

# **UNIVERSITI PUTRA MALAYSIA**

DEVELOPMENT OF CALCIUM OXIDE-BASED CATALYST DERIVED FROM WASTE SHELL FOR BIODIESEL PRODUCTION FROM Nannochloropsis oculata OIL AND PALM FATTY ACID DISTILLATE

**NUR SYAZWANI BINTI OSMAN** 

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By

**NUR SYAZWANI BINTI OSMAN** 

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

**June 2017** 

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# **DEDICATION**

Special Dedication to:

My Loving Husband:

Mohd Faiz bin Ismail

Er

My Beloved Parents:

Osman <mark>Bín Husín</mark> & Jemílah bt Jaafar

And My Family

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor Philosophy

# DEVELOPMENT OF CALCIUM OXIDE-BASED CATALYST DERIVED FROM WASTE SHELL FOR BIODIESEL PRODUCTION FROM Nannochloropsis oculata OIL AND PALM FATTY ACID DISTILLATE

By

## **NUR SYAZWANI BINTI OSMAN**

June 2017

Chairman: Prof. Taufiq Yap Yun Hin, PhD

**Faculty: Science** 

Excessive use of petroleum in transportation and industry, leads to acceleration of greenhouse gas emissions and the depletion of petroleum reserves worldwide. In order to reduce the environmental issues, research on alternative fuel which can replace the dependency on non-renewable petroleum based fuel is crucial. In this research, calcium oxide, (CaO) derived from three different waste shells (Angel Wing, Etok and Green Mussel) were used as catalyst for transesterification of microalgae oil, *Nannochloropsis oculata*. The microalgae oil was extracted after cultivating and harvesting for several weeks. Calcined angel wing shell (CAWS) at 900 °C shows highest FAME yield (84.11%) at oil:methanol molar ratio 1:150 and catalyst loading of 9 wt.% in 1 h reaction and can be reused for more than three times.

In order to reduce cost production of biodiesel, low cost feedstock such as palm fatty acid distillate (PFAD) was also used by using sulfated CAWS catalysts. CAWS precursor was sulfated using different sources of  $SO_4^{2-}$  ions with varied concentration at ambient temperature. All the catalysts were characterized by using thermogravimetric analysis (TGA), X-ray diffraction spectroscopy (XRD), Fourier transforms infrared spectroscopy (FT-IR), temperature programmed desorption of carbon dioxide (TPD-CO<sub>2</sub>), temperature programmed desorption of ammonia (TPD-NH<sub>3</sub>), BET surface area and variable pressure scanning electron microscope (VPSEM).

In addition, esterification reaction of PFAD by using a conventional reflux with the presence of  $CAWS_{(7)}$ - $H_2SO_4$  catalyst shows 98% of FAME yield at 1:15 PFAD/methanol molar ratio, 5 wt.% of catalyst loading at 80 °C for 3 h reaction. The catalyst also can be reused at least two times with 98% of FAME yield without further treatment. The reused or spent catalyst was analyzed to determine the deactivation mechanism of the reused catalyst. Besides, esterification of PFAD in supercritical methanol reaction produced 97.9% of FAME yield with PFAD/methanol molar ratio

1:6, 2 wt.% of catalyst loading at  $290^{\circ}$ C for 15 minutes. The CAWS- $_{(7)}$ H<sub>2</sub>SO<sub>4</sub> catalyst can be reused up to seven cycles with FAME yield more than 80 %.

The fuel properties were also investigated by using ASTM and European standard method and it was found that the PFAD methyl ester was met the biodiesel quality standard and has almost similar property with petrol fuel. As a conclusion, both CAWS and CAWS<sub>(7)</sub>-H<sub>2</sub>SO<sub>4</sub> show outstanding performance as low cost heterogeneous basic and acid catalyst, respectively for biodiesel production from either low or high FFA feedstocks.



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

# PEMBANGUNAN MANGKIN BERASASKAN KALSIUM OKSIDA TERBITAN SISA CENGKERANG UNTUK PENGHASILAN BIODIESEL DARIPADA MINYAK Nannochloropsis oculata DAN SULINGAN ASID LEMAK SAWIT

Oleh

## **NUR SYAZWANI BINTI OSMAN**

Jun 2017

Pengerusi: Prof. Taufiq Yap Yun Hin, PhD

Fakulti: Sains

Penggunaan petroleum yang berlebihan dalam pengangkutan dan industri, membawa kepada peningkatan pembebasan gas rumah hijau dan pengurangan rizab petroleum di seluruh dunia. Bagi mengurangkan isu alam sekitar, kajian untuk menghasilkan bahan bakar alternatif yang boleh menggantikan kebergantungan bahan api berasaskan petroleum yang tidak boleh diperbaharui adalah penting. Dalam kajian ini, kalsium oksida, CaO berasal daripada tiga sisa cengkerang yang berbeza telah digunakan sebagai mangkin dalam transesterifikasi minyak mikroalga, *Nannochloropsis oculata*. Minyak mikroalga diekstrak selepas proses menanam dan menuai selama beberapa minggu. Sisa Angel Wing (CAWS) yang dikalsin pada suhu 900°C menunjukkan hasil FAME tertinggi (84.11%) pada nisbah molar minyak:metanol 1:150 dan muatan berat mangkin sebanyak 9% dalam 1 jam masa tindak balas dan ia boleh digunakan semula lebih daripada tiga kali.

Untuk mengurangkan kos pengeluaran biodiesel, bahan mentah kos rendah seperti sulingan asid lemak sawit (PFAD) telah digunakan dengan menggunakan mangkin sulfat CAWS. CAWS prekursor telah disulfat menggunakan pelbagai sumber ion  $SO_4^{2-}$  dengan kepekatan yang divariasikan pada suhu ambien. Semua mangkin dicirikan dengan menggunakan analisis terma gravimetri (TGA), pembelauan sinar-X (XRD), Fourier mengubah inframerah spektroskopi (FT-IR), program-suhu-nyahjerapan karbon dioksida (TPD-CO<sub>2</sub>), program-suhu-nyahjerapan ammonia (TPD -NH<sub>3</sub>), analisis luas permukaan BET dan tekanan ubah mikroskop imbasan elektron (VPSEM).

Di samping itu, tindak balas pengesteran PFAD dengan menggunakan refluks konvensional dengan kehadiran mangkin CAWS<sub>(7)</sub>-H<sub>2</sub>SO<sub>4</sub> menunjukkan hasil 98% FAME pada 1:15 PFAD nisbah molar metanol, berat mangkin 5 wt.% pada 80 °C selama 3 jam masa tindak balas. Mangkin ini juga boleh digunakan semula sekurangkurangnya dua kali dengan 98% hasil FAME tanpa rawatan selanjutnya. Mangkin

digunakan semula dianalisis untuk menentukan mekanisme penyahaktifan yang pemangkin digunakan semula. Selain itu, pengesteran PFAD dalam reaksi superkritikal metanol menghasilkan 97.9% hasil FAME dengan nisbah molar PFAD: metanol 1:6, 2 wt. % berat mangkin pada 290°C selama 15 minit. Mangkin CAWS<sub>(7)</sub>-H<sub>2</sub>SO<sub>4</sub> boleh digunakan semula sehingga tujuh kitaran dengan hasil FAME lebih daripada 80%.

Sifat-sifat bahan api juga telah dikaji dengan menggunakan ASTM dan kaedah piawai Eropah dan didapati PFAD metil ester memenuhi kualiti piawaian biodiesel dan mempunyai sifat yang hampir sama dengan minyak petrol. Kesimpulannya, CAWS and CAWS<sub>(7)</sub>-H<sub>2</sub>SO<sub>4</sub> menunjukkan prestasi cemerlang sebagai mangkin heterogen bes dan asid kos rendah dalam penghasilan biodiesel daripada sumber minyak rendah atau tinggi kandungan FFA.



