa, A. A., Braga, P. R., de Macedo, J. L., Dias, J. A., & Dias, S. C. (2012). Structural effects of WO 3 incorporation on USY zeolite and application to free fatty acids esterification. *Microporous and Mesoporous Materials*, 147(1), 142-148.

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

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

Demirbas, A. (2006). Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics. *Energy conversion and Management*, 47(15), 2271-2282.

Demirbas, A. H., & Demirbas, I. (2007). Importance of rural bioenergy for developing countries. *Energy Conversion and Management*, 48(8), 2386-2398.

Ding, Y., Sun, H., Duan, J., Chen, P., Lou, H., & Zheng, X. (2011). Mesoporous Li/ZrO 2 as a solid base catalyst for biodiesel production from transesterification of soybean oil with methanol. *Catalysis communications*, *12*(7), 606-610.

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

Eevera, T., Rajendran, K., & Saradha, S. (2009). Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions. *Renewable Energy*, 34(3), 762-765.

El Diwani, G., Attia, N., & Hawash, S. (2009). Development and evaluation of biodiesel fuel and by-products from jatropha oil. *International Journal of Environmental Science and Technology*, 6(2), 219-224.

El-Gendy, N. S., Hamdy, A., & Abu Amr, S. S. (2014). An investigation of biodiesel production from wastes of seafood restaurants. *International journal of biomaterials*, *2014*.

El Sherbiny, S. A., Refaat, A. A., & El Sheltawy, S. T. (2010). Production of biodiesel using the microwave technique. *Journal of Advanced Research*, 1(4), 309-314.

El-Mashad, H. M., Zhang, R., & Avena-Bustillos, R. J. (2008). A two-step process for biodiesel production from salmon oil. *Biosystems Engineering*, 99(2), 220-227.

Embong, N. H., Maniam, G. P., Rahim, M. H. A., Lee, K. T., & Huisingh, D. (2016). Utilization of palm fatty acid distillate in methyl esters preparation using SO42−/TiO 2–SiO 2 as a solid acid catalyst. *Journal of Cleaner Production*,116, 244-248.

Encinar, J. M., González, J. F., Martínez, G., Sánchez, N., & Pardal, A. (2012). Soybean oil transesterification by the use of a microwave flow system.*Fuel*, *95*, 386-393.

Ertl, G., Knözinger, H., & Weitkamp, J. (2008). *Preparation of solid catalysts*: John Wiley & Sons.

Eterigho, E. J., Lee, J. G., & Harvey, A. P. (2011). Triglyceride cracking for biofuel production using a directly synthesised sulphated zirconia catalyst.*Bioresource technology*, *102*(10), 6313-6316.

Falasca, S., Ulberich, A., & Acevedo, A. (2014). Identification of Argentinian saline drylands suitable for growing *Salicornia bigelovii* for bioenergy. *International Journal of Hydrogen Energy*, *39*(16), 8682–8689

Fischer, C. R., Klein-Marcuschamer, D., & Stephanopoulos, G. (2008). Selection and optimization of microbial hosts for biofuels production. *Metabolic engineering, 10*(6), 295-304.

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

Fukuda, H., Kondo, A., & Noda, H. (2001). Biodiesel fuel production by transesterification of oils. *Journal of bioscience and bioengineering*, 92(5), 405-416.

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

Gole, V. L., & Gogate, P. R. (2013). Intensification of synthesis of biodiesel from non-edible oil using sequential combination of microwave and ultrasound.*Fuel processing technology*, 106, 62-69.

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

Haas, M. J. (2005). Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock. *Fuel Processing Technology*, *86*(10), 1087-1096.

Hawash, S., Kamal, N., Zaher, F., Kenawi, O., & Diwani, G. E. (2009). Biodiesel fuel from Jatropha oil via non-catalytic supercritical methanol transesterification. *Fuel*, 88(3), 579-582.

Hayyan, A., Alam, M. Z., Mirghani, M. E., Kabbashi, N. A., Hakimi, N. I. N. M., Siran, Y. M., & Tahiruddin, S. (2011). Reduction of high content of free fatty acid in sludge palm oil via acid catalyst for biodiesel production. *Fuel Processing Technology*, *92*(5), 920-924.

