BIODIESEL PRODUCTION USING HETEROGENEOUS CATALYST AND DEVELOPMENT OF QUALITY FAST CHECK TEST KIT

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SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH

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DECLARATION

I hereby declare that the materials in this thesis are original except for quotations, summaries and references, each of which have been duly acknowledged.

16th March 2015

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CERTIFICATION

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ABSTRACT

Biodiesel is receiving increasing attention as an alternative, non-toxic, biodegradable, and renewable diesel fuel. The cost of feedstock in the form of neat vegetable oils is significantly 70-95% of the total cost of the biodiesel production. Low quality oil is potential low cost feedstock to be used in biodiesel production. However, it contains high concentrations of free fatty acids (FFA) and water contain. The conventional technology is not suitable to adopt basic homogeneous catalyst due to saponication between basic catalyst and the FFA. In order to efficiently utilize these low cost feedstocks for biodiesel synthesis, development a new class of high efficiency heterogeneous catalysts, which has, high FFA and water-tolerance that could show promising performances of transesterification is necessary. FFA and water adsorption characteristics of both zeolites were investigated according to batch method under varying conditions, namely different shaking time, initial concentration and solid – solution ratio. The concentration of FFA (as Total Acid Number) and water in all samples was determined according to the EN14104 and EN14101 standard method respectively. Percent FFA and water adsorption by both natural zeolite and $NaOCH_3$-Zeolite increases with shaking time (attaining equilibrium after 60 min) and solid – solution ratio. The FFA adsorption conforms strongly to pseudo – 2nd order kinetics (R^2 = 0.9894 and R^2 = 0.9989) and Freundlich (R^2 = 0.9972 and R^2 = 0.9979) whereas the water adsorption by both zeolites conforms strongly to pseudo – 2nd order kinetics (R^2 = 0.9801 and R^2 = 0.9740) and Langmuir isotherm (R^2 = 0.9953 and R^2 = 0.9957). For the biodiesel transesterifiation, the effects of various factors consist of the reaction time, molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and catalyst reusability were investigated. The experimental treatments of a 20:1 molar ratio of methanol to oil, addition of 5wt% $NaOCH_3$-zeolite catalyst, 70°C reaction temperature and 5 cycles reusability using low quality crude jatropha oil resulted in optimum yield in which the biodiesel content reached 97.4wt% at 6 h without soap formation. This biodiesel was characterized for its physical and chemical properties as ASTM or EN-compliant biodiesel. Performance (BSFC, BTE and EGT) and emission characteristics (smoke density) of this biodiesel with diesel fuel were examined and compared in a direct injection (DI) diesel engine. Brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) for biodiesel was higher than diesel fuel with 13.12% and 0.41% for mean value, respectively. A comparison of exhaust emissions showed that smoke density of biodiesel is lower than those of diesel fuel by 44.4%. Fast check analysis method with special measuring device and chemical solvent mixture were developed to provide on-site analysis check for biodiesel quality monitoring. Biodiesel Test Kit have shown comparable result with ASTM D7371 with correlation coefficient (R^2 > 0.99) for biodiesel-diesel blends B5, B10 and B20 of Palm, Jatropha and Soybean based biodiesel. Triglycerides Test Kit have shown good correlation coefficient (R2 > 0.99) for triglycerides 3, 4 and 5%(v/v). The developed methods are providing fast, simple and affordable on-site fast check analysis in measuring FAME content in diesel & triglycerides content in final FAME product economically especially in rural area.