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I certify that a Thesis Examination Committee has met on 5 June 2017 to conduct the final examination of Nur Syazwani binti Osman on her thesis entitled "Development of Calcium Oxide-Based Catalyst Derived from Waste Shell for Biodiesel Production from *Nannochloropsis oculata* Oil and Palm Fatty Acid Distillate" 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 Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

# Gwendoline Ee Cheng Lian, PhD

Professor Faculty of Science Universiti Putra Malaysia (Chairman)

## Zulkarnain bin Zainal, PhD

Professor Faculty of Science Universiti Putra Malaysia (Internal Examiner)

# Salmiaton binti Ali, PhD

Associate Professor Faculty of Engineering Universiti Putra Malaysia (Internal Examiner)

# Didik Prasetyoko, PhD

Professor Sepuluh Nopember Institute of Technology Indonesia (External Examiner)

# NOR AINI AB. SHUKOR, PhD

Professor and Deputy Dean School of Graduate Studies Universiti Putra Malaysia

Date: 8 August 2017

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

# Taufiq Yap Yun Hin, PhD

Professor Faculty of Science Universiti Putra Malaysia (Chairman)

# Umer Rashid, PhD

Associate Professor Institute of Advanced Technology Universiti Putra Malaysia (Member)

# Mohd Izham Saiman, PhD

Senior Lecturer Faculty of Science Universiti Putra Malaysia (Member)

# ROBIAH BINTI YUNUS, PhD

Professor and Dean School of Graduate Studies Universiti Putra Malaysia

Date:

# **Declaration by Members of Supervisory Committee**

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature:
Name of Chairman of Supervisory Committee: <u>Taufiq Yap Yun Hin</u>
Signature:
Name of Member of Supervisory Committee: <u>Umer Rashid</u>
Signature:
Name of Member of Supervisory Committee: Mohd Izham Bin Saiman

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## LIST OF ABBREVIATIONS

AAS Atomic Absorption Spectroscopy

AOAC Association of Official Analytical Chemist ASTM American Society for Testing and Materials

ATR-FTIR Attenuated Total Reflection-Fourier Transform Infrared

AV Acid Value

BET Brunauer-Emmett-Teller

CHNS Carbon, Hydrogen, Nitrogen, Sulfur element analysis

CO<sub>2</sub>-TPD Temperature Programmed Desorption CO<sub>2</sub>

CAWS Calcined Angel Wing Shell

CES Calcined Etok Shell

CGMS Calcined Green Mussel Shell
Com-CaSO<sub>4</sub> Commercial Calcium Sulfate

CP Cloud Point DGs Diglycerides

EDX Energy Dispersive X-ray
EN European Standard
FAME Fatty acid methyl ester
FFA Free fatty acid

FTIR Fourier Transform Infrared Spectroscopy

FWHM Full-Width Half Maximum

GC-FID Gas Chromatography- Flame Ionization Detector
GC-MS Gas Chromatography- Mass Spectrometer

GHG Life-cycle Greenhouse Gas

H<sub>2</sub>SO<sub>4</sub> Sulfuric acid MGs Monoglycerides

MPOB Malaysian Palm Oil Board

NH<sub>3</sub>-TPD Ammonia-Temperature Programmed Desorption

NO<sub>x</sub> Nitrogen dioxide

PFAD Palm Fatty Acid Distillate

PP Pour Point

SEM Scanning Electron Microscopy

SV Saponification Value

TGs Triglycerides

## **CHAPTER 1**

#### INTRODUCTION

# 1.1 Research Background

The world is struggling to confront with the double crisis of fossil fuels declination and environmental pollution. The indiscriminate extraction and extremely high consumption of oil based fuel every year have led to a reduction in petroleum reserves and increment of greenhouse gasses (GHG) emissions. This phenomenon's will change the global climate and continuously lead to unsustainable environment. Figure 1.1 shows the world total liquid oil consumption and production from 1990 to 2035 (BP Energy Outlook 2035, 2015). Generally, both of total oil consumption and production are directly proportional to rapid growth population over the years since 1990 to date. The trends envision to be increasing until 2035 (Figure 1.1). Furthermore, oil consumption is expected to be high demand compared to the oil production in 2020 to 2035.

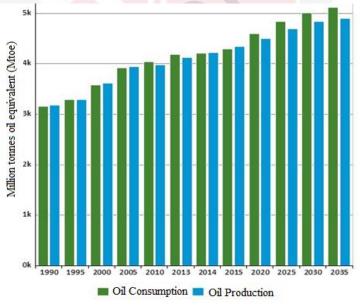


Figure 1.1: The world's total oil consumption and production from 1990 to 2035 (BP Energy Outlook 2035, 2015).

Unfortunately, fossil fuels are non-renewable source that will diminish later and burning fossil fuels significantly contribute towards global warming by emissions of GHG (Demirbas, 2011). Le Quere et al. (2014) investigated assessment of anthropogenic carbon dioxide (CO<sub>2</sub>) emissions to study global carbon cycle. As demonstrated in Figure 1.2, emissions of CO<sub>2</sub> increase rapidly since 1990. In addition, the global atmospheric CO<sub>2</sub> concentration reached 392.52±0.10 ppm averaged over

2012. From estimations, the  $CO_2$  concentration will increase about 2.1% to 9.9±0.5 GtC in 2013, 61% above emissions in 1990.

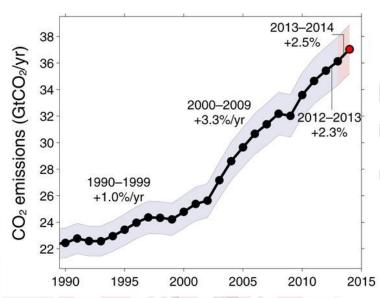


Figure 1.2: Global fossil fuel and cement emissions from 1990 to 2013 adapted from (Le Quéré et al., 2014).

Due to these scenarios, there are vital to find alternative fuels to replace the petroleum based fuel in order to fulfill the high demand of energy and provide sustainable environment. Liquid biofuel, which consists of bioethanol and biodiesel has a potential to replace the non-renewable energy without causing harm to human and environment. Both biofuel can be derived from natural renewable resources. However, in this work, only biodiesel has been focused and investigated as the alternative fossil fuel replacement.

## 1.2 Biodiesel and its Advantages

Biodiesel or mono alkyl ester of long chain fatty acids is a promising alternative fuel which has similar properties as fossil fuels in terms of the chemical structure and energy content (Lam and Lee, 2011). Moreover, since it can be produced from renewable resources, it is also one of renewable energy. According to Atabani et al.,(2012), biodiesel is highly biodegradable and has minimal toxicity, that could replace petroleum fuel in various applications without major modifications. Besides, biodiesel also non-flammable and produces lower GHG emissions (CO<sub>2</sub>, HC, SO<sub>x</sub>, and NO<sub>x</sub>) compared to fossil fuels (Shahabuddin et al., 2012), leads to the complete combustion and reduced emission due to have a lot of free oxygen (Atabani et al., 2012).

Biodiesel can be used as a pure fuel (B100) or blended with petroleum in any percentage. It offers full blending potential with conventional diesel where a high cetane number giving improved combustion in compression ignition engines, and low emissions of sulphur and particulates. For instance, there are B20 (a blend of 20 percent by volume biodiesel with 80 percent by volume petroleum diesel), B2 (a blend of 2 percent by volume biodiesel with 98 percent by volume petroleum diesel), and B5 (a blend of 5 percent by volume biodiesel with 95 percent by volume petroleum diesel) which are common fuel blends used today (Szybist et al., 2007).

# 1.3 Catalyst in Biodiesel Production

To be general, biodiesel can be produced from transesterification or esterification reaction of vegetable oils/animal fats which can be done in the presence of enzymes or catalysts (acids or bases) with alcohol (methanol and ethanol). Utilization of homogeneous catalysts in the reaction process has disadvantages due to complexity in purification step for biodiesel production (Granados et al., 2007). The catalyst cannot be recovered and must be neutralized and separated from the methyl ester phase at the end of the reaction, with the consequent generation of a large volume of wastewater. The method for the removal of the catalyst after reaction is technically difficult which increase the overall cost of the process. As a consequence, the total cost of the biodiesel production based on homogeneous catalysis, is not yet sufficiently competitive as compared to the cost of diesel production from petroleum.

