UNIVERSITI PUTRA MALAYSIA

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

SALAM HUSSEIN HAYDER AL-JABERI

FS 2017 17
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By

SALAM HUSSEIN HAYDER AL-JABERI

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

February 2017
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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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SALAM HUSSEIN HAYDER AL-JABERI

February 2017

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

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

In this research, biodiesel was produced by esterification of palm fatty acid distillate (PFAD) with methanol using heterogeneous manganese-nickel doped on sulfated zirconia catalyst (MnO-NiO-SO\textsubscript{4}^2-/ZrO\textsubscript{2}). Initially, the catalyst was synthesized using simple wet impregnation method in five different concentrations of manganese 5%-25% and nickel (5%-25%) supported on zirconia. After catalyst screening, two out of five showed significant FFA conversion when concentration of manganese was 10%Mn and the concentration of nickel was 15%NiO after doping manganese and nickel on zirconia under the best concentration and then the catalyst activity was improved by increasing the acidity via treatment with chlorosulfonic acid to form 10%Mn-15%NiO-4%SO\textsubscript{4}^2-/ZrO\textsubscript{2}. The best catalyst was characterized using different characterization techniques in order to study the physic-chemical properties of the catalyst. The optimization of esterification reaction conditions of PFAD using heterogeneous solid catalysts was performed. The TPD-NH\textsubscript{3} result of the synthesized...
solid acid catalyst proved the catalytic activity of the catalyst, having achieved 97.7% FFA conversion due to high strength of acid sites. Moreover, the catalyst was reused for at least 5 cycles before complete deactivation of the catalytic active phase.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

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

Oleh

SALAM HUSSEIN HAYDER AL-JABERI

Februari 2017

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

Dalam kajian ini, biodiesel dihasilkan melalui proses pengesteran asid lemak kelapa sawit tersulung (PFAD) bersama metanol menggunakan mangkin heterogen mangan-nikel terdop ke atas zirkonia bersulfur (MnO-NiO-SO_42-/ZrO_2). Pada mulanya, mangkin telah disintesis menggunakan kaedah pengisitepuan basah dalam lima kepekatan mangan yang berbeza (5%-25%) dan nikel (5%-25%) yang disokong ke atas zirkonia. Selepas penyaringan mangkin, dua daripada lima mangkin menunjukkan penukaran asid lemak bebas (FFA) yang signifikan apabila kepekatan mangan dan nikel masing-masing adalah sebanyak 10 % dan 15 %. Selepas mangan dan nikel didop ke atas zirkonia pada kepekatan yang dipilih dan aktiviti mangkin ditambah baik dengan meningkatkan keasidan mangkin melalui rawatan dengan menggunakan asid
klorosulfonik untuk menghasilkan 10%Mn-15%NiO- 4%SO4²⁻/ ZrO₂. Mangkin terbaik yang dipilih dicirikan menggunakan pelbagai teknik pencirian untuk mengkaji sifat fizikokimia bagi mangkin tersebut. Pengoptimuman tindak balas pengesteran PFAD menggunakan mangkin heterogen pepejal telah dilakukan. Keputusan atur cara-suhu-nyahjerapan ammonia (TPD-NH₃) bagi mangkin asid pepejal membuktikan aktivit mangkin mencapai sehingga 97.7% penukaran FFA yang disebabkan oleh kekuatan tapak asid. Tambah pula, mangkin dapat diguna semula sekurang-kurangnya lima kali kitaran tindak balas sebelum ternyahaktif.
ACKNOWLEDGMENTS

Bismillah AL-Rahman AL-Rahim. Alhamdullilah, Thanks to Allah S.W.T the almighty for giving me the strength, patience and faith to pursue my dream and also his blessings which led me through the journey of completing this research.

First and foremost, I have to thank my mother for her love and support throughout my life. Thank you for my family, both for giving me strength to reach for the stars and chase my dreams. My sister and my brothers deserve my wholehearted thanks as well. I would like to sincerely thank my supervisor, Prof. Dr. Taufiq Yap Yun Hin, for his guidance and support throughout this study, and especially for his confidence in me. I would also like to thank, Dr. Mohd Izham Bin Saiman for serving as a member on my thesis committee. Thanks also to Dr. Umer Rashid. I would also like to thank my friend Dr. Faris Al-Doghachi, in a special way, I express my heartfelt gratefulness for her guide and support that I believed I learned from the best.

To all my friends, thank you for your understanding and encouragement in my many, many moments of crisis. Your friendship makes my life a wonderful experience. I cannot list all the names here, but you are always on my mind. Thank you.
I certify that a Thesis Examination Committee has met on 23 February 2017 to conduct the final examination of Salam Hussein Hayder on his thesis entitled "Esterification of Palm Fatty Acid Distillate by Using Manganese Oxide and Nickel Oxide Supported on Zirconia for Biodiesel Production" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing And Materials</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CHSN</td>
<td>CHSN - Elemental Analyser</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-Dispersive X-Ray Spectroscopy</td>
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<tr>
<td>EN</td>
<td>European Standard</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty Acid Methyl Ester</td>
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<tr>
<td>FFA</td>
<td>Free Fatty Acid</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography Mass Spectrometry</td>
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<tr>
<td>PFAD</td>
<td>Palm Fatty Acid Distillate</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy.</td>
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<tr>
<td>TGA</td>
<td>Thermo Gravimetric Analysis</td>
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<tr>
<td>TPD- NH₃</td>
<td>Ammonia-Temperature Programmed Desorption</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Power Diffraction</td>
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<tr>
<td>XRF</td>
<td>X-Ray Fluorescence Spectrometry</td>
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CHAPTER 1

