STUDY ON ENGINE PERFORMANCE AND EXHAUST POLLUTANT USING ISOBUTANOL – *Calophyllum inophyllum* BIODIESEL – DIESEL TERNARY BLENDS IN A DIESEL ENGINE

MOHD AZHAM BIN MOHD ALWI

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2021

STUDY ON ENGINE PERFORMANCE AND EXHAUST POLLUTANT USING ISOBUTANOL – *Calophyllum inophyllum* BIODIESEL – DIESEL TERNARY BLENDS IN A DIESEL ENGINE

MOHD AZHAM BIN MOHD ALWI

DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING SCIENCE

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2021

UNIVERSITY OF MALAYA

ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: **Mohd Azham bin Mohd Alwi**

Registration/Matric No: **KGA150007 / 17042556/1**

Name of Degree: **Master of Engineering Science**

Title of Thesis: **STUDY ON ENGINE PERFORMANCE AND EXHAUST POLLUTANT USING ISOBUTANOL – *Calophyllum inophyllum* BIODIESEL – DIESEL TERNARY BLENDS IN A DIESEL ENGINE**

Field of Study: **Energy**

I do solemnly and sincerely declare that:

(1) I am the sole author/writer of this work;
(2) This work is original;
(3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyrighted work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this work;
(4) I do not have any actual knowledge, nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyrighted work;
(5) I hereby assign all and every right in the copyright to this Work to the University of Malaya (UM), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
(6) I am fully aware that if in the course of making this work, I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate's Signature Date:

Subscribed and solemnly declared before,

Witness's Signature Date:

Name:

Designation:

ABSTRACT

Renewable energy sources such as biodiesel and bio-alcohol are desirable and are alternative to meet energy demand and control emission, from renewable sources such as ethanol, methanol, butanol, and pentanol. Biodiesel has a notable interest in offering many advantages with few disadvantages and needs to be extended for comprehensive use. Applying greater alcohols such as butanol with biodiesel in fuel blends is a beneficial technic to enhance the fuel characteristics and use biodiesel and alcohol efficiently. Isobutanol is an organic compound that has very low volatility, higher-chain alcohols have energy densities close to gasoline. It is not as volatile or corrosive as ethanol and does not readily absorb water. Furthermore, branched chain of alcohols such as isobutanol have higher-octane numbers resulting in less knocking in engines. The molecule has nearly 20 percent higher energy density compared to ethanol. The chemical structure and its production from renewable sources can enhance energy security and environmental challenges. To assess the suitability of isobutanol with biodiesel diesel blends and reveal the effects of it, 5%, 10% and 15% of isobutanol were blended with 5%, 10% and 15% of *Calophyllum inophyllum* biodiesel to enhance the fuel features and make them more viable with better engine efficiency. The experiment was carried out under distinct load circumstances on a single-cylinder compression ignition diesel engine, four-stroke, water-cooled, direct injection diesel engine, 1.97 bar to 7.88 bar brake mean effective pressure (BMEP). The fuel characteristics, engine efficiency, and exhaust pollutants were assessed and compared to biodiesel blends and diesel from petroleum. From the experiment, it is been discovered that the diesel engine operating with higher alcohol-biodiesel blended fuels has shown higher brake specific energy consumption and exhaust gas temperature, but lower brake thermal efficiency. Then, the HC, CO, and CO_2 are decreased for all higher alcohol-biodiesel blended fuels. However, NOx, showed an increasing trend due to the increase of injection quantity and lower cetane number. It can be proved that isobutanol may be utilized as a preferential substitution with biodiesel and petroleum diesel.

ABSTRAK

Bahan api bio seperti biodiesel dan bio-alkohol daripada sumber yang boleh diperbaharui seperti etanol, metanol, butanol, dan pentanol adalah penyelesaian alternatif yang wajar bagi memenuhi permintaan penggunaan tenaga dan mengawal keluaran emisi. Biodiesel telah mendapat banyak faedah yang luar biasa serta memberikan banyak kelebihan dan kelemahan dan perlu dikaji dan diperluaskan lagi untuk kegunaan secara meluas. Penggunaan jenis alkohol peringkat tinggi seperti butanol dicampurkan bersama dengan biodiesel merupakan jalan positif bagi memperbaiki sifat-sifat bahanapi serta kepenggunaan yang lebih cekap. Isobutanol adalah sebatian organik yang mempunyai kemeruapan yang sangat rendah serta mempunyai rantaian atom yang lebih tinggi dan kepadatan tenaga yang hampir sama dengan petrol. Ianya bukan bersifat tidak menentu atau menghakis seperti etanol, dan juga tidak mudah menyerap air. Selain itu, rantaian bercabang alkohol isobutanol mempunyai nombor oktana yang lebih tinggi dimana dapat mengurangkan ketukan dalam enjin. Molekul ini mempunyai kepadatan tenaga hampir 20 peratus lebih tinggi berbanding dengan etanol. Struktur molekul dan dihasilkan daripada bahan mentah yang boleh diperbaharui boleh membantu memperbaiki masalah yang mencabar dari segi keselamatan tenaga dan juga isu-isu alam sekitar. Untuk menentukan kesesuaian dan mendapat pendedahan tentang kesan penambahan isobutanol, sampel minyak dicampurkan sebanyak 5%, 10% dan 15% isobutanol bersama dengan 5%, 10% dan 15% biodiesel *Calophyllum inophyllum* supaya dapat tingkatkan ciri-ciri bahanapi dan menjadikannya lebih padan dengan menghasilkan pencapaian enjin yang lebih bermutu. Eksperimen ini dilakukan pada enjin diesel penyalaan mampatan silinder tunggal, empat lejang, penyejukan air, suntikan langsung di bawah keadaan beban yang berbeza, 1.97 bar kepada 7.88 Tekanan Berkesan Min Brek (BMEP). Keadaan bahan bakar, pencapaian enjin, dan bahan pencemar ekzos disiasat dan bandingkan antara semua gabungan biodiesel dan diesel petrolem. Daripada eksperimen ini, didapati bahawa enjin diesel yang beroperasi dengan bahan api campuran alkohol yang lebih tinggi biodiesel telah menunjukkan penggunaan tenaga tertentu dan suhu gas ekzos yang lebih tinggi, tetapi kecekapan haba brek rendah. Kemudian, HC, CO, dan CO_2 berkurang untuk semua bahan api campuran alkohol-biodiesel yang semakin tinggi kandungan. Kecuali untuk NOx, menunjukkan kecenderungan meningkat disebabkan peningkatan jumlah suntikan dan jumlah cetane yang lebih rendah. Ia boleh dibuktikan bahawa isobutanol boleh digunakan sebagai pengganti pilihan untuk biodiesel dan diesel.

ACKNOWLEDGMENTS

First, I would like to thank ALMIGHTY ALLAH S.W.T. who has given me bravery and patience to carry out this thesis. I would especially like to thank both of my supervisors, Dr. Nurin Wahidah Binti Zulkifli, Dr. Nazatul Liana Binti Sukiman, and advisor, Professor Md Abul Kalam for their useful advice, encouragement, and assistance. Without their assistance, advancement in this thesis would never have been possible. I would also like to extend my sincere appreciation for monetary assistance to the Ministry of Higher Education (MOHE) for My Brain 15 Scholarship and the Fundamental Research Program (FRGS) through project no. FRGS/1/2015/TK07/UM/01/1.

I would also like to thank all members of the Center for Energy Science, Department of Mechanical Engineering, Faculty of Engineering, University of Malaya for their precious thoughts and discussions. I am grateful for their inspirational advice and opinion, positive criticism and advice.

I also want to thank my beloved family. Words cannot convey how thankful I am to them for all their sacrifices on my behalf. I was supported by their prayers on this journey

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

ASTM : The American standard for testing materials

BP : Brake Power

BS : British Standard

BMEP : Brake mean effective pressure

BSEC : Brake Specific Energy Consumption

BSFC : Brake Specific Fuel Consumption

BTE : Brake thermal efficiency

CA : Crank angle

CO : Carbon monoxide

CO_2 : Carbon dioxide

CI : *Calophyllum inophyllum*

cm : Centimeter

CN : Cetane number

CP : Cloud point

DI : Direct Injection

EGT : Engine gas temperature

EN : European Union

EHN : Ethyl hexyl nitrate

FAC : Fatty acid composition

FAME : Fatty acid methyl ester

FFA : Free fatty acid

GC : Gas chromatograph

HC : Hydrocarbon

IC : Internal Combustion

IP : Induction period
ISO : International standard organization
IEA : International Energy Agency
kg : Kilogram
kW : Kilowatt
LHV : Lower heating value
MJ : Mega Joule
mm : Millimeter
MW : Molecular weight
NO : Nitric oxide
NO_X : Oxides of Nitrogen
PM : Particulate matter
PP : Pour point
ppm : Pert Per Million
RON : Research octane number
rpm : Revolution per Minute

CHAPTER 1: INTRODUCTION

1.1 Introduction

Since the industrial revolution started in the 18th and early 19th centuries, energy has become an important factor for humans in maintaining the needs of living and preserving economic growth. In Europe, coal is available abundantly as primary source of energy and played a vital role in industrial revolution. In 20th century, use of electricity, automobiles, and aircraft was increased tremendously and energy needs were fulfilled by petroleum products. Since then, coal and petroleum are the primary energy sources for people. Due to huge use, however, petroleum resources are depleted on a daily basis. Furthermore, fossil fuel usage is the most significant implications of environmental issues. Nowadays climate is changing, and global warming is a significant problem around the globe. Several scientists had concluded that when global temperatures rise above 2 °C then over 1 million animals, 100 million human beings and plants will be at risk . At present, many environmental problems have arisen as a result of global temperature rises, such as earthquakes, inundations, increases in sea level, torrent, cyclones, droughts and stronger erosion at beachfront levels all over the world (Hassan, Yacob, & Ghani, 2005). The Four Review Report (AR4), published in 2007, showed that the reason for greenhouse gas emissions such as carbon monoxide, carbon dioxide, nitrous oxide, and global warming had increased significantly for the past 50 years, reported by IPCC (Intergovernmental Panel on Climate Change, USA) (Anand, Kannan, & Karthikeyan, 2013). This study also stated that the burning of petroleum-based fuels in diesel vehicles is the primary reason for environmental greenhouse gas pollution, that mostly engines exhausted carbon monoxide, carbon dioxide, and methane emission gases. Moreover, fossil fuel is a major source of energy that uses to generate electricity, transport, industry and manufacturing sectors, while carbon dioxide is a major part of fossil fuels. Hence, the primary reason for raising global warming is more carbon dioxide emissions from exhaust gases. On the other side, the world's entire reservation of fossil fuel is restricted. In the near future, over-dependence on fossil fuels and huge industrial development around the globe are affecting the fossil reserves. Therefore, world researchers should encourage to use another alternative renewable energy to decrease the reliance on fossil fuel and greenhouse gas emissions (Ashraful et al., 2014). Now researchers from all over world are currently working together to search for appropriate alternative and sustainable renewable energy sources including geothermal, biomass, biofuel, solar, wind and ocean wave energy. Renewable power sources, however, rely on countries' geographical status. In fact, Malaysian government already took more than one biofuel policy like as 5th fuel policy with the aim to encourage wide uses of new renewable bioenergy resources like palm, waste wood as well as rice husk as a supplement of the conventional energy (H., 2002). Malaysia has an enormous quantity of arable soil and forest crops, which can be potentially source of planting biomass. Malaysia is a developing nation; its financial and industrial growth will increase its power demand every day while the power demand is expected to reach around a hundred million tons by 2030. **Figure 1.1** shows the chart of energy consumption by sector in Malaysia. But instead, to satisfy energy demand and reduce exhaust gas emissions, Malaysia should guarantee sustainable and efficient energy sources from renewable sources.

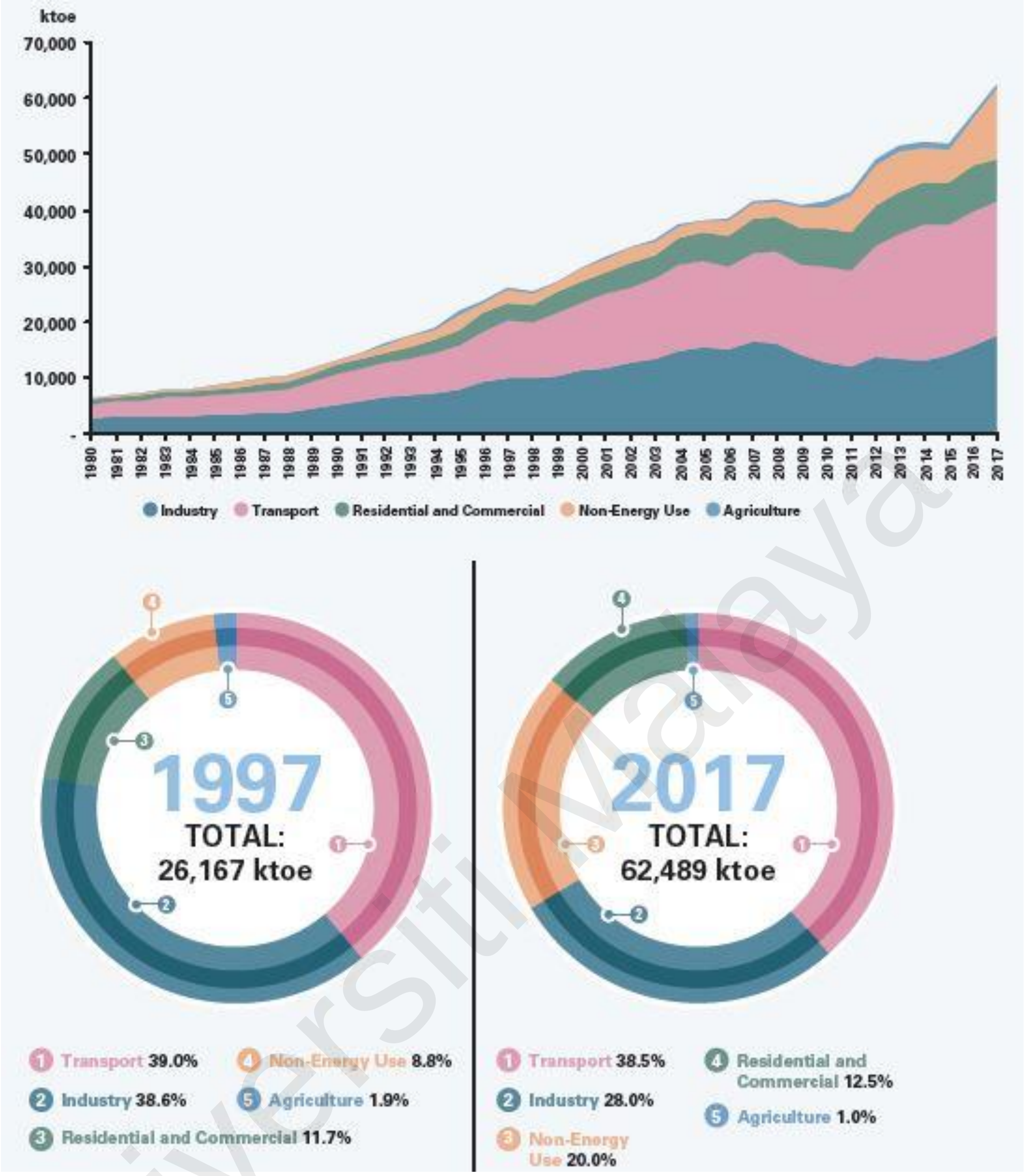


Figure 1.1: Energy consumption by sector in Malaysia (Commission, 2019)

1.2 Problem statement

Currently, biodiesel is the most potential and promising future fuel option for diesel engines from various renewable sources with various advantages and few liabilities. It obtained higher viscosity, density, and low calorific value causes the improper atomization of fuel during the combustion phase and decreases the overall performance of engine. More biodiesel is used during injection because of its high-density which increases BSFC and NO_x as a result. In addition, at the combustion stage premixed biodiesel and its blends get ignited sooner as compared to fossil diesel fuel due to shorter ignition delay. Biodiesel-diesel blended fuel utilization limited up to 20% blending ratio because of higher viscosity and lower energy content of biodiesel in addition to it is higher pour point and cloud point.

Both the length of the premixed combustion stage and the length of the diffusion combustion stage improved with all biodiesel-diesel blends compared to neat diesel. Higher premixed combustion stage length of biodiesel-diesel blends is accountable for enhancing NOx emissions. Furthermore, the reduced volatility of biodiesel causes the difficulty in the adequate mixing of the biodiesel with air during diffusion combustion, thus resulting in a decrease in engine efficiency. Research has been ongoing and many alternative and advanced methods have been applied to improve biofuels and increase their feasibility and use globally. Oxygenated additives like alcohols were used with biodiesel blends undertaking the issues and discovered that these alcohol additives such as ethanol and butanol are very good in enhancing properties of biodiesel fuel. Although the use of oxygen-enriched alcohols increases the premixed and diffusive combustion phases, but their low cetane number (CNs), low calorific values (CV), poor miscibility and stability problems, poor auto-ignition quality and inadequate lubrication conduct restrict the utilization of alcohols as a neat fuel for diesel engine (Campos-Fernandez, Arnal, Gomez, Lacalle, & Dorado, 2013). By comparison, greater alcohol can resist low-alcohol issues. The highly carbonated alcohols like butanol (four carbons) have better miscibility, good CV, high CN, and are able to be used as additives in fuel to enhance the pour point and fluidity of biodiesel at low temperatures (Atmanli, Ileri, Yuksel, & Yilmaz, 2015; Sahin, Durgun, & Aksu, 2015). Alcohols that contain more C-atoms can be an efficient and optimistic technique for increasing the rate of combustion and enhancing fuel characteristics as well as exhaust emissions by enabling more oxygen content and enhancing the number of cetanes.