Thus, heterogeneous catalysts were used for biodiesel production as they have many benefits such as easily separated, non-corrosive, can be reused and regenerated (long catalyst lifetimes) and economical friendly (Liu et al., 2008). Heterogeneous catalysts also give high purity of glycerol and do not produce soap through free fatty acid neutralization and triglyceride saponification (Refaat, 2010).

## 1.4 Problem Statement/Hypothesis

Due to highly abundant waste shells which are one of the sources of calcium oxide, CaO, it was widely used for biodiesel production as heterogeneous base catalyst. CaO obtained from different sources gives different physico-chemical properties. Screening of CaO derived from the different waste shells is important to produce highly active catalyst, hence increase biodiesel yield. However, utilization of highly basic metal oxide of CaO is not suitable for high free fatty acid (FFA) oil such as PFAD since it will cause an unfavour saponification reaction.

Recently, microalgae oil has gained research interest as third generation biodiesel feedstock. This is due to its high grow roots and lipid content. In fact, microalgae do not compete for arable land with food crops and other products since it can be grown in various environments that are not suitable for growing other crops for instance, salt water, non arable land, fresh, brackish and also wastewater (Sharma et al., 2012).

Hence, utilization of microalgae as biodiesel feedstock was expected to bring more sustainable environment.

Highly cost biodiesel production makes the biodiesel not compatible in the global market. It has been found that the cost of feedstocks accounts for 75% of the total cost of biodiesel fuel (Atabani et al., 2012). Thus, consumption of palm fatty acid distillate (PFAD) which easily available and known as low-cost feedstock for biodiesel production can reduce the production cost, but it is only suitable for acid catalyst instead of basic catalyst since consist of high free fatty acid (FFA) value.

Basically, esterification reaction of PFAD , high FFA feedstock were performed by using homogeneous acid catalyst such as sulfuric acid,  $H_2SO_4$  (Chongkhong et al., 2009; Rahmi, 2013), phosphoric acid,  $H_3PO_4$  (Metre and Nath, 2015) and methanesulfonic acid (Aranda et al.,2008) while sulfated transition metal oxide for instance sulfonated mesoporous  $ZnAl_2O_4$  (Soltani et al., 2016) and sulfonated carbon-based such as sulfonated-glucose (Lokman et al., 2015) was used as heterogeneous acid catalyst. However, these catalysts were expensive and needs complex catalyst synthesis process. Thus, modification of CaO derived from the waste shell by a simple sulfation process with sulfate group,  $SO_4$  to activate the acid site of the catalyst is expected to produce low cost solid acid catalyst which suitable to be used in esterification of high FFA feedstocks.

The esterification reaction was carried out by using the common conventional reflux at mild condition and the effect of the reaction in supercritical methanol was investigated. Basically, supercritical methanol reaction was performed in non-catalytic reaction for biodiesel production. However, it consumes very high temperature and large amount of methanol (Saka and Kusdiana, 2001). Thus, the main idea was to introduce the presence of heterogeneous acid sulfated CaO catalyst in the supercritical methanol reactor to generate the reaction at low reaction temperature in shorter time.

## 1.5 Objectives

This dissertation aims to synthesize and modify calcium oxide catalysts derived from waste shell. This study also concerned with the physical and chemical properties of synthesized catalysts and the feasibility of biodiesel production from microalgae oil and PFAD through transesterification and esterification reaction with methanol. In order to achieve the main aim, there are six research objectives have been addressed as follows:

- To synthesize, screen and characterize calcium oxide derived from different waste shells.
- 2. To optimize the condition for transesterification reaction of microalgae oils by using CaO derived from the waste shell catalysts.
- 3. To synthesize and investigate physico-chemical characteristics of sulfated CaO derived from waste shell.
- 4. To optimize the parameter condition for esterification of PFAD.

- 5. To investigate the effect of supercritical temperature on esterification of PFAD
- 6. To determine and evaluate the properties of PFAD biodiesel.

## 1.6 Scope of Research

This research involved the synthesis and sulfation of CaO derived from waste shells of Angel Wing as heterogeneous acid catalysts for biodiesel production from PFAD. Prior to the sulfation process, the CaO was synthesized from three different waste shells (Angel Wing, Etok and Green Mussel). The suitable calcination temperature for CaO synthesis was investigated and characterized by using TGA, XRF, XRD, FT-IR, TPD-CO<sub>2</sub>, TPD-NH<sub>3</sub>, BET and SEM. Then, the best calcined shell catalyst was chosen for optimization study by using crude microalgae oil synthesized after cultivation, harvest and extraction process. The condition of the transesterification reactions of microalgae oil was also studied by investigating the effect of variable parameters such as methanol to oil weight ratio, catalyst loading, and reaction time. The reusability of the CaO catalyst was determined and the leaching of calcium species into the reaction product was confirmed by using atomic absorption spectroscopy (AAS) elemental analysis.

Next, the calcined shell (CaO) was sulfated and the effect of catalyst preparation *i.e*, sulfate agent, and concentration of sulfate agent in catalyst performance was investigated. The physico-chemicals properties of sulfated catalysts were performed by using several methods (XRD, FT-IR, TPD-CO<sub>2</sub>, TPD-NH<sub>3</sub>, BET and SEM). The basicity and acidity properties of the modified catalysts were evaluated in terms of numbers and strength of the basic and the acidic site through CO<sub>2</sub> and NH<sub>3</sub>-temperature programmed desorption techniques. In addition, the structural characteristics and the surface properties of the modified catalyst was carried out using XRD and BET surface area, respectively.

The performance of the sulfated catalysts was carried out in esterification reaction of PFAD in two reaction systems: conventional reflux and supercritical methanol. The relationship between concentration of sulfate agent and acidity of the catalyst was discussed. The entire biodiesel product in the reaction was analyzed and the FAME yield was calculated by using gas chromatography (GC-FID). Additionally, the spent catalyst analysis also performed to investigate deactivation of catalyst after reused. The leaching of Ca and sulfur content was also analyzed by using AAS and CHNS, respectively. Lastly, the biodiesel fuel standard quality properties were determined by using ASTM D6751 and European 14212 standard specifications.

# 1.7 Organization of the Thesis

This thesis contains ten chapters. **Chapter One** introduces research background, the advantages of biodiesel and catalysts involved in biodiesel production. It also consists of problem statement and hypothesis, the objectives and scope of the proposed research. **Chapter Two** reveals a comprehensive literature review relating to the past

and current status of biodiesel as one of transportation fuel, the generations of biodiesel feedstocks, biodiesel production by using heterogeneous basic and acid catalyst as well as the reports on utilizing CaO derived from waste shell in biodiesel production. Moreover, recent technologies in biodiesel production also were discussed. Chapter Three is the methodology section which covers all issues associated with catalyst preparation, the characterizations and the experimental setup along with the transesterification/esterification reaction and the cultivation, harvest and extraction method of microalgae oil. The characterization of feedstocks and biodiesel also was considered. Chapter Four screen and present the characterization of CaO derived from Angel Wing shell, Etok shell and Green Mussel shell. Chapter Five shows the optimization result for transesterification of microalgae oil by using CAWS900 catalyst as well as the reusability and leaching of the catalyst. Chapter Six present the characterization of sulfated CAWS by using sulfuric acid and chlorosulfonic acid. Moreover, the characterization of sulfated CAWS with different concentration of sulfuric acid also was presented. Chapter Seven and Eight explain the optimization of PFAD esterification by using conventional reflux and supercritical methanol, respectively. The deactivation of the spent catalyst also is described. Chapter Nine shows the PFAD biodiesel fuel properties analysis according to EN14121 and ASTM D6751. Chapter Ten summarizes, highlights and concludes the contribution and the main findings of this research study along with the recommendations for future research.