ABSTRAK

PENGHASILAN BIODIESEL MENGGUNAKAN MANGKIN HETEROGEN DAN PEMBANGUNAN KIT ANALYSIS KUALTI

Biodiesel mendapat sambutan hangat sebagai bahan bakar alternatif yang tidak bertoksik, boleh terbiodegradasi serta boleh dikitar semula. Minyak berkualiti rendah yang juga merupakan bahan mentah berkos rendah berpotensi untuk digunapakai dalam penghasilan biodiesel. Walau bagaimanapun, ia mengandungi kepekatan asid lemak bebas (FFA) dan kandungan air yang tinggi. Ini menyebabkan ia tidak sesuai digunakan dalam teknologi lama untuk penghasilan biodiesel iaitu menggunakan mangkin homogen beralkali yang boleh menyebabkan proses penyabunan antara mangkin alkali dengan FFA. Untuk mengoptimunkan penggunaan bahan mentah yang berkos rendah, penghasilan kelas mangkin berprestasi tinggi yang dapat mengatasi kandungan FFA dan air yang tinggi perlu dilakukan. Sifat penyerapan FFA dan air pada zeolit masing-masing dikaji berdasarkan kaedah berkumpulan menggunakan keadaan seperti tempoh pengacauan berbeza, kepekatan awal dan nisbah pepejal-cecair. Kepekatan FFA (dalam bentuk jumlah nombor keasidan) dan air dalam semua sampel ditentukan berdasarkan kaedah piawai EN14104 dan EN14101. Kadar peratus penyerapan FFA dan air meningkat dengan tempoh pengacauan (mencapai keseimbangan selepas 60 minit) dan pengacauan mengikut nisbah pepjal-cecair tertentu. Penyerapan FFA dibuktikan melalui pseudo-kinetik tertib kedua (R^2 = 0.9894 dan R^2 = 0.9989) dan Freundlich (R^2 = 0.9972 dan R^2 = 0.9979) manakala penyerapan air oleh kedua-dua zeolit dibuktikan melalui pseudo-kinetik tertib kedua (R^2 = 0.9801 dan R^2 = 0.9740) dan isoterma Langmuir (R^2 = 0.9953 dan R^2 = 0.9957). Bagi transesterifikasian biodiesel, faktor yang dikaji adalah tempoh tindak balas, nisbah molar metanol dengan minyak, suhu tindak balas, nisbah berat mangkin dengan minyak dan kebolehgunaan semula mangkin. Eksperimen untuk nisbah 20:1 metanol kepada minyak, 5wt% mangkin $NaOCH_3$-zeolite, suhu tindak balas 70°C dan 5 kitaran kebolehgunaan semula menggunakan minyak jarak pagar mentah menghasilkan biodiesel dengan hasil optimum mencapai 97.4wt% dalam tempoh 6 jam tanpa berlakunya pembentukan sabun. Pencirian fiziko kimia biodiesel ini mematuhi ciri biodiesel dalam ASTM atau EN. Prestasi (BSFC, BTE dan EGT) dan ciri emisi (ketumpatan asap) biodiesel ini dengan diesel dikaji dan dibandingkan menggunakan enjin diesel suntikan langsung (DI). Brek spesifik penggunaan bahan bakar (BSFC) dan brek kecekapan haba (BTE) untuk biodiesel adalah lebih tinggi daripada diesel dengan masing-masing nilai min 13.12% dan 0.41%. Perbandingan pelepasan ekzos menunjukkan ketumpatan asap biodiesel yang lebih rendah daripada diesel sehingga 44.4%. Kaedah analisis pemeriksaan pantas dengan menggunakan alat khas dan campuran bahan kimia dibangunkan untuk memberi pemeriksaan analysis in-situ untuk pemantauan kualiti biodiesel. Kit analisis menunjukkan hasil setaraf dengan ASTM D7371 dengan korelasi pekali (R^2 > 0.99) untuk campuran biodiesel-diesel B5, B10 dan B20 bagi biodiesel berasaskan sawit, jarak pagar dan kacang soya. Kit pemeriksaan trigliserida menunjukkan korelasi pekali yang baik (R_2 > 0.99) trigliserida 3, 4 and 5%(v/v).

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ABBREVIATIONS AND SYMBOLS

~	-	about
±	-	plus/minus
⇆	-	equilibrium
[ ]	-	concentration
ASTM	-	American Society for Testing and Materials
B5	-	5vol% biodiesel blending with diesel
CJO	-	Crude Jatropha Oil
cm^3	-	cubic centimeter
EN	-	European Standard
FAME	-	Fatty Acid Methyl Ester
FFA	-	free fatty acid
FTIR	-	Fourier transform infrared spectroscopy
g	-	gram
J/g	-	joule per gram
mg KOH/g	-	milligram Potassium Hydroxide per gram
mg/L	-	milligram per liter
$NaOCH_3$	-	Sodium methoxide
$NaOCH_3$-Zeolite	-	Sodium methoxide Zeolite
NaOH-Zeolite	-	Sodium hydroxide Zeolite
R^2	-	Correlation Coefficient
rpm	-	rotation per minute
s	-	second
μm	-	micrometer
Vol%	-	volume percentage
wt%	-	weight percentage

