DEVELOPMENT OF BISMUTH-NICKEL OXIDE AND BISMUTH-ZINC OXIDE CATALYTS FOR BIODIESEL PRODUCTION FROM CRUDE PALM OIL

By

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

November 2019

FS 2019 93

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

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Faculty : Science

The depletion of non-renewable petroleum reserve, the consequent rising price of diesel as well as environmental concerns about air pollution caused by the combustion of conventional fuel has stimulated the interest on the development of alternative fuel. Biodiesel is a suitable substitute for petrol-based diesel that can be used directly in transports without engine modifications and it has a nearly same engine performance as petrol-diesel. However, the cost of biodiesel production mostly contributed from the cost of feedstock applied. Thus biodiesel production from crude palm oil is very crucial to reduce the cost and its compatibility and reusability with the suitable acid catalyst. In this study, varying composition of bismuth-nickel oxide (Bi-Ni) and bismuth-zinc oxide (Bi-Zn) catalysts were prepared using wet impregnation method. They were characterized by thermal gravimetric analysis (TGA), X-ray diffraction (XRD), X-ray fluoroscopy (XRF), Brunauer-Emmett-Teller (BET) surface area analysis, temperature programmed desorption of ammonia gas (TPD-NH_3), fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The catalytic performances of the mixed oxides were evaluated in simultaneous transesterification and esterification of free fatty acid containing crude palm oil under effects of composition of bismuth oxide, reaction temperature, reaction time, amount of catalyst and methanol to oil molar ratio. The optimum reaction conditions for Bi-Ni catalyst were at 200°C, 5 wt.% of catalyst, methanol/oil molar ratio of 30:1 and 5 h of reaction time to obtain 91.77% of yield. The reusability test of Bi-Ni shows that it can be used under the same reaction conditions for 6 times continuously before it decreased to 75.00% in the 7th run. For Bi-Zn catalyst system, 92.55% of biodiesel was achieved under 180°C with the methanol to oil molar ratio of 30:1 when 5 wt.% catalyst was added and run for 5 hours. Bi-Zn showed a higher reusability and stability since it only decreased to 76.21 % of yield after 7th runs continuously. Biodiesel production was optimized using response surface methodology (RSM). Bi-Ni achieved optimum biodiesel yield of 92.43% under the following reaction conditions: reaction temperature: 193.26°C, reaction

time: 5.34 h, catalyst amount: 5.15 wt.%, methanol to oil molar ratio: 30.18:1. Besides, under the reaction temperature: 186.97°C, reaction time: 5.24 h, catalyst amount: 5.10 wt.%, methanol to oil molar ratio: 31.91:1, the optimum biodiesel yield achieved by Bi-Zn catalyst was 95.10%. In conclusions, the high biodiesel yield using Bi-Ni and Bi-Zn catalysts and the accuracy of the 3 dimensional (3D) models between reaction parameters in RSM shows promising results and optimized yield achieved. The high reusability of both catalysts shows the high stability of the catalysts.