#### REFERENCES

- (AOCS) American Oil Chemists' Society.(n.d.). Retrieved from aocs.org (ISO) International Organization for Standardization. (n.d.).
- Abreu, F. R., Alves, M. B., Macêdo, C. C. S., Zara, L. F., & Suarez, P. A. Z. (2005). New multi-phase catalytic systems based on tin compounds active for vegetable oil transesterification reaction. *Journal of Molecular Catalysis A: Chemical*, 227(1–2), 263–267.
- Agency, E. (2010). Iea statistics. *Statistics*.
- Ahmad, A. L., Yasin, N. H. 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.
- Alam, F., Date, A., Rasjidin, R., Mobin, S., & Moria, H. (2012). Biofuel from algae- Is it a viable alternative?, 49, 221–227.
- Alhassan, F. H., Rashid, U., Al-Qubaisi, M. S., Rasedee, A., & Taufiq-Yap, Y. H. (2014). The effect of sulfate contents on the surface properties of iron-manganese doped sulfated zirconia catalysts. *Powder Technology*, 253, 809–813.
- Alhassan, F. H., Rashid, U., & Taufiq-yap, Y. H. (2015). Synthesis of waste cooking oil-based biodiesel via effectual recyclable bi-functional Fe<sub>2</sub>O<sub>3</sub>-MnO-SO<sub>4</sub><sup>2</sup>/ZrO<sub>2</sub> nanoparticle solid catalyst. *Fuel*, *142*, 38–45.
- Ali, O. M., Mamat, R., Abdullah, N. I. K. R., & Abdullah, A. A. (2008). Importance of palm biodiesel as a transportation fuel in Malaysia 2 Transportation Energy, 119–128.
- Ali, R. M., Abd, M. M., Latif, E., & Farag, H. A. (2015). Preparation and characterization of CaSO<sub>4</sub> SiO<sub>2</sub> CaO /SO<sub>4</sub><sup>2-</sup> composite for biodiesel production, *3*, 38–45.
- Allwayzy, S. H., Yusaf, T., Mccabe, B., Pittaway, P., & Aravinthan, V. (2010). Microalgae as Alternative Fuel for Compression Ignition (CI) Engines, (November), 1–5.
- Aranda, D. A. G., Santos, R. T. P., Tapanes, N. C. O., Ramos, A. L. D., & Antunes, O. A. C. (2008). Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. *Catalysis Letters*, 122(1–2), 20–25.
- Asri, N. P., Machmudah, S., Wahyudiono, Suprapto, Budikarjono, K., Roesyadi, A., & Goto, M. (2013). Palm oil transesterification in sub- and supercritical methanol with heterogeneous base catalyst. *Chemical Engineering and Processing: Process Intensification*, 72, 63–67.
- Atabani, A. E., Badruddin, I. A., Mekhilef, S., & Silitonga, A. S. (2011). A review on global fuel economy standards, labels and technologies in the transportation sector. *Renewable and Sustainable Energy Reviews*, 15(9), 4586–4610.
- 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.
- Atabani, A. E., Silitonga, A. S., Ong, H. C., Mahlia, T. M. I., Masjuki, H. H., Badruddin, I. A., & Fayaz, H. (2013). Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production. *Renewable and Sustainable Energy Reviews*, 18, 211–245.
- Azimi, G., Papangelakis, V. G., & Dutrizac, J. E. (2007). Modelling of calcium sulphate solubility in concentrated multi-component sulphate solutions. *Fluid*

- Phase Equilibria, 260(2), 300–315.
- Azizul Hakim, Tengku Sharifah Marliza, Najiha Maratun Abu Tahari, Wan Nor Roslam Wan Isahak, Muhammad Rahimi Yusop, M. W. M. H. and A. M. Y. (2016). Studies on CO<sub>2</sub> Adsorption and Desorption Properties from Various Type Iron Oxides
- Bahadar, A., & Bilal Khan, M. (2013). Progress in energy from microalgae: A review. *Renewable and Sustainable Energy Reviews*.
- Barthos, R., Lonyi, F., Onyestyak, G., & Valyon, J. (2001). An NH3-TPD and -FR study on the acidity of sulfated zirconia. *Solid State Ionics*, *141–142*, 253–258.
- Bhatti, H. N., Hanif, M. A., Qasim, M., & Ata-ur-Rehman. (2008). Biodiesel production from waste tallow. *Fuel*, 87(13–14), 2961–2966.
- Bligh, E. G., & Dyer, W. J. (1959). A rapid method of total lipid extraction and purification. *Canadian Journal of Biochemistry and Physiology*, 37(8), 911–917.
- Boey, P.-L., Maniam, G. P., & Hamid, S. A. (2009). Utilization of waste crab shell (Scylla serrata) as a catalyst in palm olein transesterification. *Journal of Oleo Science*, 58(10), 499–502.
- Boey, P.-L., Maniam, G. P., & Hamid, S. A. (2011). Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review. *Chemical Engineering Journal*, 168(1), 15–22.
- Boey, P. L., Maniam, G. P., & Hamid, S. A. (2009). Biodiesel production via transesterification of palm olein using waste mud crab (Scylla serrata) shell as a heterogeneous catalyst. *Bioresource Technology*, 100(24), 6362–6368.
- Boey, P. L., Maniam, G. P., Hamid, S. A., & Ali, D. M. H. (2011). Utilization of waste cockle shell (Anadara granosa) in biodiesel production from palm olein: Optimization using response surface methodology. *Fuel*, 90(7), 2353–2358.
- Boro, J., Deka, D., & Thakur, A. J. (2012). A review on solid oxide derived from waste shells as catalyst for biodiesel production. *Renewable and Sustainable Energy Reviews*, 16(1), 904–910.
- Boro, J., Thakur, A. J., & Deka, D. (2011). Solid oxide derived from waste shells of Turbonilla striatula as a renewable catalyst for biodiesel production. *Fuel Processing Technology*, 92(10), 2061–2067.
- BP Energy Outlook 2035. (2015). http://www.bp.com/content/dam/bp/pdf/Energy-Economics/energy-Outlook-2015/Energy\_Outlook\_2035\_booklet.pdf, (February).
- Brown, A. S. C., & Hargreaves, J. S. J. (1999). Sulfated metal oxide catalysts. *Green Chemistry*, *I*(1), 17–20.
- Brunauer, S., Deming, L. S., Deming, W. E., & Teller, E. (1940). On a theory of the van der Waals adsorption of gases. *Journal of The American Chemical Society*, 62(7), 1723–1732.
- Buasri, A., Chaiyut, N., Loryuenyong, V., Worawanitchaphong, P., & Trongyong, S. (2013). Calcium oxide derived from waste shells of mussel, cockle, and scallop as the heterogeneous catalyst for biodiesel production. *The Scientific World Journal*, 2013.
- Buasri, A., Ksapabutr, B., Panapoy, M., & Chaiyut, N. (2012). Biodiesel production from waste cooking palm oil using calcium oxide supported on activated carbon as catalyst in a fixed bed reactor. *Korean Journal of Chemical Engineering*, 29(12), 1708–1712.
- Chabukswar, D. D., Heer, P. K. K. S., & Gaikar, V. G. (2013). Esterification of Palm Fatty Acid Distillate Using Heterogeneous Sulfonated Microcrystalline Cellulose Catalyst and Its Comparison with H<sub>2</sub>SO<sub>4</sub> Catalyzed Reaction.
- Cheryl-Low, Y. L., Theam, K. L., & Lee, H. V. (2015). Alginate-derived solid acid catalyst for esterification of low-cost palm fatty acid distillate. *Energy*