CHAPTER 1

INTRODUCTION

1.1 Biodiesel

Biodiesel is receiving increasing attention as an alternative, renewable, non-toxic, biodegradable, carbon neutral and environmentally benign fuel for diesel engines has been attracting considerable interest all over the world which can significantly reduce global warming and the dependence on conventional fossil fuels (Atabani *et al.,* 2013; Yahyaee *et al.,* 2013). Biodiesel is a mono alkyl ester of fatty acids obtained by transesterification of the triglycerides contained in vegetable oils and animals fats which involves alcohol and vegetable oil in the presence of a catalyst to yield biodiesel and glycerol (Chattopadhyay *et al.,* 2011; Salamanca *et al.,* 2012; Pinzi *et al.,* 2013). The triglyceride used for biodiesel production could be vegetable oils such as soybean, canola, palm and sunflower oils or animal fats such as, beef tallow and even waste cooking oils and algae oil (Corro *et al.,* 2013; Lapuerta *et al.,* 2013; Liu *et al.,* 2013; Man *et al.,* 2013; Zhao *et al.,* 2013).

Biodiesel offers some technical advantages as compared to conventional petroleum diesel such as biodegradability, higher flash point, higher cetane number, reduced exhaust emissions (Kannan *et al.,* 2012; Fazal *et al.,* 2013). Biodiesel can be used as fuel for diesel engines, either pure or mixed with petroleum distillates to attain blends defined with the abbreviation BX, where B stands for biodiesel and X stands for the biodiesel percentage (volume/volume) (Fernando *et al.,* 2007; Bunce *et al.,* 2010). In order to give a quality assurance to the users, the biodiesel produced must meet the specification of ASTM D6751 and EN 14214 so that it can be used directly to run the existing diesel engines without major modifications or as a biodiesel blended with petrol diesel to create less hazardous emissions (Oliveira *et al.,* 2006; Hoekman *et al.,* 2012). European Standard EN 14214 specifies a minimum percentage of 96.5 wt% ester content in biodiesel purity which is significantly influence the performance of diesel engines. The limits for physical and chemical properties specified in these standards guarantee the safe use of biodiesel in internal combustion engines when used in the pure form or when mixed with conventional diesel at different percentages (Ciubota-Rosie *et al.,* 2013).

1.2 Conventional Methods for Biodiesel Production

Various conventional methods have been used for biodiesel production through transesterification from various types of oil feedstock. Transesterification can be catalyzed by both acidic-catalysts (e.g. HCl and H_2SO_4) and basic-catalysts (e.g. KOH and NaOH) (Ma & Hana, 1999). Alkaline catalysts are widely investigated because the rate of transesterification reaction by alkaline catalysts is much faster than that by acid catalysts (Marchetti *et al.,* 2007). Currently many heterogeneous catalysts have been used in the transesterification process to produce biodiesel at lower cost and environmentally friendly. Heterogeneous transesterification method is more superior compared to the homogenous transesterification method especially on the separation and purification of the product (FAME) (Demirbas, 2007; Zabeti, 2009).

1.3 Current Standard Methods for Biodiesel Quality Monitoring

Many analytical techniques have been developed for the quantification of biodiesel content in the biodiesel-diesel blend (Knothe, 2006; Pimentel *et al.,* 2006). Methods based on Fourier transform mid-infrared (FT-IR) absorption spectroscopy (Santos *et al.,* 2005; Aliske *et al.,* 2007; Lira *et al.,* 2010), liquid and gas chromatography (Nicola *et al.,* 2008; Ragonese *et al.,* 2009), nuclear magnetic resonance spectroscopy (Knothe, 2006; Monteiro *et al.,* 2009;), ultraviolet absorption spectroscopy (Zawadzki *et al.,* 2007), near infrared spectroscopy (Oliveira *et al.,* 2006; Pimentel *et al.,* 2006; Fernandes *et al.,* 2011) have been reported.

For biodiesel purity assessment, international standard methods, such as EN14105 and ASTM 6584, among others are used to do the quality control of biodiesel which use gas chromatography technique. Results from these analyses can give information about whether or not the sample is adulterated with unreacted raw vegetable oils which will lead to injector fouling and may also contribute to the formation of deposits at injection nozzles, pistons, and valves (Dhar *et al.,* 2012).

1.4 Problems Encounter in the Biodiesel Production

For biodiesel production, high FFA and water content in the oil are the two limitations of transesterifying vegetable oils with alcohol using conventional alkaline catalyst (Ma & Hana, 1999; Satyarthi *et al.,* 2010; Thiruvengadaravi *et al.,* 2012). High acidic oils normally present high amounts of free fatty acids (FFA), varying from 3% to 40%, which make non-recommendable its usage with the conventional technology that employs a basic homogeneous catalyst (Chung *et al.,* 2008). There are advantages and limitations of the conventional methods in transesterification using low quality oil. This give rise the search for alternative approaches.

