FEASIBILITY OF DIESEL-BIODIESEL-ALCOHOL BLEND FUELS FOR DIESEL ENGINE

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ABSTRACT

The energy policies and the ever-growing energy demand of the world require an alternative to fossil fuels. Among the alternative fuels, diesel–ethanol blend or the diesohol blend or the diesel-biodiesel blends might be good options. But these binary blends possess some problems. Diesel-biodiesel blends possess higher density, higher viscosity, lower heating value, poor cold flow properties and higher CN etc., which hinders its use. When biodiesel is added to diesel-bioethanol blends or bioethanol is added to diesel-biodiesel blends then the physicochemical properties of the ternary blends become almost similar to fossil diesel fuel and also remains stable. Thus, the use of ternary blends will eradicate the problems of using binary blends, make the biodiesel and bioethanol more feasible for the CI engines and in the meantime will increase the portion of the oxygen content of the fuel. The objectives of this study is to first develop a density and kinematic viscosity models to calculate the density and viscosity of ternary blends using bioethanol and biodiesel with diesel fuel and compare performance and emission of diesel-biodiesel-bioethanol blends with diesel-biodiesel-propanol, diesel-biodiesel-butanol, diesel-biodiesel-pentanol and diesel-biodiesel-hexanol blends. Five different biodiesels (palm, coconut, soybean, mustard and calophyllum inophyllum biodiesel) have been used with anhydrous bioethanol (99.9% pure) and neat diesel. Initially, density and viscosity models of neat diesel, 5 different biodiesels and bioethanol have been developed with respect to temperature (15°C-100°C). Later, 30 different diesel-biodiesel-bioethanol blends were prepared (each biodiesel×6 blends=30 blends) to measure the density and viscosity at different temperatures. To calculate the density of the diesel-biodiesel-bioethanol blends at 15°C, one density model is proposed with respect to components portion and their individual density which has a very high accuracy rate. To calculate the kinematic viscosity of diesel-biodiesel-bioethanol blends at 40°C, three correlation equations are proposed. To compare the performance and emission between ternary blends, the biodiesel has been kept constant while replacing the alcohol in the blend. Palm biodiesel (PBD) has been selected as the test biodiesel fuel which is considered as the most prospective renewable energy sources of Malaysia in recent years. Initially neat diesel and B20 (80% diesel+20% palm biodiesel) have been tested in the single cylinder Yanmar CI engine. Later, ternary blends of diesel-biodiesel-alcohol were tested. In all the ternary blends, the amount of diesel and PBD were kept constant which were 70% and 20% respectively while only varying the alcohol. Engine tests were conducted at variable speed, ranging from 1000 rpm to 2400 rpm and constant load at full throttle. Engine performance parameters like brake specific fuel consumption (BSFC), brake thermal efficiency (BTE) and engine emissions like nitrogen oxides (NO_x), hydrocarbons (HC) and carbon monoxide (CO) were measured. Performance and exhaust emissions variation of the ternary blends from the baseline fuels, i.e. neat diesel and P20, were compared for the assessment of the improvement quantitatively.

