UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF HETEROGENEOUS CATALYSTS FOR TRANSESTERIFICATION OF NON-EDIBLE OIL TO BIODIESEL

LEE HWEI VOON

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By

LEE HWEI VOON

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

May 2012

DEDICATION

Dedication to my family with love

I would like to dedicate this dissertation to my loving parents, Lee Kian Guan and Chong Siew Ying, my lovely brother and sister, Lee Yen Yen and Lee Hwei May for their priceless support and endless encouragement.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

DEVELOPMENT OF HETEROGENEOUS CATALYSTS FOR TRANSESTERIFICATION OF NON-EDIBLE OIL TO BIODIESEL

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Chairman: Professor Taufiq-Yap Yun Hin, PhD, CChem, FRSC (UK)

Faculty: Science

The critical problem arises from the fossil fuels has stimulated recent interests in alternative sources for petroleum-based fuel. An alternative fuel should be technically feasible, readily available, environment acceptable and techno-economically competitive. Biodiesel, which is considered as a potential replacement of conventional diesel fuel is commonly, composed of mono-alkyl ester of long chain that can be prepared from triglycerides which is available in renewable feedstock (vegetable oils or animal fats) utilizing transesterification technology. The feedstock used for the production of biodiesel mainly come from edible vegetable oil which is highly available in most of the countries around the world. However, the competition between food and fuel economies towards the same oil resources may bring global imbalance to the food supply and demand market. The focus on this research is to produce biodiesel using non-edible feedstock (*Jatropha Curcas* oil) via heterogeneous catalyzed transesterification reaction. The solid base mixed metal oxide catalysts (CaO-MgO, CaO-ZnO, MgO-ZnO and CaO-La_2O_3) were synthesized via co-precipitation method. The physico-chemical properties of

binary oxide catalysts were characterized by using X-ray diffraction (XRD), temperature-programmed desorption of carbon dioxide (CO_2-TPD), temperature- programmed desorption of ammonia (NH_3 -TPD), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDX), N_2 adsorption (BET), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS). Furthermore, the catalytic activity of mixed metal oxides with different stoichiometric ratios (0.5- 10.0 atomic ratio) of Ca/Mg, Ca/Zn, Mg/Zn and Ca/La corresponding to CaO-MgO, CaO-ZnO, MgO-ZnO and CaO-La_2O_3, respectively, was investigated. The optimum ratios for each binary metal oxides catalyst with highest activity were CaO-MgO with 0.5 atomic ratio (90 %), CaO-ZnO with 8.0 atomic ratio (94 %), MgO-ZnO with 8.0 atomic ratio (83 %) at transesterification temperature of 120 ^oC, 25 methanol/oil molar ratio, 3 wt.% of catalyst loading within 3 h reaction time. Whereas, CaO-La_2O_3 with 8.0 atomic ratio (98 %) showed the highest activity among the series at 160 ^oC reaction temperature, 25 methanol/oil molar ratio, 3 wt.% of catalyst loading and 3 h reaction time. The transesterification activity was greatly influenced by the basicity of the active site on the catalyst. Optimization study for jatropha-based biodiesel production using CaO-MgO, CaO-ZnO, CaO-La_2O_3 and MgO-ZnO mixed oxides solid base catalysts was conducted in this study. The effects of variables including reaction temperature (40-200 ^oC), catalyst loading (1-5 wt. %), methanol/oil molar ratio (15-30) and reaction time (1-5 h) on biodiesel yield was examined and optimized using response surface methodology (RSM) coupled with central composite design (CCD). Confirmation experiment was further conducted to validate the efficacy of the model. The CaO-MgO, CaO-ZnO, MgO-ZnO and CaO-La_2O_3 catalyzed reaction model generated from RSM showed reasonable predictability and sufficient accuracy of the examined catalyzed

reaction. Furthermore, the physical and chemical characteristics of the jatropha-based biodiesel produced from CaO-MgO, CaO-ZnO, MgO-ZnO and CaO-La_2O_3 catalyzed transesterification reaction was tested with compliance to ASTM D7851 and EN 14124 standards.

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

PEMBANGUNAN PEMANGKIN HETEROGEN BAGI TRANSESTERIFIKASI MINYAK BUKAN KONSUMSI UNTUK MENGHASILKAN BIODIESEL

By

LEE HWEI VOON

Mei 2012

Pengerusi: Profesor Taufiq-Yap Yun Hin, PhD, CChem, FRSC (UK)