- Conversion and Management, 106, 932-940.
- 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.
- 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.
- de Almeida, R. M., Noda, L. K., Gonçalves, N. S., Meneghetti, S. M. P., & Meneghetti, M. R. (2008). Transesterification reaction of vegetable oils, using superacid sulfated TiO<sub>2</sub>-base catalysts. *Applied Catalysis A: General*, *347*(1), 100–105.
- De Sousa, F. P., Dos Reis, G. P., Cardoso, C. C., Mussel, W. N., & Pasa, V. M. D. (2016). Performance of CaO from different sources as a catalyst precursor in soybean oil transesterification: Kinetics and leaching evaluation. *Journal of Environmental Chemical Engineering*, 4(2), 1970–1977.
- Demirbas, A. (2007). Biodiesel from sunflower oil in supercritical methanol with calcium oxide. *Energy Conversion and Management*, 48, 937–941.
- Demirbas, A. (2011). Biodiesel from oilgae, biofixation of carbon dioxide by microalgae: A solution to pollution problems. *Applied Energy*, 88(10), 3541–3547.
- Demirbas, M. F. (2011). Biofuels from algae for sustainable development. *Applied Energy*, 88(10), 3473–3480.
- Dias, J. M., Alvim-Ferraz, M. C. M., & Almeida, M. F. (2009). Production of biodiesel from acid waste lard. *Bioresource Technology*, *100*(24), 6355–6361.
- Dias, J. M., Alvim-Ferraz, M. C. M., Almeida, M. F., Méndez Díaz, J. D., Polo, M. S., & Utrilla, J. R. (2012). Selection of heterogeneous catalysts for biodiesel production from animal fat. *Fuel*, *94*, 418–425.
- Dragone, G., Fernandes, B., Vicente, A., & Teixeira, J. (2010). Third generation biofuels from microalgae. *Current Research, Technology and Education Topics in Applied Microbiology and Microbial Biotechnology*, 1355–1366.
- Duan, Y., Wu, Y., Shi, Y., Yang, M., Zhang, Q., & Hu, H. (2016). Esterification of octanoic acid using SiO<sub>2</sub> doped sulfated aluminum-based solid acid as catalyst. *Catalysis Communications*, 82, 32–35.
- Eghbali, F., Soraya, B., Salman, H., & Soltani, M. (2016). Sulfonated Beet Pulp as Solid Catalyst in One-Step Esterification of Industrial Palm Fatty Acid Distillate. *Journal of the American Oil Chemists' Society*, *93*(3), 319–327.
- 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.
- Endalew, A. K., Kiros, Y., & Zanzi, R. (2011). Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. *Biomass and Bioenergy*, *35*(9), 3787–3809.
- Er, E. I., Corma, A., Forn6s, V., Juan-Rajadell, M. I., & L6pez Nieto, J. M. (1994). applied catalysis A Influence of preparation conditions on the structure and catalytic properties of SO<sub>4</sub>-2/ZrO<sub>2</sub> superacid catalysts. *Applied Catalysis A: General*, 116, 151–163.
- Farooq, M., Ramli, A., & Naeem, A. (2015). Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones. *Renewable Energy*, 76, 362–368.

- Feldmann, T., & Demopoulos, G. P. (2012a). The crystal growth kinetics of alpha calcium sulfate hemihydrate in concentrated CaCl2-HCl solutions. *Journal of Crystal Growth*, 351(1), 9–18.
- Galadima, A., & Muraza, O. (2014). Biodiesel production from algae by using heterogeneous catalysts: A critical review. *Energy*, 78, 72–83.
- Gapor Md Top, A. (2010). Production and utilization of palm fatty acid distillate (PFAD). *Lipid Technology*, 22(1), 11–13.
- Ghoreishi, S. M., & Moein, P. (2013). Biodiesel synthesis from waste vegetable oil via transesterification reaction in supercritical methanol. *Journal of Supercritical Fluids*, 76, 24–31.
- Granados, M. L., Poves, M. D. Z., Alonso, D. M., Mariscal, R., Galisteo, F. C., Moreno-Tost, R., ... Fierro, J. L. G. (2007). Biodiesel from sunflower oil by using activated calcium oxide. *Applied Catalysis B: Environmental*, 73, 317–326.
- Guner, F. S., Sirkecioglu, A., Yilmaz, S., Erciyes, A. T., & Erdem-Senatalar, A. (1996). Esterification of oleic acid with glycerol in the presence of sulfated iron oxide catalyst. *JAOCS, Journal of the American Oil Chemists' Society*, 73(3), 347–351.
- Guo, F., & Fang, Z. (2011). Biodiesel Production with Solid Catalysts. *Biodiesel Feedstocks and Processing Technologies*, 1–21.
- Gupta, A. R., Yadav, S. V., & Rathod, V. K. (2015). Enhancement in biodiesel production using waste cooking oil and calcium diglyceroxide as a heterogeneous catalyst in presence of ultrasound. *Fuel*, *158*, 800–806.
- 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. *Plant Journal*.
- Huang, G., Chen, F., Wei, D., Zhang, X., & Chen, G. (2010). Biodiesel production by microalgal biotechnology. *Applied Energy*, 87(1), 38–46.
- Ibrahim M.Lokman, Umer Rashid, Zulkarnain Zainal, Robiah Yunus, Y. H. T.-Y. (2014). Microwave-assisted Biodiesel Production by Esterification of Palm Fatty Acid Distillate. *Journal of Oleo Science*, 63(9), 849–855.
- Islam, A., Taufiq-Yap, Y. H., Chu, C.-M., Chan, E.-S., & Ravindra, P. (2012). Studies on design of heterogeneous catalysts for biodiesel production. *Process Safety and Environmental Protection*, (January), 1–14.
- Istadi, I., Anggoro, D. D., Buchori, L., Rahmawati, D. a, & Intaningrum, D. (2015). Preparation and Characterization of Sulphated Zinc Oxide Acid Catalyst for Biodiesel Production by Transesterification of Soybean Oil with Methanol. *Procedia Environmental Sciences*, 23 (Ictcred 2014), 1–24.
- Jin, T., Wang, B., Zeng, J., Yang, C., Wang, Y., & Fang, T. (2015). Esterification of free fatty acids with supercritical methanol for biodiesel production and related kinetic study. *RSC Adv.*, *5*(64), 52072–52078.
- John, R. P., Anisha, G. S., Nampoothiri, K. M., & Pandey, A. (2011). Bioresource Technology Micro and macroalgal biomass: A renewable source for bioethanol. *Bioresource Technology*, *102*(1), 186–193.
- Karmakar, A., Karmakar, S., & Mukherjee, S. (2010). Properties of various plants and animals feedstocks for biodiesel production. *Bioresource Technology*, *101*(19), 7201–7210.
- Kaur, K., Wanchoo, R. K., & Toor, A. P. (2015). Sulfated Iron Oxide: A Proficient Catalyst for Esterification of Butanoic Acid with Glycerol. *Industrial & Engineering Chemistry Research*, *54*(13), 3285–3292.
- Kawashima, A., Matsubara, K., & Honda, K. (2009). Acceleration of catalytic activity of calcium oxide for biodiesel production. *Bioresource Technology*, 100(2), 696–