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

PEMBANGUNAN PEMANGKIN BISMUT-NIKEL OKSIDA DAN BISMUT-ZINK OKSIDA UNTUK PENGHASILAN BIODIESEL DARI MINYAK SAWIT MENTAH

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Kekurangan petroleum yang tidak boleh diperbaharui, kenaikan harga diesel serta kebimbangan alam sekitar mengenai pencemaran udara yang disebabkan oleh pembakaran sumber tenaga konvensional telah merangsang minat terhadap pembangunan tenaga alternative. Biodiesel adalah pengganti yang sesuai untuk diesel berasaskan petrol yang boleh digunakan secara langsung dalam pengangkutan tanpa perubahan atas enjin dan mempunyai prestasi enjin yang hampir sama seperti petrol-diesel. Walau bagaimanapun, kos pengeluaran biodiesel kebanyakan disumbangkan daripada kos bahan mentah yang digunakan. Oleh itu, pengeluaran biodiesel dari minyak sawit mentah sangat penting untuk mengurangkan kos dan keserasian dan penggunaan semula dengan pemangkin asid yang sesuai. Dalam kajian ini, pelbagai komposisi pemangkin bismut-nikel oksida (Bi-Ni) dan bismut-zink oksida (Bi-Zn) telah disediakan menggunakan kaedah impregnasi basah. Mereka dicirikan dengan analisis gravimetri terma (TGA), analisis pembelauan sinar-X (XRD), pendarfluor sinar-X (XRF), analisis luas permukaan Brunauer-Emmett-Teller (BET), nyahjerapan NH_3 terprogram suhu (TPD-NH_3), spektroskopi inframerah transformasi Fourier (FT-IR) dan mikroskopi electron pengimbasan (SEM). Prestasi pemangkinan campuran oksida telah dinilai melalui transesterifikasi dan esterifikasi secara serentak minyak kelapa sawit mentah yang mengandungi asid lemak bebas di bawah kesan komposisi bismut oksida, suhu tindak balas, masa tindak balas, amaun pemangkin dan nisbah metanol kepada minyak. Keadaan tindak balas optimum untuk pemangkin Bi-Ni adalah pada 200°C, amaun pemangkin 5 wt.%, nisbah metanol kepada minyak bersamaan 30: 1 dan jangka masa tindak balas 5 jam untuk mencapai hasil 91.77%. Ujian penggunaan semula atas pemangkin menunjukkan bahawa Bi-Ni boleh digunakan di bawah keadaan reaksi yang sama selama 6 kali secara berterusan sebelum ia menurun hingga 75.00% pada kali ke-7. Untuk sistem pemangkin Bi-Zn, 92.55% hasil biodiesel dicapai di bawah 180 ° C dengan nisbah metanol kepada minyak bersamaan 30: 1

apabila 5 wt.% pemangkin telah ditambah dan dijalankan selama 5 jam. Bi-Zn menunjukkan penggunaan semula dan kestabilan yang lebih tinggi kerana ia hanya menggurangkan kepada hasil 76.21% selepas tindak balas ke-7 secara berterusan. Penghasilan biodiesel dioptimumkan dengan menggunakan kaedah permukaan tindak balas (RSM). Bi-Ni mencapai hasil biodiesel optimum 92.43% di bawah keadaan tindak balas berikut: suhu tindak balas: 193.26°C, masa tindak balas: 5.34 jam, amaun pemangkin: 5.15 wt.%, nisbah metanol kepada minyak: 30.18:1. Selain itu, di bawah suhu tindak balas: 186.97°C, masa tindak balas: 5.24 jam, amaun pemangkin: 5.10 wt.%, nisbah metanol kepada minyak: 31.91:1, hasil biodiesel optimum yang dicapai oleh pemangkin Bi-Zn adalah 95.10%. Kesimpulannya, hasil biodiesel yang tinggi menggunakan pemangkin Bi-Ni dan Bi-Zn dan ketepatan model 3 dimensi (3D) antara parameter tindak balas dalam RSM menunjukkan hasil yang menjanjikan dan hasil yang dioptimumkan dicapai. Penggunaaan yang kerap bagi kedua-dua pemangkin menunjukkan kestabilan yang tinggi pemangkin tersebut.

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my countless and utmost appreciation and gratitude to my supervisor, Dr. Tan Yen Ping for her dedicated supervision, continuous support and invaluable advices throughout the research. Special thanks are extended to my co-supervisors Prof. Datuk ChM. Ts. Dr.Taufiq-Yap Yun Hin and Asssociate Prof. Dr. Irmawati Ramli who constantly inspired and advised me in the research.

Besides, I would like to express my millions of thanks, appreciation and gratitude to all those who had contributed to the success of this project work directly or indirectly include all the staffs of Chemistry Department. I would like to say thanks to my parents and siblings who always continue support and understanding me all the time. Moreover, I also want to thanks to my lovely boyfriend Leong Mun Teik who always inspired and take care of me whenever I am sad or happy.

Sincere thanks also given to all my friends and labmates who indirectly provide advice and assistance for my research project work. Finally, I gratefully acknowledge the financial support from Universiti Putra Malaysia as well as IOI group, Malaysia for providing crude palm oil for research purpose.