1.3 Research objectives

I. To investigate the physicochemical properties of blended fuels (5%, 10% and 15%) compared to biodiesel and neat diesel.

II. To compare the engine performance characteristics by using blended fuels, biodiesel, and neat diesel.

III. To establish the best fuel blends ratio to improve engine performance and reduced exhaust emissions.

1.4 Scope of study

The main focus of this research is to inspect the behavior of *Calophyllum inophyllum* biodiesel and its blends with higher carbon atoms alcohols like isobutanol (5%, 10% and 15% by volume) Moreover, physicochemical properties of *Calophyllum inophyllum* biodiesel and all of its blends are also investigated to explore their potential as a diesel engine fuel. All these properties are also compared with the 20:80 % blend of biodiesel:

diesel fuel only because the previous researcher revealed that among various blends mostly 20:80 % biodiesel: diesel blend enhances the engine performance (Arbab et al., 2015). In addition, few researchers also mentioned that more than 20% of alcohol addition in biodiesel causes engine knocking. Therefore, 5%, 10% and 15% by vol. of isobutanol as additives were selected. The physicochemical properties such as kinematic viscosity, density, acid value, lower heating values, cloud point, pour point and flash point of the blended fuels (i.e *Calophyllum inophyllum* biodiesel and diesel) were also evaluated in accordance with ASTM D7467, ASTM D6751, and EN 14112 standards. Moreover, the fatty acid composition of the *Calophyllum inophyllum* based biodiesel has also determined by GC analysis. Engine testing was executed at the maximum, 1,200 RPM with varies load of 25% to 100% of brake mean effective pressure (BMEP).

Engine performance was measured in terms of brake thermal efficiency (BTE), brake power (BP), and brake specific energy consumption (BSEC). Regulated exhaust emissions including carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbon (HC), and nitrogen oxide (NOx) were also investigated and compared with base fuels to see the effects of alcohol addition in biodiesel.

1.5 Dissertation outline

This dissertation contains five solid chapters. The summary of all the chapters is defined below:

Chapter 1 provides a perspective on the current situation and sources of biofuel and its use in the transport industry as fuel in order to diminish the current and future energy crises. Biodiesel's potential as a diesel engine fuel with some intrinsic problems is identified and solutions to alleviating these problems have been discussed in order to set goals of this research.

Chapter 2 highlights the introduction of biodiesel; it is blending with higher carbon oxygenated alcohol (isobutanol) and evaluation of their physicochemical properties according to standards. Investigation of feasibility of high c-atom alcohol usage in the diesel engine as an additive with biodiesel was deliberated. As this work was already undertaken by numerous scientists and their results and impacts on engine efficiency are also discussed.

Chapter 3 presents the materials and methods for using different equipment and the investigational process mostly to finish up the research experiment.

Chapter 4 discusses the results achieved by all test, followed by an assessment and discussion of the revealed facts.

Chapter 5 provides the findings with some notable experimental outcomes and highlights some suggestions and recommendations for future research.

CHAPTER 2: LITERATURE REVIEW

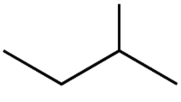
2.1 Introduction

This section shows significant high-impact journal publications and reports that will provide insight and understanding about the topic and related issues. This chapter described the origin, sustainability, and chemistry of alcohol-based biofuels. This section also discussed the selection of feedstock, selection of the production method of biodiesel and its quality standard as well as the problem of biodiesel use in a diesel engine as engine fuel. Finally, up-to-date critical assessments and the outcomes of the past engine and emission studies are discussed.

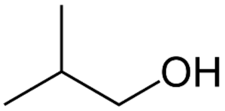
2.2 Butanol as an alternative fuel

Butanol is four-carbon primary alcohol having the molecular formula of C_4H_9OH and exist in four isomers: *n*-butanol $CH_3CH_2CH_2CH_2OH$, *sec*-butanol $CH_3CH_2CHOHCH_3$, *iso*-butanol $(CH_3)_2CH_2CHOH$ and *tert*-butanol $(CH_3)_3COH$. All of the isomers producing the same energy but each of them has different manufacturing methods. All four isomers have the same amount of heat energy and formulae but have a different molecular structure that affects each property (Brandao & Suarez, 2018).

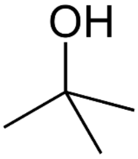
n-butanol



sec-butanol



iso-butanol



tert-butanol

Figure 2.1: Isomers of butanol structural formula (Pan et al., 2020)

Butanol is a colorless liquid with a distinct odor and its vapor has an irritant effect on mucous membranes and a narcotic effect in higher concentrations. Butanol is completely miscible with organic solvents and partly miscible with water.

2.3 Production of butanol

Since the late 1990s, the interest in butanol as sustainable automobile fuel has increased and directed to research to enhancing bio-butanol production process that stands more cost-effective than petrochemical production process. The current commercial butanol production via microbial fermentation is not a new concept. Sugar cane, sugar beet, cereal crops, and some others could produce Biobutanol. It can be synthesized with cellulose raw materials. Bio-butanol production is a vibrant study area from the 19th century (Atsumi et al., 2010; Gheshlaghi, Scharer, Moo-Young, & Chou, 2009; Green, 2011). As a substitute fuel, bio-butanol offers many different advantages from ethanol, like good miscibility with current fuels having high energy content, poor water absorption, and a problem-free utilization in conventional engines (Durre, 2008). The traditional production of butanol is a fermentation of acetone-butanol-ethanol (ABE).

ABE butanol cannot compete with synthetically manufactured butanol on a company scale because of the cost, relatively low yield along with slack fermentation, and problems associated with phase transition and final product inhibition. Therefore, most ABE manufacturing has ceased with the progress of the petrochemical industry. Louis Pasteur was referenced and commercially applied by Chaim Weizmann regarding the manufacturing of microbial butanol (Gheshlaghi et al., 2009). 1-butanol or isobutanol may be extracted by using a biotechnological method (Atsumi, Hanai, & Liao, 2008). ABE fermentation can be used with lingo cellulosic products such as local agricultural waste enriched with fiber or cellulose (Lopez-Contreras, Claassen, Mooibroek, & De Vos, 2000).

2.4 Biodiesel standard and characteristics

Biodiesel is the main essential solution to replace diesel fuel as diesel reservoirs are depleting day by day. Biodiesel is synthesized mainly from animal fats and crop seed oils. It can be used as pure or blended with diesel fuel to be used in any standard or customized diesel engine. The advantages of biodiesel are less polluting compared with pure diesel and are renewable, non-toxic and biodegradable (Nagaraj, Ponnusamy, Muthukutti, & Ponnusamy, 2019). It has comparable features and properties to regular diesel. It is getting swift famous as it considerably decreases greenhouse gas emissions. When the engine is fuelled with biodiesel or its blends with diesel fuel than its efficiency changes and also impacts the exhaust pollutant of a diesel engine (Atabani et al., 2013; Ong, Masjuki, Mahlia, Silitonga, Chong, & Leong, 2014). Many researchers reported that biodiesel shown result of improved on torque and brake power. They also found biodiesel and its blends improve reducing hydrocarbon (HC) and carbon monoxide (CO) of exhaust emission (Ong, Masjuki, Mahlia, Silitonga, Chong, & Yusaf, 2014; Silitonga, Masjuki, Mahlia, Ong, & Chong, 2013)

Table 2.1: Biodiesel Fuel Standard Specification (B100) (M. N. A. M. Yusoff et al., 2020)

Property	Units	Test Method	ASTM D6751 (US Standard)	EN 14214 (European Standard)
Density at 15 °C	kg/m^3	ASTM D 4052 / EN ISO 3675 / EN ISO 12185	-	860 - 900
Kinematic viscosity at 40 °C	mm^2/s	ASTM D 445 / EN ISO 310	1.9 – 6.0	3.5 – 5.0
Kinematic viscosity at 100 °C	mm^2/s	ASTM D 445 / EN ISO 310	-	-
Flash point	°C	ASTM D 93 / EN ISO 3679	93 min	120 min
Calorific value	MJ/kg	ASTM D 240 /	-	-
Acid value	KOH/g	ASTM D 664 /	0.5 max	0.5 max
Ester content	% mass	EN 14103	-	96.5 min

2.5 History and potential of biodiesel

Biodiesel is also called fatty acid methyl ester of respective vegetable oils. Biodiesel has been found to have comparable structure and characteristics compared to petroleum-derived diesel generated from other procedures. By means of the transesterification technique, biodiesel is synthesized with multiple plant oils or animal fats. Biodiesel is the most popular biofuel with several benefits compared to diesel derived from petroleum. The history of biodiesel starts in the mid-1800s. Since then, the process of transesterification was used to separate the glycerin from vegetable oils. In 1900s, Rudolf Diesel said the first small diesel engine exhibited by the Otto company that fueled with peanut oil in the Paris World Fair, France. In 1920s, vegetable oil eliminated from the market due to cheaper price and high availability of petroleum diesel. In the 1970s, oil producers' companies focused on vegetable oil as an alternative fuel because of the limited supply of fossil fuel. However, because of low volatility and high viscosity of vegetable oil is directly used, it is no longer suitable for a diesel engine. Due to this reason vegetable oil is required to be refined to make quality fuel. Pyrolysis, blending (Ma & Hanna, 1999; Pramanik, 2003) and micro emulsification (A. Srivastava & Prasad, 2000) are several methods for reducing the viscosity of vegetable oils. However, those methods have some problem including carbon deposition and contamination (Sarin, Sharma, Sinharay, & Malhotra, 2006). In 1977, first biodiesel production process began by a Brazilian scientist expedite. In 1979, biodiesel production and refining processes initiated in South Africa. In the late 1990s, commercially biodiesel productions had continued. During this period, many European countries constructed several biodiesel plants. Within the 2000s, many other countries around the world such as France, United state started commercial biodiesel production. "National Biodiesel Board" in United State had reported that in 1999s, produced 1.9

million liters of biodiesel, in the 2000s, it had increased 25.4 million liters ("EIA (Energy Information Administration) Biodiesel Performance, Cost and Use 2005.Available from www.eia.doe.gov," 2005). In 2004, the Philippine government had made obligatory 1% coconut biodiesel blend mix with diesel fuel and commercially used in their government vehicles (A. K. Srivastava, Soni, Sharma, & Jain, 2018). In 2005, the United States' mandate was to use at least 2% of biodiesel blend with diesel fuel nationwide. In the same year, American society of testing material published new biodiesel blend specification. After this publication biodiesel has been widely introduced in many countries. Now many service stations of those countries' biodiesel production are available. While, in 2008, 11 million metric tonnes of biodiesel was produced around the world, and total biodiesel production increased to more than 20 million tonnes in 2010.

2.6 Fuel properties of alcohol – biodiesel – diesel blended

The solubility and physical characteristics of the biodiesel-ethanol- diesel mixture in a diesel engine were estimated by Kwanchareon, Luengnaruemitchai, and Jai-In (2007). By comparing fuel characteristics, the flash point measurement of the ethanol mixture fuel was not quite the same as the fossil diesel. Ethanol mixed fuel have a calorific value that was not as distinctive as fossil diesel. Bhale, Deshpande, and Thombre (2009) inspected the effects of ethanol as additive on the cold flow properties of *mahua* oil biodiesel while commercial additives and kerosene were also added. The cloud point of the mixture decreased at 20% of ethanol from 18 °C to 8 °C. The author found that cold flow properties of *mahua* biodiesel improved up to 20 percent by adding kerosene and ethanol in it. A greater percentage of ethanol in mixtures is demoralized as the overall calorific quality may reduce. The cloud point of *mahua* methyl ester was reduced up to 13 °C when 20% kerosene was blended with it. While by mixing 20% ethanol in *mahua* biodiesel, cloud point reached to 10 °C (Rashedul et al., 2014). Joshi, Moser, Toler, Smith, and Walker (2010) recorded the blending of poultry fat methyl ester (PFME) with butanol and isopropanol increased the viscosity but when ethanol mixed with biodiesel, the mixture has a minimal viscosity. Similarly, butanol blends had greater flash point than fuel mixed with isopropanol and ethanol. Joshi, Moser, Toler, Smith, and Walker (2011) also identified 3°C – 4 °C decrease in PP, 4°C – 5 °C decrease in CP and about 3 °C decrease in CFPP.

Yasin, Yusaf, Mamat, and Yusop (2014) conducted a 5 percent methanol experiment in biodiesel to assess the efficiency and exhaust pollutant characteristics on the multi-cylinder diesel engine. Additional methanol has been observed that it reduces the blending density from 0.845 gram per centimeter to 0.8429 gram per centimeter, the viscosity from 4.5 cSt to 3.13 cSt and the flash point result from 110 °Celsius to 92 °Celsius. Butanol's characteristics, such as cetane number, hydrophobic, and latent vaporization heat are similar to neat diesel with lower type alcohols (Siwale et al., 2013). The reduced alcohol has greater latent heat of vaporization which increases ignition delay as compared to neat diesel. The n-butanol offers full miscibility with fossil diesel and has shown enhanced combustion in diesel engines owing to reduced vaporization heat, making it greater heating (Atmanli, Ileri, & Yuksel, 2015). Imtenan et al. (2014) used butanol as oxygen additive in the palm - jatropha biodiesel mixtures and examine its impacts on diesel engine efficiency and on emissions. It was discovered that n-butanol combined biodiesel fuel has declined in density and viscosity. When low heating value additives added in P20 and J20 blends then calorific values and flash point of these blends also reduced. (Z. H. Zhang & R. Balasubramanian, 2014) showed that huge percentage of butanol in the mixtures considerably lowers the calorific value of mixtures and results in a larger fuel mass required to produce a greater BSFC energy output. Atmanli, Ileri, and Yuksel (2014) noted that the blending of cotton oil with n-butanol enhanced their solubility than the solubility of diesel – cotton oil at a temperature of -15 degrees Celsius. This is because n-butanol is better miscible with vegetable oils at low temperatures. Laza et al. (2011) discovered when adding 20% iso-butanol with rapeseed biodiesel, it reduces significantly on CFPP up to −1.5 ° Celsius. Rapeseed oil oxidation stability and blends were found to be around 4.3 hours. Li, Wang, Wang, and Xiao (2015) added pentanol in biodiesel and diesel blends to assess combustion and exhaust pollutant characteristics of diesel engines. The researcher stated that because of greater viscosity, the biodiesel has shown the bad atomization properties than neat diesel. Wang, Liu, Zheng, and Yao (2015), noticed that the addition of pentanol could be enhanced. Because pentanol has a comparatively lower boiling point, by adding it to the mixed fuels could result in rapid vaporization, thus improving the quality of atomization.

2.7 Performance studies of alcohol – biodiesel – diesel blends

In a DI single-cylinder water-cooled diesel engine, Banapurmath and Tewari (2010) used honge and jatropha biodiesel with 0 percent, 5 percent, 10 percent, and 15 percent of ethanol. They clarified that the ethanol mixed biodiesel fuel's brake thermal efficiency improved at general working circumstances with a rise in ethanol content in the mixed fuels. Zhu, Cheung, Zhang, and Huang (2011) indicated that 5% addition of ethanol in biodiesel-diesel blends slightly improved the engine efficiency. Meanwhile, How, Masjuki, Kalam, and Teoh (2014) noted for the equal percentage of ethanol and coconut methyl ester, they discovered greater BTE and BSFC. Due to the reduced cetane index and calorific value of ethanol mixed fuel, the torque and output strength were greater (Rahimi, Ghobadian, Yusaf, Najafi, & Khatamifar, 2009). Because the heating price was smaller, ethanol and biodiesel showed greater BSFC regarding the percentage of the mixed fuels when blended with diesel (Hulwan & Joshi, 2011; Rahimi et al., 2009). Furthermore, because the heating cost was lower, when mixed with petrol, ethanol and biodiesel showed increased BSFC regarding the percentage of the blends. (Yilmaz & Sanchez, 2012). Complete combustion of biodiesel occurred with addition of methanol and ethanol. It also increases brake thermal efficiency and lubricity of the mixture (Hüseyin Aydin & İlkılıç, 2010; Mat Yasin, Yusaf, Mamat, & Fitri Yusop, 2014). Even though greater alcohol-mixed fuel blends acquired reduced heating values than 20 percent biodiesel mixed fuels, the combustion effectiveness was enhanced owing to elevated oxygen content, reduced density and viscosity resulting in reduced BSFC. (Imtenan, Masjuki, Varman, & Fattah, 2015). Maroa and Inambao (2019) had done an analysis of waste plastic pyrolysis oil (WPPO) and blend it with ethanol, conventional diesel, WPPO and ethanol with 2-ethyl hexyl nitrate (EHN) and run in a natural aspirated single-cylinder diesel engine power generator. The result has shown slight increase in BSFC and improved BTE.

The addition of ethanol and methanol in biodiesel reduced its calorific value and increased BSFC because oxygen content in mixtures increased. But ethanol and methanol in biodiesel has been fully combusted and contributes to the increased lubricity of the mixture (H. Aydin & Ilkilic, 2010; Mat Yasin et al., 2014). Cheng et al. (2008) researched on the efficiency of a diesel engine in mixed and fumigation mode using 10 percent methanol with biodiesel. They noted that the blended mode tended to improve the engine's brake thermal efficiency at low engine loads, while methanol's cooling effect decreased efficiency at heavy load operation. Yasin et al. (2013)

individually using 5 percent of methanol in the B20 blend and fossil diesel. He noted increase in BTE because of presence of higher mass of pre-premixed fuel combustion.