- 700.
- Kim, J., Yoo, G., Lee, H., Lim, J., Kim, K., Kim, C. W., ... Yang, J. W. (2013). Methods of downstream processing for the production of biodiesel from microalgae. *Biotechnology Advances*, 31(6), 862–876.
- Kong, B., Yu, J., Savino, K., Zhu, Y., & Guan, B. (2012). Synthesis of ??-calcium sulfate hemihydrate submicron-rods in water/n-hexanol/CTAB reverse microemulsion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 409, 88–93.
- Kouzu, M., & Hidaka, J. S. (2012). Transesterification of vegetable oil into biodiesel catalyzed by CaO: A review. *Fuel*, *93*, 1–12.
- Kouzu, M., Hidaka, J. S., Komichi, Y., Nakano, H., & Yamamoto, M. (2009). A process to transesterify vegetable oil with methanol in the presence of quick lime bit functioning as solid base catalyst. *Fuel*, 88(10), 1983–1990.
- Kouzu, M., Kasuno, T., Tajika, M., Sugimoto, Y., Yamanaka, S., & Hidaka, J. (2008). Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. *Fuel*, 87, 2798–2806.
- Kuwahara, Y., Kaburagi, W., Nemoto, K., & Fujitani, T. (2014). Esterification of levulinic acid with ethanol over sulfated Si-doped ZrO<sub>2</sub> solid acid catalyst: Study of the structure-activity relationships. *Applied Catalysis A: General*, 476, 186–196.
- Lam, M. K., & Lee, K. T. (2011). Mixed methanol-ethanol technology to produce greener biodiesel from waste cooking oil: A breakthrough for SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>-SiO<sub>2</sub> catalyst. *Fuel Processing Technology*, 92(8), 1639–1645.
- Lam, M. K., & Lee, K. T. (2012). Microalgae biofuels: A critical review of issues, problems and the way forward. *Biotechnology Advances*, 30(3), 673–690.
- Lam, M. K., & Lee, K. T. (2013a). Catalytic transesterification of high viscosity crude microalgae lipid to biodiesel: Effect of co-solvent. *Fuel Processing Technology*, 110, 242–248.
- 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.
- 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.
- Le Quéré, C., Peters, G. P., Andres, R. J., Andrew, R. M., Boden, T. A., Ciais, P., ... Zaehle, S. (2014). Global carbon budget 2013. *Earth System Science Data*, 6(1), 235–263.
- Lee, D. W., Park, Y. M., & Lee, K. Y. (2009). Heterogeneous base catalysts for transesterification in biodiesel synthesis. *Catalysis Surveys from Asia*, 13, 63–77.
- Lee, J., Yoo, C., Jun, S., Ahn, C., & Oh, H. (2010). Bioresource Technology Comparison of several methods for effective lipid extraction from microalgae. *Bioresource Technology*, 101(1), S75–S77.
- Lee, S. L., Wong, Y. C., Tan, Y. P., & Yew, S. Y. (2015). Transesterification of palm oil to biodiesel by using waste obtuse horn shell-derived CaO catalyst. *Energy Conversion and Management*, *93*, 282–288.
- Lee, H. V., Taufiq-Yap, Y. H., Hussein, M. Z., & Yunus, R. (2013). Transesterification of jatropha oil with methanol over Mg-Zn mixed metal oxide catalysts. *Energy*, 49, 12–18.
- Li, Q., Du, W., & Liu, D. (2008). Perspectives of microbial oils for biodiesel production. *Applied Microbiology and Biotechnology*.
- Li, S. K. (2011). Synthesis of Sulphated Transition Metal Oxides Supported on

- Mesoporous Silica using Direct Impregnation Method and Their Catalytic Activities Primary Supervisor: Roger WHITING
- Li, Y., Lian, S., Tong, D., Song, R., Yang, W., Fan, Y., ... Hu, C. (2011). One-step production of biodiesel from Nannochloropsis sp. on solid base Mg-Zr catalyst. *Applied Energy*, 88(10), 3313–3317.
- 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., He, H., Wang, Y., Zhu, S., & Piao, X. (2008). Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel*, 87, 216–221.
- Lokman, I. M. (2016). Meso- and macroporous sulfonated starch solid acid catalyst for esterification of palm fatty acid distillate. *Arabian Journal of Chemistry*, 9(2), 179–189.
- Lokman, I. M., Goto, M., Rashid, U., & Taufiq-Yap, Y. H. (2016). Sub- and supercritical esterification of palm fatty acid distillate with carbohydrate-derived solid acid catalyst. *Chemical Engineering Journal*, 284(JANUARY), 872–878.
- Lokman, I. M., Rashid, U., Hin, Y., & Yunus, R. (2015). Methyl ester production from palm fatty acid distillate using sulfonated glucose-derived acid catalyst, 81, 347–354
- Lokman, I. M., Rashid, U., & Taufiq-Yap, Y. H. (2015). Production of biodiesel from palm fatty acid distillate using sulfonated-glucose solid acid catalyst: Characterization and optimization. *Chinese Journal of Chemical Engineering*, 23(11), 1857–1864.
- Lokman, I. M., Rashid, U., Yunus, R., & Taufiq-Yap, Y. H. (2014). Carbohydrate-derived Solid Acid Catalysts for Biodiesel Production from Low-Cost Feedstocks: A Review. *Catalysis Reviews*, *56*(2), 187–219.
- López, D. E., Goodwin, J. G., Bruce, D. A., & Lotero, E. (2005). Transesterification of triacetin with methanol on solid acid and base catalysts. *Applied Catalysis A: General*, 295(2), 97–105.
- 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.
- Marchetti, J. M., & Errazu, A. F. (2008). Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides. *Biomass and Bioenergy*, 32(9), 892–895.
- Mata, T. M., Martins, A. A., & Caetano, N. S. (2010). Microalgae for biodiesel production and other applications: A review. *Renewable and Sustainable Energy Reviews*.
- Metre, A. V, & Nath, K. (2015). Super phosphoric acid catalyzed esterification of Palm Fatty Acid Distillate for biodiesel production: physicochemical parameters and kinetics, 88–96.
- Miao, X., & Wu, Q. (2006). Biodiesel production from heterotrophic microalgal oil. *Bioresource Technology*, 97(6), 841–846.
- Mishra, T., & Parida, K. M. (2006). Effect of sulfate on the surface and catalytic properties of iron-chromium mixed oxide pillared clay. *Journal of Colloid and Interface Science*, 301(2), 554–559.
- Mo, X., Lotero, E., Lu, C., Liu, Y., & Goodwin, J. G. (2008). A novel sulfonated carbon composite solid acid catalyst for biodiesel synthesis. *Catalysis Letters*, 123(1–2), 1–6.
- Muhammad, Y., Mohd, W., Wan, A., & Aziz, A. R. A. (2013). Journal of Environmental Chemical Engineering Solid acid-catalyzed biodiesel production

- from microalgal oil The dual advantage. Biochemical Pharmacology, I(3), 113-121.
- Muñoz Morán, J. a., Kretzschmar, B. H., & Lepage, O. M. (2007). The use of calcium sulphate (plaster of Paris) in a two step surgery for the treatment of a facial fracture in a foal. *Equine Veterinary Education*, 19, 370–373.
- Musa, I. A. (2016). The effects of alcohol to oil molar ratios and the type of alcohol on biodiesel production using transesterification process. *Egyptian Journal of Petroleum*, 25(1), 21–31.
- Muthu, H., Selvabala, V. S., Varathachary, T. K., Selvaraj, D. K., Nandagopal, J., & Subramanian, S. (2010). Synthesis of biodiesel from neem oil using sulfated zirconia via tranesterification. *Brazilian Journal of Chemical Engineering*, 27(4), 601–608.
- Nakatani, N., Takamori, H., Takeda, K., & Sakugawa, H. (2009). Transesterification of soybean oil using combusted oyster shell waste as a catalyst. *Bioresource Technology*, 100(3), 1510–1513.
- National Center for Biotechnology Information. PubChem Compound Database; CID=24497. (n.d.). Retrieved December 29, 2016, from https://pubchem.ncbi.nlm.nih.gov/compound/24497
- Niju, S., Meera Sheriffa Begum, K. M., & Anantharaman, N. (2014). Enhancement of biodiesel synthesis over highly active CaO derived from natural white bivalve clam shell. *Arabian Journal of Chemistry*.
- Nur Syazwani, O., Rashid, U., & Taufiq Yap, Y. H. (2015). Low-cost solid catalyst derived from waste Cyrtopleura costata (Angel Wing Shell) for biodiesel production using microalgae oil. *Energy Conversion and Management*, 101, 749–756.
- Nurfitri, I., Maniam, G. P., Hindryawati, N., Yusoff, M. M., & Ganesan, S. (2013). Potential of feedstock and catalysts from waste in biodiesel preparation: A review. *Energy Conversion and Management*, 74, 395–402.
- Oh, S. W., Bang, H. J., Bae, Y. C., & Sun, Y. K. (2007). Effect of calcination temperature on morphology, crystallinity and electrochemical properties of nanocrystalline metal oxides (Co<sub>3</sub>O<sub>4</sub>, CuO, and NiO) prepared via ultrasonic spray pyrolysis. *Journal of Power Sources*, 173(1), 502–509.
- Olutoye, M. A., Wong, C. P., Chin, L. H., & Hameed, B. H. (2014). Synthesis of FAME from the methanolysis of palm fatty acid distillate using highly active solid oxide acid catalyst. *Fuel Processing Technology*, 124, 54–60.
- Osterwalder, N., Loher, S., Grass, R. N., Brunner, T. J., Limbach, L. K., Halim, S. C., & Stark, W. J. (2007). Preparation of nano-gypsum from anhydrite nanoparticles: Strongly increased Vickers hardness and formation of calcium sulfate nanoneedles. *Journal of Nanoparticle Research*, 9(2), 275–281.
- Pan, Z., Lou, Y., Yang, G., Ni, X., Chen, M., Xu, H., ... Huang, Q. (2013). Preparation of calcium sulfate dihydrate and calcium sulfate hemihydrate with controllable crystal morphology by using ethanol additive. *Ceramics International*, 39(5), 5495–5502.
- Park, Y. M., Lee, D. W., Kim, D. K., Lee, J. S., & Lee, K. Y. (2008). The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel. *Catalysis Today*, 131(1–4), 238–243.
- Patel, A., Brahmkhatri, V., & Singh, N. (2013). Biodiesel production by esterification of free fatty acid over sulfated zirconia. *Renewable Energy*, *51*, 227–233.
- Patil, P. D., & Deng, S. (2009). Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel*, 88(7), 1302–1306.