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 Philosphy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

GHG	Greenhouse Gas
IEA	International Energy Agency
°	Degree
%	Percentage
°C	Degree Celsius
°C/min	Degree Celsius per minute
m^2/g	Square metre per gram
mm^2/s	millimetre per second
ml/min	millilitre per minute
kg/m^3	kilogram per cubic meter
h	hour
g	gram
mg/g	milligram per gram
g/mol	gram per molarity
wt.%	weight percent
min	minute
nm	nanometer
mm	millimeter
mol	mole
μmol/g	micromole per gram
Bi-Ni	Bismuth-nickel mixed oxide
Bi-Zn	Bismuth-zinc mixed oxide
CPO	Crude Palm Oil
RSM	Response Surface Methodology

TGA	Thermal Gravimetric Analysis
XRD	X-ray Diffraction
XRF	X-ray Fluorescence spectroscopy
FT-IR	Fourier-Transform Infrared spectroscopy
BET	Brunauer-Emmett-Teller
TPD-NH_3	Temperature-Programmed Desorption with Ammonia Gas
SEM	Scanning Electron Microscopy
FFA	Free Fatty Acid
FAME	Fatty Acid Methyl Ester
Ton	Tonnage
TG	Triglyceride
DG	Diglyceride
MG	Monoglyceride
CCD	Central Composite Design
ANOVA	Analysis of Variance
GC	Gas Chromatography
$K\alpha$	K alpha
2θ	2-theta
ICDD	International Centre for Diffraction Data
μm	Micrometre
rpm	Revolutions per minute
AAS	Atomic Absorption Spectroscopy
FID	Flame Ionization Detector
EDX	Energy Dispersive X-Ray

CHAPTER 1

INTRODUCTION

1.1 Energy

Energy is often described as the capacity or a source of power that required in performing a work. The word “energy” is originated derived from the Greek word called “en-ergon” that has the meaning of “content of work” or “in-work”. The production of work done is actually depends on the amount of energy going into the system (Khan, 2006). In the term of energy, energy neither can be described as created nor depleted but can convert into other form. Generally, mechanical, electrical, thermal, chemical, gravitational and etc., are the most common forms of energy but mainly can classified into potential energy and kinetic energy or combination of the two in many ways.

Energy has been very important in the end-less progress of human civilizations. Thus, energy consumptions is continuous increasing followed by the development of human living standards that involves most sectors such as domestic activities, transportation, industrial, electronics and agriculture (Khan, 2006). The sources of energy can be categorized into two groups, which are conventional energy sources and non-conventional energy sources.

1.2 Conventional Energy Sources

Conventional energy sources are also called non-renewable energy sources which the resources can be used once only and cannot be recycled, reused and reproduced. Conventional energy resources are conventionally used many decades and the examples of resources are nuclear energy and fossil fuels (Khan, 2006).

Fossil fuels consist of coal, petroleum and natural gas. In the past decades, more than three quarters of the global energy market is monopolized by the combustion of fossil fuels (EIA, 2010). It shows that human are greatly dependent to the energy resources to maintain their countries’ economic growth and preserve better quality of life. Fossil fuels are non-renewable hydrocarbon resources which are finite and do not get replenished after used. Fossil fuels took millions of years to form from the decomposition of dead living organisms, where they were trapped, heated and compacted underground of Earth.

1.3 Non-conventional Energy Sources

Non-conventional or renewable energy sources are the natural resources sources of energy which can be generated and replenished by nature continuously. The example of energy sources are wind energy, geothermal energy, solar energy, tidal energy, biomass, and etc. The supply resources do not have any influence to the rate of their consumption as they can be renewed by nature again and again.

Taking account from its sustainability and environment friendly advantages, it shows that it is the best alternative energy to replace fossil fuel resources due to their uncertainty in future supply and its disadvantages to the environment. Moreover, the less maintenance and low operation cost of a renewable energy facility is much more favorable than conventional energy fossil based electricity generator (Smith & Taylor, 2008).

