TRANSESTERIFICATION OF CROTON MEGALOCARPUS OIL OVER TUNGSTEN TRIOXIDE LOADED ON SILICA MESOPOROUS-MACROPARTICLES

KHALIDAH BINTI PUAD

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Science (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

DECEMBER 2015

A special dedication to my beloved parents,

Puad Mat Yassin and Shariffah Osman

To my siblings, my beloved nephews

&

To all my friends

Thank you for everything.

ACKNOWLEDGEMENT

Alhamdulillah, all prise and thanks to Allah. Peace and blessing to our prophet Nabi Muhammad S.A.W, his families and all muslims. Special thanks go to my supervisor, Prof Dr. Sugeng Triwahyono and co-supervisor Associate Prof Dr. Aishah Abdul Jalil and Associate Prof Dr Zainab Ramli for their supervison throughout the course of this project. Without their time and patience much of this work could not have been accomplish. I have gained a lot of knowledge and experience during this project.

I would like to express my deepest gratitude to the Zamalah UTM schorship for the agreement and financial support. Millions thanks goes to my senior,Aiza, Munirah, Peng, and Dayah. A lot of appreciation also goes to all my GTAM lab members for their hands and cooperation. And lastly my appreciation goes to all of my friends for all the encouragement and helps throughout the study.

Last but not least, I wish to express my sincere appreciation to my beloved family for their continuous support, advices,and motivation for me to complete my project. Thank you so much.

ABSTRACT

Production of biodiesel has been seen as a quantum jump in recent years due to its ability to mitigate greenhouse gas (GHG). Biodiesel produces better quality of exhaust gas emission that helps in minimizing the greenhouse effect. In this study, non-edible *Croton megalocarpus* oil was converted to biodiesel by transesterification process in heterogeneous catalysis over tungsten trioxide supported on silica mesoporous-macroparticles (WO_3/SMP). The SMP was successfully synthesized by hydrolysis of TEOS in the mixed solvent of water and acetone using CTAB as template at room temperature. Meanwhile, WO_3/SMP catalysts were prepared by impregnation, followed by drying and calcination at 823 K. The properties of WO_3/SMP were characterized using XRD, FTIR, N_2 physisorption, FESEM and TEM. The 2WO_3/SMP catalyst has high surface area, large pore size, and high acidity. The enhancement of Lewis acid sites induced high activity in the transesterification of *Croton megalocarpus* oil. Increased acidity effectively enhanced the catalytic performance of 2WO_3/SMP as a heterogenous catalyst in biodiesel production. The optimal parameters obtained for the transesterification process were: reaction temperature (348 K), reaction time (68 min), and methanol to oil molar ratio (1:7), and catalyst dosage (4.wt%). Response surface methodology (RSM) based on central composite design (CCD) was used to optimize the catalyst dosage (3 to 6 wt.%), methanol to oil molar ratio (4 to 13), reaction temperature (318 to 363 K), and reaction time (45 to 112 min) of the transesterification process. Using the optimal conditions determined by RSM, the conversion yield of *Croton megalocarpus* oil reached 93.1 % at 345 K with the methanol to oil molar ratio of 9:1, reaction time of 45 min, and catalyst dosage of 4.5 wt.%, respectively. Overall, this study shows that WO_3/SMP has the potential to be applied as a catalyst in future biodiesel production.

ABSTRAK

Penghasilan biodiesel menyaksikan lonjakan besar sejak kebelakangan ini disebabkan keupayaannya untuk mengurangkan gas rumah hijau (GHG). Biodiesel menghasilkan pelepasan gas ekzos dengan kualiti lebih baik yang dapat membantu meminimumkan kesan rumah hijau. Dalam kajian ini, minyak *Croton megalocarpus* tidak boleh dimakan telah ditukar kepada biodiesel melalui proses transesterifikasi dalam pemangkinan heterogen menggunakan tungsten trioksida berpenyokong silika mesoliang-zarah makro (WO_3/SMP). SMP telah berjaya disintesis melalui hidrolisis TEOS di dalam pelarut campuran air dan aseton dengan menggunakan CTAB sebagai templat pada suhu bilik. Sementara itu, mangkin WO_3/SMP telah disediakan melalui kaedah pengisitepuan, diikuti dengan pengeringan dan pengkalsinan pada 823 K. Sifat mangkin WO_3/SMP telah dicirikan menggunakan XRD, FTIR, penjerapan-penyahjerapan gas nitrogen, FESEM dan TEM. Mangkin 2WO_3/SMP mempunyai luas permukaan yang tinggi, saiz liang yang besar, dan keasidan yang tinggi. Peningkatan tapak asid Lewis WO_3/SMP telah mendorong kepada kenaikan aktiviti transesterifikasi minyak *Croton megalocarpus*. Peningkatan keasidan telah meningkatkan prestasi pemangkinan 2WO_3/SMP dengan berkesan sebagai mangkin heterogen dalam penghasilan biodiesel. Parameter optimum yang diperoleh untuk proses transesterifikasi ini adalah: suhu tindak balas (348 K), masa tindak balas (68 min) dan nisbah molar metanol kepada minyak (1:7), dan dos mangkin (4.wt%). Kaedah permukaan respons (RSM) berdasarkan reka bentuk komposit pusat (CCD) digunakan untuk mengoptimumkan dos mangkin (3 hingga 6 wt.%), nisbah molar metanol kepada minyak (4 hingga 13), suhu tindak balas (318 hingga 363 K), dan masa tindak balas (45 hingga 112 min) bagi proses transesterifikasi. Dengan menggunakan keadaan optimum yang ditentukan oleh RSM, hasil pertukaran minyak *Croton megalocarpus* mencapai 93.1% pada 345 K metanol kepada minyak dengan nisbah molar 9:1, masa tindak balas 45 min, dan dos mangkin ialah 4.5 wt%, masing-masing. Pada keseluruhannya, kajian ini menunjukkan bahawa WO_3/SMP berpotensi digunakan sebagai mangkin dalam pengeluaran biodiesel pada masa hadapan.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

