UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF NANOPARTICLES SOLID ACID AND BI-FUNCTIONAL ZIRCONIA SUPPORTED CATALYSTS FOR PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL

FATHELRAHMAN HAMID ELHASSAN HAMID

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By

FATHELRAHMAN HAMID ELHASSAN HAMID

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

October 2014

DEDICATION

I would like to dedicate my thesis to soul of my beloved parents, Hamid and Ayesha, am asking Allah always to forgive them and reward them Janet Alferrdous Al-Aalaa. I will never forget my father who had wished me since my childhood to achieve this stage of education and pure love of my mother. Particularly, to the love of my life, my wife Sania and my daughters, Fatimaalzahra, Leena, Roduina and Deyala who's their love, support, patience, sacrifice and inspiration have enlightened and entertained me throughout the course of this journey.

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 NANOPARTICLES SOLID ACID AND BI-FUNTIONAL ZIRCONIA SUPPORTED CATALYSTS FOR PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL

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Chairman: Prof. Taufiq-Yap Yun Hin, PhD

Faculty: Science

Fossil-based oil has been the most important energy and fuel source since the mid of nineteenth century but there has been growing distress about an energy crisis caused by potential fossil-based oil depletion, high oil prices and the effect of gas emissions from petroleum on the environment. Thus, a need for a better energy security and an alarm about high petroleum prices has guided the scientific society to look for sustainable, renewable energy resources to decrease the reliance on fossil fuels.

Biodiesel, which is considered as a potential substitute of fossil based-diesel fuel is commonly composed of the mono-alkyl ester of a long chain fatty acid that can be produced from vegetable oils, waste cooking oil and animal oil utilizing the esterification and transesterification reactions. However, competition between food and fuel economies towards the same oil resources may bring global crisis to the food supply and demand market. In this respect, the main goal of the research is to develop new nanoparticle solid acid catalysts that can be used in place of homogeneous catalysts for production of biodiesel from waste cooking oil. The new proposed catalytic system needs to be more eco-friendly, economically visible and technically applicable with a minimum level of complexity in terms of preparation and use. Moreover, the production of biodiesel from waste cooking oil offers a triplet aspect solution: economical, environmental and waste management.

The developed nanoparticle solid acid and bi-functional catalysts are synthesized via precipitation and impregnation methods. The physico-chemical properties of the developed nanoparticle catalysts are characterized by using X-ray diffraction (XRD), temperature programming desorption (TPD-NH_3/CO_2), thermogravimetric analysis (TGA), energy dispersive spectroscopy (EDS), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), fourier transform infrared (FT-IR) and X-ray fluorescence (XRF) analyses.

In addition, the catalytic activity of all synthesized catalysts for the production of biodiesel and the effect of variables, such as reaction temperature, reaction time, waste cooking oil/methyl alcohol molar ratio as well as the catalyst loading at the fixed stirring of 600 rpm on the biodiesel yield, has been evaluated. On the other hand, an examination of the reusability and leaching of ferric, manganese as well as sulphur species into the biodiesel is carried out. Moreover, extensive modification is done over a pre-selected catalyst sample with secured heterogeneous performance in an attempt to select the most active and industrially applicable catalysis system for biodiesel production.

The central composite design (CCD) is used to design the experiments and the optimization of the process has been performed using response surface methodology (RSM) to understand the relationship between the factors and the yield of biodiesel besides that the optimum conditions for synthesis of the biodiesel is also determined.

Results revealed that Fe/Mn-SO_4^{2-}/ZrO_2 is showed the best catalytic activity in the methanolysis of waste cooking oil to biodiesel. This is followed by the Fe/Mn-WO_3/ZrO_2 and Fe/Mn-WO_3/MoO_3 catalysts that appeared with the least catalytic activity. A good reusability of the catalysts with insignificant leaching of ferric, manganese and sulphur species into the biodiesel has also been obtained.

According to the extensive modification on the surface of the Fe/Mn-SO_4^{2-}/ZrO_2, the ferric-manganese doped sulphated zirconia -16wt% SO_4^{2-} nanoparticle bi-functional solid catalyst is found to be the best catalyst amongst the entire proposed developed nanoparticle heterogeneous catalytic system for the simultaneous synthesis of waste cooking oil based-biodiesel which attributed to its highest strength and active site density of both types, large surface area and a big pores size as well as the inconsiderable leaching of sulphur.

The response surface methodology has been illustrated that the expected and experimental yield of waste cooking oil biodiesel based-biodiesel is found to be 97.0% and 97.2%, respectively, under the optimized conditions of 160 °C, 10.0 stoichiometric ratio, 3.0% wt/wt catalyst loading, reaction time of 4 h and stirring at 600 rpm.