- Patil, P. D., Gnaneswar, V., Mannarswamy, A., Cooke, P., Nirmalakhandan, N., Lammers, P., & Deng, S. (2012). Comparison of direct transesterification of algal biomass under supercritical methanol and microwave irradiation conditions. *Fuel*, 97, 822–831.
- Petchmala, A., Laosiripojana, N., Jongsomjit, B., Goto, M., Panpranot, J., Mekasuwandumrong, O., & Shotipruk, A. (2010). Transesterification of palm oil and esterification of palm fatty acid in near- and super-critical methanol with SO<sub>4</sub>-ZrO<sub>2</sub> catalysts. *Fuel*, 89(9), 2387–2392.
- Piker, A., Tabah, B., Perkas, N., & Gedanken, A. (2016). A green and low-cost room temperature biodiesel production method from waste oil using egg shells as catalyst. *Fuel*, *182*, 34–41.
- Rahmi, I. D. (2013). The Influence of Molar Ratio of Methanol to PFAD and Esterification Reaction Time towards Biodiesel Characteristics Palm Fatty Acids Distillate Produced. *Advanced Science Engineering Information Technology*, 3(5), 9–13.
- Rainforest Foundation Norway. (2016). Palm Fatty Acid Distillate ( PFAD ) in biofuels.
- Rashid, N., Ur Rehman, M. S., Sadiq, M., Mahmood, T., & Han, J.-I. (2014). Current status, issues and developments in microalgae derived biodiesel production. *Renewable and Sustainable Energy Reviews*, 40, 760–778.
- Rashid, U., Anwar, F., & Knothe, G. (2011). Biodiesel from Milo (Thespesia populnea L.) seed oil. *Biomass and Bioenergy*, 35(9), 4034–4039.
- 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.
- Rauschmann, M. A., Wichelhaus, T. A., Stirnal, V., Dingeldein, E., Zichner, L., Schnettler, R., & Alt, V. (2005). Nanocrystalline hydroxyapatite and calcium sulphate as biodegradable composite carrier material for local delivery of antibiotics in bone infections. *Biomaterials*, 26(15), 2677–2684.
- Rawat, I., Ranjith Kumar, R., Mutanda, T., & Bux, F. (2013). Biodiesel from microalgae: A critical evaluation from laboratory to large scale production. *Applied Energy*.
- Refaat, A. A. (2010). Biodiesel production using solid metal oxide catalysts. International Journal of Environmental Science & Technology, 8(1), 203–221.
- Ropero-Vega, J. L., Aldana-Pérez, a., Gómez, R., & Niño-Gómez, M. E. (2010). Sulfated titania [TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>]: A very active solid acid catalyst for the esterification of free fatty acids with ethanol. *Applied Catalysis A: General*, 379(1–2), 24–29.
- Roschat, W., Siritanon, T., Yoosuk, B., & Promarak, V. (2016). Biodiesel production from palm oil using hydrated lime-derived CaO as a low-cost basic heterogeneous catalyst. *Energy Conversion and Management*, 108, 459–467.
- Saka, S., & Kusdiana, D. (2001). Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. *Fuel*, 80(2), 225–231.
- Saravanan, K., Tyagi, B., Shukla, R. S., & Bajaj, H. C. (2015a). Esterification of palmitic acid with methanol over template-assisted mesoporous sulfated zirconia solid acid catalyst. *Applied Catalysis B: Environmental*, 172–173, 108–115.
- Shahabuddin, M., Masjuki, H. H., Kalam, M.A., Hazrat, M.A., Mofijur, M., Nazira, V., & Varman, M., Liaquat, A. M. (2012). Biofuel: Potential Energy Source in Road Transportation Sector in Malaysia. *Innovation for Sustainnable and Secure Energy*, (November).
- Shahid, E. M., & Jamal, Y. (2008). A review of biodiesel as vehicular fuel, 12(x),

- 2484-2494.
- Sharma, K. K., Schuhmann, H., & Schenk, P. M. (2012). High Lipid Induction in Microalgae for Biodiesel Production, 1532–1553.
- Shin, H. Y., Lee, S. H., Ryu, J. H., & Bae, S. Y. (2012). Biodiesel production from waste lard using supercritical methanol. *Journal of Supercritical Fluids*, 61, 134– 138.
- 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(7–8), 1002–1008.
- Shuit, S. H., & Tan, S. H. (2014). Feasibility study of various sulphonation methods for transforming carbon nanotubes into catalysts for the esterification of palm fatty acid distillate. *Energy Conversion and Management*, 88, 1283–1289.
- Shuit, S. H., & Tan, S. H. (2015). Biodiesel Production via Esterification of Palm Fatty Acid Distillate Using Sulphonated Multi-walled Carbon Nanotubes as a Solid Acid Catalyst: Process Study, Catalyst Reusability and Kinetic Study. *Bioenergy Research*, 8(2), 605–617.
- Singh, S. P., & Singh, D. (2010). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable and Sustainable Energy Reviews*, 14, 200–216.
- Sirisomboonchai, S., Abuduwayiti, M., Guan, G., Samart, C., Abliz, S., Hao, X., ... Abudula, A. (2015). Biodiesel production from waste cooking oil using calcined scallop shell as catalyst. *Energy Conversion and Management*, 95, 242–247.
- Slade, R., & Bauen, A. (2013). Micro-algae cultivation for biofuels: Cost, energy balance, environmental impacts and future prospects. *Biomass and Bioenergy*, 53, 29–38.
- Soltani, S., Rashid, U., Yunus, R., & Taufiq-Yap, Y. H. (2016). Biodiesel production in the presence of sulfonated mesoporous ZnAl2O4 catalyst via esterification of palm fatty acid distillate (PFAD). *Fuel*, *178*, 253–262.
- Sprules, F. J., & York, N. (1950). UNITED STATES PATENT OFFICE.
- Sree, R., Babu, N. S., Prasad, P. S. S., & Lingaiah, N. (2008). Transesterification of edible and non-edible oils over basic solid Mg / Zr catalysts. *Fuel Processing Technology*, 90(1), 152–157.
- Su, C.-H. (2013). Kinetic study of free fatty acid esterification reaction catalyzed by recoverable and reusable hydrochloric acid. *Bioresource Technology*, *130*, 522–8.
- Suryaputra, W., Winata, I., Indraswati, N., & Ismadji, S. (2013). Waste capiz (Amusium cristatum) shell as a new heterogeneous catalyst for biodiesel production. *Renewable Energy*, 50, 795–799.
- Syazwani, O. N., Teo, S. H., Islam, A., & Taufiq-Yap, Y. H. (2017). Transesterification activity and characterization of natural CaO derived from waste venus clam (Tapes belcheri S.) material for enhancement of biodiesel production. *Process Safety and Environmental Protection*, 105, 303–315.
- Szybist, J. P., Song, J., Alam, M., & Boehman, A. L. (2007). Biodiesel combustion, emissions and emission control. *Fuel Processing Technology*.
- Talebian-kiakalaieh, A., Aishah, N., Amin, S., Zarei, A., & Noshadi, I. (2013). Transesterification of waste cooking oil by heteropoly acid (HPA) catalyst: Optimization and kinetic model, *102*, 283–292.
- Tang, Y., Chen, G., Zhang, J., & Lu, Y. (2011). Highly active cao for the transesterification to biodiesel production from rapeseed oil. *Bulletin of the Chemical Society of Ethiopia*, 25(1), 37–42.
- Tang, Y., Gu, X., & Chen, G. (2013). 99 % yield biodiesel production from rapeseed