K	-	Kelvin
h	-	Hour
mL	-	Mililiter
nm	-	Nanometer
min	-	Minute
θ	-	Theta
wt.%	-	Weight percentage
%	-	Percentage
2θ	-	Bragg Angle
^{o}C	-	Degree Celcius
g	-	gram

LIST OF SCHEMES

LIST OF ABBREVIATIONS

SMP	-	Silica mesopororous-macroparticles
WO_3	-	Tungsten trioxide
TEOS	-	Tetraethyl orthosilicate
CTAB	-	Cetyltrimethylammonium bromide
XRD	-	X-Ray Diffraction
FESEM	-	Field Emission Scanning Electron Microscopoic
TEM	-	Transmission Emission Microscopic
BET	-	Brunauer Emmet and Teller
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transformer Infra-Red
GC	-	Gas Chromatography
FAME	-	Fatty acid methyl ester
FFA	-	Free fatty acid
RSM	-	Response surface methodology
ASTM	-	American Society for Testing and Materials
ENs	-	European Standards
CCD	-	Centre composite site

LIST OF APENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, global warming and crisis of fuels are of the main global current issues. Many countries have encouraged alternatives to overcome these problems. In recent years, biodiesel has received great attention in the production of engine fuels. Biodiesel can be defined as liquid fuel similar to petroleum diesel but with better quality of exhaust gas emission compared to the petroleum diesel (Helwani *et al.*, 2009 and Singh *et al*., 2010). This is due to combustion process of using biodiesel which does not contribute to a net rise in the level of carbon dioxide in the atmosphere and hence, it minimizing the intensity of greenhouse effect. In addition, biodiesel is better than diesel fuels in terms of sulphur content, flash point, aromatic content and biodegradability. Biodiesel is also a non-toxic, biodegradable, renewable fuel that can be produced from a range of organic feedstock including fresh or waste vegetable oils, animal fats, and oil seed plants (Prafulla *et al*., 2009).

The major component in vegetable oils and animal fats for the biodiesel production is triacylglycerol (TAG). In biodiesel production, when triglyceride reacts with an alcohol, the three fatty acid chains are released from the glycerol skeleton and combined with methanol to yield fatty acid methyl esters (FAME) and glycerol as the by product (Ramachandran e*t al.*, 2013 and Corro *et al.*, 2013). The resulting biodiesel typically comprises of alkyl fatty acid (chain length C_{14}-C_{22}) esters of short-chain alcohols, primarily, methanol or ethanol.

The source of biodiesel comes from vegetable oils and animal fats. Most of the biodiesel produce using vegetable oils. Vegetable oils can be classified into two which are edible oil and non-edible oil. Edible oil such as soybeans oil, rapeseed oil, canola oil, sunflower oil, and coconut oil is defined as the oil derived from plants which can be consumed as a part of food for human. Non-edible oil is derived from vegetables that cannot be eaten by human such as jatropha oil, croton oil, tobacco seed oil, sesame oil and others. Currently, more than 95% of the biodiesel is synthesized from edible oil using various types of catalyst. However, there are many claims that a lot of problems may arise due to the competition between food supply and automotive fuels. It is believed that large-scale production of biodiesel from edible oils may bring global imbalance to the food supply and demand market. Moreover, edible oil feedstocks costs are far expensive to be used as fuel (Ivana *et al*., 2012). However, there will always be a competition between edible and non-edible oil plants for land usage (Searchinger *et al.,* 2008).

In many countries, edible oils are not produced enough to meet requirements for human and they must be imported. Hence, the price of biodiesel produced from edible oils much higher than that of petrodiesel. Therefore, non-edible oils from jatropha, karanja, neem, mahua and other plants are the only possibility for biodiesel production (Jain and Sharma, 2010). Croton megalocarpus oil is one of the most promising potential oil sources for biodiesel production. It is a non-edible transparent liquid of brownish colour obtained from the seeds of croton megalacorpus plant. Besides, it is a low-cost and economical non-edible crop that is suitable for biodiesel production (Kafuku *et al.,* 2010b). The croton plant is indigenous to the northern part of Tanzania and has been used locally to provide shade. Compared to other non-edible oil crops such as jatropha curcas, croton megalocarpus requires relatively less water footprint and fertilization during cultivation stage which can reduce land usage for the plants (Kafuku *et al.,* 2010a).