Yilmaz, Vigil, Benalil, Davis, and Calva (2015) examined the effects of biodiesel-butanol mixtures on DI-diesel combustion and exhaust emission, results showing an enhanced BSFC compared to neat butanol-biodiesel mixtures. Labeckas, Slavinskas, and Mazeika (2014) discovered that ethanol mixed RME-biodiesel blends had high diesel engine efficiency, but it increased brake-specific fuel consumption as compared to normal diesel, while comparable heat brake thermal efficiency was discovered for the equal working situation. Atmanli, Yuksel, Ileri, and Karaoglan (2015) researched the efficiency and exhaust pollutant of diesel engines by using fuels blending with greater proportions (20 percent - 60 percent) of n-butanol in cotton oil-diesel blends at fully load with variable speeds. The author reported that increasing the percentage of n-butanol in the blends in the fuel decreased the average brake torque, brake power, brake thermal efficiency (BTE) exhaust gas temperature of the blend and increased brakes specific fuel consumption (BSFC). More quantity of n-butanol in blends results in an enhanced kinematic viscosity, density, and cold filter plug point, and this can be attributed to the collapse of the calorific value and cetane index of the blends. Jayabal, Thangavelu, and Velu (2019) studied the effect of adding n-butanol in waste sapota seeds biodiesel and run in single-cylinder common rail direct injection (CRDi). There were significant improvements in BTE and reduce BSFC compared to fossil diesel.

Li, Wang, Wang, and Xiao (2015) analyzed the impacts of the addition of pentanol to biodiesel-diesel blends to determine the combustion and emission performance on the diesel engine. In comparison with mineral diesel in all experiment circumstances, it was found that pentanol showed greater thermal efficiency in experimental loads (0.5 - 1.0 MPA IMEP). Pentanol released more heat by shortened combustion duration so it can be used as additives in diesel fuel. L. J. Wei, C. S. Cheung, and Z. H. Huang (2014) added 10 percent, 20 percent, 30 percent of *n*-pentanol with fossil diesel and examined their impact on DI diesel engine's efficiency. The lower BSFC was discovered with a greater percentage of *n*-pentanol in the fuel mixtures but did not influence the brake thermal efficiency.

Table 2.2: List of various researchers investigates on engine performance by using alcohol - biodiesel - diesel blended fuels

Engine specification	Operation condition	Biodiesel used	Alcohol used	BP	BTE	BSFC	Reference
4 strokes, 1-cylinder, direct injection, naturally aspirated.	Speed: 1200 rpm. Load: 0, 4, 8, 12, 16, 20 and 24 Nm	Jatropha-diesel blends	Ethanol (5% by vol.)	-	Adding ethanol in biodiesel-diesel: BTE increase.	Adding ethanol with neat biodiesel and diesel-biodiesel: BSFC increase.	(Kannan et al., 2012)
1-cylinder, direct injection, naturally aspirated.	Load: five level. Speed: 1,500 rpm Torque: 170.0 Nm.	Cottonseed oil biodiesel	Ethanol (5%, 10%, and 15%).	-	Adding ethanol in biodiesel-diesel: BTE increases with increasing load.	-	(Anbarasu et al., 2012)
4 strokes, 2-cylinder, Horizontal liquid-cooled, direct injection, naturally aspirated.	Load: No 0%, low 46%, medium 69%, and high 92%.	Used cooking oil biodiesel	5%, 10%, and 20% of butanol	-	-	Increase the percentage of butanol and increase load: BSFC decreases.	(Yilmaz et al., 2014b)
4 strokes, 4-cylinder in-line, direct injection.	Load: BMEP-(0.05 MPa) Speed: 2500 rpm	Mineral biodiesel (B20)	Methanol (5% by volume)	Adding 5% methanol to biodiesel: BP decrease.	-	Adding 5% methanol in biodiesel: BSFC increase.	(Mat Yasin et al., 2014)
4-cylinder in-line, direct injection.	Load: 80.0 Nm Variable speed: 1,000 rpm to 3,000 rpm.	*Calophyllum inophyllum* biodiesel	5%, 10% of n-butanol	-	Increase the percentage of butanol in the blends: BTE increases.	Increase the percentage of butanol: BSFC decrease.	(S. Imtenan et al., 2015)
4s, 1-cylinder (retrofitted from 4-cylinder), direct injection.	Load: 0.50-1.00 MPa IMEP Speed: 1600 constant	30% of biodiesel	30 % by vol. of pentanol	-	Adding Pentanol in biodiesel-diesel: BTE increase.	Adding pentanol blends: BSFC decrease.	(L. Li et al., 2015b)

2.8 Emission studies of alcohol blended biodiesel

Yilmaz, Vigil, Donaldson, and Darabseh (2014) studied the emission of CI engines by using cooking oil biodiesel with 3%, 5%, 15%, and 25% ethanol as diesel additives. In conclusion, the introduction of ethanol in combinations showed less NO emissions but greater CO emissions than diesel fuel. Increased ethanol mixture percentage increases HC emissions according to engine operating conditions. How et al. (2014) indicated that 5 percent of ethanol in coconut biodiesel blended fuels had less NOx, CO emissions and smoke opacity than fossil diesel. Fang, Fang, Zhuang, and Huang (2013) run the engine on low-temperature combustion mode to assess the impact of ethanol addition in biodiesel – diesel blended fuels on engine emissions. The writers noted that LTC mode released the greater latent heat of vaporization, which lesser NOx emissions and reduced CO and HC emissions as compared to neat diesel fuel. The greater proportion of oxygen and extended ignition delay also reduce smoke emissions, especially at increased loads. Because ethanol in the mixture has completely burned and the combustion temperature has risen, the emission of NOX is increasing. In addition, the reduced ethanol cetane number is also accountable for the greater formation of NOx (Banapurmath & Tewari, 2010). However, CO emissions for both blends at low speed and medium speed were reduced as oxygen enrichment, but greater speeds result in an increased emission of CO. Cheung, Zhu, and Huang (2009) researched the output of Euro 5 diesel engine which used biodiesel – diesel blended fuels with 5 percent, 10 percent, and 15 percent methanol in the blends. It has been revealed that mixing of methanol in fuel reduced emissions like particulate matter (PM) and oxides of nitrogen (NOx) due to formation of oxygen deficiency and lower in-cylinder temperatures for fuel-lean mixtures and fuel-rich, correspondingly (Sanli, Canakci, Alptekin, Turkcan, & Ozsezen, 2015).

CO emissions were better compared to those generated by biodiesel or fossil diesel, where HC emissions increased more than biodiesel but lesser than fossil diesel. Zhu, Cheung, Zhang, and Huang (2010) proved similar outcomes, while 5 percent of alcohol mixed with biodiesel, it reduced both HC and CO emissions. In mixed and fumigation mode, Cheng et al. (2008) methanol mixed biodiesel fuel was combusted in diesel engines to explore the performance and emission characteristics. The author found that in both modes carbon dioxide (CO_2) and NOx emissions were lowered with the addition of 10 percent of methanol in the blended fuels.

Adding n-butanol with biodiesel enhanced nitrogen oxides (NO and NOx) formations, significantly reducing hydrocarbon (HC) and carbon monoxide (CO) emissions (Atmanli, Ileri, & Yuksel, 2015). In addition, the entire number of particles, entire particulate-phase polycyclic aromatic hydrocarbon emissions, element carbon, levels of particulate mass and cytotoxicity of particulate extracts and carcinogenic potential reduced by the addition of butanol relative to B20. Whereas the increase of butanol in ternary fuel also increases the percentage of organic carbon (OC) in particles (Z.-H. Zhang & R. Balasubramanian, 2014). Imtenan, Masjuki, Varman, Fattah, et al. (2015) mixed 5-10% butanol with *Jatropha Curcas* methyl ester mixtures and concluded that HC emissions of diesel engines improved with an addition of n-butanol, while both 5 percent and 10 percent of n-butanol merged with blended fuels had a decreased emission of smoke and oxides of carbon. Yilmaz et al. (2015) monitored and founded that the addition of butanol reduced NOx emissions as the percentage of butanol in the blended fuels increases, the emission of NOx increases as well. Five carbon alcohol such as pentanol in biodiesel-diesel blended fuels decreased the exhaust pollutions like soot and oxides of nitrogen (NOx) at low and medium loads. In addition, use of oxygenated fuel blends in diesel engines also reduced the emissions including total unburnt hydrocarbons and carbon monoxide at lower engine loads (Li, Wang, Wang, & Liu, 2015).

Table 2.3: List of various researchers investigates on exhaust pollutant by using alcohol - biodiesel - diesel blended fuels

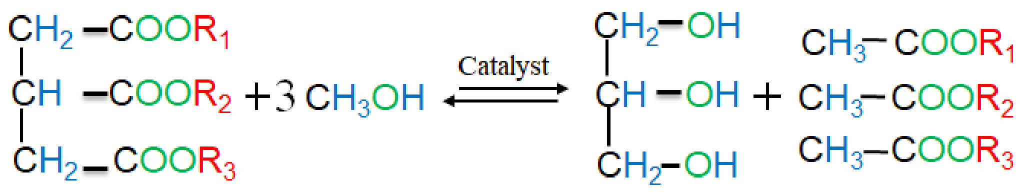
Engine specification	Operating Condition	Biodiesel used	Alcohol used	HC emissions	CO emissions	CO$_2$ emissions	NO$_X$ emissions	Smoke opacity	Reference
4 strokes, 1-cylinder, direct injection, naturally apirated.	Load: 0, 4, 8, 12, 16, 20 and 24 N-m. Speed: 1200 rpm constant	Jatropha biodiesel-diesel blends	Ethanol 5%	-	Adding 5% ethanol in blends: Increase load, CO Increase. Decrease load, CO reduces.	-	Increase load, NOx increase. Decrease load, NO$_X$ reduces.	Increase load: Smoke increase. Decrease load, Smoke opacity reduces.	(Kannan et al., 2012)
1-cylinder, direct injection, naturally apirated.	Load: five level. Speed: 1,500 rpm. Torque $_{max}$: 170.0 Nm	Cottonseed biodiesel	Ethanol (5%, 10% & 15%)	Adding 5% ethanol in blends: HC decrease. Increase the percentage of ethanol: HC rate increase.	5% ethanol in blends: CO reduces. Increase percentage of ethanol will increase the CO rate.	-	The low percentage of ethanol: NO$_X$ reduce. While increasing the percentage of ethanol: NO$_X$ increase.	The low percentage of ethanol: Smoke opacity reduce but increase the percentage of ethanol: Smoke opacity increase.	(Anbarasu et al., 2012)
4 strokes, 2-cylinder, Horizontal liquid-cooled, indirect injection, naturally apirated.	Load: No, 0%, low 46%, medium 69% and high 92%.	Used cooking oil biodiesel	Butanol (5%, 10%, and 20%)	Adding 20% butanol in blends: HC decrease.	Adding 0% and 46% load: Increase the percentage of butanol will increase the CO rate.	-	Adding butanol: NO$_X$ reduce but increase the percentage of butanol: NO$_X$ increase.	-	(Yilmaz et al., 2014b)
4 strokes, 4-cylinder in-line, indirect	Load: BMEP-	Mineral	Methanol (5%		Adding 5%	Adding 5% of	Adding 5% of		(Mat Yasin

injection, naturally apirated. .	0.050 Mpa. Speed: 2,500 rpm.	biodiesel (B20)	by vol.)	-	methanol in biodiesel: CO reduces.	methanol in biodiesel: CO_2 reduce.	methanol in biodiesel: NO_X increase.	-	et al., 2014)
4-cylinder in-line, indirect injection, naturally apirated.	Load: 80.0 Nm constant Speed: 1,000 rpm – 3,000 rpm.	*Calophyllum inophyllum* biodiesel	n-butanol (5% & 10%)	Increase the percentage of n-butanol: HC increase.	Increase the percentage of butanol: CO reduce.	-	-	Increase the percentage of butanol: Smoke opacity reduce.	(S. Imtenan et al., 2015)
4 strokes,1-cylinder (retrofitted from 4-cylinder), direct injection.	Load: 0.5-1.0 MPa IMEP Speed: 1600 constant.	30% of biodiesel	Pentanol (30% by vol.)	-	Adding pentanol in blends: CO reduces.	-	Low to medium loads: NO_X reduce compared to normal diesel fuel.	-	(L. Li et al., 2015b)

2.9 Production of *Calophyllum inophyllum* biodiesel

Unrefined oil of *Calophyllum inophyllum* oil contained about 8% free fatty acid (FFA) i.e. acid value (AV) of oil was 16. As acidic value was more than 1 so pretreatment of oil was performed first to reduce free fatty acids content. This pretreatment included steam distillation, alcoholic extraction, and acidic catalyzed esterification process. In the esterification process, FFA of oil reacted with methanol, while acidic catalyst was also used to accelerate the reaction. Acidic catalysts are mainly preferred in the esterification process because these are simple and can easily transform FFA's into biodiesel. Normally, the esterification process is chosen mainly due to its simplicity and acid catalysts can easily turn FFAs into biodiesel (Tapanes et al., 2008, Koh & Ghazi, 2011).

During the esterification process, 1.5 liters of *Calophyllum inophyllum* crude oil was poured into a 3 L FAVORIT double jacket reactor. Then, 50% (vol/vol of oil) methanol along with 1% sulfuric acid (H_2SO_4) vol/vol of oil were also added. This mixture was stirred at 1000 rpm with the help of "IKA Eurostar motor stirrer" for 2 hours. While reaction temperature was sustained at 60°C by circulating hot water from "WiseCircu". After 2 hours, this product was transferred into separating funnel for 1 hour to separate catalyst layer and esterified product. Afterward, the lower layer of esterified product was taken out and excess methanol and water were removed by using rotary evaporator (IKA RV10 Control). Then transesterification process was carried out by pouring esterified product into double jacket reactor and mixed it with 25% methanol (v/v of oil) and 1% of KOH catalyst (w/w of oil) for 2 hours at 63°C. This transesterification process produced biodiesel and glycerol as shown described by equation 3.1.



$$\begin{array}{l} CH_2-COOR_1 \\ | \\ CH-COOR_2 \\ | \\ CH_2-COOR_3 \end{array} + 3\,CH_3OH \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + \begin{array}{l} CH_3-COOR_1 \\ CH_3-COOR_2 \\ CH_3-COOR_3 \end{array} \quad (3.1)$$

Triglyceride of oil Methanol Glycerol Biodiesel

After completion of the reaction, the product was left in separating funnel for 12 hrs. Two immiscible layers were formed, upper layer contained biodiesel (methyl ester) while lower layer had glycerol and impurities in it. The upper layer of biodiesel was separated out and washed with 60°C warm water to remove impurities. Excess methanol and water were removed by using rotary evaporator and then this biodiesel was filtered to remove catalyst by using filter papers. After the purification process, the *Calophyllum inophyllum* methyl ester (CIME) was mixed with isobutanol and diesel at various ratios to produce the biodiesel blends.

CHAPTER 3: METHODOLOGY

3.1 Introduction

This chapter summarizes the experimental setup, the complete sequence of experimental work to synthesize biodiesel and the testing procedures along with standards. It also provides the complete procedure details of all the equipment utilized to estimate fatty acid composition and physicochemical properties of the biodiesel synthesized from *Calophyllum inophyllum* oil. This chapter illustrates the formation of biodiesel blends with alcohol, their performance, and emission analysis along with operating conditions. The flow chart of experimental work is illustrated in Fig. 3.1.

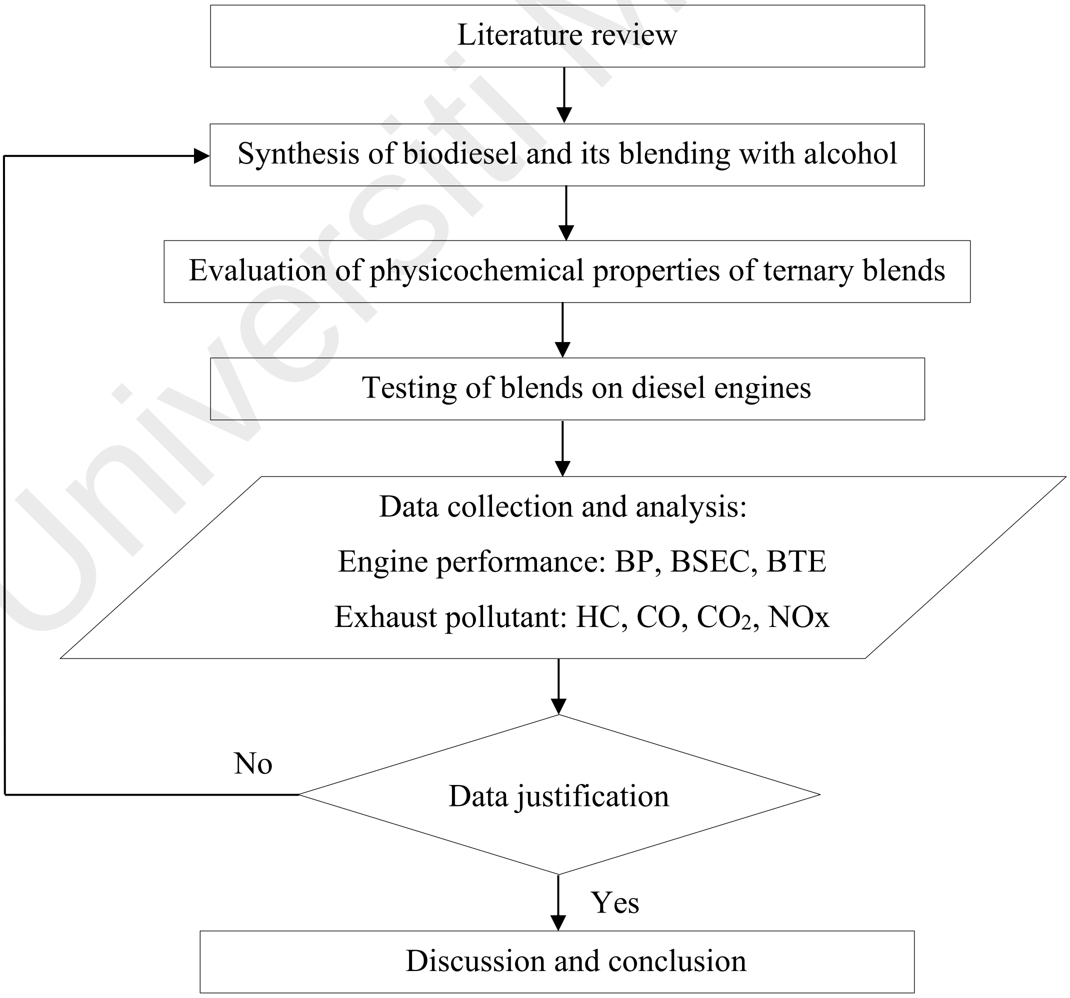


Figure 3.1: Research methodology flowchart

3.2 *Calophyllum inophyllum* oil

In this research, *Calophyllum inophyllum* was chosen as biodiesel feedstocks because it was abundantly available in Malaysia and obtained from the non-edible source. The kernels of *Calophyllum inophyllum* have very high oil content range from 60 – 70%. About 100 kg of seeds are harvested annually from a mature tree of *Calophyllum inophyllum*, which gives almost 18 kg of oil.