Hoekman, S. K., Broch, A., Robbins, C., Ceniceros, E., & Natarajan, M. (2012). Review of biodiesel composition, properties, and specifications. *Renewable and Sustainable Energy Reviews*, 16(1), 143-16.

Hu, Q., Sommerfeld, M., Jarvis, E., Ghirardi, M., Posewitz, M., Seibert, M., & Darzins, A. (2008). Microalgal triacylglycerols as feedstocks for biofuel production: perspectives and advances. *The Plant Journal*, 54(4), 621-639.

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

Islam, A., Taufiq-Yap, Y. H., Chu, C. M., Chan, E. S., & Ravindra, P. (2013). Studies on design of heterogeneous catalysts for biodiesel production. *Process Safety and Environmental Protection*, *91*(1), 131-144.

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

Jacobson, K., Gopinath, R., Meher, L. C., & Dalai, A. K. (2008). Solid acid catalyzed biodiesel production from waste cooking oil. *Applied Catalysis B: Environmental*, 85(1), 86-91.

Jentoft, F. C., Hahn, A., Kröhnert, J., Lorenz, G., Jentoft, R. E., Ressler, T., ... & Köhler, K. (2004). Incorporation of manganese and iron into the zirconia lattice in promoted sulfated zirconia catalysts. *Journal of Catalysis*, 224(1), 124-137.

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.

Kafuku, G., & Mbarawa, M. (2010). Biodiesel production from Croton megalocarpus oil oil and its process optimization. *Fuel*, 89(9), 2556-2560.

Kaya, C., Hamamci, C., Baysal, A., Akba, O., Erdogan, S., & Saydut, A. (2009). Methyl ester of peanut (Arachis hypogea L.) seed oil as a potential feedstock for biodiesel production. *Renewable Energy*, *34*(5), 1257-1260.

Karmakar, A., Karmakar, S., & Mukherjee, S. (2010). Properties of various plants and animals feedstocks for biodiesel production. *Bioresource technology*, 101(19), 7201-7210.

Karmee, S. K., & Chadha, A. (2005). Preparation of biodiesel from crude oil of Pongamia pinnata. *Bioresource Technology*, 96(13), 1425-1429.

Knothe, G., & Steidley, K. R. (2009). A comparison of used cooking oils: a very heterogeneous feedstock for biodiesel. *Bioresource technology*, *100*(23), 5796-5801.

Knothe, G. (2005). Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel processing technology*, *86*(10), 1059-1070.

Koopmans, C., Iannelli, M., Kerep, P., Klink, M., Schmitz, S., Sinnwell, S., & Ritter, H. (2006). Microwave-assisted polymer chemistry: Heck-reaction, transesterification, Baeyer–Villiger oxidation, oxazoline polymerization, acrylamides, and porous materials. Tetrahedron, 62(19), 4709-4714.catalyst: effect of stoichiometric composition. *Chemical Engineering Journal*, 178, 342-347.

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

Lam, M. K., Tan, K. T., Lee, K. T., & Mohamed, A. R. (2009). Malaysian palm oil: Surviving the food versus fuel dispute for a sustainable future. *Renewable and Sustainable Energy Reviews*, 13(6), 1456-1464.

Lau, P. C., Kwong, T. L., & Yung, K. F. (2016). Effective heterogeneous transition metal glycerolates catalysts for one-step biodiesel production from low grade non-refined Jatropha oil and crude aqueous bioethanol. *Scientific reports*, 6.

Lee, H. V., Juan, J. C., & Taufiq-Yap, Y. H. (2015). Preparation and application of binary acid–base CaO–La 2 O 3 catalyst for biodiesel production. *Renewable Energy,* 74, 124-132.

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.

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.

Liaw, K. J. (2013). *Biodiesel synthesis via solid acid catalyst by using palm fatty acid distillate (PFAD) as feedstock* (Doctoral dissertation, UTAR).

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.