Vegetable oils can be converted into biodiesel using four ways such as blending, micro-emulsions, pyrolysis and transesterification (Ma and Hanna, 1999; Srivastava and Pasad, 2000). The reversible transesterification reactions are the most common method of converting triglycerides from oils into biodiesel. In addition, the main factors affecting transesterification reaction and produced esters yield are type of catalyst, reaction temperature, reaction time, pressure and molar ratio of alcohol and oil. The transesterification reaction can be non-catalyzed or catalyzed by an acid, a base or an enzyme. In traditional transesterification process, KOH or NaOH is used as the homogenous catalyst and methanol as the lower alcohol. The advantage of this process is that it produces high yield of methyl esters under mild condition and in shorter the reaction time (Surbhi *et al.,* 2011). Although the transesterification rate is very rapid when these homogenous alkaline catalysts are used, a large amount of water is required to wash the produced biodiesel leading to generation of large amount of wastewater containing liquids of high basicity or acidity which are not environmentally benign (Guan *et al.,* 2009). Thus, the use of heterogenous catalysts brings advantages such as reusability, easier catalyst and product separation, reduction in the amount of wastewater produces and less sensitivity to the presence of water in feedstock (Kafuku *et al*., 2010a). Besides, heterogenous catalysts are non-corrosive and are environmentally benign, thus being ecologically and economically important in catalysis filed systems with no disposal problems.

Recently, researchers have been focusing on heterogenous catalyst that could be used to replace the homogenous catalyzed in the biodiesel reaction. Heterogenous catalytic reaction converts triglyceride into methyl ester and glycerol as the by products slowly but produces biodiesel in a very feasible and economical way due to the reusability and easier separation (Sakai *et al.,* 2009). Different heterogenous catalytic activities exist for various feedstock with different process conditions. The effectiveness of the heterogenous catalytic reaction is based on the activity of the solid catalyst used. There are two types of heterogenous catalyst for biodiesel production, such as base and acid catalyst. In general, solid base catalysts are more active than solid acid catalysts requiring relatively shorter reaction times and lower reaction temperatures (Borges and Diaz, 2012). However, solid acid catalysts have several advantages over solid base catalyst, in which the reaction is less affected by the presence of water and free fatty acids (FFA). Besides, it has the ability to carry out the esterification of free fatty acids by utilizing the high free fatty acids contained in the feedstock.

Currently, all researchers are focusing on exploring new and sustainable solid acid catalysts for biodiesel production. In addition, it is understood that solid acid catalysts have strong potential to replace liquid acid catalyst. Besides, it can carry out esterification and transesterification simultaneously (Jitputti *et al*., 2006). The ideal solid acid catalyst for transesterification reaction should have characteristics such as an interconnected system of large pores, a hydrophobic surface area and high concentration of strong acid sites (Lotero *et al.*, 2005). One of the potential catalysts is Heteropolyacid (HPA) as it possesses strong Brönsted acidity and high water tolerance. Besides, other materials such as clays, zeolite, ion exchange resin, carbon material, metal oxide as well as sulphated metal oxides, WO_3/ZrO_2, supported on different supports such as zirconia, activated carbon, silica and tantalum are also used as the heterogeneous catalysts. These catalysts have uniform pore structures that provide an advantage on the surface. The surfaces are hydrophobic in order to promote preferential adsorption of oily hydrophobic species on the catalyst surface and it avoids deactivation of catalytic sites by strong adsorption of polar by products like glycerol or water.

Therefore, this study focuses on the non-edible croton megalocarpus oil for production of biodiesel using of tungsten trioxide (WO_3) supported by silica mesoporous-macroparticles (SMP) as catalyst. It is expected that WO_3 would increase the acidity of the catalyst and increase the performance of the catalytic activity. Silica is more prefered to be used as a support because it can provide a high surface area that can increase the dispersion of the metal. Besides, based on literatures, a few important properties of support should be implemented in order to increase the catalytic activity of the catalyst. The main properties for the catalyst are spherical shape, high surface area, high pore size and stability at a high temperature.

Therefore, the aim of the present work is to prepare the silica mesoporous-macroparticles (SMP) and tungsten trioxide loaded on silica mesoporous-macroparticles (WO_3/SMP) and to analyze of the characterization of the physical and chemical properties. The catalytic performance of these catalysts will be investigated in the biodiesel production from croton megalocarpus oil and the biodiesel will be tested according to the ASTM standard. Besides that, response surface methodology

(RSM) will be used to statistically evaluate and optimize the biodiesel production process catalyzed by WO_3/SMP catalyst with four different variables such as methanol to oil molar ratio, temperature, catalyst loading and time.

1.2 Problem Statement and Hypothesis

Croton oil is a non-edible oil that has not been explored widely in the biodiesel production. According to Kafuku *et al.*, (2010b), croton oil is a promising non-edible feedstock for biodiesel production, for which it has been successful in achieving the conversion of fatty methyl ester (FAME) up to 88%. During the process, it uses homogenous catalyst in the reactions which needs additional neutralization and separation steps for the final reaction mixture. Because of these problems, a great deal of interest has recently been observed for use of heterogenous catalyst.

Since Croton oil has high FFA content (>2 %), the selection of solid acid catalyst would be preferable. However, research on direct use of solid acid catalyst for biodiesel production has not been encouraged due to its limitations such as slow reaction rate and possible undesirable side reactions. The catalytic performance of a reaction dependent on structure, strength of acidity/basicity, surface area and stability of solid acid/base catalyst (Corma, 1995).