Moreover, it has very good physicochemical properties that are compatible with commercially available petroleum-based fuels, as mentioned by numerous researchers (Imdadul et al., 2016). This feedstock was provided by a local market supplier at Kuala Lumpur, Malaysia. *Calophyllum inophyllum* Linn belongs to Guttiferae or Clusiaceae family. It is a medium-sized tree up to 7 to 20 meters in height. Initially, it was abundantly available in Southeast and East Asia but now it is also widely cultivated in other tropics. *Calophyllum inophyllum* oil has a dark green color, insipid taste, and aromatic odor.

3.3 Advantages of *Calophyllum inophyllum*

Calophyllum inophyllum has the following benefits and advantages

- *Calophyllum inophyllum* is highly viable in nature and maintains high yields until 50 years.
- As it is non-edible, so it has no competition with other food crops.
- Its trees can easily grow on the seashore, where they can reduce abrasion, serve as windbreaks, protect crops, provide ecotourism, and maintain coastal demarcation.
- Its oil yielding capacity is higher than other raw materials like Jatropha.

- *Calophyllum inophyllum* oil-based biodiesel meets European Union EN 14214 and US ASTM D6751 standards.
- Its biodiesel has a high calorific value and better lubrication than that of pure diesel.
- Its biodiesel can be used as a potential alternative fuel to petroleum diesel.

3.4 Determination of Fatty acid composition

The *Calophyllum inophyllum* methyl ester's fatty acid composition (FAC) was determined by Gas Chromatography (GC) Agilent 7890. **Table 3.1** describes the GC operating conditions for the experiment.

Table 3.1: The GC operation modes to determine FAC

Parameters	Specification
Gas Used	Helium (83kPa)
Fuel Injection System	Split or split less than 1177, full EFC control
Temperature	250 °Celsius
Injection volume	1µL
Column	HP-INNO Wax (crossed-linked PEG), 0.32 mm X 30 mm, 0.25µm
Column 2 flow	Helium at 1 mL per minute constant flow
Oven	210 °Celsius isothermal
Column temperature	60 ° Celsius for 2 min. 10 ° Celsius per minute to 200 ° Celsius 5 ° Celsius per minute to 240 ° Celsius Hold 240 ° Celsius for 7 minutes
Split flow	100 mL per minute
Detector	250° Celsius, FID, full EFC control

3.5 Physicochemical properties measurement

The physicochemical properties of pure biodiesel and blended fuels have been performed at Energy Laboratory and Engine Tribology Laboratory at Mechanical Engineering Department, University of Malaya, Kuala Lumpur. The detail of all the machines, types of equipment, and methods used to investigate the fuel properties was shown in **Table 3.2.**

Table 3.2: Apparatus for measuring fuel properties

Properties	Appliances	Maker	Standard	Precision
Kinematic viscosity	SVM 3000, Automatic.	Anton Paar, UK.	D 445	± 0.35%
Density	SVM 3000, Automatic.	Anton Paar, UK.	D 4052	± 0.15 kg/m^3
Calorific value	C2000 Basic Calorimeter, Automatic.	IKA, UK.	D 240	± 0.15%
Flash Point	Pensky - Martens Flash Point, Automatic NPM 440.	Normalab, France.	D 93	± 0.12 °C

3.5.1 Determination of viscosity and density

Kinematic viscosity and density were investigated following ASTM D 445 and ASTM D 4052 by using automatic viscometer SVM 3000 (Brand: Anton Paar) as presented in **Figure 3.3.** Both density and kinematic viscosity of biodiesel and blends were measured together at the temperature of 15 °C and 40 °C respectively. While ASTM standard-setting was selected from the mode setting menu of the viscometer. When the viscometer is turned ON, it initializes to test itself then it gets ready to estimate the density and kinematic viscosity and displays the values on the measuring window. The measuring process repeats itself and shows the deviation for density and kinematic viscosity. When values of the first repetition are similar and within the prescribed limit, then ‘RESULT VALID’ appears on the screen. If these values are not within the limit, then it requires one more refill until results get within the limit automatically.

Figure 3.2: Anton Paar Viscometer (SVM 3000)

Table 3.3: Anton Paar (SVM 3000) Viscometer Technical data

Parameter	Values
Kinematic viscosity	0.2 mPa.s to 20,000 mPa.s
Density	0.65 g/cm^3 to 3.0 g/cm^3
Temperature	15 °Celsius to 105 °Celsius
Repeat variation of viscosity	0.1%
Repeat variation of density	0.0001 g/cm^3
Space requirements L×W×H	440 mm × 315 mm × 220 mm

3.5.2 Calorific value measurement

IKA C 2000 Bomb calorimeter with constant volume was used to measure the entire calorific and heating value of pure biodiesel in conformance with DIN 51900, ASTM 5468, and ASTM 4809, BS 1016 T5, ISO 1928 standard. The prescribed amount of biodiesel was combusted by using electric energy. A bomb calorimeter is shown in **Figure 3.4.** The details of all parameters of the calorimeter are mention in **Table 3.4.**

Figure 3.3: IKA C 2000 Bomb Calorimeter

Table 3.4: IKA C 2000 Bomb Calorimeter Technical Data

Monitoring	Details
The cycle of duties	Ongoing operations
Ambiance temperature	20°Celsius to 25°Celsius
Ambiance humidity	Approx. 80%
Usage level	2,000 m above sea level
Measuring limit	40,000 Joule

Measuring mode	Isoperibolic 25°Celsius Dynamic 30°Celsius Isoperibolic 30°Celsius Dynamic 25°Celsius
Isoperibolic measuring time	Approx. 20 minutes
Dynamic measuring time	Approx. 15 minutes
Oxygen operating pressure	30 bar
Oxygen tests pressure	40 bar
Cooling medium	Water via line
Dimensions	440 mm x 450 mm x 500 mm (W x D x H)
Weight	30 kg
Flow quantity	Min. 60 liters per hour Max. 70 liters per hour

To start, 0.5 ±0.02 g of biodiesel sample was weighted in the small crucible. This crucible was placed into a bomb head and thread was used to ignite the biodiesel sample completely. The bomb head was tightened up and oxygen-filled in the bomb from its pinhole at 20 atm pressure. Then the oxygen bomb and steel container were placed into the calorimeter. Next, poured 2000 ml of distilled water into the steel container and attached electrodes with the bomb. The calorimeter was covered with its lid, which also had a stirrer to make the water temperature constant. After that, standard-setting was selected on the panel of the calorimeter and the test was turned ON. After completion of the test, readings were noted down, bomb removed from the calorimeter, open the knurled valve knob to release the residual oxygen gas pressure. Then, unscrew and remove the bomb head unit. It was observed that all the samples got ignited. The heating and calorific value were measured from the rise of water temperature and by the mass of the biodiesel sample consumed in this procedure. The details of the entire calorific value of biodiesel samples were determined by:

- The weight of the biodiesel sample
- The heat capacity value of the calorimeter system.
- The increase in water temperature in the calorimeter's steel container.

3.5.3 Flash Point Measurement

The value of biodiesel’s flash point was determined by following standard method ASTM D93 on HFP 380 Pensky-Martens flash point tester is shown in **Table 3.5.** About 70 mL of biodiesel sample was transferred into the cup of the tester and placed inside the flash point-device and turned ON. The regulators of the device regulated the temperatures until the boiling point was achieved. The biodiesel samples were stirred continuously and checked from time to time until the flash point reached. The device recorded the temperature readings of a flash point on the panel.

Figure 3.4: Norma Lab (France) NPM 440 Flash Point Tester

Table 3.5: Norma Lab (France) NPM 440 Flash Point Tester

Monitoring	Values
Temperature limits	40 °Celsius to 360 °Celsius
Ignition type	Gas / electric
Stirring speeds	120rpm / 250 rpm
Sensing system	Differential-thermocouple
Dimension (L×W×H)	230 mm × 470 mm × 460 mm

3.5.4 Acid value, cetane number, and iodine value determination

The acid value is the amount of KOH in milligrams required to neutralize the free fatty acids in 1 gram of the oil sample. The acid value was determined from this equation 3.1:

$$AV = \frac{MW \times N \times V}{W} \tag{3.1}$$

Where,

MW ≡ Molecular weight of potassium hydroxide (KOH)

N≡ Normality of potassium hydroxide (KOH) solution.

V≡ Volume of potassium hydroxide (KOH) solution used in the titration.

W ≡ Weight of the biodiesel sample

The saponification number (SN), iodine value (IV), and cetane number (CN) were also measured by the following given equations (S. Imtenan, H. H. Masjuki, M. Varman, I. M. Rizwanul Fattah, et al., 2015), where Ai, D, and MWi symbolizes the proportion of each component, the number of double bonds and mass of each component respectively.

$$\mathrm{SN} = \sum \left(\frac{560 \text{ x Ai}}{\mathrm{MWi}} \right) \tag{3.2}$$

$$\mathrm{IV} = \sum \left(\frac{254 \text{ x D x Ai}}{\mathrm{MWi}} \right) \tag{3.3}$$

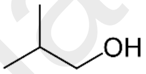
$$\mathrm{CN} = 46.3 + \left(\frac{5458}{\mathrm{SN}} \right) - (0.225 \text{ x IV}) \tag{3.4}$$

3.6 Selection of alcohol

The biodiesel blends with alcohol (as an additive) is an optimal solution for increasing commercial utilization (Rashedul et al., 2014). However, previous literature showed blends of diesel with low carbon chain alcohol or biodiesel, when burnt in diesel engine, have poor blending solubility, low cetane no, less miscibility, low calorific value, and long ignition delay (Atmanlı et al., 2015). In contrast, high carbon alcohols such as isobutanol lead to overcome these problems of lower types of alcohol. Because long carbon chain alcohols blends with diesel have:

- A higher calorific worth prompts a lower fuel utilization.
- Higher vitality than ethanol.
- Higher cetane no as compared to ethanol.
- Greater oxygen content as compared to biodiesel.
- Good miscibility and higher breaking point as compared to ethanol.
- Isobutanol as different alcohols is an oxygen-improved fuel with an oxygen substance of roughly 21.5%, which can fundamentally animate the burning procedure.

Table 3.6: Detail of isobutanol used for this research

Properties	Additives Used
CAS Number	78-83-1
Name	isobutanol
Chemical formula	$C_4H_{10}O$
Physical state	Colorless liquid
Molecular mass (g.mol)	74.122
Density@ 40 °Celsius (kg/m^3)	802
Viscosity @ 40 °Celsius (mm^2/s)	3.78
Boiling point	107.89°C
Flash point	35°C
Structure	

3.7 Preparation of the samples

The samples selected and determination of all physicochemical properties of biodiesel-diesel samples were carried out in laboratories of Mechanical Engineering Department, University of Malaya. The proportions of 5%, 10%, and 15% of isobutanol were added together with 5%,10% and 15% of *Calophyllum inophyllum* methyl ester to petroleum diesel for producing different fuel blends (CIB10, CIB20, iBu5CIB5, iBu10CIB10 and iBu15CIB15) to analyze the diesel engine characteristics. **Table 3.7** contains information about the fuel sample details that had been used for the experiment. The fuel blends were made by using a homogenizer mixer tool, which was clamped on a vertical stand and rotated at a speed of 3000 rpm for 30 minutes as shown in **Figure 3.6**. The properties of blends were measured and also compared with neat diesel and diesel-biodiesel blends.

Table 3.7: Fuel samples and blend information used for the research.

No	Type of Fuels	Specifications
1.	Diesel	100% diesel
2.	CIB10	10% *calophyllum inophyllum* biodiesel + 90% diesel
3.	CIB20	20% *calophyllum inophyllum* biodiesel + 80% diesel
4.	iBu5CIB5	5% iso-butanol + 5% *calophyllum inophyllum* biodiesel + 90% diesel
5.	iBu10CIB10	10% iso-butanol + 10% *calophyllum inophyllum* biodiesel + 80% diesel
6.	iBu15CIB15	15% iso-butanol + 15% *calophyllum inophyllum* biodiesel + 70% diesel

Figure 3.5: Setup for the homogenous fuel blending process

3.8 The engine test bed

Heat Engine Laboratory of Mechanical Engineering Department at UM was used to perform tests. A 4-stroke, single-cylinder, water-cooled, naturally aspired, DI diesel engine was used for this study. The engine requirements are set out in **Table 3.8.** The velocity of the engine was measured and adjusted from the eddy current dynamometer. To estimate exhaust gas and entry air temperatures, lubricating oil, and cooling water temperature, thermocouples of the K-type were linked. To evaluate the fuel flow, a Kobold ZOD positive displacement-type flow meter was used.

The engine fuel system consists of two tanks connected with two-way valves for normal diesel and test fuel, lead to combustions and enable rapid fuel exchange. Performance information was gathered from the Dynomax 2000 data acquisition system, which was tracked using the Dynomax 2000 software.

Table 3.8: Specification of a single-cylinder diesel engine in Heat Engine Laboratory, Department of Mechanical Engineering, University of Malaya

Details of Engine	
Model	TF-120-M
No of cylinder / stroke	1 / 4
Cylinder bore / stroke	92 mm / 96 mm
Displacement	638 cc
Compression ratio	17.7
Type of Injection	Direct injection (DI)
Injection timing / pressure (kg/cm^2)	17 º BTDC / 200
Maximum Speed	2400 rpm
Rated output	7.7 kW
Maximum rated output	8.8 kW at 2400 rpm
Cooling system	Radiator cooling system
Injection System	Pump line nozzle
Dynamometer Details	
Model	SAJ SE-20 eddy current
Max power	20 kW
Max speed	10,000 rpm
Max torque	80 Nm
Water consumption for max power	14 l/min
Water pressure	23 lbf/in^2
Electricity requirement	220 V, 60 Hz, 0.5 A

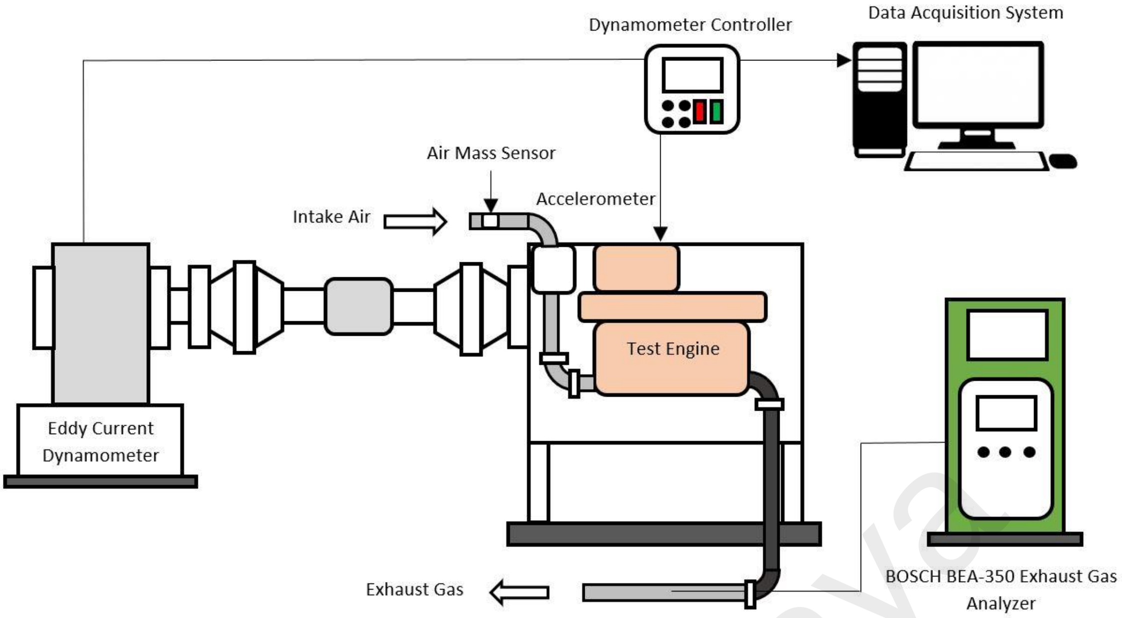


Figure 3.6: Engine setup for the experiment

3.9 Operating conditions of the engine

The experiment was conducted at varying loads starting from 1.97, 2.95, 3.93, 4.92, 5.91, 6.89, and 7.88 brake mean effective pressure (BMEP) bar at the constant throttle condition. The temperature of lubrication oil in the engine was maintained from 85 °Celsius to 90 °Celsius. Before each run, the ambient condition was made sure to be almost identical which are around 27-28 °C temperature and relative humidity around 45-55 %. In the beginning, the engine stabilized by running with neat diesel than it was run on alcohol – biodiesel mixtures. After the steady-state was achieved, the engine was run on neat diesel and information was saved in the data acquisition system for the different engine loading conditions. All the data from every tested blend were saved and noted when the engine constant and stable at the needed operating conditions. After the first test end, the engine was let run for another 60 seconds for ensuring the remaining fuel in the fuel system was removed. For the next test, repeat the previous procedure with the rest of fuel samples.

