THERMAL CHARACTERIZATION AND KINETICS OF OIL PALM BIODIESEL BLENDS AND ITS EFFECT ON ENGINE COMBUSTION

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A thesis submitted in fulfilment of the requirements for the award of the degree of Master of Philosophy

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DEDICATION

This thesis is dedicated to my family members and friends whom are always there to keep me motivated and keep going. Their stories have been my source of inspiration.

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ABSTRACT

Numerous studies have been done on palm biodiesel on engine performance and emissions. The thermal stability study has received increasing attention and past studies have been trying to relate it with oxidation properties of produced biodiesel. Low thermal stability will cause high viscosity due to oxidation, among the disadvantage of biodiesel storage but it is an advantage in engine combustion. Likewise, the thermal characteristics of palm biodiesel with different blends have not yet been fully explored and are still unclear. The purposes of this study are to investigate the fuel properties of the palm biodiesel blends, the thermal characteristics and the engine performance and emissions in comparison with commercial diesel. The thermal characteristic is done with thermal stability study using the thermal gravimetric analysis (TGA) with different heating rate of 5, 10 and 15 °C/min. The thermal characteristic mainly activation energy (E_a) is computed using the direct Arrhenius and Coats-Redfern kinetic method. The engine performance is carried out in a four-stroke direct injection engine with one vertical cylinder, one intake valve and one exhaust valve to observe important parameters; brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE). The engine emissions are mainly on carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides (NO_x) and hydrocarbon (HC). The findings showed that all palm biodiesel blends met the diesel standard specification in ASTM D6751. The TGA analysis showed that B30 has the least stable thermal characteristic correlating with the direct Arrhenius and Coats-Redfern method by having an average of 20% lower E_a among the palm biodiesel blends. 15 °C/min heating rate showed a high temperature of full fuel conversion up to 420 °C. BSFC of palm biodiesel always have a minimum of 5% higher than diesel at BMEP 1.0 to 2.7 bar tested. BTE of palm biodiesel blends and diesel are close except at BMEP 2.7 bar where BTE of diesel is 11% higher. The CO and CO₂ of palm biodiesel and diesel formed irregular pattern, same as HC except that at BMEP 2.2 bar, HC of full palm biodiesel, B100 is at the lowest meanwhile consistently 19% higher NO_x emissions for palm biodiesel blends than diesel.

ABSTRAK

Banyak kajian telah dilakukan pada biodiesel kelapa sawit mengenai prestasi dan keluaran enjin. Kajian kestabilan termal telah meraih perhatian dan kajian lepas cuba menghubung kaitkan dengan sifat pengoksidaan biodiesel yang terhasil. Kestabilan termal yang rendah menyebabkan kelikatan tinggi kerana pengoksidaan, ianya antara kelemahan penyimpanan biodiesel tetapi ia adalah kelebihan dalam pembakaran enjin. Seterusnya, ciri-ciri termal biodiesel kelapa sawit dengan adunan berbeza masih belum diterokai sepenuhnya dan masih tidak jelas. Tujuan kajian ini adalah untuk menyiasat sifat-sifat bahan bakar campuran biodiesel kelapa sawit, ciriciri termal dan prestasi serta keluaran enjin berbanding diesel komersial. Ciri-ciri termal adalah dilakukan dengan menggunakan analisis termal gravitian (TGA) dengan kadar pemanasan berbeza 5, 10 dan 15 °C/min. Ciri-ciri termal terutamanya tenaga pengaktifan (E_a) dikira menggunakan kaedah kinetik Arrhenius dan Coats-Redfern terus. Prestasi enjin dijalankan pada enjin empat lejang suntikan terus jenis satu silinder tegak, satu injap masuk dan satu injap keluar untuk memerhati parameter penting; penggunaan bahan bakar brek (BSFC) dan kecekapan termal brek (BTE). Keluaran enjin adalah karbon monoksida (CO), karbon dioksida (CO₂), nitrogen oksida (NO_x) dan hidrokarbon (HC). Kajian menunjukkan semua adunan biodiesel kelapa sawit memenuhi spesifikasi standard diesel ASTM D6751. Analisis TGA menunjukkan B30 mempunyai ciri-ciri termal paling tidak stabil melalui kaedah Arrhenius dan Coats-Redfern terus dengan purata Ea 20% lebih rendah antara semua adunan biodiesel kelapa sawit. Kadar pemanasan 15 °C/min menunjukkan suhu tinggi bahan api terbakar sepenuhnya mencecah 420 °C. BSFC biodiesel kelapa sawit sentiasa minimum 5% lebih tinggi daripada diesel pada BMEP 1.0 hingga 2.7 bar. BTE biodiesel kelapa sawit dan diesel adalah hampir kecuali pada BMEP 2.7 bar, BTE diesel adalah 11% lebih tinggi. CO dan CO₂ biodiesel kelapa sawit dan diesel membentuk corak tidak tetap, sama seperti HC kecuali pada BMEP 2.2 bar, HC biodiesel kelapa sawit penuh, B100 paling rendah manakala NO_x adunan biodiesel kelapa sawit adalah 19% lebih tinggi secara konsisten berbanding diesel.