According to Makoto *et al.*, (1988), WO_3 posses high acidity and can be a potential candidate to be used in this study. It has been found that the use of mesoporous silica contributed to a better diffusion. Silica mesoporous-macroparticles is a good support catalyst due to the high surface area, macropartices size with circle shape and high pore size. Therefore, it is expected that SMP can be effectively used as a support for WO_3 and further enhances its catalytic activity.

1.3 Objectives of study

The objectives of this study are to:

i. prepare and characterize the physicochemical silica mesoporous-macroparticles (SMP) and tungsten trioxide supported on SMP (WO_3/SMP) catalysts.
ii. investigate the catalytic performance of the catalyst prepared for the biodiesel production from croton megalocarpus oil.
iii. optimize the transesterification of the Croton oil by Response Surface Methodology (RSM).

1.4 Scope of Study

In order to complete the objectives of this study, this research cover three aspects. The first aspect is to synthesize SMP by sol-gel method. The WO_3 will be loaded on SMP with various WO_3 loading (1, 2, 3.5, and 5 wt.%) by impregnation method (Ruslan *et al.*, 2011 and Choung *et al.*, 1983). Then, characterization of the physicochemical properties of the catalysts will be conduted using X-Ray diffractometer (XRD), N_2 adsorption-desorption, transmission electron microscope (TEM), field emission scanning electron microscope-energy dispersion X-Ray (FESEM-EDX), Fourier transform infrared (FTIR) spectroscopy and IR adsorbed pyridine. Adsorption of pyridine as a probe molecule for FTIR has been accepted as a general practice to classify the type of acids, either a Lewis or Bronsted acid site on the surface of the catalyst.

The second aspect is to test the catalytic performance of WO_3/SMP catalyst for the biodiesel production from croton megalocarpus oil. The croton megalocarpus oil was investigated for the production of biodiesel while reaction factors such as molar ratio of methanol to oil (4 to 13) (Parafulla *et al.*, 2009), reaction temperature (318 to 363K) (Kafuku *et al.*, 2010a), catalyst dosage (3 to 6 wt.%) (Mandeep *et al.*, 2011), and reaction time reaction time (45 to 112 min) (Kafuku *et al.,* 2010c) were investigated in order to obtain the optimal process conditions.

In this study, statistical analysis of FAME yield was performed using Statsoft Statistica 7.0 software. The FCCCD was used to study the interaction of process variables and to predict the optimum process condition for FAME yield by applying Response Surface Methodology (RSM). Independent variables considered important were reaction temperature (X_1), reaction time (X_2), reaction catalyst (X_3), and reaction of molar ratio (X_4). The independent variables were coded to (-1, 1) interval where the low and high levels were coded as -1 and +1, respectively. According to FCCCD, the total number of experiments conducted is 30 with 2^4 factorial points, 8 axial points and 2 replicates at the center points. The FAME yield was taken as the response of the experiment design.

1.5 Significance of Study

The finding of this study showed that WO_3/SMP has the potential to be applied in the production of biodiesel for croton megalocarpus oil. The solid acid heterogenous catalyst is suitable to be used with high free fatty acids (FFA) content of non-edible oil. Besides, the advantages of using solid acid catalyst are; the simultaneous esterification and transesterification process, insensitivity to free fatty acid content, and easy separation of the catalyst from the reaction mixtures resulting in lower product contaminations. One of the possible alternative oil crops for biodiesel production is non-edible croton megalocarpus oil primarily available in the African continent. Croton megalocarpus is a pioneer species, grown in cleared parts of natural forest, forest margins, or as a canopy tree. The non-edible croton megalocarpus plant can be grown in areas with mean annual rainfall of 800-1600 mm, mean annual temperature 11-27^{o}C and the production life span of the plant is more than 40 years. The ecosystem in Malaysia is one of the most complex tropical rainforests in the world. The average temperature is 27^{o}C with an everage rainfall of

2500 mm a year. This provides a perfect setting for the cultivation of Croton megalocarpus in the country.

1.6 Thesis Outline

This study is divided into five chapters. In Chapter 1, the introduction about the importance of the biodiesel as an alternative for liquid fuel and the application of non-edible oil in the transesterification process using the heterogeneous catalysts were outlined. The research motivation of WO_3/SMP as a catalyst in the production of biodiesel from Croton oil is also clarified. The problem statement of the current research is stated to give clear objectives of this present study. The scope of study covers the research works performed to meet these objectives.

Chapter 2 or literature reviews covers the research background of biodiesel productions as well as the type of feedstocks and catalysts used in the processes. The properties and mechanistic behavior of the reported catalysts are also reviewed. The principles of optimization by RSM are also included.

Chapter 3 or methodology describes the details of the materials and chemical reagents that are used in the present work, the procedure for the catalyst preparations, characterizations, and transesterification process which include the experiments, setup and data analysis.

In Chapter 4, the results and discussion are presented and comprehensively discussed in three parts.The first part is the characterization of the properties that are possessed by the catalysts. In the second part, the catalytic performance of the catalysts in the transesterification of Croton oil under variable parameters are discussed. Lastly, the properties of the biodiesel are also determined.

Finally, Chapter 5 includes the conclusions of this study and the recommendations for future studies.

REFERENCES

Abreu, R. F., Daniella, G. L., Elias, H. H., Carlos, W., and Paulo, A. Z. S. (2004). Utilization of Metal Complexes as Catalyst in Transesterification of Brazilian Vegetables Oils with Different Alcohols. *Journal of Molecular Catalysis A: Chemical.* 209: 29-33.