3.10 Analysis of engine performance

3.10.1 Brake specific energy consumption

Brake specific energy consumption (BSEC) is defined as a ratio of energy obtained by burning fuels for an hour to the actual energy obtained at the wheels. BSEC of diesel engines depends on the relationship between Brake-specific fuel consumption (BSFC) and the calorific value of any fuel (Mishra & Nayak, 2018). BSFC is defined as the ratio of mass fuel consumption with brake effective power and it is inversely proportional to thermal efficiency (Enweremadu & Rutto, 2010).

Specific fuel consumption of biodiesel fuel is expected to be increased by 13% as compared to the specific fuel consumption of diesel fuel because biodiesel has low heating value (N. Kumar, Varun, & Chauhan, 2013). In other words, the heating value of biodiesel is compensated by greater fuel consumption.

The following equation (3.1) was used to calculate the brake specific fuel consumption

$$BSFC(gm/kWh) = \frac{m_f}{BP} \tag{3.1}$$

Where,

m_f = Fuel consumption, kg/h,

BP = Brake power, kW

The brake specific energy consumption (BSEC) is indicative of the efficiency of obtaining energy from the fuel to produce unit power. The BSEC is a more exact measure than specific fuel consumption for comparing calorific values of different fuels. BSEC is calculated as a product of its lower heating value and BSFC (Nanthagopal et al., 2019). The brake specific energy consumption calculated using the following equation (3.2) :

$$BSEC = BSFC \; x \; C.V \qquad [3.2]$$

Where,

$C.V$ = Calorific value of the fuel.

3.10.2 Brake power

Brake power (BP) is the engine's ultimate output defined as the engine torque product and angular speed. The engine braking force is directly proportional to the engine's torque and speed. Some research has shown that the oxygen content of biodiesel is lower than that of fossil fuels, resulting in a decreased calorific value (Yesilyurt, Arslan, & Eryilmaz, 2018). High values of kinematic viscosity and density affect the atomization of fuel, slowing down the rate of mixing between air and fuel. Weak atomization rates contribute to erratic combustion and ultimately reduced brake power (Abedin et al., 2014).

Brake power was measured from the following equation (3.3):

$$BP = \frac{2\pi NT}{60} \qquad [3.3]$$

Where N is the speed of the engine in rpm and where T is the torque of the engine.

3.10.3 Brake thermal efficiency

Brake Thermal Efficiency is the energy-generated ratio of fuel injection (Basha, Gopal, & Jebaraj, 2009). The opposite of thermal efficiency is therefore often called brake specific energy consumption. For experimental engine analysis, brake energy is widely used to evaluate thermal efficiency, the result obtained is brake-specific efficiency. In addition to their heating value, this parameter is more suitable for comparing the efficiency of various fuels than energy usage. Some scientists (N. Kumar et al., 2013; Sayin, Gumus, & Canakci, 2012) would have seen no obvious change in thermal efficiency in the use of biodiesel. The brake thermal efficiency was calculated from the following equation (3.3):

$$BTE\ (\%) = \frac{BP\ (kW) \times 100}{C\ \left(\frac{MJ}{kg}\right) \times m_f (g/kwh)} \qquad \textbf{[3.3]}$$

Where, m_f = Fuel consumption and C = Calorific value

3.11 Analysis of exhaust emission

Biodiesel is renewable and environmentally friendly fuel than ordinary petroleum-based diesel. In this research, the test of test blended fuel's emissions was measured on a diesel engine and compared with emissions of neat diesel fuel. The carbon monoxide, carbon dioxide, hydrocarbons and nitrogen oxides emissions were evaluated using an exhaust gas analyzer. The gas analyzer reading was varied every two seconds, so at five different times, five readings were taken. The average values from all three reading were recorded. Smoke opacity was evaluated using the smoke tester device earlier listed in the experiment's user equipment section 3.6. The first fuel to be used as the baseline was neat diesel and the average fuel run time in the engine was 15 minutes. The emission reading data were taken after the exhaust and cooling water temperatures of the engine were stable. The emissions were analyzed using an exhaust gas analyzer and a special computer program recorded readings of each emission to determine the mean values. For other blended fuels, the exact process has been repeated.

3.11.1 Exhaust gas analyzer

The fuel burnt in the diesel engine and exhaust emissions of the engine were measured using the Bosch series BEA-350 exhaust analyzer. Bosch series RTM-430 was used to measure the intensity of smoke. The emission data was recorded three times and average values were taken to retain the accuracy of the measurement. Also, the data was collected after 10 to 15 minutes, when the engine achieved a stable condition and during the test run for each fuel sample. **Figure 3.7** shows the image of the BOSCH gas analyzer and the gas analyzer information.

Figure 3.7: BOSCH BEA-350 exhaust gas analyzer

Table 3.9: Data accuracy of exhaust gas analyzer

Equipment	Measuring method	Measurement	Upper limit	Accuracy
Gas analyzer	Non-dispersive infrared	CO	0 to 10% by volume	±0.00099
	Non-dispersive infrared	HC	0 to20,000 ppm	±1.1 ppm
	Electrochemical	NO	0 to 5,000 ppm	±1.2 ppm

CHAPTER 4: RESULT AND DISCUSSION

4.1 Introduction

The results and findings of the study are described in both text and graphic form following the desired goals in this chapter. Detailed analysis and review of the findings are given in each step with the correct comparison and scientific explanation. The classification of crude oils, biodiesel's fatty acid composition made from crude *Calophyllum inophyllum* oil and their biodiesel physicochemical properties and their mixtures together and without isobutanol were discussed. The performance and emission profiles of the modified and unmodified fuels were subsequently illustrated graphically.

4.2 Crude oils and biodiesel characterization

4.2.1 Crude *Calophyllum inophyllum* oil

As shown in **Table 4.1**, crude *Calophyllum inophyllum* has a far lower kinematic viscosity, density and acid value.. The main reason for the higher amount of catalyst required for biodiesel production lies in *Calophyllum inophyllum* oil. *Calophyllum inophyllum* oil has a high acid value and must first be esterified before transesterification of biodiesel production.

Table 4.1: Physicochemical properties of crude *Calophyllum inophyllum* oils

Properties	Units	Standards	*Calophyllum inophyllum* oil
Density at 15 °C	kg/m^3	ASTM D 4052	935
Kinematic viscosity at 40 °C	mm^2/s	ASTM D 445	52.50
Kinematic viscosity at 100 °C	mm^2/s	ASTM D 445	11.68
Flash point	°C	ASTM D 93	219
Calorific value	MJ/kg	ASTM D 240	39.3
Acid value	mg KOH/g	ASTM D 664	15

4.2.2 The fatty acid composition of *Calophyllum inophyllum* biodiesel

Saturated fatty acids contain only one or a single bond. It is classified as an unsaturated fatty acid that comprises two, double or more bonds. Gas Chromatography (GC) Analyzer calculated the fatty ester profile of *Calophyllum inophyllum* methyl ester used in this study. **Table 4.2** demonstrates the fatty acid composition of *Calophyllum inophyllum* biodiesel. It also shows *Calophyllum inophyllum* biofuel's quantitative fatty acid composition results, found to contain 32.6 percent saturated and 66.6 percent unsaturated acids.

Table 4.2: Fatty acid composition of *Calophyllum inophyllum* biodiesel

Carbon structure	Name of fatty acid composition	Chemical formula	Molecular mass	Composition (wt.%)
				CIME
C12:00	Laurate	$CH_3(CH_2)_{10}COOCH_3$	214.34	–
C14:00	Myristate	$CH_3(CH_2)_{12}COOCH_3$	242.4	–
C16:00	Palmitate	$CH_3(CH_2)_{14}COOCH_3$	270.45	14.7
C16:01	Palmitoleate	$CH_3(CH_2)_5CH=CH(CH_2)_7COOCH_3$	268.43	0.2
C18:00	Stearate	$CH_3(CH_2)_{16}COOCH_3$	298.5	16.6
C18:01	Oleate	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH3$	296.49	38.2
C18:02	Linoleate	$CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOCH_3$	294.47	27.6
C18:03	Linolenate	$CH_2(CH_2CH=CH)_3(CH_2)_7COOCH_3$	292.46	0.3
C20:00	Arachidate	$CH_3(CH_2)_{18}COOCH_3$	326.56	0.9
C20:01	Eicosenoate	$CH_3(CH_2)_{16}CH=CHCOOCH_3$	324.54	0.3
C22:00	Behenate	$CH_3(CH_2)_{20}COOCH_3$	354.61	0.3
C24:00	Lignocerate	$CH_3(CH_2)_{22}COOCH_3$	382.66	0.1
Saturated				32.6
Monounsaturated				37.8
Polyunsaturated				27.9
Unsaturated				65.7

4.2.3 Fuel properties analysis

The fuel's physicochemical properties, such as viscosity, flash point, calorific value, cetane number, and density, have a significant impact on engine performance and emission features. Many researchers focused on kinematic viscosity, flash point, density, and calorific value to assess fuel performance (Kalam et al., 2003; Machacon et al., 2001; Ndayishimiye & Tazerout, 2011; Sahoo et al., 2009). Density and viscosity are the most critical parameters of fuel among these properties because fuel flows through various orifices, nozzles, and pipes. Density and viscosity also have a major influence on the atomization of fuel, which affects the quality of combustion, characteristics of performance and emission. Biodiesel is lower in density and viscosity than diesel. The higher types of alcohols have slightly lower calorific values than biodiesel, which means the blends must gain equivalent calorific values than diesel and biodiesel. There is also a dropping flash point. A flash point above 66 °Celsius is usually considered safe (Agarwal & Das, 2001). All the mixtures are therefore safe to use in a diesel engine. Normally, the injection system of diesel engines calculates the fuel by volume, hence the engine's output power is the difference in the density of fuel and the mass injected. In addition, the large fuel modulus depends on the density of the fuel and shows how incompressible it is. Low compressible fluid in the fuel line speeds up the pressure to rapidly inject into the combustion chamber, while it has recently been pumped into the combustion chamber for extremely compressible fuel. Thus advanced injection timing for high density fuel. **Table 4.3** displays the calculated values and their blends of various physicochemical properties of *Calophyllum inophyllum* biodiesel. Biodiesel's kinematic viscosity usually depends on the unsaturated fat element (A. Sanjid et al., 2014). **Table 4.3** demonstrates a reduction of the kinematic viscosity of biodiesel mixtures as compared with that of pure biodiesel. In this research, *Calophyllum inophyllum* biodiesel's kinematic viscosity met the standards of ASTM D6751 and EN 14214.

The current study shows a 4.3 percent greater density and 30.6 percent higher viscosity than diesel was obtained from the pure *Calophyllum inophyllum* biodiesel. Once mixed with diesel, however, the density and viscosity of the biodiesel are increasing.

Table 4.3: Physicochemical properties of diesel, *Calophyllum inophyllum* biodiesel, and blended fuels

Parameters	Unit	ASTM standard	Diesel	iBu100	CIB100	CIB10	CIB20	iBu5CIB5	iBu10CIB10	iBu15CIB15
Density @ 15°C	(kg/m^3)	D4052	830.80	805.20	868.20	834.69	838.43	831.54	832.13	832.72
Kinematic viscosity @ 40°C	(mm^2/s)	D445	3.39	2.55	4.88	3.68	3.83	3.57	3.75	3.91
Flash point	(˚C)	D93	68.70	29.00	92.50	71.23	73.61	67.99	67.31	66.52
Calorific value	(MJ/kg)	D240	44.89	35.25	39.37	44.49	43.94	44.28	43.52	42.77
Acid value	(mgKOH/g)	D664	0.075	0.026	0.400	0.113	0.155	0.094	0.118	0.131
Cetane number	-	D4737	48	13	56	49	50	47	45	44

4.3 Engine performance characteristics

4.3.1 Brake specific energy consumption

Brake specific energy consumption (BSEC) is the efficient of energy obtained from given fuel. BSEC also defined as the product of BSFC times to calorific value of fuel and compared those fuel with different calorific values. BSEC is a more precise measure for comparing fuels with different calorific values. It is understood that the lower amount of BSEC is notably desirable and proving that more operative the utilization of fuel energy to produce effective work. **Figure 4.1** shows the variation of the BSEC as a function of engine load (BMEP). The BSEC of all the tested blends decreases with an increase in engine load. It can also be observed that the BSEC for CIB10, CIB20, iBu5CIB5, iBu10CIB10, and the iBu15CIB15 blend is higher compared to neat diesel, with an average increase of 7.7%, 6.4%, 9.3%, 14.2% and 17.5%, respectively. The slight increase of BSEC for all the fuel blends was caused by the lower energy content of the biodiesel and its modified blends (Satputaley, Zodpe, & Deshpande, 2018). The heating value of CIME and isobutanol is lower than neat diesel with 11% and 26%, respectively, resulting in lower per unit mass of heating values of the modified blends. Therefore, a higher amount of fuel blend is needed to produce the same engine power output of a diesel engine in comparison to the neat diesel. Similar findings were observed by Ashok, Nanthagopal, and Vignesh (2018) who determines the conceivable reason of BSEC to increased were because of low calorific value, high boiling point and a viscosity value of the fuel. By increasing the percentage of biodiesel in the blended fuels, BSEC will increase due to the decrease of calorific value in the blended fuels.

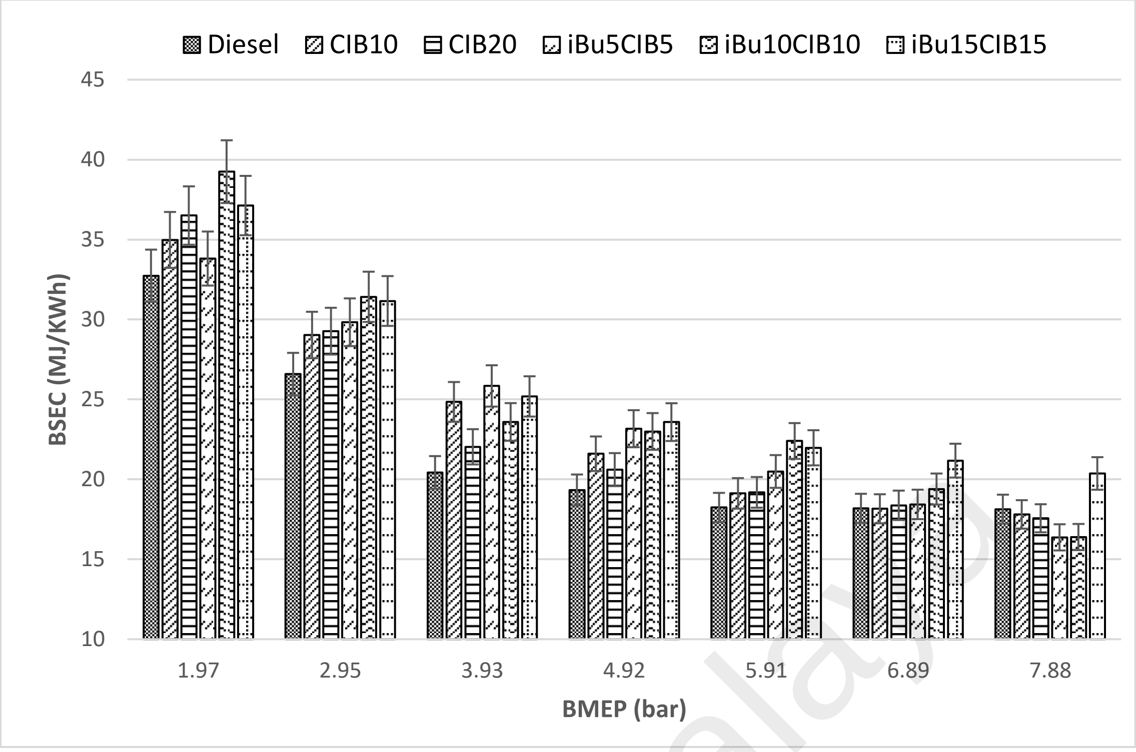


Figure 4.1: Trend of Brake Specific Energy Consumption (BSEC) with varying load BMEP.

4.3.2 Brake thermal efficiency

Brake thermal efficiency (BTE) is a measure of the efficiency of an engine to produce brake power from thermal input over the fuel amount supplied. BTE can be expressed as the ratio of brake power (the amount of power available at the crankshaft with frictional losses) and fuel power (the product of the calorific value of fuel and mass flow rate). **Figure 4.2** represents the variation of brake thermal efficiency of the tested fuel at different engine loads (BMEP). It can be observed that the results of the BTE are a stark contrast with a variation of BSFC of the tested fuel blends in Figure 4.2. The BTE was low at lower engine load and subsequently increase with higher engine load. Besides that, the maximum BTE of the tested fuel blends was observed at the highest engine load (BMEP) of 7.88 bar, whereby the CIB10, CIB20, iBu5CIB5, iBu10CIB10, and iBu15CIB15 blend produced the maximum BTE of 22.14%, 21.29%, 22.99%, 22.57%, and 17.84%, respectively. It can be seen that the CIB10, CIB20, iBu5CIB5, iBu10CIB10, and iBu15CIB15 blend shows an average reduction of 6.3%, 5.1%, 8.7%, 12.3%, and 19.3%, respectively, relative to neat diesel. The increasing isobutanol content in the blend causes a slight drop in BTE. This is due to the lower energy content of isobutanol compared to net diesel and biodiesel. Similar findings were noted by (Sanli et al., 2015), whereby the BTE of the biodiesel and alcohol blend was lower than diesel.