INTRODUCTION

1.1 Background

Science and technological revolution that started over a century ago was meant to modified and improved human activities such as industrialization for the production of goods and services, modern transport system, mechanized agriculture and modern telecommunication. The aforementioned human activities are solely depending on energy which could be solar, hydro, coal or petrochemical based sources. Nowadays, the most used source of energy is petrochemical based which is fossil in nature. Fossil fuel is now considered as conventional source of energy for the production of goods and services in the industries as well as modern transportation. However, as a result of global rapid growth of human population from developing nations, possible future depletion of the fossil fuel reserved and concern over environmental issues such as global warming, fossil fuel is generally no longer considered as reliable sustainable source of energy in the future. These and other factors led to the search in renewable alternative sources of energy such as biofuels that could replace the diminishing fossil fuel. Biodiesel was found one of the most promising alternatives to conventional diesel due to its biodegradability, less poisonous exhaust, availability of feedstocks, low cost of production when compared to crude oil exploration and refining. Apart from the aforementioned advantages, biodiesel possesses similar chemical properties to that of conventional fossil fuel such as high flash point, enhanced cetane number and density. The production of biodiesel or fatty acid methyl ester (FAME) involve the reversible chemical reaction of triglycerides (TGs) a major component of vegetable oil or free fatty acid (FFA) a major component of Palm Fatty Acid Distillate (PFAD) with lower chain methyl alcohol (methanol) facilitated by good catalytic system under temperature and pressure over a period of time. Traditionally, biodiesel or FAME is produced using homogeneous catalyst such as NaOH, H$_2$SO$_4$, KOH, in which the catalyst and the feedstock are in the same phase. These catalysts are very active as they can convert vegetable oil to biodiesel at low reaction conditions. However, homogeneous catalysts are only fit to high grade vegetable oil (containing <1% FFA) which would make biodiesel production very expensive considering the high cost of fresh vegetable oil. A part from that, homogeneous catalysts are associated with difficulty in separation after the reaction which involves regular water washing that could pollute the environment and make biodiesel production difficult. Continual usage of high grade vegetable oil suitable for homogeneous catalysts for the production of biodiesel is no longer sustainable considering the consequences of food versus fuel competition which would pose hunger threats and environmental degradation through agricultural practices. Besides, homogeneous catalysts require considerable amount of energy for the purification of products and catalyst separation, additionally the catalysts are not reusable. In order to overcome such challenges, low grade feedstocks such as waste cooking oil (WCO), PFAD would be adopted as feedstock for the production of biodiesel considering their low cost. About 70% of total cost of biodiesel production goes to feedstock, hence using low cost feedstock like PFAD would make the production cost low and sustainable. However, low grades feedstock like PFAD and waste cooking oil have high FFA content usually >1. PFAD contain more than 85% FFA which cannot be handled by homogeneous catalyst for
biodiesel. Heterogeneous acid or base catalysts have revealed less marked operational difficulty when compared to conventional homogeneous catalysts for biodiesel production considering their easy separation which has minimum environmental effect compared to their counterpart. One of the most important aspects about biodiesel is that it possessed all the chemical and physical properties as contained to conventional fossil fuel.

1.2 Catalyst

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

![Figure 1.1: The effect of catalyst on the activation energy of the reaction](image)

1.3 Problem Statement and Hypothesis

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

In this study, biodiesel was produced from low cost PFAD using heterogeneous acid catalyst (MnO-NiO-SO\textsubscript{4}^{2-}/ZrO\textsubscript{2}), which is believed to reduce biodiesel production cost and make significant contribution towards its commercialization in the near future. The heterogeneous solid catalyst could be separated easily and reused severally before total loss of activity. Solid catalysts are less corrosive and more environmentally benign in terms of disposal after use.

1.4 Objectives of the Research

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

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

1.5 Scope of the Research

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

1- The solid acid catalyst (MnO-NiO-SO\textsubscript{4}^{2-}/ZrO\textsubscript{2}) would be synthesized using simple wet impregnation method from the oxides of nickel and manganese as dopants on surface of sulphated zirconia, in array to develop their catalytic activity towards the synthesis of biodiesel from high FFA feedstock.

2- The catalytic activity of the synthesized catalyst would be tested through biodiesel production using direct esterification reaction of PFAD with short chain alcohol (methanol), catalyst and temperature as reaction conditions.

3- Physico-chemical properties of the synthesized solid acid catalyst would be explored and evaluated using different characterization techniques to understand the features that control their catalytic activity as well as recyclability, regeneration and the leaching problems of active sites.

4- Optimization of biodiesel production parameters would be assessed over the most active catalyst within the screened synthesized solid catalysts under the reaction conditions (catalyst loading, methanol oil ratio, temperature and reaction time).
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