ABSTRAK

Dasar-dasar tenaga dan permintaan tenaga yang semakin berkembang di dunia, memerlukan alternatif kepada bahan api fosil. Antara bahan api alternatif, campuran diesel-etanol atau campuran diesohol atau diesel-biodiesel campuran mungkin menjadi pilihan yang baik. Tetapi ini campuran binari mempunyai beberapa masalah. campuran Diesel-biodiesel mempunyai ketumpatan yang lebih tinggi, kelikatan yang lebih tinggi, nilai pemanasan yang lebih rendah, sifat aliran sejuk miskin dan nombor setana yang lebih tinggi dan lain-lain, yang menghalang penggunaannya. Apabila biodiesel ditambah kepada campuran diesel-bioethanol atau bioethanol ditambah kepada campuran diesel-biodiesel maka sifat-sifat fizikokimia campuran pertigaan menjadi hampir sama dengan bahan api diesel fosil dan juga kekal stabil. Oleh itu penggunaan campuran pertigaan akan membasmi masalah menggunakan campuran binari, membuat biodiesel dan bioethanol lebih layak untuk enjin CI dan dalam masa yang sama akan meningkatkan bahagian kandungan oksigen dalam bahan api. Objektif kajian ini ialah dengan membangunkan ketumpatan dan model kelikatan kinematik untuk mengira ketumpatan dan kelikatan campuran pertigaan menggunakan bioetanol dan biodiesel dengan bahan api diesel dan bandingkan prestasi dan pelepasan diesel-biodiesel-bioethanol campuran dengan diesel-biodiesel-propanol, diesel-biodiesel-butanol, diesel-biodiesel-pentanol dan campuran diesel-biodiesel-hexanol. Five Biodiesel berbeza (kelapa sawit, kelapa, kacang soya, sawi dan Calophyllum inophyllum biodiesel) telah digunakan dengan bioethanol anhydrous (99.9% tulen) dan diesel kemas. Pada mulanya, model ketumpatan dan kelikatan diesel kemas, 5 Biodiesel berbeza dan bioethanol telah dibangunkan dengan merujuk kepada suhu (15°C-100°C). Kemudian, 30 berbeza campuran diesel-biodiesel-bioethanol telah disediakan (setiap biodiesel × 6 = 30 campuran campuran) untuk mengukur ketumpatan dan kelikatan pada suhu yang berbeza. Untuk mengira ketumpatan campuran diesel-biodiesel-bioethanol pada 15°C, satu model ketumpatan yang dicadangkan berkenaan dengan komponen bahagian dan ketumpatan masing-masing yang mempunyai kadar ketepatan yang sangat tinggi. Untuk mengira kelikatan kinematik campuran diesel-biodiesel-bioethanol pada 40°C, tiga persamaan korelasi dicadangkan. Untuk membandingkan prestasi dan pelepasan antara campuran pertigaan, biodiesel yang telah disimpan berterusan manakala menggantikan alkohol di dalam campuran. Palm biodiesel (PBD) telah dipilih sebagai bahan api biodiesel ujian yang dianggap sebagai yang paling bakal sumber tenaga boleh diperbaharui daripada Malaysia pada tahun-tahun kebelakangan ini. Pada mulanya diesel kemas dan B20 (80% diesel + 20% biodiesel sawit) telah diuji dalam silinder tunggal Yanmar CI enjin. Kemudian, campuran pertigaan diesel-biodiesel alkohol telah diuji. Dalam semua campuran pertigaan, jumlah diesel dan PBD telah disimpan berterusan yang masing-masing 70% dan 20% manakala hanya yang berbeza-beza alkohol. ujian enjin dijalankan pada kelajuan berubah-ubah, dari 1000 rpm 2400 rpm di pendikit penuh. parameter prestasi Brek penggunaan bahan api tentu dan brek kecekapan haba dan enjin pelepasan seperti nitrogen oksida, hidrokarbon dan karbon monoksida dan kelegapan asap diukur. Prestasi dan pelepasan ekzos variasi campuran pertigaan dari bahan api asas, iaitu diesel kemas dan P20, dibandingkan untuk penilaian peningkatan kuantitatif.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF NOTATIONS AND ABBREVIATIONS

ASTM	American Society of Testing Materials
BSFC	Brake Specific Fuel Consumptions
BTE	Brake Thermal Efficiency
CaME	Calophyllum Methyl Ester
CI	Cetane Index
CME	Coconut Methyl Ester
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CP	Cloud Point
CN	CN
DI	Direct Injection
EGR	Exhaust Gas Recirculation
EPA	Energy Protection Agency
EN	European Union
ETF	Engine Test Fuel
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GHG	Greenhouse gas
HC	Hydrocarbon
IC	Internal Combustion

IEA	International Energy Agency
IV	Iodine Value
kW	Kilowatt
ME	Methyl Esters
MJ	Mega Joule
MME	Mustard Methyl Ester
Mtoe	Million Tons of Oil Equivalents
N-m	Newton Meter
NOx	Oxides of Nitrogen
OECD	Organization for Economic Co-operation and Development
PME	Palm Methyl Ester
PP	Pour Point
ppm	Part Per Million
RPM	Revolution Per Minute
SAE	Society of Automotive Engineers
SME	Soybean Methyl Ester
SV	Saponification Value
Wt%	Percentage Weight
Ha	Hectare
Vol.%	Percentage Volume