1.4 Potential Renewable Energy-Biofuels

Due to the global energy issues, many countries are looking for other alternative energy resources that will not contribute to global warming issue, decrease the import of oil and able to supply clean source energy to those less developed regions. The reasons biofuels are suggested as one of the long term resolution to replace fossil fuels as environment friendly fuels because they are renewable, biodegradable, carbon neutral, produce less pollutant gases and sustainable to environmental and economic (Ashraful *et al.*, 2014; Fischer *et al.*, 2009; Mishra & Goswami, 2018).

Biofuels have been claimed to have potential to reduce environment pollution, greenhouse gas emissions, minimize the usage of fossil fuels, improve energy security, and enhance economic growth (Demirbas, 2008; Fischer*, et al.*, 2009).

Biofuel is an alternative renewable fuel (Mofijur *et al.*, 2015) that derived from plant based oils (vegetable oils, seeds oils, non-edible oils and algae oil), animal fats (tallow, lard, fish oils and white or yellow grease) and used or recycled oils (used cooking and fry oils). In most of the cases when composition of the fuels has more than 95% of renewable biomass is classified as biofuels (Alex, 2017).

Figure 1.1 illustrates category of biofuels. Basically, biofuels are divided into two classes: primary fuels and secondary fuels. Normally primary fuels use unprocessed materials as main sources while secondary fuels are further classified into 3 generations. Biofuels made from sugars and vegetable oils are considered to be first generation while the sources for second generation biofuels production are come from non-edible biomass and animal waste such as Jatropha oil, cottonseed oil, waste cooking oil and animal fat. Lastly, the third generation of biofuel is derived from algae (Alex, 2017; Nigam & Singh, 2011). Biodiesel is a substitution for diesel engine while bioethanol is produced for gasoline by microbial fermentation process from sugars, starches or cellulose.

Biofuels normally claimed as one of the resource that able to minimize the emission of greenhouse gas (GHG), improve the security of energy, and facilitate rural development (Fischer, *et al.*, 2009). This biofuel industry can develop a lot of opportunities in the majority developing countries, and thus economic growth in those rural areas can be boost. In the transportation sector, it occupies as the second largest consumer of fossil fuels and release out approximately 23% of GHG into atmosphere. Biofuels can substitute current fossil fuels in order to minimize the climate change effect (Lora *et al.*, 2011). Currently, biofuel's share in the transportation fuel are predicted only have 12 percent in the developed countries and 8 percent for developing countries by 2030 (Fischer, *et al.*, 2009).