Liu, Y., Wang, L., & Yan, Y. (2009). Biodiesel synthesis combining pre-esterification with alkali catalyzed process from rapeseed oil deodorizer distillate. *Fuel Processing Technology*, 90(7), 857-862.

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

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.

Lowell, P. S., Schwitzgebel, K., Parsons, T. B., & Sladek, K. J. (1971). Selection of metal oxides for removing SO2 from flue gas. *Industrial & Engineering Chemistry Process Design and Development*, 10(3), 384-390.

Lu, J., Nie, K., Xie, F., Wang, F., & Tan, T. (2007). Enzymatic synthesis of fatty acid methyl esters from lard with immobilized Candida sp. 99-125. *Process Biochemistry*, 42(9), 1367-1370.

Mabaleha, M., Mitei, Y., & Yeboah, S. (2007). A comparative study of the properties of selected melon seed oils as potential candidates for development into commercial edible vegetable oils. *Journal of the American Oil Chemists' Society*, 84(1), 31-36.

Fulton, L., Howes, T., & Hardy, J. (2008). Biofuels for transport: an international perspective, *International Energy Agency (IEA),* Paris, France. 2004 [Internet].

Marchetti, J. M., Miguel, V. U., & Errazu, A. F. (2008). Techno-economic study of different alternatives for biodiesel production. *Fuel Processing Technology*,89(8), 740-748.

Martínez, S. L., Romero, R., Natividad, R., & González, J. (2014). Optimization of biodiesel production from sunflower oil by transesterification using Na2O/NaX and methanol. *Catalysis Today*, 220, 12-20.

Meher, L., Vidya Sagar, D., & Naik, S. (2006). Technical aspects of biodiesel production by transesterification—a review. *Renewable and sustainable energy reviews*, 10(3), 248-268.

Mofijur, M., Masjuki, H., Kalam, M., Atabani, A., Fattah, I., & Mobarak, H. (2014). Comparative evaluation of performance and emission characteristics of Moringa oleifera and Palm oil based biodiesel in a diesel engine. *Industrial Crops and Products*, 53, 78-84.

Motasemi, F., & Ani, F. N. (2012). A review on microwave-assisted production of biodiesel. *Renewable and Sustainable Energy Reviews*, 16(7), 4719-4733.

Mross, W. D. (1983). Alkali doping in heterogeneous catalysis. *Catalysis Reviews Science and Engineering*, 25(4), 591-637.

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

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

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

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

Perrichon, V., & Durupty, M. C. (1988). Thermal stability of alkali metals deposited on oxide supports and their influence on the surface area of the support. *Applied catalysis*, 42(2), 217-227.

Pienkos, P. T., & Darzins, A. (2009). The promise and challenges of microalgal-derived biofuels. Biofuels, *Bioproducts and Biorefining*, 3(4), 431-440.

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

Pinto, A. C., Guarieiro, L. L., Rezende, M. J., Ribeiro, N. M., Torres, E. A., Lopes, W. A.,. Andrade, J. B. d. (2005). Biodiesel: an overview. *Journal of the Brazilian Chemical Society,* 16(6B), 1313-1330.

Qing, S. H. U., Jixian, G. A. O., Yuhui, L. I. A. O., & Jinfu, W. A. N. G. (2011). Reaction kinetics of biodiesel synthesis from waste oil using a carbon-based solid acid catalyst. *Chinese Journal of Chemical Engineering*, 19(1), 163-168.

Raheman, H., Jena, P. C., & Jadav, S. S. (2013). Performance of a diesel engine with blends of biodiesel (from a mixture of oils) and high-speed diesel. *International Journal of Energy and Environmental Engineering*, 4(1), 1-9.

Rashid, U., & Anwar, F. (2008b). Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. *Fuel*, 87(3), 265-273.

Rashid, U., & Anwar, F. (2008a). Production of biodiesel through base-catalyzed transesterification of safflower oil using an optimized protocol. *Energy & Fuels,* 22(2), 1306-1312.

Rashid, U., Anwar, F., Moser, B. R., & Ashraf, S. (2008). Production of sunflower oil methyl esters by optimized alkali-catalyzed methanolysis. *Biomass and Bioenergy*, 32(12), 1202-1205.