CHAPTER 1 : INTRODUCTION

1.1 Overview

Human civilization has always been flourished by a steady growth of energy consumption. Industrialization has raised the average per capita energy consumption by almost 50% in the last 40 years (Eden, 1993). Limited availability with the ever-increasing demand for energy in power generation and transport sectors have triggered a serious threat to the energy security of this globe. According to British Petroleum (Petroleum, 2012), only from 2010 to 2011, fuel consumption grew to 0.6 million barrels per day, which is a 40% increment compared to 2010. Again, according to European Commission (Commission, 2006), primary energy consumption of the world will be 22.3 Giga tons of oil equivalent (Gtoe) by 2050, whereas at present it is only 10 Gtoe. In this situation the most important concern is that, the present reserve of fuel (oil) has the ability to fulfil only half of the usual demand of energy till 2023 (Owen, Inderwildi, & King, 2010). Since, the fossil fuels have played a significant role in the progress of global civilization, such declining storage of fossil fuels is really a matter of great concern. Fossil fuels are finite resources. Therefore, in the near future, it is most likely that the alternative sources of energy are going to power the human civilization.

Fossil fuel burning has direct effect on the environment due to its carbon dioxide (CO_2) emission which is one of the primary greenhouse gases (GHG) and a primary cause of global warming. Although there are other gases which trap more heat within the earth's atmosphere compare to CO_2, their production and use are limited. Atmospheric emissions of carbon dioxide (CO_2) results primarily from the combustion of fossil fuels. It is forecasted that energy related CO_2 emissions will increase from 32.3 billion metric tons in 2012 to 35.6 billion metric tons in 2020 and to 43.2 billion metric tons in 2040 ("International Energy Outlook 2016," May 2016). In 2009, at Copenhagen summit, it had been shown that, sustainable energy resources; i.e. renewable and clean fuels can decrease GHGs keeping the food security intact and enhance economic development reducing the poverty. Therefore, environmental issues due to burning of petroleum fuels and of course the trade-off between the demand and supply of the fossil fuels have intensified the requirement of biofuels like biodiesels and bioethanol at present. However, biodiesels have some inherent problems regarding its usage in internal combustion (IC) engines; and eradicating those problems to make biodiesels more feasible for the IC engines is the key to modern biofuel research activities.

1.2 Background

Energy consumption from all sources increases ("International Energy Outlook 2016," May 2016). Concerns about energy security, effects of fossil fuel emissions on the environment, and sustained high world oil prices in the long-term support expanded use of non-fossil or renewable energy sources and nuclear power, as well as natural gas, which is the least carbon-intensive fossil fuel. With government policies and incentives promoting the use of non-fossil energy sources in many countries, renewable energy is the world's fastest-growing source of energy, at an average rate of 2.6%/year, while nuclear energy use increases by 2.3%/year, and natural gas use increases by 1.9%/year as shown in the below figure 1.1. From the figure it is seen that, coal is the world's slowest growing form of energy, at an average growth rate of 0.6%/year (compared with an average increase of 1.4%/year in total world energy demand). From the figure it can be seen that the fossil fuels continue to provide most of the world's energy in 2040, liquid fuels, natural gas, and coal account for 78% of total world energy consumption. Petroleum and other liquid fuels remain the largest source of energy, although their share of total world marketed energy consumption declines from 33% in 2012 to 30% in 2040. Worldwide, most of the increase in liquid fuels consumption occurs in the transportation and industrial sectors, with a small increase in the commercial sector and decreases in the residential and electric power sectors. The declines in the use of liquid fuels in the residential and power sectors result from rising world oil prices, which lead to switching from liquids to alternative fuels where possible ("International Energy Outlook 2016," May 2016).