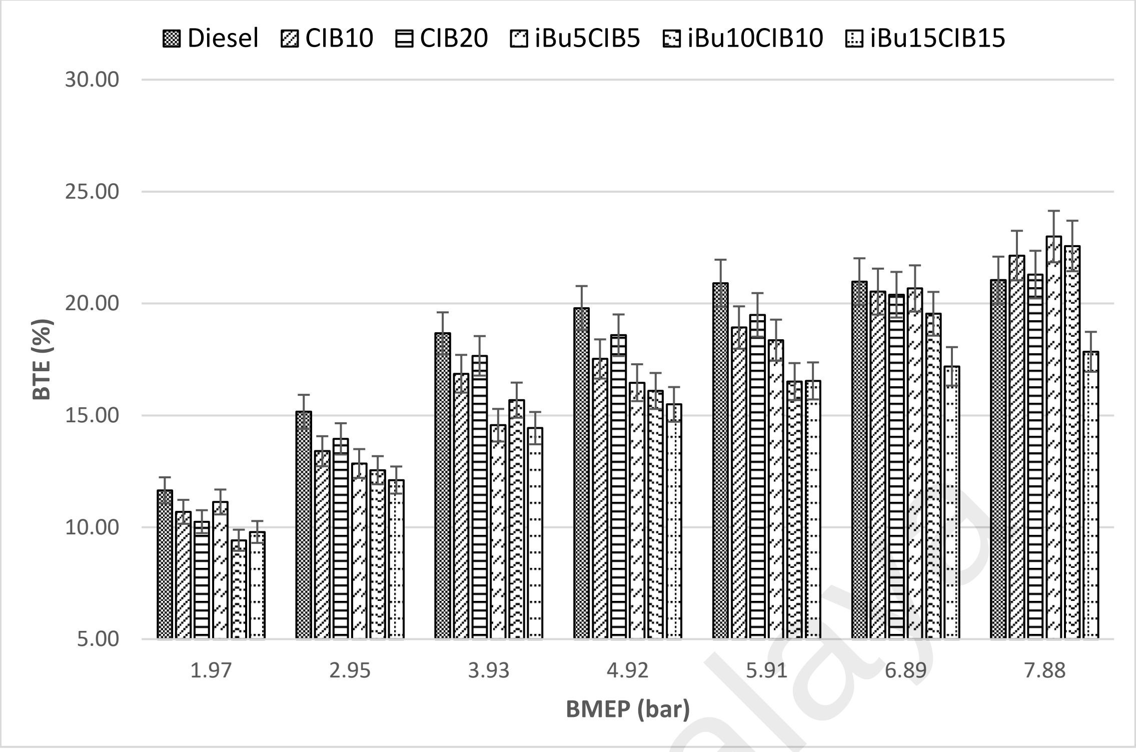


Figure 4.2: Trend of Brake Thermal Efficiency (BTE) with varying load BMEP.

4.3.3 Exhaust gas temperature

Exhaust Gas Temperature (EGT) is a measure of the gas temperature at the exhaust manifold. The EGT can be used for optimizing fuel economy, diagnosis and prognosis of an engine (Von Moll, Behbahani, Fralick, Wrbanek, & Hunter, 2014). **Figure 4.3** shows the variation of exhaust gas temperature (EGT) of the tested blend at different engine load (BMEP). It can be noted that the EGT of all the tested fuels was increased with the increase of engine load. The EGT of all tested fuels reaches maximum (290 – 420 °C) at engine load (BMEP) of 7.88 bar. The EGT for all the fuel blends increases with the increase of engine load is due to higher fuel consumption of the fuel inside the engine to meet load requirements. Besides that, it can be observed that the EGT of the CIB10, CIB20, iBu5CIB5, iBu10CIB10, and iBu15CIB15 blend shows an average increment of 24.5%, 27.2%, 21.8%, 17.6%, and 22.2%, respectively, relative to neat diesel. The presence of isobutanol as the ternary blend would result in a reduction of EGT in comparison with the binary blend of CIME in diesel. In fact, the CIB5iBu5 and CIB10iBu10 blend give a lower increment of EGT than CIB10 and CIB20, respectively. This may due to the higher heat of vaporization and lower cetane number of isobutanol than the CIME, which is reflected by a drop in EGT (M. Yusoff et al., 2018). Nevertheless, the increasing amount of the CIME in the blends would result in lower vapor pressure, which results in the delayed ignition, poor atomization, and problematic combustion, and eventually causes a more distinct rise of EGT.

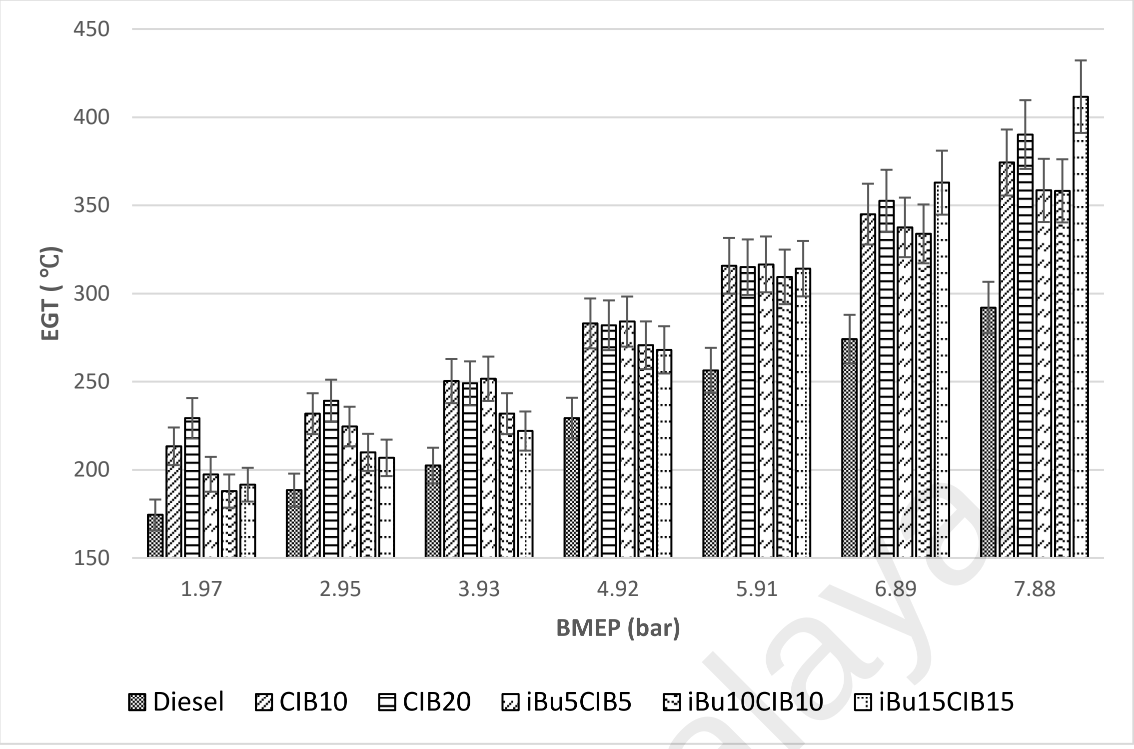


Figure 4.3: Trend of Exhaust Gas Temperature (EGT) with varying load BMEP.

4.4 Engine emission characteristics

4.4.1 Hydrocarbons (HC)

Hydrocarbon emitted by the burning of heterogeneous air/fuel mixture in an engine. **Figure 4.4** shows the result of HC emissions for all tested fuel at different engine load (BMEP). It can be monitored that the HC emission concentration of all the tested fuel was higher at lower load condition, while decreases with increasing engine load (1.97 bar to 9.88 bar). Besides that, it can be observed that CIB10 blend produced the lowest concentration of HC emissions among the tested fuel blends with an average reduction of 26.85% relative to that of neat diesel. The CIB20 and CIB5iBU5 blend were produced a lower concentration of HC emissions by an average reduction of 20.06% and 12.04%, respectively with respect to neat diesel. However, the additional of isobutanol in the blends increase the concentration of HC emissions. In fact, the CIB10iBu10 and CIB15iBu15 blend show a higher concentration of HC emissions, with an average increment of 15.12% and 20.68%, respectively with respect to neat diesel. This condition is due to a higher number of cetane that results in shorter delays and better combustion. This reveals the strong atomization of CIB10, thereby demonstrating a shorter time frame and leading to improved combustion due to low HC emissions (Suhaimi et al., 2018). The higher form of the HC emissions from blends with alcohols were because of incomplete combustion in the cylinder engine, whereby the inhomogeneous charge of fuel mixing and air which cause an increase of HC emissions. It is also can be found that the presence of isobutanol in fuel blends increase the formation of HC emissions. This is due to the higher heat of vaporization of isobutanol than the diesel fuel, which then results in higher HC formation (Rakopoulos et al., 2010). Besides that, isobutanol has a lower cetane number than diesel fuel, thus it reduces the cetane number of the ternary blends of CIB10iBu10 and CIB15iBu15, which marks in a longer ignition delay for the blended fuel. Therefore, it requires additional time for the fuel blend to evaporate, lead to increasing lean outer flame zone and eventually increase in HC emission formation (L. Wei, C. Cheung, & Z. Huang, 2014).

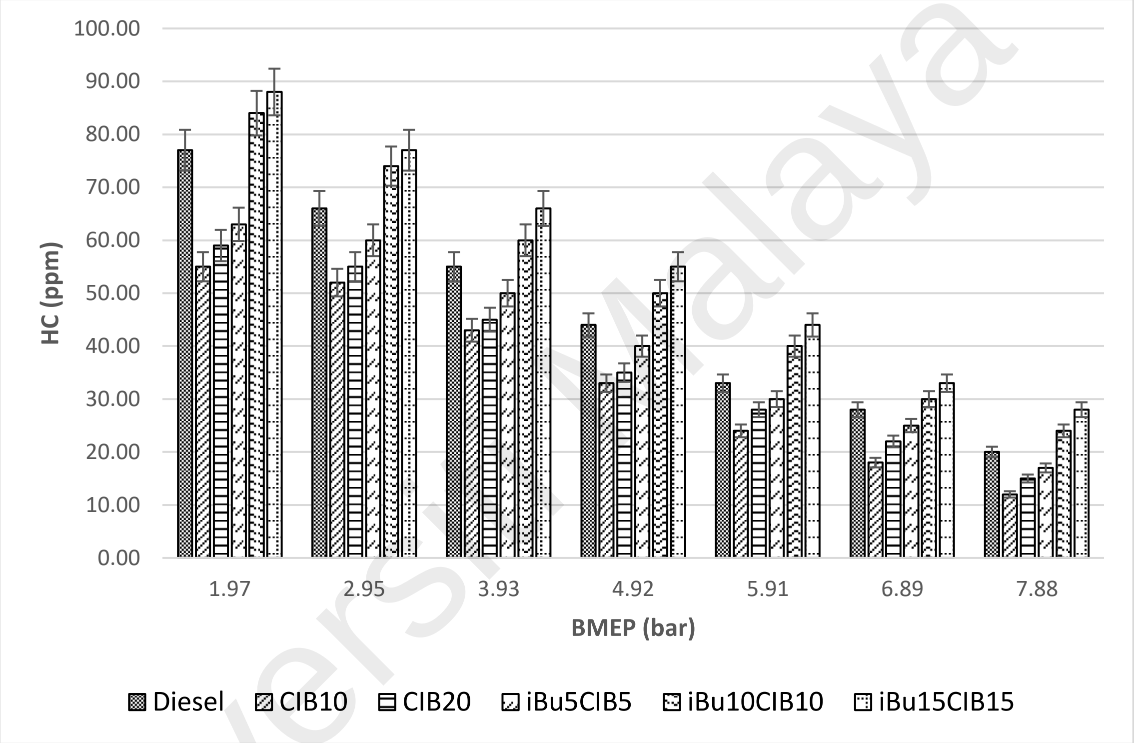


Figure 4.4: Trend of Hydrocarbons (HC) emission with varying BMEP.

4.4.2 Carbon monoxide (CO)

Carbon monoxide (CO) is produced in the incomplete combustion of carbon-containing fuel in an internal combustion engine. **Figure 4.5** shows the result of CO emission with varying engine load (BMEP). The trend of CO emissions is nearly to HC emissions, where the concentration of CO emissions is higher at lower engine load and vice versa. The formation of CO emission is lower at higher engine load due to higher in-cylinder temperature (L. Wei et al., 2014). It is apparent that the CIB10, CIB20, iBu5CIB5, iBu10CIB10, and iBu15CIB15 blend produces a lower concentration of CO emissions relative to that of neat diesel, with an average reduction of 6.6%, 10.2%, 16.7%, 25.8%, 33.9%, respectively. The significant reduction of CO emissions is due to the presence of oxygen in isobutanol and CIME, which then improves the combustion of fuel, and consequently results in lower incomplete combustion product of CO emissions. A similar result were observed by B. R. Kumar, Saravanan, Rana, and Nagendran (2016) and Alptekin (2017).

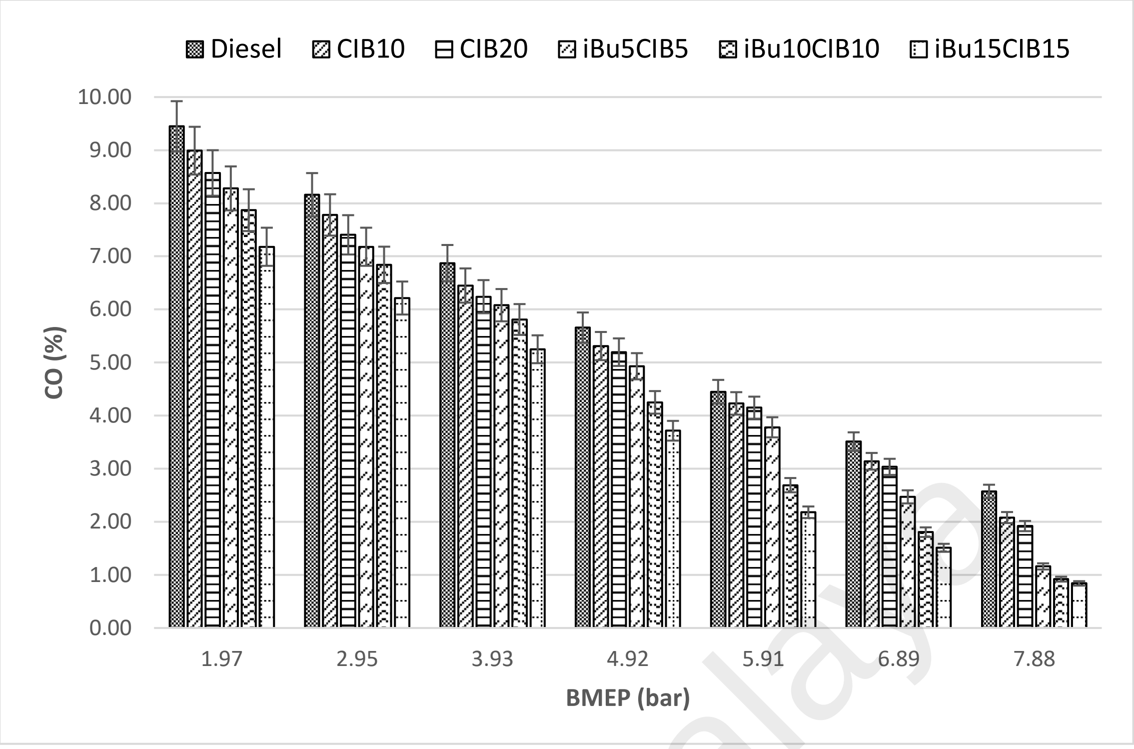


Figure 4.5: Trend of Carbon monoxide (CO) emission with varying BMEP.

4.4.3 Carbon dioxide (CO_2)

All fuels, which contain carbon in their molecular structure produce CO_2 after combustion. The CO_2 emissions from the exhaust of the engine describe the full combustion of the fuel inside the engine. **Figure 4.6** shows the result of CO_2 emission with varying engine load (BMEP). From the graph, it can be observed that the concentration of CO_2 emissions of blends fuel containing biodiesel and isobutanol are higher than neat diesel at all engine load range. On average, it is shown that the concentration of CO_2 emissions of the CIB10, CIB20, iBu5CIB5, iBu10CIB10, and iBu15CIB15 blend increased by 5.7%, 10.8%, 8.8%, 4.6% and 7.7%, respectively, relative to neat diesel. A greater amount of CO_2 emissions produced by the engine is due to the presence of more oxygen contents in fuel blends, which then produces more complete combustion, as well as reducing incomplete combustion products such as CO emissions (Jayabal, Thangavelu, & Subramani, 2020). A similar finding was observed whereby the presence of the oxidizing agent in the biodiesel such as hydroxyl radical OH and oxygen contents enhanced the conversion of CO to CO_2 in the emissions (Karabektas & Hosoz, 2009). Therefore, this indicates that the fuel combustion could be improved by the addition of biodiesel and isobutanol in the blend. The findings from exhaust emissions show that the increased CO_2, as the combustion becomes more complete, is coherent with the decreasing CO and HC emissions (Alptekin, 2017).