For biodiesel quality monitoring, the problem and limitation of current analysis technology is cost and the availability of advanced facilities which is not available on engine operation site. The analysis methods and analysis devices utilizing gas chromatography and FTIR have some disadvantages, such as sample preparation, which is time consuming, use of more than one internal standard, a longer analysis time, and an expensive technique employed (Soares *et al.,* 2008; Kay *et al.,* 2012). Therefore, development of alternative methods that combine low cost, fast and accurate results and portability is necessary as alternative approaches.

1.5 Hypothesis

To solve the biodiesel production problem as mentioned, it is necessary to develop a new heterogeneous catalysts, which has, high FFA and water-tolerance that could show promising performances in terms of methyl ester (biodiesel) yield, reaction conversion, potentiality and sustainability, as well as simplicity to greatly simplify the biodiesel refining process.

As a solution for biodiesel quality monitoring, there is necessary to develop a new biodiesel test kit and triglyceride test kit to providing fast, simple and affordable *in situ* fast check analysis in measuring FAME content in diesel & triglycerides content in final FAME product economically.

1.6 Objectives

The objectives of this study were as follows:

a. to develop a new heterogeneous catalytic approach for the biodiesel production,
b. to develop new fast check test kit for biodiesel blending percentage monitoring and triglycerides content of biodiesel purity monitoring
c. to determine the quality of biodiesel, and
d. to determine biodiesel percentage of biodiesel-diesel blend

1.7 Scope of Study

In this study, removal of FFA and water by natural zeolite and modified zeolite were carried out on the crude jatropha oil sample through adsorption (batch) experiments under different experimental conditions, namely varying shaking time, initial FFA or water concentration and solid – solution ratio. The effect of zeolite modification on transesterifications was investigated at different reaction time, type of cation saturation on zeolite, temperature, catalyst dosage, methanol – oil ratio and particle size of zeolite. Also, physical and chemical characteristics were investigated for all sample of oil, biodiesel and diesel fuel according to EN 14214 and ASTM D6751. Subsequently, performance (Brake specific fuel consumption, BSFC and brake thermal efficiency, BTE, exhaust gas temperature, EGT) and emission characteristics (smoke density) of these biodiesel with diesel fuel were examined and compared in a direct injection (DI) diesel engine. Apart from that, Biodiesel Test Kit and Triglycerides Test Kit were invented to develop *in situ* fast check analysis methods which provide fast, simple and affordable *in situ* fast check analysis in measuring FAME content in diesel & triglycerides content in final FAME product, respectively.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Biodiesel

Depletion of world petroleum reserves and the impact of environmental pollution of increasing exhaust emissions have led to the search for suitable alternative fuels for diesel engines such as biodiesel are being increasingly sought (Demirbas, 2011; Koh and Ghazi, 2011; Taufiq-Yap *et al.,* 2011; Salvi and Panwar, 2012; Ismail *et al.,* 2013). There are various reasons for the search of an alternative fuel that is technically feasible, environmentally acceptable, economically competitive, and readily available (Talebian-Kiakalaieh *et al.,* 2013). Biodiesel is receiving increasing attention as an alternative, renewable, non-toxic, biodegradable, carbon neutral and environmentally benign fuel for diesel engines has been attracting considerable interest all over the world which can significantly reduce global warming and the dependence on conventional fossil fuels (Singh and Singh, 2010; Ahmad *et al.,* 2011; Chakraborty *et al.,* 2011; Lam *et al.,* 2010; Atabani *et al.,* 2013; Yaakob *et al.,* 2013; Yahyaee *et al.,* 2013).

Biodiesel is a diesel fuel alternative produced from vegetable oils and animal fats (Fukuda *et al.,* 2001). Biodiesel defined by ASTM as the mono alkyl ester produced from vegetable oils or animal fats, one of the most promising alternatives (Marchetti and Errazu, 2010). Biodiesel is a mixture of mono alkyl esters of long-chain (C16-C18) fatty acids, usually methyl or ethyl esters, obtained by transesterification of the triglycerides contained in vegetable oils and animals fats (Salamanca *et al.,* 2012). Biodiesel can be used as fuel for diesel engines, either neat or when blended with petroleum diesel (Fernanda *et al.,* 2006; Núbia *et al.,* 2007). Biodiesel can be used pure or mixed with petroleum distillates to attain blends defined with the abbreviation BX, where X stands for the biodiesel percentage (v/v). The designation of pure biodiesel is B100 and the mixtures are named by the BXX abbreviation, which indicates the B100 volume (in percent) in the mixture with diesel (Ragonesea *et al.,* 2009).