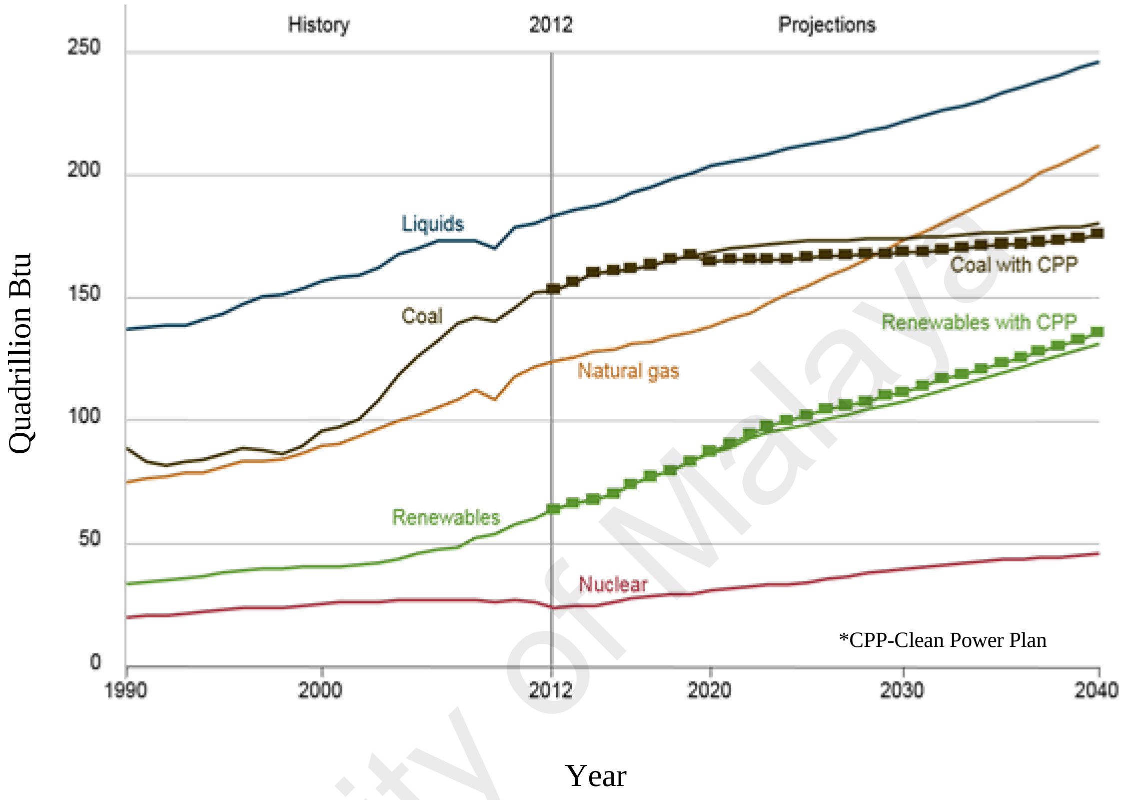


Figure 1.1: World energy consumption by energy source, 1990-2040 ("International Energy Outlook 2016," May 2016)

In prevention of global warming, Kyoto Protocol established the contributions of using the biofuels. There they addressed biofuel as “carbon neutral fuel” because unlike the fossil fuels, which release carbon that has been deposited beneath the earth‘s surface for millions of years, biodiesel emits carbon to the atmosphere through carbon dioxide which itself was captivated from the air by feedstock crops for the sake of photosynthesis (Balat & Balat, 2008). Thus, biodiesels have the immense potential to mitigate the GHGs as well as reduce the energy crisis replacing the fossil-based fuels.

As a renewable and sustainable energy source, biodiesel and bioethanol are increasingly gaining acceptance worldwide. This is unanimous that, conventional diesel can be replaced by biodiesels up to a certain extent to serve both concerns; energy crisis and legislative emission standards. Consequently, new target has been set for the European members that, at least 10% biofuel have to be used on all forms of transport by 2020 (D. Rakopoulos, 2013). Therefore, in the automotive fuel market, the share of the biodiesel is going to be increased.

Biodiesels are mono alkyl esters of fatty acids derived from vegetable oil or animal fat (Knothe, 2006). The most widespread chemical treatment to produce biodiesel from vegetable oil or animal fat or waste cooking oil is called trans-esterification process (Balat & Balat, 2008) being widely used in diesel engines presently (McCarthy, Rasul, & Moazzem, 2011). Biodiesels and biodiesel blends possess quite similar properties as diesel fuel and meet ASTM and EN standard specifications of properties (Machacon, Shiga, Karasawa, & Nakamura, 2001).