Furthermore, the physical and chemical characteristics of waste cooking oil-based biodiesel properties of the produced biodiesel are tested with compliance to EN14214 and ASTM D6751 standards.

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

PEMBANGUNAN MANGKIN NANOZARAH PEPEJAL BERASID DWIFUNGSI BERPENYOKONG ZIRCONIA BAGI PENGHASILAN BIODIESEL DARIPADA SISA MINYAK MASAK

Oleh

FATHELRAHMAN HAMID ELHASSAN HAMID

Oktober 2014

Pengerusi: Prof. Taufiq-Yap Yun Hin, PhD
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Minyak berasaskan fosil merupakan tenaga dan sumber bahan api yang paling penting sejak pertengahan abad ke-sembilan belas, walaubagaimanapun terdapat masalah yang semakin meningkat tentang krisis tenaga disebabkan kemungkinan kekurangan minyak berasaskan fosil kerana ia adalah sumber yang tidak boleh diperbaharui, harga minyak yang tinggi dan kesan pembebasan gas daripada petroleum terhadap alam sekitar. Oleh itu, keperluan kepada keselamatan dan petunjuk tenaga yang lebih baik tentang kenaikan harga petroleum mendorong masyarakat saintifik mencari sumber tenaga yang mampan dan boleh diperbaharui bagi mengurangkan kebergantungan kepada bahan api fosil.

Biodiesel mempunyai potensi sebagai pengganti bahan bakar diesel berasaskan fosil dan biasanya terdiri daripada ester mono-alkil rantai panjang asid lemak yang boleh dihasilkan daripada minyak sayur-sayuran, sisa minyak masak dan lemak haiwan melalui proses pengesteran dan transesterifikasi. Walau bagaimanapun, persaingan antara makanan dan ekonomi bahan api terhadap sumber minyak yang sama boleh membawa kepada krisis global untuk bekalan makanan dan permintaan pasaran. Dalam hal ini, tujuan utama kajian ini adalah untuk membangunkan sistem mangkin pepejal heterogen baru yang boleh menggantikan mangkin homogen dalam penghasilan biodesel berasaskan sisa minyak masak. Sistem mangkin baru yang dicadangkan ini perlulah lebih mesra alam dan dapat meminimumkan masalah teknikal dari segi penyediaan dan penggunaannya. Selain itu, penghasilan biodiesel daripada sisa minyak

masak dapat memberi penyelesaian kepada tiga aspek iaitu: ekonomi, alam sekitar dan pengurusan sisa.

Mangkin nanozarah pepejal asid dan mangkin bi-fungsi yang dibangunkan telah disintesis melalui kaedah pemendakan dan impregnasi dan sifat-sifat mangkin telah dicirikan menggunakan analisis pembelauan sinar-X (XRD), penyahjerapan berprogramkan suhu dalam ammonia/ karbon dioksida (TPD-NH_3/CO_2), analisis termogravimetri (TGA), spektroskopi serakan tenaga (EDS), elektron mikroskop transmisi (TEM), spektroskopi fotoelektron sinar-X (XPS), analisis inframerah (FT-IR) dan analisis pendarfluor sinar-X (XRF).

Tambahan, kesemua mangkin yang disintesis telah diuji untuk penghasilan biodiesel. Parameter yang diambilkira dalam pengeluaran biodiesel termasuk suhu tindak balas, masa tindak balas, nisbah molar sisa minyak masak terhadap metil alkohol dan muatan mangkin pada masa pengacauan yang telah ditetapkan iaitu 600 rpm. Selain daripada itu, larut lesap spesis ferric, mangan dan sulfur dalam biodiesel itu dianalisa terhadap semua sampel pemangkin yang telah disintesis. Seterusnya, pengubahsuaian yang menyeluruh telah dijalankan ke atas sampel mangkin terpilih bagi memilih sistem pemangkinan yang paling aktif untuk industri penghasilan biodiesel.

Reka bentuk Komposit Pusat (CCD) telah digunakan untuk membentuk eksperimen dan mengoptimumkan tindak balas proses itu dijalankan dengan menggunakan kaedah gerak balas permukaan (RSM) untuk memahami hubungan antara faktor dan hasil biodiesel dan untuk memastikan keadaan yang optimum untuk sintesis biodiesel.