Azam, M. M., Watul, A., and Nahar, N. M. (2005). Prospects and Potential of Fatty Acid Methyl Esters of Some Non-traditional Seed Oils for use as Biodiesel in India. *Biomass and Bioenergy.* 29: 292-302.

Azambre, B., Zenboury, L., Weber, J. V., and Burg, P. (2010). Surface Characterization of Acidic Ceria-Zirconia Prepared by Direct Sulfation. *Applied Surface Science. 2*56: 4570-4581.

Aziz, M. A. A., Jalil, A. A., Triwahyono, S., and Sidik, S. M. (2014). Methanation of Carbon Dioxide on Metal-Promoted Mesostructed Silica Nanoparticles. *Applied Catalyst. A.* 486115-122.

Bagby, M. O. (1987). Vegetables Oils for Diesel Fuel: Opportunities for Development *American Society of Agricultural Engineers.* 87: 1588.

Bamgboye, A., and Hansen, A. C. (2008). Prediction of Cetane Number of Biodiesel Fuel from the Fatty Acid Methyl Ester (FAME) Composition. *International Agrophysics*. 22: 21-29.

Baoshan, L., Zhengxing, L., Jiangjun, L., Zhiyuan, Z., Xiaohui, G., Xinmei, P., Huiting, S. (2011). Preparation, Characterization and Application in Deep Catalytic of the Mesoporous Silica Pillared Clay Incorporated with Phosphotungstic Acid. *Journal of Colloid and Interface Scien*ce. 362: 450 456.

Bas, D., and Boyaci, I. H. (2007). Modeling and Optimization I: Usability of Response Surface Methodology. *Journal of Food Engineering*. 78: 836-845.

Batista, A. F., Abiney, L. C., and Marcio, J. D. S. (2012). Tin-Catalyzed Esterification and Transesterification Reaction. *ISRN Renewable Energy.*

Borges, M. E. and Diaz, L. (2012). Recent Developments on Heterogeneous Catalyst for Biodiesel Production by Oil Esterification and Transesterification Reaction: A Review. *Renewable and Sustainable Energy Reviews* 16: 2839 2849.

Cairo, G., Umapada, P., and Nallely, T. (2013). Biodiesel Production from Jatropha Curcas Crude Oil Suing ZnO/SiO_2 Photocatalyst for Free Fatty Acids Esterfication. *Applied Catalysis B: Environmental.* 129: 39-47.

Carmo, J. A. C., Souza, L. K. C., Costa, C. E. F., Longo, E., Zamian J. R., Rocha, F. G. N. (2009). Production of Biodiesel by Esterification of Palmitic Acid over Mesoporous Aluminosilicate Al-MCM-41. *Fuel* 88:461–8.

Chatterjee, S., Kumar, A., Basu, S., and Dutta, S. (2012). Application of Response Surface Methodology for Methylene Blue Dye Removal from Aqueous Solution using Low Cost Adsorbent. *Chemical Engineering Journal.* 181: 289-299.

Choung, S. J., and Sol, W. W. (1983). Oxygen Chemisorption and Olefin Disproportination Activity of WO_3/SiO_2. *Industrial & Engineering Chemistry Process Design and Development.* 22: 662-665.

Corma, A. (1995). Inorganis Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions. *Chemical Review.* 95 : 559-614.

Corro, G., Pal, U., and Tellez, N. (2013). Biodiesel Production from Jatropha Curcas Crude Oil using ZnO/SiO_2 Photocatalyst for Free Fatty Acids Esterification. *Applied Catalysis B: Environmental*: 129: 39-47.

Dam, J. T., Badloe, D., Ramanathan, A., Djanashvili, K., Kapteijn, F., and Hanefeld, U. (2013). Synthesis, Characterization and Catalytic Performance of a Mesoporous Tungsten Silicates: W-TUD-1. *Applied Catalyst A.* 468:150 159.

Demirbas, A. (2002). Biodiesel from Vegetables Oils via Transesterificationin Supercritical Methanol. *Energy Conversion and Management.* 43: 2349-2356.

Fan, M., Jianglei, H., Jing, Y., and Pingbo, Z. (2013). Biodiesel Production by Transesterification Catalyzed by an Efficient Choline Ionic Liquid Catalyst. *Applied Energy*. 108: 333-339.

Fang, C., Fenghua, C., Fengying, Z., Yang, C., Xiaohong, W. and Zhongmin, S. (2007). Transesterification of Vegetables Oil to Biodiesel using Heteropoly Solid Catalyst. *Advanced Synthesis and Catalysis.* 349: 1057-1065.

Frangrui, M., and Milford, A. H. (1999). Biodiesel Production: A Review. *Bioresource Technology*. 70: 1-15

Ganapathy, T., Gakkhar, R. P. and Murugesan, K. (2011). Influence of Injection Timing on Performance, Combustion and Emission Characteristics on Jatropha Biodiesel Engine. *Applied Energy*. 88: 4376-4386.

Garcia, C. M., Teixeira, S., Marciniuk, L. L., Schuchardt, U. (2008). Transesterification of Soybean Oil Catalyzed by Sulfated Zirconia. *Bioresource Technology*. 99: 6608-6613.