Rashid, U., Ibrahim, M., Yasin, S., Yunus, R., Taufiq-Yap, Y. H., & Knothe, G. (2013). Biodiesel from Citrus reticulata (mandarin orange) seed oil, a potential non-food feedstock. *Industrial Crops and Products*, 45, 355-359.

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

Serrano, E., Rus, G., & García-Martínez, J. (2009). Nanotechnology for sustainable energy. *Renewable and Sustainable Energy Reviews*, 13(9), 2373-2384.

Sharma, Y., & Singh, B. (2009). Development of biodiesel: current scenario. *Renewable and Sustainable Energy Reviews*, 13(6), 1646-1651.

Sharma, Y., Singh, B., & Upadhyay, S. (2008). Advancements in development and characterization of biodiesel: a review. *Fuel*, 87(12), 2355-2373.

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.

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

Shu, Q., 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.

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

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

Siatis, N. G., Kimbaris, A. C., Pappas, C. S., Tarantilis, P. A., & Polissiou, M. G. (2006). Improvement of biodiesel production based on the application of

ultrasound: monitoring of the procedure by FTIR spectroscopy. *Journal of the American Oil Chemists' Society*, 83(1), 53-57.

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

Song, H., Qiu, X., & Li, F. (2009). Promotion of carbon nanotube-supported Pt catalyst for methanol and ethanol electro-oxidation by ZrO 2 in acidic media. *Applied Catalysis A: General*, 364(1), 1-7.

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

Taufiq-Yap, Y. H., Lee, H. V., Yunus, R., & Juan, J. C. (2011). Transesterification of non-edible Jatropha curcas oil to biodiesel using binary Ca–Mg mixed oxide

Tewari DN (2007) Jatropha and biodiesel. (1st edn), Prabhat Prakashan, New Delhi, India

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

Trakarnpruk, W. (2012). Biodiesel production from palm fatty acids distillate using tungstophosphoric acid-and Cs-salt immobilized-silica. *Walailak Journal of Science and Technology (WJST),* 9(1), 37-47.

Veljković, V., Lakićević, S., Stamenković, O., Todorović, Z., & Lazić, M. (2006). Biodiesel production from tobacco (Nicotiana tabacumL.) seed oil with a high content of free fatty acids. *Fuel*, 85(17), 2671-2675.

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

Worapun, I., Pianthong, K., & Thaiyasuit, P. (2010). Synthesis of biodiesel by two-step transesterification from crude jatropha curcus L. oil using ultrasonic irradiation assisted. *KKU Engineering Journal*, *37*(3), 169-179.

Xie, W., & Li, H. (2006). Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. *Journal of Molecular Catalysis A: Chemical*, *255*(1), 1-9.

Yadav, G. D., & Murkute, A. D. (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(1), 218-223.

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

Zäch, M., Hägglund, C., Chakarov, D., & Kasemo, B. (2006). Nanoscience and nanotechnology for advanced energy systems. *Current Opinion in Solid State and Materials Science*, 10(3–4), 132-143.

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

Zhang, J., Cui, C., Chen, H., & Liu, J. (2014a). The Completion of Esterification of Free Fatty Acids in Zanthoxylum Bungeanum Seed Oil with Ethanol. *International Journal of Green Energy*, 11(8), 822-832.

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

Zhang, J., & Jiang, L. (2008). Acid-catalyzed esterification of Zanthoxylum bungeanum seed oil with high free fatty acids for biodiesel production. *Bioresource technology*, *99*(18), 8995-8998.

Zhang, Y., Wong, W. T., & Yung, K. F. (2013). One-step production of biodiesel from rice bran oil catalyzed by chlorosulfonic acid modified zirconia via simultaneous esterification and transesterification. *Bioresource technology*, 147, 59-64.

Zhang, Y., Wong, W. T., & Yung, K. F. (2014b). Biodiesel production via esterification of oleic acid catalyzed by chlorosulfonic acid modified zirconia. *Applied Energy*, 116, 191-198.