Hasil penelitian menunjukkan bahwa Fe/Mn-SO_4^{2-}/ZrO_2 telah menunjukkan aktiviti pemangkinan yang tertinggi untuk metanolisis sisa minyak masak kepada biodiesel. Ini diikuti dengan mangkin Fe/Mn-WO_3/ZrO_2 dan Fe/Mn-WO_3/MoO_3 yang muncul dengan aktiviti pemangkinan paling rendah. Tahap kebolehgunaan semula yang baik diperolehi dengan larut lesap spesis ferric, mangan dan sulfur spesis dalam biodiesel yang tidak ketara juga diperoleh.

Berdasarkan pengubahsuaian yang menyeluruh kepada permukaan mangkin Fe/Mn-SO_4^{2-}/ZrO_2, nanozarah pepejal heterogen bi-fungsi ferric-mangan yang didopkan pada kumpulan zirkonia tersulfat - 16 wt% SO_4^{2-} merupakan mangkin yang terbaik di antara seluruh sistem pembangunan mangkin heterogen yang dicadangkan untuk sintesis biodiesel berasaskan sisa minyak masak secara serentak itu disebabkan oleh kekuatan tertinggi dan ketumpatan tapak aktif kedua-dua jenis di samping luas permukaan yang besar serta saiz liang besar dan larut lesap sulfur yang tidak bererti.

Kaedah gerak balas permukaan menunjukkan hasil yang dijangka dan hasil eksperimen daripada biodiesel berasaskan sisa minyak masak ini masing-masing ialah 97.0% dan 97.2% pada keadaan optimum iaitu 160 °C, nisbah stoikiometri 10.0, muatan mangkin 3.0 wt%, masa tindak balas 4 jam dan pengacauan 600 rpm. Seterusnya, sifat-sifat fizik dan kimia biodiesel berasaskan sisa minyak masak didapati menepati piawai EN14214 dan ASTM D6751.

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I certify that a Thesis Examination Committee has met on 13 October 2014 to conduct the final examination of Fath Elrahman Hamid Elhassan Hamid on her thesis entitled "Development of Nanoparticles Solid Acid and Bi-Functional Zirconia Supported Catalysts for Production of Biodiesel from Waste Cooking Oil" 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.

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This 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.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
BET	Baunauer-Emmett-Teller
CCD	Central composite design
DOE	Design of Experiment
EN	European standard
EDX	Energy dispersive spectroscopy
FAME	Fatty acid methyl ester
FMSZ	Ferric-manganese sulphated zirconia
FID	Flame ionization detector
FFAs	Free fatty acid
FMMZ	Ferric-manganese molybdated zirconia
FMWM	Ferric-manganese tungstated molybdena
FMWZ	Ferric-manganese tungstated zirconia
FWHM	Full width at half maximum
FT-IR	Fourier transform infrared
GC	Gas chromatography
JCPDS	Joint committee on powder diffraction standard
NO_x	Nitrogen dioxide
CP	Cloud Point
PP	Pour Point
RSM	Response Surface Methodology
S_{BET}	Specific surface area
SCOME	Spent cooking oil methyl ester
TEM	Transmission Electron Microscopy
TCD	Thermal conductivity detector
TG	Triglycerides
TGA	Thermo-gravimetric analysis
TPD	Temperature-Programmed Desorption
WCOME	Waste cooking oil methyl ester
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-Ray Fluorescence Spectrometry

CHAPTER 1

INTRODUCTION

1.1 Back ground of research

The rising worldwide population and global economy growth have led to a significant energy utilisation and has consequently resulted in the limitation of energy resources. Consumption of fossil fuels in the forms of petroleum, natural gas and coal has caused the world to be greatly dependent on these non-sustainable sources. The exploitation of fossil fuels as an energy supply has led to various issues about global warming and remarkable climate change. Insecurity about fossil fuel resources and extreme greenhouse gas emissions through their combustion has become the main challenge faced in the near future. Accordingly, looking for new renewable forms of energy sources is important. Thus, broad groundwork has begun based on new technology expansion to utilise different types of catalysts for the production of a clean energy source that is possibly produced from greenhouse gas emissions. Moreover, the heterogeneous catalysed production of biodiesel has developed as a preferred process for the production of biodiesel.

Generally, a catalyst is defined as any material or substance that speeds up the rate of a chemical reaction by lowering its activation energy. It is added in a very little amount in comparison to the quantities of the reactants, and is not consumed in the chemical transformation; it is known as an initiator. However, in some cases, the catalyst effects the reaction by being consumed and regenerated whilst in other cases it seems not to be included in the process and functions by a high calibre of surface characteristics (Ertl *et al*., 2008).