- oil using benzyl bromide CaO catalyst, 203–208.
- Tariq, M., Ali, S., & Khalid, N. (2012). Activity of homogeneous and heterogeneous catalysts, spectroscopic and chromatographic characterization of biodiesel: A review. *Renewable and Sustainable Energy Reviews*, 16(8), 6303–6316.
- 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.
- Tay, B., Ping, Y., & Yusof, M. (2009). Characteristics and Properties of Fatty Acid Distillates from Palm Oil. *Oil Palm Bulletin*, *59*(November), 5–11.
- Taylor, P., Abdelaziz, A. E. M., Leite, G. B., & Hallenbeck, P. C. (2013). Addressing the challenges for sustainable production of algal biofuels: II. Harvesting and conversion to biofuels. *Environmental Technology*, *34*(13–14), 1807–1836.
- Teo, S. H., Islam, A., Yusaf, T., & Taufiq-Yap, Y. H. (2014). Transesterification of Nannochloropsis oculata microalga's oil to biodiesel using calcium methoxide catalyst. *Energy*, 78, 63–71.
- Teo, S. H., & Ng, F. L. (2014). Alumina supported / unsupported mixed oxides of Ca and Mg as heterogeneous catalysts for transesterification of Nannochloropsis sp. microalga's oil.
- Thitsartarn, W., & Kawi, S. (2011). Transesterification of oil by sulfated Zr-supported mesoporous silica. *Industrial and Engineering Chemistry Research*, 50(13), 7857–7865.
- Thommes, M., Kaneko, K., Neimark, A. V, Olivier, J. P., Rodriguez-reinoso, F., Rouquerol, J., & Sing, K. S. W. (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution ( IUPAC Technical Report ).
- Trakarnpruk, W. (2012). Biodiesel Production from Palm Fatty Acids Distillate Using Tungstophosphoric Acid- and Cs-salt Immobilized-Silica. *Jurnal Teknik Kimia Indonesia*, 11(2), 101–107.
- U.S Energy Information Administration. (2016). *International Energy Outlook 2016* (Vol. 484). Retrieved from http://www.eia.gov/forecasts/ieo/world.cfm
- Umdu, E. S., Tuncer, M., & Seker, E. (2009). Transesterification of Nannochloropsis oculata microalga's lipid to biodiesel on Al2O3 supported CaO and MgO catalysts. *Bioresource Technology*, 100(11), 2828–2831.
- Vieira, S. S., Magriotis, Z. M., Gra??a, I., Fernandes, A., Ribeiro, M. F., Lopes, J. M. F. M., ... Saczk, A. A. (2017). Production of biodiesel using HZSM-5 zeolites modified with citric acid and SO42???/La2O3. *Catalysis Today*, 279, 267–273.
- Viriya-Empikul, N., Krasae, P., Nualpaeng, W., Yoosuk, B., & Faungnawakij, K. (2012). Biodiesel production over Ca-based solid catalysts derived from industrial wastes. *Fuel*, 92(1), 239–244.
- Viriya-empikul, N., Krasae, P., Puttasawat, B., Yoosuk, B., Chollacoop, N., & Faungnawakij, K. (2010). Waste shells of mollusk and egg as biodiesel production catalysts. *Bioresource Technology*, *101*(10), 3765–3767.
- Wan, Z., Lim, J. K., & Hameed, B. H. (2015). Chromium-tungsten heterogeneous catalyst for esterification of palm fatty acid distillate to fatty acid methyl ester. *Journal of the Taiwan Institute of Chemical Engineers*, 54, 64–70.
- Wang, H., Gao, L., Chen, L., Guo, F., & Liu, T. (2013). Integration process of biodiesel production from filamentous oleaginous microalgae Tribonema minus. *Bioresource Technology*, *142*, 39–44.
- Wang, J., Wang, A., Tian, X., Wang, H., Xu, M., & Yang, L. (2017). Development of palygorskite-SO42–/ZnAl2O4 composites as a novel solid acid catalyst for the esterification of acetic acid with n-butanol. *Applied Clay Science*, *135*, 596–602.

- Wang, Y.-W., Kim, Y.-Y., Christenson, H. K., & Meldrum, F. C. (2012). A new precipitation pathway for calcium sulfate dihydrate (gypsum) via amorphous and hemihydrate intermediates. *Chemical Communications*, 48(4), 504.
- Wei, Z., Xu, C., & Li, B. (2009). Application of waste eggshell as low-cost solid catalyst for biodiesel production. *Bioresource Technology*, 100(11), 2883–2885.
- 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, 1–9.
- Y.C.Wong, Y.P.Tan, Y.H.Taufiq Yap, I. R. (2014). Effect of Calcination Temperatures of CaO/Nb<sub>2</sub>O<sub>5</sub> Mixed Oxides Catalysts on Biodiesel Production. *Sains Malaysiana*, 43(5), 783–790.
- Y.H. Taufiq-Yap, H.V.Lee, P. L. L. (2012). Transesterification of jatropha curcas oil to biodiesel by using short necked clam (orbicularia orbiculata) shell derived catalyst. *Energy Exploration & Exploitation*, 30(5), 853–866.
- Yan, S., Lu, H., & Liang, B. (2008a). Supported CaO catalysts used in the transesterification of rapeseed oil for the purpose of biodiesel production. *Energy and Fuels*, 22(14), 646–651. http://doi.org/10.1021/ef0701050
- Yang, J. C., Wu, H. Da, Teng, N. C., Ji, D. Y., & Lee, S. Y. (2012). Novel attempts for the synthesis of calcium sulfate hydrates in calcium chloride solutions under atmospheric conditions. *Ceramics International*, 38(1), 381–387.
- Yang, Z., & Xie, W. (2007). Soybean oil transesterification over zinc oxide modified with alkali earth metals. *Fuel Processing Technology*, 88(6), 631–638.
- Yin, X., Ma, H., You, Q., Wang, Z., & Chang, J. (2012). Comparison of four different enhancing methods for preparing biodiesel through transesterification of sunflower oil, 91, 320–325.
- Yoshikawa, G., Murashima, Y., Wadachi, R., Sawada, N., & Suda, H. (2002). Guided bone regeneration (GBR) using membranes and calcium sulphate after apicectomy: A comparative histomorphometrical study. *International Endodontic Journal*, 35(3), 255–263.
- Yu, H., Zhang, Z., Li, Z., & Chen, D. (2014). Characteristics of tar formation during cellulose, hemicellulose and lignin gasification. *Fuel*, *118*, 250–256.
- 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.
- Zabeti, M., Wan Daud, W. M. A., & Aroua, M. K. (2009). Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology*, 90(6), 770–777.
- Zhang, J., & Nancollas, G. H. (1992). Influence of calcium/sulfate molar ratio on the growth rate of calcium sulfate dihydrate at constant supersaturation. *Journal of Crystal Growth*, 118(3–4), 287–294.
- 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. (2014). Biodiesel production via esterification of oleic acid catalyzed by chlorosulfonic acid modified zirconia. *Applied Energy*, 116, 191–198.

## **APPENDICES**