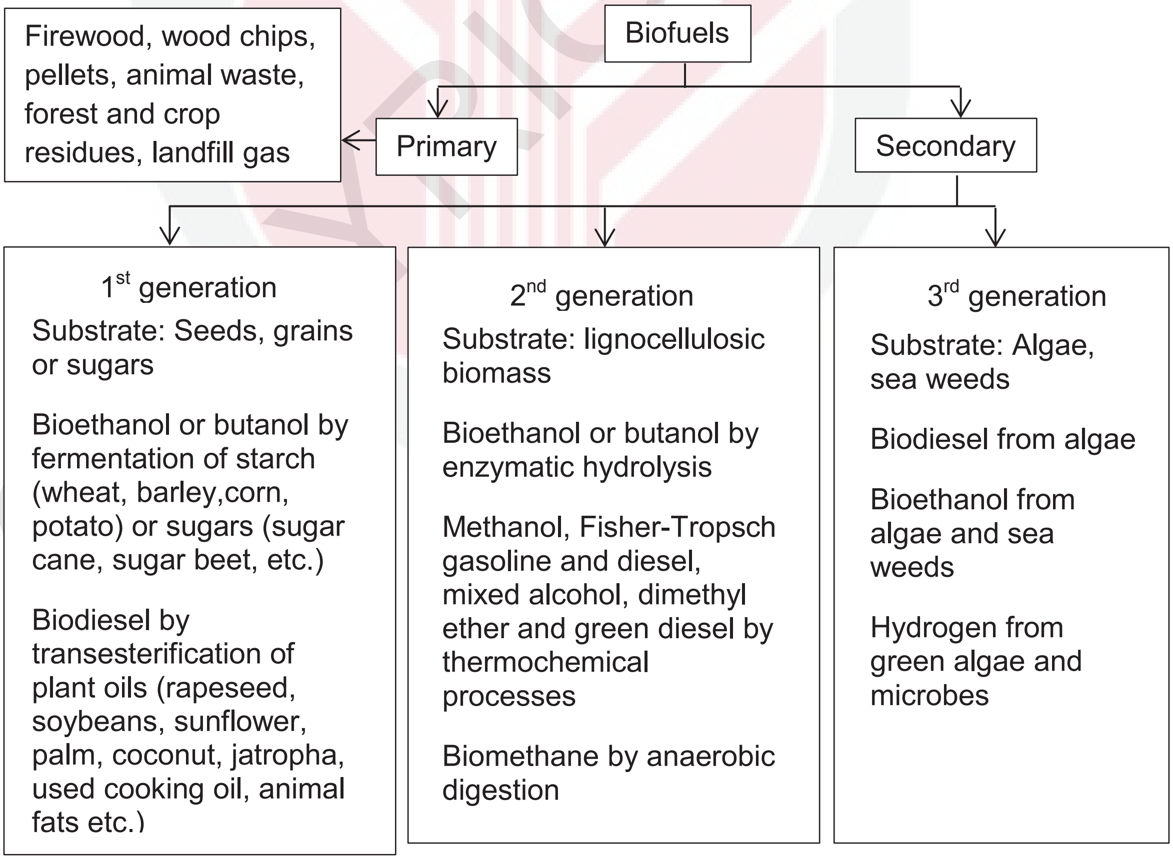

Figure 1.1 : Biofuels Classification (Nigam & Singh, 2011)

1.5 Catalytic Reactions for Biodiesel Production

A catalyst is a substance that help to speed up the rate of reaction by providing another alternative route, which is lower the activation energy of reactant. Catalysts can be reused, recovered and unchanged during the reaction. During transesterification of triglycerides, the catalysts that used basically divide into homogeneous, heterogeneous and enzyme type. Excess amount of catalyst used during the process would not only reduce the yield but also adding extra cost to the biodiesel production (Ma & Hanna, 1999).

1.5.1 Homogeneous Catalysts

A type of substance where the reaction takes place under same medium with reactants and products is called homogeneous catalyst. Homogeneous acid catalyst is commonly involves with (H_2SO_4 or HCl) whereas homogenous basic catalyst uses (KOH or NaOH) in transesterification process. Although homogeneous basic catalyst can promote higher reaction rate than heterogeneous catalyst, but separation process of catalyst from the mixture after reaction is complicated (Du *et al.*, 2004; Liu *et al.*, 2008).

1.5.2 Heterogeneous Catalysts

A heterogeneous catalyst is a type of substance which is different phase with the reactants and products. Normally catalyst is in solid phase. There are a lot of advantages when use this type of catalyst, including easier to separate out from reaction mixture, non-corrosive, environmental friendly (less of disposal) and are designed to promote higher rate of reaction and long shelf life (Gryglewicz, 1999). In the transesterification process, catalyst that usually applied were alkaline earth metal oxides, anion exchange resins, various alkali metal compounds supported on alumina and various type of zeolite. However, most of anion exchange resins and supported alkali metal catalyst were easily corrode by methanol and thus shorter shelf life. As stated in Supes *et al.* (2004) study, alkaline earth metal oxides compound is suggested as the best catalyst in transesterification reaction as it slightly soluble in organic solvents.

1.6 Palm oil

Palm oil is one of the vegetable oil that extracts from fruit flesh of the oil palm *Elaeis guineensis* (Ng *et al.*, 2000). Each oil palm fruit is consists of a hard kernel that covers by mesocarp shell. According to studies of Abdullah & Sulaiman, (2013), oil palm was first introduced into Malaysia as the first agriculture crop in the Botanical Gardens, Singapore at 1870. Oil palm is known as tropical plant, and thus it can be easily cultivated in Malaysia. According to literatures reported, the first commercial oil palm estate was established at 1917, located at Tennamaran Estate, Selangor (Abdullah & Sulaiman, 2013; Sumathi *et al.*, 2008). Moreover, it can be seen by The Oil Palm Wastes, Malaysia that the overall average shelf life of oil palm is range from 25 years to 30 years.