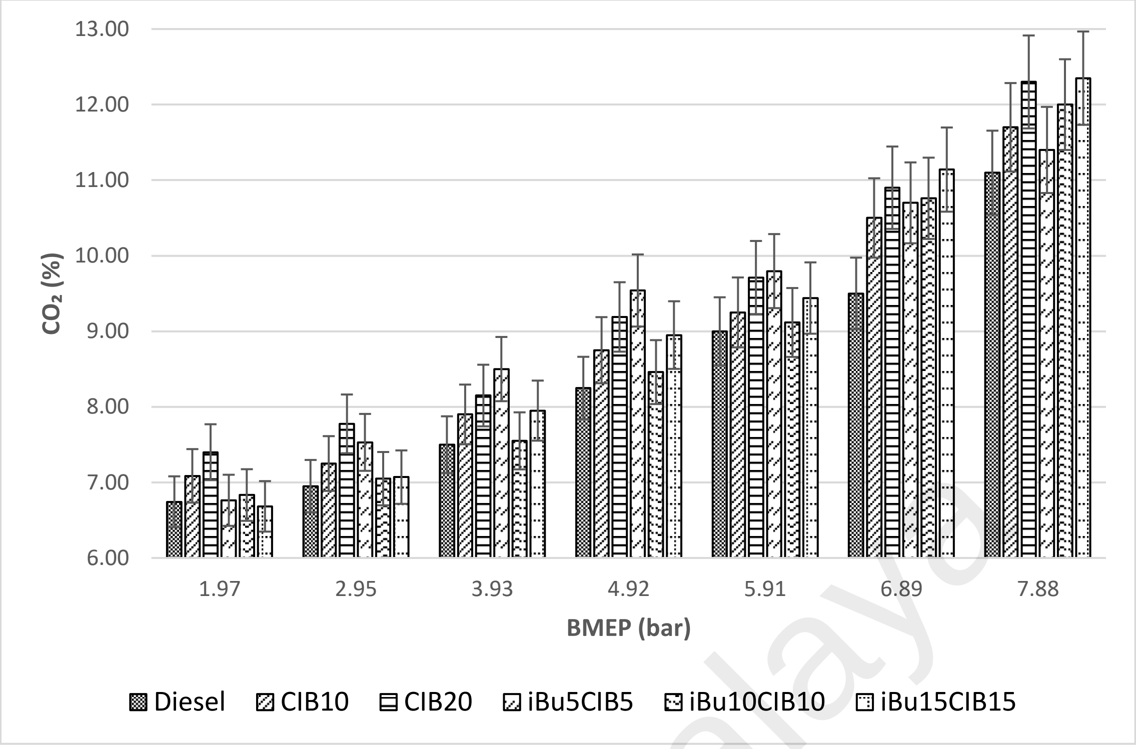


Figure 4.6: Trend of Carbon dioxide (CO_2) emission with varying BMEP.

4.4.4 Nitrogen oxides (NOx)

Nitrogen oxides (NOx) are produced by the endothermic reaction of nitrogen and oxygen takes place inside the engine cylinder during the combustion cycle at high temperature. **Figure 4.7** depicts the result of NOx emission with varying engine load (BMEP). It can be noted that by increasing the engine load, the concentration of NOx emissions of the blends fuel containing biodiesel and isobutanol is significantly higher than the neat diesel. The NOx emissions increase at higher engine load are due to more injection and combustion of fuel inside the cylinder (Yang, Wei, Cheung, Tang, & Huang, 2017). On average, the concentration of the CIB10, CIB20, iBu5CIB5, iBu10CIB10, and iBu15CIB15 blend increased by 10.96%, 23.11%, 4.56%, 16.19% and 6.86%, respectively, relative to neat diesel. The increase of NOx emissions is due to the higher oxygen concentration of the fuel blends containing biodiesel and isobutanol, which leads to a higher temperature of the mixture during combustion of the fuel and EGT, especially at higher engine load. As alcohol fuels contained more oxygen contents as compared to petroleum diesel fuel, this extra oxygen content in the fuel increase the temperature of the combustion mixture. This higher temperature of the combustion process enhanced the formation of NOx emissions (Sayin et al., 2012). Besides that, it can be observed that the presence of isobutanol in the ternary blends could reduce the formation of NOx emissions in comparison with the binary blend of CIME in diesel. In fact, the ternary blend of iBu5CIB5 and iBu10CIB10 produces lower CO emissions in comparison to a binary blend of CIB10 and CIB20 with an average of 5.76 and 5.62%, respectively. Isobutanol which has a higher heat of vaporization and lower cetane number reduces the exhaust gas temperature and consequently releases lower NOx emission concentration (Jayabal et al., 2020).

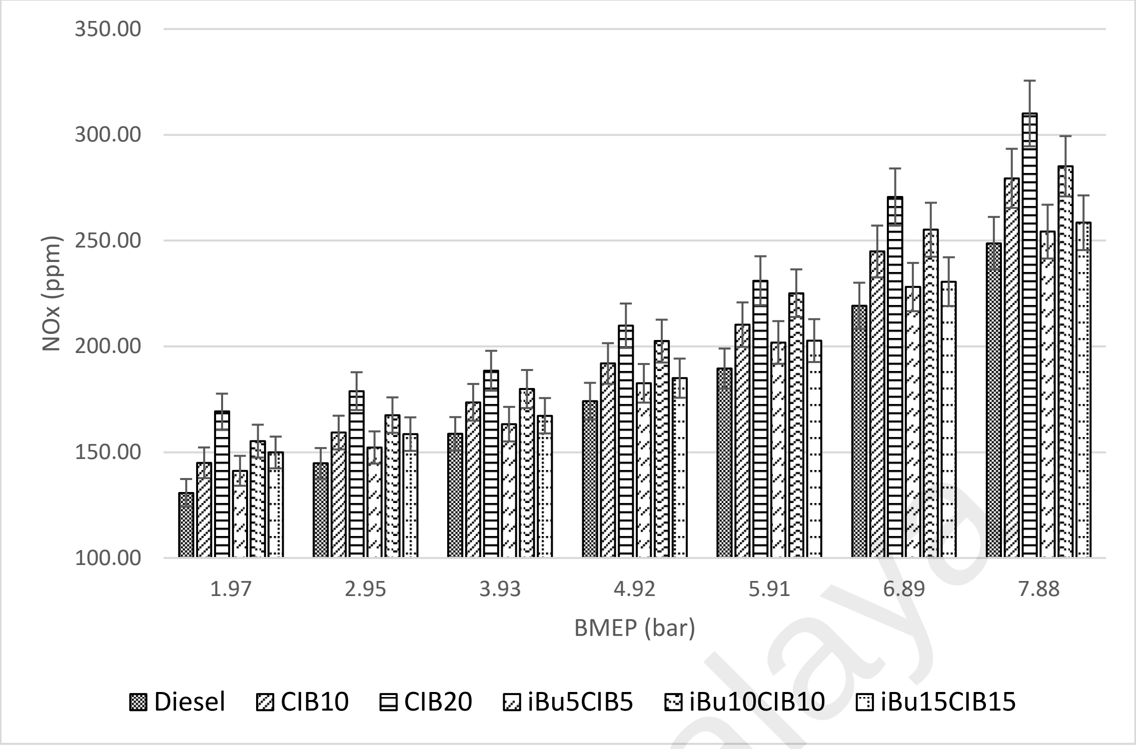


Figure 4.7: Trend of Nitrogen oxides (NOx) emission with varying BMEP.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this research, the effect on engine performance and exhaust emission characteristics of isobutanol-blended with *Calophyllum inophyllum* biodiesel and diesel were examined and compared with neat diesel fuel in a single cylinder diesel engine at various engine load with BMEP (1.97–7.88 bar). The following conclusions are drawn based on the results of this experiment:

- The ternary fuel blends containing isobutanol in biodiesel-diesel shows reduction in density, kinematic viscosity, flash point and cetane number relative to that of the binary fuel blends. However, both binary and ternary fuel blends have lower calorific value with respect to neat petroleum diesel.
- The addition of isobutanol and CIB in the fuel blend shows a slight increase in BSEC and EGT and a minimal drop in BTE as compared to that of neat diesel. Besides that, the presence of isobutanol in ternary blend reduces EGT with respect to the binary blend due to lower cetane number and higher heat of vaporization of the alcohol.
- In terms of exhaust emission characteristics, the CIB10 blend shows the largest reduction of HC emissions among the tested fuel blends. The addition of isobutanol in fuel blends increases the formation of HC emissions relative to neat. Meanwhile, all the tested fuel blends containing isobutanol and CIB show a decreasing trend in CO emissions and minimal increase in CO_2 emissions due to improving complete combustion. The fuel blends show a slight increase in NOx emissions. However, the addition of isobutanol in the ternary blend reduces

NOx formation in comparison with the binary blend due to a lower higher temperature of the mixture during combustion and EGT.

In general, the addition of isobutanol with *Calophyllum inophyllum* biodiesel showed the deficient result of the engine performance but improves on exhaust emission characteristics. The remarkable properties of isobutanol and CIB in the fuel blends reduce exhaust emissions of a diesel engine. Therefore, it can be concluded that higher alcohol can be blended with a lower volume ratio in order to achieve the desired engine performance and compromise emissions level.

5.2 Recommendations

The following are recommendations for future studies.

- Consideration to attempt to blend isobutanol with other kinds of biodiesel fuel supply to improve the fuel characteristics for the next research.
- The experiment focuses on performance and emission analysis but, for a deeper understanding of the impact of greater alcohols on biodiesel diesel blends, the combustion characteristics can be studied in the future.
- Further testing of multi-cylinder engines is suggested so that more test information may be generated which can be used to study mixed impacts of combustion and recirculation of engine gas.

REFERENCES

Abedin, M. J., Masjuki, H. H., Kalam, M. A., Sanjid, A., Rahman, S. M. A., & Fattah, I. M. R. (2014). Performance, emissions, and heat losses of palm and jatropha biodiesel blends in a diesel engine. *Industrial Crops and Products, 59*, 96-104. doi:10.1016/j.indcrop.2014.05.001

Alptekin, E. (2017). Emission, injection and combustion characteristics of biodiesel and oxygenated fuel blends in a common rail diesel engine. *Energy, 119*, 44-52. doi:10.1016/j.energy.2016.12.069

Anand, R., Kannan, G. R., & Karthikeyan, P. (2013). A Study of the Performance Emission and Combustion Characteristics of a Di Diesel Engine Using Waste Cooking Oil Methyl Ester-Ethanol Blends. *International Mechanical Engineering Congress and Exposition - 2012, Vol 6, Pts a and B*, 935-942.

Arbab, M. I., Varman, M., Masjuki, H. H., Kalam, M. A., Imtenan, S., Sajjad, H., & Fattah, I. M. R. (2015). Evaluation of combustion, performance, and emissions of optimum palm-coconut blend in turbocharged and non-turbocharged conditions of a diesel engine. *Energy Conversion and Management, 90*, 111-120. doi:10.1016/j.enconman.2014.11.017

Ashok, B., Nanthagopal, K., & Vignesh, D. S. (2018). Calophyllum inophyllum methyl ester biodiesel blend as an alternate fuel for diesel engine applications. *Alexandria Engineering Journal, 57*(3), 1239-1247. doi:10.1016/j.aej.2017.03.042

Ashraful, A., Masjuki, H., Kalam, M., Rizwanul Fattah, I., Imtenan, S., Shahir, S., & Mobarak, H. (2014). Production and comparison of fuel properties, engine performance, and emission characteristics of biodiesel from various non-edible vegetable oils: A review. *Energy Conversion and Management, 80*, 202-228.

Atabani, A. E., Silitonga, A. S., Ong, H. C., Mahlia, T. M. I., Masjuki, H. H., Badruddin, I. A., & Fayaz, H. (2013). Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production. *Renewable & Sustainable Energy Reviews, 18*, 211-245. doi:10.1016/j.rser.2012.10.013

Atmanli, A., Ileri, E., & Yuksel, B. (2014). Experimental investigation of engine performance and exhaust emissions of a diesel engine fueled with diesel-n-butanol-vegetable oil blends. *Energy Conversion and Management, 81*, 312-321. doi:10.1016/j.enconman.2014.02.049

Atmanli, A., Ileri, E., & Yuksel, B. (2015). Effects of higher ratios of n-butanol addition to diesel-vegetable oil blends on performance and exhaust emissions of a diesel engine. *Journal of the Energy Institute, 88*(3), 209-220. doi:10.1016/j.joei.2014.09.008

Atmanli, A., Ileri, E., Yuksel, B., & Yilmaz, N. (2015). Extensive analyses of diesel-vegetable oil-n-butanol ternary blends in a diesel engine. *Applied Energy, 145*, 155-162. doi:10.1016/j.apenergy.2015.01.071

Atmanli, A., Yuksel, B., Ileri, E., & Karaoglan, A. D. (2015). Response surface methodology based optimization of diesel-n-butanol -cotton oil ternary blend ratios to improve engine performance and exhaust emission characteristics. *Energy Conversion and Management, 90*, 383-394. doi:10.1016/j.enconman.2014.11.029

Atsumi, S., Hanai, T., & Liao, J. C. (2008). Non-fermentative pathways for synthesis of branched-chain higher alcohols as biofuels. *Nature, 451*(7174), 86-U13. doi:10.1038/nature06450

Atsumi, S., Wu, T. Y., Eckl, E. M., Hawkins, S. D., Buelter, T., & Liao, J. C. (2010). Engineering the isobutanol biosynthetic pathway in Escherichia coli by comparison of three aldehyde reductase/alcohol dehydrogenase genes. *Applied Microbiology and Biotechnology, 85*(3), 651-657. doi:10.1007/s00253-009-2085-6

Aydin, H., & Ilkilic, C. (2010). Effect of ethanol blending with biodiesel on engine performance and exhaust emissions in a CI engine. *Applied Thermal Engineering, 30*(10), 1199-1204. doi:10.1016/j.applthermaleng.2010.01.037

Aydin, H., & İlkılıç, C. (2010). Effect of ethanol blending with biodiesel on engine performance and exhaust emissions in a CI engine. *Applied Thermal Engineering, 30*(10), 1199-1204. doi:http://dx.doi.org/10.1016/j.applthermaleng.2010.01.037

Banapurmath, N. R., & Tewari, P. G. (2010). Performance, combustion, and emissions characteristics of a single-cylinder compression ignition engine operated on ethanol-biodiesel blended fuels. *Proceedings of the Institution of Mechanical Engineers Part a-Journal of Power and Energy, 224*(A4), 533-543. doi:10.1243/09576509jpe850

Basha, S. A., Gopal, K. R., & Jebaraj, S. (2009). A review on biodiesel production, combustion, emissions and performance. *Renewable & Sustainable Energy Reviews, 13*(6-7), 1628-1634. doi:10.1016/j.rser.2008.09.031

Bhale, P. V., Deshpande, N. V., & Thombre, S. B. (2009). Improving the low temperature properties of biodiesel fuel. *Renewable Energy, 34*(3), 794-800. doi:10.1016/j.renene.2008.04.037

Brandao, L. F. P., & Suarez, P. A. Z. (2018). Study of Kinematic Viscosity, Volatility and Ignition Quality Properties of Butanol/Diesel Blends. *Brazilian Journal of Chemical Engineering, 35*(4), 1405-1414. doi:10.1590/0104-6632.20180354s20170376

Campos-Fernandez, J., Arnal, J. M., Gomez, J., Lacalle, N., & Dorado, M. P. (2013). Performance tests of a diesel engine fueled with pentanol/diesel fuel blends. *Fuel, 107*, 866-872. doi:10.1016/j.fuel.2013.01.066

Cheng, C. H., Cheung, C. S., Chan, T. L., Lee, S. C., Yao, C. D., & Tsang, K. S. (2008). Comparison of emissions of a direct injection diesel engine operating on biodiesel with emulsified and fumigated methanol. *Fuel, 87*(10-11), 1870-1879. doi:10.1016/j.fuel.2008.01.002

Cheung, C. S., Zhu, L., & Huang, Z. (2009). Regulated and unregulated emissions from a diesel engine fueled with biodiesel and biodiesel blended with methanol. *Atmospheric Environment, 43*(32), 4865-4872. doi:10.1016/j.atmosenv.2009.07.021

Commission, E. (2019). *Malaysia Energy Statistics Handbook 2019*. Retrieved from https://meih.st.gov.my/documents/10620/bcce78a2-5d54-49ae-b0dc-549dcacf93ae

Durre, P. (2008). Fermentative butanol production - Bulk chemical and biofuel. *Incredible Anaerobes: From Physiology to Genomics to Fuels, 1125*, 353-362. doi:10.1196/annals.1419.009

EIA (Energy Information Administration) Biodiesel Performance, Cost and Use 2005.Available from www.eia.doe.gov. (2005).

Enweremadu, C. C., & Rutto, H. L. (2010). Combustion, emission and engine performance characteristics of used cooking oil biodiesel-A review. *Renewable & Sustainable Energy Reviews, 14*(9), 2863-2873. doi:10.1016/j.rser.2010.07.036

Fang, Q., Fang, J. H., Zhuang, J., & Huang, Z. (2013). Effects of ethanol-diesel-biodiesel blends on combustion and emissions in premixed low temperature combustion. *Applied Thermal Engineering, 54*(2), 541-548. doi:10.1016/j.applthermaleng.2013.01.042

Gheshlaghi, R., Scharer, J. M., Moo-Young, M., & Chou, C. P. (2009). Metabolic pathways of clostridia for producing butanol. *Biotechnology Advances, 27*(6), 764-781. doi:10.1016/j.biotechadv.2009.06.002

Green, E. M. (2011). Fermentative production of butanol - the industrial perspective. *Current Opinion in Biotechnology, 22*(3), 337-343. doi:10.1016/j.copbio.2011.02.004

H., M. (2002). Malaysian energy situation. EC-ASEAN COGEN program phase III. Malaysia: Shah Alam. See also: http://www.cogen3.net/presentations/asean/malaysia_energy_situation.pdf;.

Hassan, M. A., Yacob, S., & Ghani, B. A. (2005). Utilization of biomass in Malaysia: potential for CDM business. *University Putra Malaysia, Faculty of Biotechnology*.