Whereas, catalysis represents the vital technology for accelerating essential chemical conversions; it is key to recognising environmentally friendly and commercially feasible reactions for transforming energy carriers to directly usable energy. However, use of nanocatalysts not only decreases the total input energy needed for energy producing processes but also improves two considerable catalyst aspects, i.e., selectivity and thermal stability, thus leading to ecologically benign green skills.

Recently, nanocatalysts have been known as the field which includes the use of nanomaterials as catalysts for a range of liquid and solid catalysis applications. Meanwhile, solid catalysts are characterised as one of the previous industrial uses of different types of nanoparticles, which have been widely employed for main chemical processes (Serrano *et al*., 2009; Zäch *et al.*, 2006).

Thus, catalysis plays a fundamental role in the improvement of sustainable reactions, which are principal to permit the present and future universal production and exploitation of energy and chemicals whilst circumventing harmful consequences to the surroundings and has the significance of being a key technology.

Fossil-based oil has been the most important energy and fuel source since the mid nineteenth century. Around ninety percent of recent vehicular fuel desires are met by petroleum. Petroleum is the essential feedstock for several chemical industries, including plastics, pharmaceuticals, solvents, fertilizers and pesticides as well (Simanzhenkov and Idem, 2003; Speight and Ozum, 2001). Still, there has been growing distress about an energy crisis caused by potential fossil-based oil depletion since it is a non-renewable resource. This requires better energy security, and an alarm about high petroleum prices has guided people to look for sustainable, renewable energy to decrease the reliance on fossil fuels. The result of gas emissions from petroleum on the environment is another dynamic factor to seek for eco-friendly fuels (Demirbas, 2009b; Mizsey and Racz, 2010). Biomass and biofuel-based energy resources have the possibility to become the main providers of energy in the next century. Amongst the many renewable fuels currently available around the world, biodiesel offers an immediate impact to the energy sector.

The utilization of biodiesel as biodegradable, renewable, sustainable, non-toxic and eco-friendly clean fuel or blends with fossil-based diesel are interesting (Agarwal, 2007). Similar to conventional diesel in composition (Table 1.1) chemically, recognized as the mono-alkyl esters of long chain triglycerides, it has become gradually attractive globally as it is derived from renewable resources and combines high performance with ecological advantages (Gerpen, 2005; Sharma *et al.*, 2008). In conventional processes, virgin vegetable oils, normally used as feedstock, undergo the transesterification reaction with methyl or ethyl alcohol, via homogeneous base catalysts (commonly sodium hydroxide and potassium hydroxide). To be more commercially feasible, the use of high grade vegetable oils, which contribute to about 88% of the entire expected cost of biodiesel production, could be substituted with a cheaper feedstock, such as waste cooking oil. Nevertheless, the production of biodiesel from this acid feedstock is difficult because of water and FFA content. The pretreatment steps, including an acid catalyzed pre-esterification combined with water removal, are required to decrease the acid value and water to below onset limits prior to being processed by using a traditional biodiesel production method. In addition to catalyze esterification process, heterogeneous solid acid catalysts are capable to catalyze the transesterification of triglycerides giving rise to the utilization of the acid catalysts to carry out the simultaneous esterification of free fatty acid and transesterification of triglycerides.

Biodiesel has high oxygen content around (11%) and consequently, being a fuel with high combustion properties, reduces net carbon-dioxide emissions by 78% on a lifecycle basis when compared to petroleum based-diesel fuel and hence decreases smoke owing to free soot. It is considered as an ideal fuel since it is biodegradable, sustainable, non-toxic, renewable, readily available, portable and non-flammable has less sulphur and is environmentally benign. It offers about a 90% drop in harmful disease possibility. It has many additional socio-economic advantages, for instance, rural regeneration, establishment of new jobs and less universal warming. The biodiesel cetane number is higher than petroleum-based diesel. It can be easily produced compared to the production of conventional diesel. Furthermore, it has a higher flash point than conventional diesel and so it safer for handling. In addition, only biodiesel (B20) can be used directly in vehicle engines without modification. However, slight engine modification may be required for higher blends. Nonetheless, biodiesel has a drawback; it has less energy content compared to petroleum-based fuel, which results in a rising fuel consumption. Furthermore, a higher cloud point, pour point and higher nitrogen oxide emissions than petroleum based-diesel with comparatively higher viscosity than conventional diesel causes the formation of residues in the engine due to imperfect combustion properties and lower oxidation stability than that of conventional diesel. Therefore, it can be easily oxidised so corrosion can easily attack engine injectors and storage tanks (Table 1.1). It generates relatively higher amounts of NO_x than conventional diesel and contributes to the issue of food versus fuel.