Goodrum, J. W (2002). Volatility and Boiling Points of Biodiesel from Vegetables Oil and Tallow. *Biomass and Bioenergy*. 22: 205-211.

Guan, G., Kusakabe, K., Sakurai, N., and Moriyama, K (2010). Transesterification of Vegetable Oil to Biodiesel Fuel using Catalysts in The Presence of Dimethyl Ether. *Fuel* 88: 81-86.

Haaland, P. D. (1989). Experimental Design in Biotechnology, Marcel Dekker Inc New York. Potential Source of Bio-Diesel. *Biomass and Bioenergy*. 34: 1495 1499.

Han, X. , He, Y., Hung, C., Liu, L. L., Huang, S. J., and Liu, S. B. (2005). Efficient Catalyst for The Esterification of Acetic Acid using N-Butyl Alcohol. *Journal of Molecular Catalysis A: Chemical*. 237: 146-154.

Helwani, Z., Othman, M. R., Aziz, N., Kim, J. and Fernando, W. J. N. (2009). Solid Heterogenous Catalysts for Trasnesterification of Triglycerides with Methanol: A Review. *Applied Catalysis A: General*. 363: 1-10

Hino, M. and Arata, K. (1988). Synthesis of Solid Superacid of Tungsten Oxide Supported on Zirconia and its Catalytic Action for Reactions of Butane and Petane.*Chemical Communication.* 18:1259-1260.

Issariyakul, T., Mangesh, G. K., Lekha, C. M., Ajay, K. D and Narendra, N. B. (2008). Biodiesel Production from Mixtures of Canola Oil and used Cooking Oil. *Chemical Engineering Journal.* 140: 77-85.

Ivana, B. B. I., Olivera, S. S. and Vlada, B. V. (2012). Biodiesel Production from Non Edible Plant Oils. *Renewable and Sustainable Energy Reviews.* 16: 3621-3647.

Jain, S, and Sharma, M. P. (2010). Prospects of Biodiesel from Jatropha in India: A Review. *Renewable and Sustainable Energy Reviews. 14*: 763-771.

Jentys, A., and Lercher, J. A. (2001). Chapter 8 Techniques of Zeolite Characterization. *Studies in Surface Science and Catalysis.* 137: 345-386.

Jiang, Y., Lu, J., Sun, K., Ma, L. and Ding, J. (2013). Esterification of Oleic Acid with Ethanol Catalyzed by Sulfonated Carbon Exchange Resin; Experimental and Kinetic Studies. *Energy Conversion and Mangagement.* 76: 980-985.

Jitputti, J., Kitiyanan, B., Rangsunvigit, P., Bunyakiat, K., Attanatho, L., and Jenvanitpanjakul, P. (2006). Transesterification of Crude Palm Kernel Oil and Crude Coconut Oil by Different Solid Catalysts. *Chemical Engineering Journal* 116: 61-66

Joshi, M. R., and Micheal, J. P (2007). Flow Properties of Biodiesel Fuel Blends at Low Temperatures. *Fuel.* 86: 143-151.

Kafuku, G., Kansedo, J and Mbarawa, M. (2010a). Biodiesel Production from Croton Megalocarpus oil and Its Process Optimization. *Fuel.* 89: 2556-2560.

Kafuku, G., Man, K. L., Keat, T. L., and Mbarawa M. (2010b). Croton Megalocarpus Oil: A Feasible Non-Edible Oil Source for Biodiesel Production. *Bioresouce Technology*.101: 7000-7004.

Kafuku, G., Man, K., L., Jibrail, K., Keat, T. L., and Makame, M. (2010c). Heterogenous Catalyzed Biodiesel Production from Moringa Oleifera Oil. *Fuel Processing Technology*. 91: 1525-1529.

Kansedo, J, and Keat, T. L. (2013). Process Optimization and Kinetic Study for Biodiesel Production from Non-Edible Sea Mango (CerberaOdollam) Oil using Response Surface Methodology. *Chemical Engineering Journal*. 214 157-164.

Kansedo, J., Keat, T. L., and Subhash, B. (2009). Biodiesel Production from Palm Oil via Heterogeneous Transesterification. *Biomass and Bioenergy*. 33: 271 276.

Kaya, C., Hamamci, C., Baysal, A., Akba, O., Sait, E., and Saydut, A. R. (2009). Methyl Ester of Peanut (Arachis Hypogea L.) Seed Oil as a Potential \ Feedstock for Biodiesel Production. *Renewable Energy*. 34: 1257-1260.

Kivevele, T. T., Mbarawa, M. M., Bereczky, A., Laza, T. and Madarasz, J. (2011). Impact of Antioxidant Aditives on The Oxidation Stability of Biodiesel Produced from Croton Megalocarpus Oil. *Fuel Processing Technology*. 92: 1244-1248.

Klepel, O., Bohlmann, W., Ivanov, E. B., Riede, and Papp, H. (2004). Incorporation of Tungsten into Mcm-41 Framework. *Microporous and Mesoporous Materials*. 76: 105-112.

Knothe G. (2005). Dependence of Biodiesel Fuel Properties on the Structure of Fatty Acid Alkyl Esters. *Fuel Processing Technology*. 86: 1059-1070.

Kozhevnikov, I.V. (1998) Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-phase Reactions. *Chemical Reviews* 98: 171-198.

Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., and Beck, Ordered (1992). Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism, *Nature*. 359: 710-712

Kumar, R., and Pal, P. (2012). Response Surface-Optimized Fenton's Pre-Treatment for Chemical Precipitation of Striated And Recycling of Water Through Downstream Nanofiltration. *Chemical Engineering Journal*. 210: 33-44.

Leung, D. Y. C. and Guo, Y (2005). Transesterification of Neat and Used Frying Oil: Optimization For Biodiesel Feedstocks: Vegetable Oil Soapstock. *Fuel Process Technology*. 86: 1087-1096.

Lide, D. R., ed. (2005). Magnetic Susceptibility of the Elements and Inorganic Compounds. *Handbook of Chemistry and Physics* (86th ed.). Boca Raton (FL).

Lotero, E., Yijun, L., Dora, E. L, Kaewta, S., David, A. B. and James, G. G. (2005). Synthesis of Biodiesel via Acid Catalysis. *Industrial and Engineering Chemistry Research*. 44: 5353-5363.

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

Makoto, H. and Kazushi, A. (1988). Synthesis of Solid Superacid of Tungsten Oxide Supported on Zirconia and Its Catalytic Action for Reactions of Butane and Pentene Journal of the Chemical Society. *Chemical Communication*. 1259-1260.

Mandeep, K. and Amjad, A. (2010). Lithium Ion Impregnated Calcium Oxide As Nano Catalyst for The Biodiesel Production from Karanja And Jatropha Oil. *Renewable Energy*. 36: 2886-2871.

Meneghetti, S. M. P., Mario, R. M., Carlo,s R. W, Eid, C. S, Gilvan, E. S. L, Laelson D, L. S., Tatiana M. S., Fernanda C., and Lenise G. D. O. (2006). Biodiesel from Castor Oil: A Comparison of Ethanolysis versus Methanolysis. *Energy and Fuels*. 20: 2262-2265.

Millini, R., E. Massara, P., Perego, G. and Bellussi, G. (1992). Framework Composition of Titanium Silicalite-1. *Journal of Catalysis.* 137: 497-503.

Molnar A. (2011). Nafion-Silica Nanocomposites; A New Generation of Water Tolerant Solid Acids of High Efficiency- An Update. *Current Organic Chemistry*. 15 23: 3928-3960.

Montgomery, D. C., Design and Analysis of Experiments, fourth ed., John Wiley & Sons. New York, 1996.

Morales, J. I, Santamaría, G. J, Maireles, T. P, Jiménez, L. A (2010). Zirconium doped MCM-41 Supported WO3 Solid Acid Catalysts for the Esterification of Oleic Acid with Methanol. *Applied Catalysis A: General* 379 :61–8.

Nascimento L. A. S, Angélica R. S, Costa C. E. F, Zamian J. R, Rocha F.G. N. (2011). Comparative Study between Catalysts for Esterification prepared from Kaolins. *Applied Clay Science*.51:267–73.

Özer A., Gurbuz G. Calimi A., and Korbahti B. K. (2008). Investigation of Nickel (II) Biosorption on Enteromorpha Prolifera: *Optimization using Response Surface Analysis. Journal of Hazardous Materials* 152: 778-788.

Parry, E. P. (1963). An Infrared Study of Pyridine Adsorbed on Acidic Solids. Characterization of Surface Acidity. *Journal of Catalysis.* 2: 371-379.

Prafulla, D. P., and Shuguang D. (2009). Optimization of Biodiesel Production from Edible and non-Edible Vegetable Oils. *Fuel. 88*: 1302-306.

Prakash, C. J., Hijfur R., Prasanna K. G. V. and Rajendra M. (2010). Biodiesel Production from Mixture of Mahua and Simarouba Oils with High Free Fatty Acids. *Biomass and Bioenergy.* 34: 1108-116.

Ramachandran, K., Suganya T., Gandhi N. N and Renganathan S. (2013). Recent Developments for Biodiesel Production by Ultrasonic Assist Transesterification Using Different Heterogenous Catalyst: A Review. *Renewable and Sustainable Energy Revie*ws. 22: 410:418.

Ruslan, N.N., Ahmad, F. N. H., Karim A. H., Jalil A. A. A., and Triwahyono S. (2011). IR study of Active Site for n Hepatane Isomerization over MoO_3 ZrO_2. *Applied Catalyst A.* 405: 102-112.

Sahoo, P. K., and Das, L. M (2009). Combustion Analysis of Jatropha, Karanja and Polanga Based Biodesel as Fuel in Diesel Engine. *Fuel.* 88: 994-999.

Sakai, T., Kawashima A., and Koshikawa T (2009). Economic Assessment of Batch Biodiesel Production using Homogenous and Heterogeneous Alkali Catalyst. Bioresource Technology 100: 3268-3276.

Santos, L., Dos M. G, Rennan G. O. Araujo, Bernhard W., Silvana D. O. C and Maria G. R. V. (2009). Simultaneous Determination of Cd and Fe in Grain Products using Direct Solid Sampling and High-Resolution Continum source Electrothermal Atomic Absorption Spectrometry. *Talanta. 78*: 557 583.

Sazegar, M. R., Jalil A. A., Triwahyono S., Mukti R. R., Aziz, M. A. A. Setiabudi H. D., and Kamarudin N. H. N. (2014). Protonation of Al-grafted mesostructured silica nanoparticles (MSN): Acidity and Catalytic Activity for Cumene Conversion. *Chemical Engineering Journal.* 240: 352-361.