Among all agriculture crops, palm oil is well known as the second traded oils in the whole world since 90% of export palm oil was originated from Malaysia and Indonesia. In the Tropical Asia countries like Southeast Asia and Africa, the palm oil is quite popular and well known as cooking ingredient. Based on the studies of (Che Man *et al.*, 1999; Matthäus, 2007), it mention that the usage of this palm oil inside food industry is keep increasing because of cheap pricing and have high oxidative stability of the refined product.

If expressed in term of energy, oil palm is one of energy efficient agricultural crops. Basically, it only required less energy to produce 1 tonne of palm oil. The energy output of oil palm is nearly 3 times higher when compared with soybean and rapeseed oil. The energy expressed in the ratio of energy output to input is higher for oil palm if compared with any other commercial oil sources such as soybean and rapeseed. By studying the studies of (Basiron, 2007), it show that the overall processing palm oil products only require lower input of pesticides, fertilizers and fossil fuels to produce 1 tonne of palm oil. All these variable parameters were combined to produce out the high percentage of palm oil as the usage of the oil will decreasing the impact when generate palm oil as one of renewable energy (Sumathi, *et al.*, 2008).

1.7 Problem Statements

Energy demand is often related to advances in technology, economic growth, and socio-economic development. The overwhelming demand on energy led to global energy issues such as depletion of natural resources and the effects on environment. In view of this, the world has been searching for few decades to find alternative energy that is renewable and environmental friendly to replace the conventional energy. Biodiesel is one of the potential and reliable ‘green’ fuels that can substitute the petrol-based diesel fuel due to the similar composition of biodiesel compared to diesel.

Finding a suitable feedstock of biodiesel is necessarily in order to reduce cost of biodiesel production. Low production costs and large-scale production are the two main requirements for biodiesel feedstock selection. The availability and production of biodiesel feedstock depends on the geographical locations, climatic condition, local soil texture and conditions, and agricultural practices. Palm oil is a favorable feedstock for biodiesel production among the crops since Malaysia is the second largest producer of oil palm. On the other hand, high FFA containing crude palm oil has the lower cost as no pre-treatments were conducted. However, a suitable acid catalyst has to be synthesized due to the compatibility with the low cost, FFA containing palm oil feedstock.

Heterogeneous acid catalysts are likely to be favor selection especially for feedstock that contains high amount of FFAs and water content, they offer the advantage of reduced separation steps, recyclable catalyst and continuous operation. Therefore, bismuth-based mixed oxides were synthesized and used as in the study. Bismuth compound is extensively applied in different chemical reactions, especially in the superconductor and drug fields. It is selected due to non-corrosive, low toxicity, relatively easy to handle and its moderate to strong Lewis acidity properties. The deficient nucleus shielding by the f electrons shell of bismuth configuration (Bi = [Xe] $4f^{14}$, $5d^{10}$, $6s^{2}$, $6p^{3}$) results in its Lewis acidity (Da Silva *et al*., 2013). Moreover, it is inexpensive and tolerant of small amounts of moisture in the reaction. All these properties make bismuth compounds to gain attention from a green perspective view.

The characterization of the Bi_2O_3-NiO and Bi_2O_3-ZnO catalysts were carried out for physio-chemical properties identification. Previous study shows that Bi_2O_3-ZnO has high catalytic activity due to synergistic interaction of the two metals. Moreover, optimization studies on reaction parameters in response to biodiesel yield via response surface methodology (RSM) to ensure the catalysts more valuable.