Table 1.1: Comparison of standards between biodiesel and diesel according to the American Standard for Testing and Materials (ASTM)

Property of the fuel	***Biodiesel***	***Diesel***
Standard method	ASTM D6751	ASTM D975
Fuel composition	FAME(C12-C22)	Hydrocarbon(C10-C21)
Density(g/cm^3)	0.878	0.848
Pour point (^oC)	-15 to 16	-30 to -15
Cloud point(^oC)	-3 to 12	-15 to 5
Flash point(^oC)	100-170	60-80
Cetane number	48-60	40-55
Water (vol %)	0.05	0.05
Carbon (wt. %)	77	87
Hydrogen (wt. %)	12	13
Oxygen (wt. %)	11	0
Sulphur (wt. %)	0.05	0.05

1.2 Problem Statement

Currently special attention has been paid to biodiesel as a promising renewable fuel that could effectively substitute the fossil-based diesel fuel. Their extensively available feedstocks make biodiesel production a striking field to invest in and enlarge. Nevertheless, currently employed manufacturing processes produce an expensive renewable-based fuel in contrast to fossil-based fuel; this is attributed to feedstock and manufacturing costs. The feedstock used for the production of biodiesel mainly comes from edible oil that is highly available all around the world. The competition between food and energy economies towards the same oil resources may bring about a global crisis to the food supply and demand market. Furthermore, these vegetable oils could be more expensive to use as it will lead to a higher demand on vegetable oils.
Hence, increase the production cost. Therefore, in order for biodiesel to be a commercially feasible alternative to fossil-based diesel industry, the use of lower-cost and non-food based feedstock, such as waste cooking oil has been taken into consideration for biodiesel production.

Conventionally, the main technology used in the industrial production is fit for processing higher grade vegetable oils with methanol using basic homogeneous catalysts, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). However, the use of a homogeneous catalyst is limited to batch-mode processing and associated with a serious environmental problem arising from the waste washing water generated during the purification step.

In general, the waste cooking oil contains high free fatty acids. The homogeneous base catalyst technologies are not suitable to employ this type of feedstock because alkaline catalysts are sensitive to a high level of free fatty acid and water, which results in soap formation.

Thus, waste cooking oil with a high content of free fatty acid cannot be directly utilized with homogeneous and solid base catalysts even though the solid base or acid catalysts have revealed less marked operational difficulties compared to conventional liquid ones. However, existing solid acid and base catalysts have their own characteristic features and restrictions; whilst joining both heterogeneous catalysts in a two-stage solid base-acid catalysis scheme could add an additional manufacturing cost. Hence, there is a vital need for substituting the existing traditional technologies with a new one being more eco-friendly, commercially feasible and industrially applicable.
Forthcoming new developed nanoparticle solid acid and bi-functional zirconia supported catalysts maintain new routes being accessible to overcome the associated problems and should be capable to handle waste cooking oil and high acid feedstocks with a minimum level of difficulty converting it to a pure, cheaper and eco-friendly fuel.

1.3 Scope of the Research

The scope of this research was to use the oxides of ferric and manganese as dopants on the surface of sulphated zirconia, tungstated zirconia, molybdated zirconia and tungstated molybdena, respectively, in an array to develop their catalytic activity towards simultaneous synthesis of biodiesel from low grade oil and reduce the leaching from all synthesized catalysts. The fundamental catalytic activity of these types of promising, proposed, modified nanoparticle solid heterogeneous catalysts have been appraised for the synthesis of biodiesel via the simultaneous esterification of free fatty acid and triglyceride transesterification of low grade oil. Moreover, the physico-chemical properties have been explored to realize the features that control their catalytic activity and also their recyclability and regeneration as well as the leaching issues of active sites from all of the screened catalysts which were assessed.

The optimization of biodiesel production via the most active catalyst within the screened modified nanoparticle heterogeneous catalysts has been assessed using the response surface methodology.

1.4 Objectives

The objectives of this research study are:

1. To synthesise nanoparticle solid acid catalysts for the production of biodiesel from waste cooking oil.
2. To characterise the physico-chemical properties of the prepared acid catalysts.
3. To evaluate the catalytic activity of the developed heterogeneous acid catalysts.
4. To determine the factors affecting the biodiesel production using synthesized catalysts.
5. To examine the reusability and leaching of the developed heterogeneous catalysts.
6. To optimize the production of biodiesel via the response surface methodology using the most active catalyst within the developed solid acid catalysts.
7. To test the quality and physico-chemical properties of the produced biodiesel from waste cooking oil.

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