Schinas, P., Karavalakis G., Davaris C., Anastopoulos G., Karonis D., Zannikos F., Stournas S., And Lois E. (2009). Pumpkin (Cucurbita pepo L.) Seed Oil as Alternative Feedstock for the Production of Biodiesel in Greece. *Biomass and Bioenergy*. *33*: 44-49.

Schumacher,, L. G., Gerpen, J. V., and Adams B. (2004). Biodiesel Fuels. *Encycolpedia of Energy*. 1: 151-162.

Searchinger, T., Heimlich R., Houghton R. A., dong F., Elobeid A., Fabiosa J., Tokgoz S., Hayes D., and Yu H. T. (2008). Use of U.S Croplands for Biofuels Increase Greenhouse Gases Through Emissions from Land-Use Change. *Science Journal* 319: 1238-1240.

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

Singh S. P., and Dipti S. (2010) A. Biodiesel Production Through The Use of Different Sources and Characterization of Oils and Their Esters as the Substitute Diesel: A Review. *Renewable and Sustainable Energy Reviews.* 14 : 200-216.

Singh, Chopra D., Kumar A., Sastry, Patel M. I. S., and Basu M. B. (2014) B. Response Factor Correction for Estimation of Ester Content in *Biodiesel Chromatographia* 77 : 165-169 *Solid State Chemistry*. 184:12001-1207.

Srilatha, K, Lingaiah, N, Prabhavathi, D. B. L. A., Prasad R. B. N., Venkateswar S., Sai P. S. (2009). Esterification of Free Fatty Acids for Biodiesel Production over Heteropoly Tungstate supported on Niobia Catalysts. *Applied Catalysis A: General*. 365:28–33.

Srivastava, A. and Prasad R (2000). Triglyceride Based Diesel Fuels. *Renewable and Sustainable Energy Reviews* 4: 111-133.

Surbhi, S., Ajay K. A, Rajendra P. B., and Deepak K. T. (2011). Biodiesel Production Using Heterogenous Catalysts. *Bioresouce Technology*. 102: 2151-2161.

Tazul, I. B., Palani A., Muhammad N. A., Abdullah M. A. R., Abudawoud H., Mohammed A. A. Y and Sulaiman S. A. K. (2013). Metathesis of 2 butene to propylene over W-mesoporous molecular sieves:A comparative study between tungsten containing MCM-41 and SBA-15. *Applied Catalyst A.* 467: 224-234.

Tiwari, A. K., K. Akhilesh, and Raheman, H (2007). Biodiesel Production from Jatropha Oil with High Free Fatty Acids: An Optimized Process. *Biomass and Bioenergy*. 31: 569-575.

Trens, P, Stathopoulos, V, Hudson, M. J., and Pomonis, P. (2004). Synthesis and Characterization of Packed Mesoporous tungsten-silicate application to the Catalytic Dehydrogenation of 2-Propanol. *Applied Catalysis A* 263: 103-108 Triwahyono S., Abdullah Z., and Jalil A. A. (2006). The Effect of Sulfate Ion on the Isomerization of *n*-Butane to *iso*-Butane. *Journal of Natural Gas Chemistry*. 15: 246-252.

Triwahyono, S., Jalil A. A., Ruslan N. N., Setiabudi H. D., Kamarudin N. H. N. (2013) B. C_5-C_7 Linear Alkane Hydroisomerization over MoO_3-ZrO_2 and Pt/MoO_3Zr Catalysts, *Journal Catalyst.* 303 : 50-59.

Vilas, G. and Hifjur, R. (2005). Biodiesel Production from Mahua (Madhuca Indica) Oil having High Free Fatty Acids. *Biomass and Bioenergy*. 28: 601-605.

Vyas, P., Amish, Jaswant L, and Verma, Subrahmanyam N.(2010). A Review on FAME Production Processes. *Fuel.* 89: 1-9.

Yang, X. L, Wei L. D. , Ruihua G., and Kangnian F. (2007) B. Characterization and Catalytic Behavior of Highly Active Tungstendoped SBA-15 Catalyst in the Synthesis of Glutaradehyde using an Anyhydrous Approach. *Journal Catalyst.* 249: 278-288.

Yang, X. L., Wei L. D., Hui C., Jian H. X., Yong C., Hexing L., and Kangnian F. (2005) A, Novel Tungsten-Containing Mesoporous HMS Material: Its Synthesis, Characterization and Catalytic Application in the Selective Oxidation of Cyclopentane to Glutaraldehyde by Aqueous H_2O_2. *Applied Catalyst. A* 283: 1-8.

Zhang, J., Min, L., Anfeng Z., Kaifeng L., Chunshan S., and Xinwen G (2010). Facile Synthesis of Mesoporous Silica Nanoparticles with Controlled Morphologies using Water-Acetone Media. *Solid State Sciences.* 12: 267-273.

Zhao, X. Lu, S., Whittaker A. K., Millar G. J., and Zhu H. Y. (1997). Comprehensive Study of Surface Chemistry of MCM-41 using Si CP/MAS NMR, FTIR, Pyridine-TPD and TGA. *Journal of Physical Chemistry. B* 101: 6525-6531.

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

Zubr, J. (1997). Oil Seed Crop: Camelina Sativa. *Industrial Crops and Product*. 6: 113-119.