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LIST OF ABBREVIATIONS

ASEAN	-	Association of Southeast Asian Nations
B5	-	5% Biodiesel
B7	-	7% Biodiesel
B10	-	10% Biodiesel
B20	-	20% Biodiesel
B30	-	30% Biodiesel
B50	-	50% Biodiesel
B100	-	100% Biodiesel
TGA	-	Thermogravimetric Analysis
ASTM	-	American Society for Testing and Materials
NO _x	-	Nitrogen Oxides
ppm	-	Part Per Million
mg	-	milligram
KOH	-	Potassium Hydroxide
NA	-	Not Available
CO	-	Carbon Monoxide
CO_2	-	Carbon Dioxide
HC	-	Hydrocarbon
mm	-	millimeter
APHA	-	American Public Health Association

LIST OF SYMBOLS

Р	-	Pressure
V	-	Volume
Т	-	Temperature
q	-	Heat
BP	-	Brake Power
BSFC	-	Brake Specific Fuel Consumption
BTE	-	Brake Thermal Efficiency
BMEP	-	Brake Mean Effective Pressure
Ν	-	Engine Speeds in RPM
ŋ _c	-	Number of Revolutions per Cycle
V_d	-	Displacement Volume
m_f	-	Fuel Consumed
CV	-	Calorific Value
Κ	-	Kelvin
E_a	-	Activation Energy
BSNO _x	-	Brake Specific Nitrogen Oxide
BSCO	-	Brake Specific Carbon Monoxide
BSCO ₂	-	Brake Specific Carbon Dioxide
BSHC	-	Brake Specific Hydrocarbon

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Petroleum-based fuels in energy sector have been used for a wide range of applications in the development of industrial growth, agricultural sector and most-notably in transportation to powering internal combustion engines. These petroleum fuels are depleting over the earth's finite reserves oil and the use of it has some concerns on the environment. Such events are oil spills and the release of pollutants during the combustion. Other issues are the uneven oil prices and the economic downfall in oil and gas industry (Ahmad et al., 2015). The oil market downturn in 2014 hits energy sector hard. To cope with these issues, the usage of alternative fuel has raised to fulfil the world energy demand.

Biodiesel is one of the available alternative fuel and has been accepted in a growing number of countries around the world. According to the World Oil Outlook 2016, as the world energy demand increase, the use of alternative fuel will increase towards coming years (OPEC, 2016). Policy support and technology improvements could see investment shift in alternative fuel supply. Figure 1.1 shows the energy sector merely focus on biomass, other renewables and gas in years ahead.

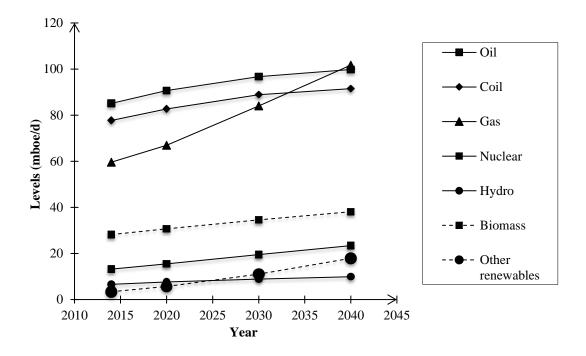


Figure 1.1 Forecast of energy demand (OPEC, 2016)

In most of countries in ASEAN, the governments are encouraging biofuel practice to deal with the energy demand and pollutions formed from the engine combustion. Such countries has started to add biofuels into their transportation fuels like Indonesia, currently implementing B20 mandate (Munthe, 2018), Thailand implementing B10 mandate (Niazi and Wells, 2016) as well as B5 mandate in Vietnam (Trinh and Linh, 2018). With abundant of palm oil feedstocks, Malaysia and Indonesia have the prospective to capture the biggest market shares with the attractive price of crude palm oil compared with crude oil (Mohammadi et al., 2016). The comparison of biodiesel policy in ASEAN countries are as in Table 1.1.