Fakulti: Sains

Kehausan bahan minyak bakar telah menjadi salah satu masalah dalam bidang sumber tenaga dan ianya telah merangsang minat para penyelidik untuk mencari sumber alternatif yang boleh diperbaharui untuk menggantikan sumber minyak fossil. Sumber minyak alternatif harus memiliki cirri-ciri seperti mudah untuk diperolehi, mesra alam, mesra teknolgi dan ia juga harus kompetitif dari segi ekonomi. Biodiesel merupakan sejenis minyak altenatif yang diakui untuk menggantikan sumber minyak fossil yang digunakan pada masa kini. Biodiesel merupakan rantai ester mono-alkil yang dihasilkan daripada sumber trigliserida yang boleh diperbaharui (minyak sayuran dan minyak haiwan) melalui proses transesterifikasi bermangkin. Majoriti bahan mentah yang digunakan untuk penghasilan biodiesel di negara ini adalah sumber minyak sayuran. Ini telah membangkitkan kebimbangan terhadap ketidakseimbangan sumber minyak sayuran yang menjadi sumber makanan digunakan untuk penghasilan biodiesel secara komersial. Penyelidikan ini tertumpu kepada penghasilan biodiesel dengan menggunakan sumber

minyak bukan-konsumsi (Minyak *Jathropa Curcas*) sebagai sumber bahan mentah dalam proses transesterifikasi dengan pemangkin heterogen. Pemangkin-pemangkin gabungan logam alkali iaitu CaO-MgO, CaO-ZnO, MgO-ZnO dan CaO-La_2O_3 telah disintesiskan melalui teknik pemendakan beriring. Sifat-sifat kimia fizik pemangkin oksida perduaan telah diuji menggunakan pembelauan sinar-X (XRD), penyahjerapan CO_2 Suhu Berprogram (CO_2-TPD), penyahjerapan NH_3 Suhu Berprogram (NH_3-TPD), mikroskopi electron imbasan dengan spektroskopi sebaran tenaga (SEM-EDX), penjerapan N_2 (BET), spektroskopi pancaran atom plasma gandingan induktif (ICP-AES) dan spektroskopi penyerapan atom (AAS). Dalam penyelikan tersebut, tindakbalas pemangkin oksida logam gabungan dengan pelbagai nisbah stoikiometri (0.5- 10.0 nisbah atom) bagi Ca/Mg, Ca/Zn, Mg/Zn and Ca/La berbanding dengan CaO-MgO, CaO-ZnO, MgO-ZnO and CaO-La_2O_3 masing-masing dalam tindakbalas transesterifikasi telah dikaji dalam nisbah molar methanol kepada minyak 25:1, suhu tindakbalas pada 120 ^oC, muatan pemangkin pada 3 wt. % dan tempoh tindakbalas pada 3 jam. Hasil kajian tersebut menunjukan penghasilan biodiesel oleh pemangkin dengan nisbah atom Ca/Mg=0.5 %, Ca/Zn=8.0%, Mg/Zn=8.0% dan Ca/La=8.0% adalah sebanyak 90 %, 94 %, 83% dan 98% masing-masing manakala CaO-La_2O_3 dengan nisbah atom 8.0% menunjukkan kadar tindak balas tertinggi pada nisbah molar methanol kepada minyak 25:1, suhu tindakbalas pada 160 ^oC, muatan pemangkin pada 3 wt. % dan tempoh tindakbalas pada 3 jam. Kajian ini menunjukkan bilangan tapak aktif pemangkin yang beralkali adalah amat penting untuk meningkatkan aktiviti transesterifikasi. Selain itu, kajian pengoptimuman tindakbalas transesterifikasi menggunakan pemangkin CaO-MgO, CaO-ZnO, CaO-La_2O_3 and MgO-ZnO turut dijalankan. Kesan-kesan pembolehubah seperti suhu tindakbalas (40-200 ^oC), muatan pemangkin (1-5 wt. %), nisbah kemolaran methanol/minyak (15-30) dan tempoh

tindakbalas (1-5h) terhadap efisiensi penghasilan biodiesel telah dikaji menggunakan kaedah tindakbalas permukaan (RSM) dengan rekabentuk komposit pusat (CCD). Model yang dijana melalui RSM ditentukurkan melalui eksperimen untuk mengesahkan ketepatan dan efikasi model tersebut. Hasil daripada eksperimen yang dijalankan menunjukkan bahawa model yang dihasilkan menunjukkan kejituan dan kepersisan yang amat memuaskan. Selain itu, ciri-ciri biodiesel yang dihasilkan melalui tindakbalas transesterifikasi dengan CaO-MgO, CaO-ZnO, MgO-ZnO dan CaO-La_2O_3 telah diuji supaya setaraf dengan kualiti diesel fosil yang digunakan pada masa kini dan mematuhi piawaian biodiesel ASTM D7851 dan EN14124.

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I certify that a Thesis Examination Committee has met on 21 May 2012 to conduct the final examination of Lee Hwei Voon on her thesis entitled "Development of Heterogeneous Catalysts for the Transesterification of Non-Edible Oil to Biodiesel" 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 degree of Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

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

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DECLARATION

I declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

LEE HWEI VOON

Date: 21 May 2012

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