How, H. G., Masjuki, H. H., Kalam, M. A., & Teoh, Y. H. (2014). Engine performance, emission and combustion characteristics of a common-rail diesel engine fuelled with bioethanol as a fuel additive in coconut oil biodiesel blends. *International Conference on Applied Energy, Icae2014, 61*, 1655-1659. doi:10.1016/j.egypro.2014.12.185

Hulwan, D. B., & Joshi, S. V. (2011). Performance, emission and combustion characteristic of a multicylinder DI diesel engine running on diesel-ethanol-biodiesel blends of high ethanol content. *Applied Energy, 88*(12), 5042-5055. doi:10.1016/j.apenergy.2011.07.008

Imdadul, H. K., Masjuki, H. H., Kalam, M. A., Zulkifli, N. W. M., Alabdulkarem, A., Rashed, M. M., . . . How, H. G. (2016). Higher alcohol-biodiesel-diesel blends: An approach for improving the performance, emission, and combustion of a light-duty diesel engine. *Energy Conversion and Management, 111*, 174-185. doi:10.1016/j.enconman.2015.12.066

Imtenan, S., Masjuki, H. H., Varman, M., & Fattah, I. M. R. (2015). Evaluation of n-butanol as an oxygenated additive to improve combustion-emission-performance characteristics of a diesel engine fuelled with a diesel-calophyllum inophyllum biodiesel blend. *Rsc Advances, 5*(22), 17160-17170. doi:10.1039/c4ra15474f

Imtenan, S., Masjuki, H. H., Varman, M., Fattah, I. M. R., Sajjad, H., & Arbab, M. I. (2015). Effect of n-butanol and diethyl ether as oxygenated additives on combustion-emission-performance characteristics of a multiple cylinder diesel engine fuelled with diesel-jatropha biodiesel blend. *Energy Conversion and Management, 94*, 84-94. doi:10.1016/j.enconman.2015.01.047

Imtenan, S., Masjuki, H. H., Varman, M., Kalam, M. A., Arbab, M. I., Sajjad, H., & Rahman, S. M. A. (2014). Impact of oxygenated additives to palm and jatropha biodiesel blends in the context of performance and emissions characteristics of a light-duty diesel engine. *Energy Conversion and Management, 83*, 149-158. doi:10.1016/j.enconman.2014.03.052

Jayabal, R., Thangavelu, L., & Subramani, S. (2020). Combined effect of oxygenated additives, injection timing and EGR on combustion, performance and emission characteristics of a CRDi diesel engine powered by sapota biodiesel/diesel blends. *Fuel, 276*. doi:ARTN 118020

Jayabal, R., Thangavelu, L., & Velu, C. (2019). Experimental Investigation on the Effect of Ignition Enhancers in the Blends of Sapota Biodiesel/Diesel Blends on a CRDi Engine. *Energy & Fuels, 33*(12), 12431-12440. doi:10.1021/acs.energyfuels.9b02521

Joshi, H., Moser, B. R., Toler, J., Smith, W. F., & Walker, T. (2010). Effects of blending alcohols with poultry fat methyl esters on cold flow properties. *Renewable Energy, 35*(10), 2207-2210. doi:10.1016/j.renene.2010.02.029

Joshi, H., Moser, B. R., Toler, J., Smith, W. F., & Walker, T. (2011). Ethyl levulinate: A potential bio-based diluent for biodiesel which improves cold flow properties. *Biomass & Bioenergy, 35*(7), 3262-3266. doi:10.1016/j.biombioe.2011.04.020

Karabektas, M., & Hosoz, M. (2009). Performance and emission characteristics of a diesel engine using isobutanol-diesel fuel blends. *Renewable Energy, 34*(6), 1554-1559. doi:10.1016/j.renene.2008.11.003

Kumar, B. R., Saravanan, S., Rana, D., & Nagendran, A. (2016). A comparative analysis on combustion and emissions of some next generation higher-alcohol/diesel blends in a direct-injection diesel engine. *Energy Conversion and Management, 119*, 246-256. doi:10.1016/j.enconman.2016.04.053

Kumar, N., Varun, & Chauhan, S. R. (2013). Performance and emission characteristics of biodiesel from different origins: A review. *Renewable & Sustainable Energy Reviews, 21*, 633-658. doi:10.1016/j.rser.2013.01.006

Kwanchareon, P., Luengnaruemitchai, A., & Jai-In, S. (2007). Solubility of a diesel-biodiesel-ethanol blend, its fuel properties, and its emission characteristics from diesel engine. *Fuel, 86*(7-8), 1053-1061. doi:10.1016/j.fuel.2006.09.034

Labeckas, G., Slavinskas, S., & Mazeika, M. (2014). The effect of ethanol-diesel-biodiesel blends on combustion, performance and emissions of a direct injection diesel engine. *Energy Conversion and Management, 79*, 698-720. doi:10.1016/j.enconman.2013.12.064

Li, L., Wang, J. X., Wang, Z., & Liu, H. Y. (2015). Combustion and emissions of compression ignition in a direct injection diesel engine fueled with pentanol. *Energy, 80*, 575-581. doi:10.1016/j.energy.2014.12.013

Li, L., Wang, J. X., Wang, Z., & Xiao, J. H. (2015). Combustion and emission characteristics of diesel engine fueled with diesel/biodiesel/pentanol fuel blends. *Fuel, 156*, 211-218. doi:10.1016/j.fuel.2015.04.048

Lopez-Contreras, A. M., Claassen, P. A. M., Mooibroek, H., & De Vos, W. M. (2000). Utilisation of saccharides in extruded domestic organic waste by Clostridium acetobutylicum ATCC 824 for production of acetone, butanol and ethanol. *Applied Microbiology and Biotechnology, 54*(2), 162-167. doi:DOI 10.1007/s002530000374

Ma, F., & Hanna, M. A. (1999). Biodiesel production: a review. *Bioresource technology, 70*(1), 1-15. doi:10.1016/s0960-8524(99)00025-5

Maroa, S., & Inambao, F. (2019). The effect of cetane number and oxygen content in the performance and emissions characteristics of a diesel engine using biodiesel blends. *Journal of Energy in Southern Africa, 30*(2), 1-13. doi:10.17159/2413-3051/2019/v30i2a5337

Mat Yasin, M. H., Yusaf, T., Mamat, R., & Fitri Yusop, A. (2014). Characterization of a diesel engine operating with a small proportion of methanol as a fuel additive in biodiesel blend. *Applied Energy, 114*(0), 865-873. doi:http://dx.doi.org/10.1016/j.apenergy.2013.06.012

Mishra, P. C., & Nayak, S. K. (2018). Pre-and post-mixed hybrid biodiesel blends as alternative energy fuels-an experimental case study on turbo-charged direct injection diesel engine. *Energy, 160*, 910-923. doi:10.1016/j.energy.2018.07.071

Nagaraj, S. K., Ponnusamy, P., Muthukutti, G. P., & Ponnusamy, R. (2019). Emission evaluation on 3-hole and 4-hole nozzle diesel engine with Jatropha and Pongamia (Karanja) mixed bio oil. *Sustainable Environment Research, 29*. doi:UNSP 13

10.1186/s42834-019-0018-3

Nanthagopal, K., Ashok, B., Saravanan, B., Pathy, M. R., Sahil, G., Ramesh, A., . . . Rasul, M. G. (2019). Study on decanol and Calophyllum Inophyllum biodiesel as ternary blends in CI engine. *Fuel, 239*, 862-873. doi:10.1016/j.fuel.2018.11.037

Ong, H. C., Masjuki, H. H., Mahlia, T. M. I., Silitonga, A. S., Chong, W. T., & Leong, K. Y. (2014). Optimization of biodiesel production and engine performance from high free fatty acid Calophyllum inophyllum oil in CI diesel engine. *Energy Conversion and Management, 81*, 30-40. doi:10.1016/j.enconman.2014.01.065

Ong, H. C., Masjuki, H. H., Mahlia, T. M. I., Silitonga, A. S., Chong, W. T., & Yusaf, T. (2014). Engine performance and emissions using Jatropha curcas, Ceiba pentandra and Calophyllum inophyllum biodiesel in a CI diesel engine. *Energy, 69*, 427-445. doi:10.1016/j.energy.2014.03.035

Pan, M. Z., Tong, C. Z., Qian, W. W., Lu, F. L., Yin, J. W., & Huang, H. Z. (2020). The effect of butanol isomers on diesel engine performance, emission and combustion characteristics under different load conditions. *Fuel, 277*. doi:ARTN 118188

10.1016/j.fuel.2020.118188

Pramanik, K. (2003). Properties and use of jatropha curcas oil and diesel fuel blends in compression ignition engine. *Renewable Energy, 28*(2), 239-248. doi:10.1016/s0960-1481(02)00027-7

Rahimi, H., Ghobadian, B., Yusaf, T., Najafi, G., & Khatamifar, M. (2009). Diesterol: An environment-friendly IC engine fuel. *Renewable Energy, 34*(1), 335-342. doi:10.1016/j.renene.2008.04.031

Rakopoulos, D., Rakopoulos, C., Hountalas, D., Kakaras, E., Giakoumis, E., & Papagiannakis, R. (2010). Investigation of the performance and emissions of bus engine operating on butanol/diesel fuel blends. *Fuel, 89*(10), 2781-2790.

Rashedul, H. K., Masjuki, H. H., Kalam, M. A., Ashraful, A. M., Rahman, S. M. A., & Shahir, S. A. (2014). The effect of additives on properties, performance and emission of biodiesel fuelled compression ignition engine. *Energy Conversion and Management, 88*, 348-364. doi:10.1016/j.enconman.2014.08.034

Sahin, Z., Durgun, O., & Aksu, O. N. (2015). Experimental investigation of n-butanol/diesel fuel blends and n-butanol fumigation - Evaluation of engine performance, exhaust emissions, heat release and flammability analysis. *Energy Conversion and Management, 103*, 778-789. doi:10.1016/j.enconman.2015.06.089

Sanli, H., Canakci, M., Alptekin, E., Turkcan, A., & Ozsezen, A. N. (2015). Effects of waste frying oil based methyl and ethyl ester biodiesel fuels on the performance, combustion and emission characteristics of a DI diesel engine. *Fuel, 159*, 179-187. doi:10.1016/j.fuel.2015.06.081

Sarin, R., Sharma, M., Sinharay, S., & Malhotra, R. K. (2006). Jatropha–Palm biodiesel blends: An optimum mix for Asia. *Fuel, 86*(10-11), 1365-1371. doi:10.1016/j.fuel.2006.11.040

Satputaley, S. S., Zodpe, D. B., & Deshpande, N. V. (2018). Performance, Combustion and Exhaust Emissions Analysis of a Diesel Engine Fuelled with Algae Oil and Algae Biodiesel. *Materials Today-Proceedings, 5*(11), 23022-23032.

Sayin, C., Gumus, M., & Canakci, M. (2012). Effect of fuel injection pressure on the injection, combustion and performance characteristics of a DI diesel engine fueled with canola oil methyl esters-diesel fuel blends. *Biomass & Bioenergy, 46*, 435-446. doi:10.1016/j.biombioe.2012.07.016

Silitonga, A. S., Masjuki, H. H., Mahlia, T. M. I., Ong, H. C., & Chong, W. T. (2013). Experimental study on performance and exhaust emissions of a diesel engine fuelled with Ceiba pentandra biodiesel blends. *Energy Conversion and Management, 76*, 828-836. doi:10.1016/j.enconman.2013.08.032

Siwale, L., Kristof, L., Adam, T., Bereczky, A., Mbarawa, M., Penninger, A., & Kolesnikov, A. (2013). Combustion and emission characteristics of n-butanol/diesel fuel blend in a turbo-charged compression ignition engine. *Fuel, 107*, 409-418. doi:10.1016/j.fuel.2012.11.083

Srivastava, A., & Prasad, R. (2000). Triglycerides-based diesel fuels. *Renewable and Sustainable Energy Reviews, 4*(2), 111-133. doi:10.1016/s1364-0321(99)00013-1

Srivastava, A. K., Soni, S. L., Sharma, D., & Jain, N. L. (2018). Effect of injection pressure on performance, emission, and combustion characteristics of diesel-acetylene-fuelled single cylinder stationary CI engine. *Environmental Science and Pollution Research, 25*(8), 7767-7775. doi:10.1007/s11356-017-1070-3

Suhaimi, H., Adam, A., Mrwan, A. G., Abdullah, Z., Othman, M. F., Kamaruzzaman, M. K., & Hagos, F. Y. (2018). Analysis of combustion characteristics, engine performances and emissions of long-chain alcohol-diesel fuel blends. *Fuel, 220*, 682-691. doi:10.1016/j.fuel.2018.02.019

Von Moll, A., Behbahani, A. R., Fralick, G. C., Wrbanek, J. D., & Hunter, G. W. (2014). *A review of exhaust gas temperature sensing techniques for modern turbine engine controls.* Paper presented at the 50th AIAA/ASME/SAE/ASEE Joint Propulsion Conference.

Wang, X., Liu, H. F., Zheng, Z. Q., & Yao, M. F. (2015). Development of a reduced n-butanol/biodiesel mechanism for a dual fuel engine. *Fuel, 157*, 87-96. doi:10.1016/j.fuel.2015.04.053

Wei, L., Cheung, C., & Huang, Z. (2014). Effect of n-pentanol addition on the combustion, performance and emission characteristics of a direct-injection diesel engine. *Energy, 70*, 172-180.

Wei, L. J., Cheung, C. S., & Huang, Z. H. (2014). Effect of n-pentanol addition on the combustion, performance and emission characteristics of a direct-injection diesel engine. *Energy, 70*, 172-180. doi:10.1016/j.energy.2014.03.106

Yang, K., Wei, L., Cheung, C. S., Tang, C. L., & Huang, Z. H. (2017). The effect of pentanol addition on the particulate emission characteristics of a biodiesel operated diesel engine. *Fuel, 209*, 132-140. doi:10.1016/j.fuel.2017.07.093

Yasin, M. H. M., Mamat, R., Yusop, A. F., Rahim, R., Aziz, A., & Shah, L. A. (2013). Fuel Physical Characteristics of Biodiesel Blend Fuels with Alcohol as Additives. *Malaysian Technical Universities Conference on Engineering & Technology 2012 (Mucet 2012), 53*, 701-706. doi:10.1016/j.proeng.2013.02.091

Yasin, M. H. M., Yusaf, T., Mamat, R., & Yusop, A. F. (2014). Characterization of a diesel engine operating with a small proportion of methanol as a fuel additive in biodiesel blend. *Applied Energy, 114*, 865-873. doi:10.1016/j.apenergy.2013.06.012

Yesilyurt, M. K., Arslan, M., & Eryilmaz, T. (2018). Experimental Investigation of the Effects of Ethanol Addition into Biodiesel-Diesel Fuel Blends on the Performance, Combustion and Emission Characteristics. *Isi Bilimi Ve Teknigi Dergisi-Journal of Thermal Science and Technology, 38*(2), 129-150.

Yilmaz, N., & Sanchez, T. M. (2012). Analysis of operating a diesel engine on biodiesel-ethanol and biodiesel-methanol blends. *Energy, 46*(1), 126-129. doi:10.1016/j.energy.2011.11.062

Yilmaz, N., Vigil, F. M., Benalil, K., Davis, S. M., & Calva, A. (2015). Effect of biodiesel-butanol fuel blends on emissions and performance characteristics of a diesel engine (vol 135, pg 46, 2014). *Fuel, 139*, 781-781. doi:10.1016/j.fuel.2014.09.019

Yilmaz, N., Vigil, F. M., Donaldson, A. B., & Darabseh, T. (2014). Investigation of CI engine emissions in biodiesel-ethanol-diesel blends as a function of ethanol concentration. *Fuel, 115*, 790-793. doi:10.1016/j.fuel.2013.08.012

Yusoff, M., Zulkifli, N., Masjuki, H., Harith, M., Syahir, A., Khuong, L., . . . Alabdulkarem, A. (2018). Comparative assessment of ethanol and isobutanol addition in gasoline on engine performance and exhaust emissions. *Journal of Cleaner Production, 190*, 483-495.

Yusoff, M. N. A. M., Zulkifli, N. W. M., Sukiman, N. L., Chyuan, O. H., Hassan, M. H., Hasnul, M. H., . . . Zakaria, M. Z. (2020). Sustainability of Palm Biodiesel in Transportation: a Review on Biofuel Standard, Policy and International Collaboration Between Malaysia and Colombia. *Bioenergy Research*. doi:10.1007/s12155-020-10165-0

Zhang, Z.-H., & Balasubramanian, R. (2014). Influence of butanol addition to diesel–biodiesel blend on engine performance and particulate emissions of a stationary diesel engine. *Applied Energy, 119*(0), 530-536. doi:http://dx.doi.org/10.1016/j.apenergy.2014.01.043

Zhang, Z. H., & Balasubramanian, R. (2014). Influence of butanol addition to diesel-biodiesel blend on engine performance and particulate emissions of a stationary diesel engine. *Applied Energy, 119*, 530-536. doi:10.1016/j.apenergy.2014.01.043

Zhu, L., Cheung, C. S., Zhang, W. G., & Huang, Z. (2010). Influence of Methanol-Biodiesel Blends on the Particulate Emissions of a Direct Injection Diesel Engine. *Aerosol Science and Technology, 44*(5), 362-369. doi:10.1080/02786821003652646

Zhu, L., Cheung, C. S., Zhang, W. G., & Huang, Z. (2011). Combustion, performance and emission characteristics of a DI diesel engine fueled with ethanol-biodiesel blends. *Fuel, 90*(5), 1743-1750. doi:10.1016/j.fuel.2011.01.024

LIST OF PUBLICATIONS AND PAPERS PRESENTED

Journal papers

- Alwi, A., Zulkifli, N.W., Sukiman, N.L. et al. Evaluation of engine performance and exhaust emission characteristics in a diesel engine using isobutanol—Calophyllum inophyllum biodiesel—diesel ternary blends. Environ Sci Pollut Res 26, 11815–11826 (2019). https://doi.org/10.1007/s11356-019-04603-6 [**ISI Q2**]

Conference paper

- Azham Alwi, N.W.M. Zulkifli, N.L. Sukiman, H.H. Masjuki, H.K. Imdadul, Z.M. Zulfattah (2017). Study on performance and emission of pentanol – biodiesel – diesel blends on a light-duty diesel engine. TECH-POST UM, Malaysia.