Table 1.1Policy of biodiesel usage in ASEAN countries (Masjuki et al., 2013)

Country	Policy and targets
Indonesia	B10 (2014), B15 (April 2015), B20 (2016) and soon B30
Thailand	B7 mandate in 2016 and B10 in 2018
Malaysia	B7 mandate and B10 in 2019
Vietnam	B5 mandate since 2009

The mandatory mandate of biodiesel blends for Malaysia has started in 2011 with B5 following the National Biofuel Policy (NBP) that was fixed in 2006. The policy promoted the continuous production and use of biofuels which governed by five policy thrust (Johari et al., 2015). Accordance to that, Biofuel Industry Act (BIA) was established in 2007 wherein under the act, the Plantation Industries and Commodities minister is authorized to raise and lower Malaysia's biodiesel mandate (Mohammadi et al., 2016).

The advantages of biodiesel which are renewable, biodegradable and clean burning fuel produce lesser toxic pollutants and greenhouse gases than petroleum diesel when burnt (Kumar and Sharma, 2016; Mekhilef et al., 2011). It is also harmless to environment in its production process compared to fossil fuels. Another desirable points for biodiesel are the similarity in composition and characteristics with diesel fuel where enable it to be directly used in diesel engine with little or almost no modification to the engine (Kumar et al., 2014; Lim and Teong, 2010). Biodiesel also has its advantage of oil palm plantations in Malaysia which give promising continuous supply of feedstocks (Abdul-Manan et al., 2014).

For engine application, the biodiesel has been proven applicable to be used in turbo-charged engine, high speed direct injection engine, diesel engine, marine craft engine and stationary engine which is unmodified (Dwivedi et al., 2013). Nevertheless, most engine studies show higher NO_x emissions and higher fuel consumption with biodiesel tested. These formations were influenced by the fuel properties such as activation energy as reported by Conconi and Crnkovic (2013).

Santos (2014) done thermal analysis to monitor the thermoxidation of biodiesel in function of time. The thermal analysis was further evaluated to determine the activation energy. Dwivedi (2016) done thermal analysis to determine the combustion kinetics and stated that it affected the emissions released from the combustion. Hence, this study intended to further evaluate the activation energy from thermal analysis. Moreover, this study also investigates the fuel properties, engine performance and emissions of palm biodiesel.

1.2 Problem Statement

Numerous studies proven that engine combustion using palm biodiesel blends have reduced carbon emissions (Abedin et al., 2014; Al-Dawody and Bhatti, 2014; Nalgundwar et al., 2016; Prabu et al., 2017). However, the high NO_x emissions in some studies give downsides of palm biodiesel (Dwivedi et al., 2013; Nagi et al., 2008). The emissions from the engine combustion with palm biodiesel blends are not conclusive. The reduced engine power and high fuel consumption are some other disadvantages of biodiesel (Fazal et al., 2011; Pullen and Saeed, 2014). A study reported that the NO_x and CO production are influenced by activation energy (Conconi and Crnkovic, 2013). The thermal analysis of palm biodiesel to discover the activation energy is still scarce. To ascertain these gaps, this study is intended to study the palm biodiesel blends fuel properties, thermal characteristics to study the activation energy and examine the engine performance and emissions. The thermal characteristic study is done using Thermal Gravimetric Analysis (TGA) to evaluate the activation energy in detail. The evaluation of activation energy was studied in detail using two different kinetic methods; Direct Arrhenius method and Coats-Redfern method. This study will benefit respective authority in future to decide higher biodiesel blends implementation and facilitates in the predictions of thermal stability behaviour, engine performance and engine emissions of palm biodiesel.

1.3 Objectives of the Study

This study intended to investigate:

- 1. The fuel properties for diesel, B30, B50 and B100 with respect to ASTM D6751
- 2. The thermal characteristics of diesel, B30, B50 and B100 at three different heating rates using TGA to study the activation energy with two kinetic methods; Direct Arrhenius and Coats-Redfern method
- 3. The performance of diesel, B30, B50 and B100 from engine combustion
- 4. The emission of diesel, B30, B50 and B100 from engine combustion

1.4 Scope of the Study

- 1. This study involved fuel properties study of four fuel samples which are diesel and palm biodiesel blends; B30, B50 and B100.
- 2. These fuel samples were tested on a direct injection (DI) diesel engine (Yanmar model L70AE) that is a four stroke, natural-aspirated and air-cooled engine to see the engine performance and emissions. The diesel engine was coupled to an eddy-current brake dynamometer equipped with a load controller to give force exerted by the torque arm of the dynamometer.
- 3. The thermal analysis was done using TGA and the thermal characteristics which are activation energy (E_a) and pre-exponential factor (A⁻¹) were calculated using two different methods; Direct Arrhenius and Coats-Redfern. The thermal analysis was discussed in detail to study the behaviour of activation energy (E_a) of palm biodiesel blends and diesel.
- Engine performances such as Brake Specific Fuel Consumption (BSFC) and Brake Thermal Efficiency (BTE) were evaluated at one constant speed and four different load of diesel engine.
- 5. Exhaust emissions such as nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO₂) and hydrocarbons (HC) were measured.

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