1.8 Objectives

The aim of the study is to investigate the activities of the synthesized bismuth-based mixed oxide catalysts on response to biodiesel yield using crude palm oil. The research was carried out with purpose to develop solid acid catalysts that possess high activity and selectivity will ensure cheaper biodiesel production and commercialization against petro-diesel. Using low cost feedstock with high FFAs would ascertain the novelty of this study.
The objectives of this study are as follows:

a) To synthesize Bi_2O_3-NiO and Bi_2O_3-ZnO mixed oxides catalysts using wet impregnation method.

b) To characterize the Bi_2O_3-NiO and Bi_2O_3-ZnO catalysts using various analysis such as thermal gravimetric analysis (TGA), X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), Fourier-transform infrared spectroscopy (FT-IR), Brunauer-Emmett-Teller analysis (BET), temperature-programmed desorption of ammonia gas ($TPD-NH_3$) and scanning electron microscopy (SEM) with energy dispersive spectrometer (EDX).

c) To evaluate the catalytic activities of the catalysts in the biodiesel production using crude palm oil as feedstock.

d) To evaluate the effects of various parameters such as reaction time, methanol to oil molar ratio, amount of catalyst and reaction temperature on the catalytic activity of bismuth-based mixed oxide catalysts in biodiesel production.

e) To optimize biodiesel yield under optimum reaction parameters conditions using response surface methodolody (RSM).

1.9 Scope of the Study

This research work has focused on catalytic activity study on heterogeneous solid acid catalysis for biodiesel synthesis from crude palm oil (CPO), which contains high free fatty acids. The raw material was supplied by IOI Group via simultaneous esterification and transesterification reactions. The oil samples with 5.60% of FFA content were used without any further purification and pre-treatment steps. The newly developed bismuth based mixed nickel oxides (Bi_2O_3-NiO) and zinc oxides (Bi_2O_3-ZnO) were synthesized using wet impregnation method. The reactions were carried out in BERGHOP high pressure autoclave reactor equipped with an external mechanical stirrer. The amount of mixed metal oxides catalysts varied from (1, 3, 5, 7 to 9 wt. %) was added into the reaction mixture of 25 g CPO with calculated amount of methanol (molar ratio from 10:1 to 50:1). The mixture was heated to desired temperature (120, 140, 160, 180, 200 and 220°C) for a certain period of (1, 3, 5 and 7 h) under constant agitation of 500 rpm. Characterizations of the catalysts were carried out to investigate their physico-chemical properties using various characterization anaylsis such as TGA, XRD, XRF, FT-IR, BET, TPD-NH_3 and SEM with EDX. The synthesized biodiesel was characterized in order to meet the biodiesel standard quality parameters. Consequently, the leaching of catalysts actives sites were investigated by studying the effect of composition of Bi_2O_3 on NiO and ZnO. The effects of the four reaction parameters such as temperature, reaction time, methanol to oil molar ratio and amount of catalyst on biodiesel conversion were studied and the optimum conditions of reaction parameters for high biodiesel conversion was obtained using response surface methodology (RSM).

1.10 Outline of the Thesis

In chapter 1, a brief discussion described about the global energy crisis, conventional and non-conventional energy resources in the conversion into biofuels. The utilization of catalysts in biodiesel production includes homogeneous or heterogeneous catalysts from crude palm oil. In chapter 2, previous studies related to the development of catalysts from homogeneous to heterogeneous catalyst. Different types of catalyst employed dependable on the acid value of feedstock which indirectly relates to the cost of production of biodiesel. Besides, this chapter reviewed some previous researches with heterogeneous acid catalysts at their optimized reaction conditions and response surface methodology (RSM) was discussed in details in the end. In the subsequent chapter, chapter 3 introduced the flow of research methodology which briefly involves the synthesis of bismuth-based mixed oxide using wet impregnation method, various characterizations on the physico-chemical properties of the synthesized catalysts, followed by the catalytic activity studies and optimization under four reaction variables include temperature, methanol to oil molar ratio ,amount of catalyst and reaction time. Chapter 4 summarized the identity, purity and all the physico-chemical properties of bismuth-based mixed oxide mentioned in the chapter 3 using characterization techniques applied. The preliminary optimization results under different variables were studies and finally the optimization using RSM was evident with the accuracy of the preliminary studies. The final chapter was the summary for the entire research for the preparation and application of the bismuth-based mixed oxides in the biodiesel production with the optimum reaction conditions were determined.

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