Malaysia produces 18 million tons of crude palm oil every year (MPOB, 2013). Although palm oil is edible, large-scale production can allow its use as automotive fuel without hampering the food chain. In 2006, the Malaysian government agreed to allocate about 40% of the country's total palm oil production for biodiesel production (M Mofijur et al., 2012). In addition, the government of Malaysia has recently mandated the use of 5% palm biodiesel with diesel fuel nationwide for all diesel vehicle (Adnan, 2014). But there are some difficulties if the portion of biodiesel in diesel-biodiesel blends is increased which can reduce the performance of the engine. To solve this problem bioethanol or other alcohols can be used in diesel-biodiesel blends. This blend is stable well below under sub-zero temperature (Fernando & Hanna, 2004; Shahir et al., 2014) and have equal or superior properties to fossil diesel fuel (Magín Lapuerta, Armas, & García-Contreras, 2009; Shahir et al., 2014). Studies have shown that the diesel-biodiesel-ethanol/bioethanol blend has improved physicochemical properties compare to diesel-biodiesel or diesel-ethanol/bioethanol blends separately (Bhale, Deshpande, & Thombre, 2009; Shahir et al., 2014). This blend has better water tolerance and stability than the diesel-ethanol blend (X Shi et al., 2005).

Therefore, being prospective renewable energy sources with satisfactory physicochemical properties, diesel-biodiesel-alcohol blends deserve profound investigation regarding their viability in the diesel engines and compare their performances against diesel, biodiesel and other higher alcohols ternary blends.

1.3 Problem statement

Using biodiesels or diesel-biodiesel blends with high portion of biodiesel in diesel engines have some inherent problems due to some of their physicochemical properties. Apart from lower calorific value, biodiesels possess higher viscosity and density and poor cold flow properties compared to diesel (Lujaji, Kristóf, Bereczky, & Mbarawa, 2011; Shahir et al., 2014). Higher density and viscosity hinder proper atomization of the blends during the combustion which results in lower performance and emission characteristics (Ozsezen, Canakci, & Sayin, 2008). Due to higher density and viscosity biodiesel blends are found to have higher NOx emission and higher BSFC. In addition biodiesel has high cetane number which also offsets the final cetane number of the binary blend which is responsible for lower ignition delay (D. Rakopoulos, 2013). Another disadvantage of using biodiesel blends is its lower volatility. On the other hand, there are also some problems associated with the diesel-bioethanol or diesohol blends. the problems associated with the two binary blends can be solved by mixing the 3 components together to make a ternary blend. In place of bioethanol, other alcohols can also be used but their effect till need to be identified properly. Later density and viscosity calculation models for diesel-biodiesel-bioethanol blends are developed. There are two unique aspects of this research, i.e., a) the effect of adding 2-propanol, iso-butanol, pentanol and 1-hexanol in a binary blend of diesel and biodiesel can be compared to the ternary blend having diesel, biodiesel and bioethanol. b) developed models can be used to calculate density and viscosity of any ternary blend of diesel, biodiesel and bioethanol at temperature ranging from 15°-75°C with high accuracy.

1.4 Research Objectives

The objectives of this study are:

a) To characterize physicochemical properties of diesel-biodiesel-alcohol blends using palm biodiesel and 5 alcohols (bioethanol, 2-propanol, iso-butanol, iso-amyl alcohol/pentanol and 1-hexanol).

b) To investigate the performance and emission characteristics of diesel-biodiesel-bioethanol blends compare to diesel-biodiesel-propanol, diesel-biodiesel-butanol, diesel-biodiesel-pentanol and diesel-biodiesel-hexanol blends.

c) To develop density and viscosity calculation models for ternary (diesel-biodiesel-bioethanol) blends based on statistical and experimental analysis.

1.5 Scope of study

This study aims to compare and investigate the physicochemical properties, engine performance and emission characteristics of diesel-palm biodiesel, diesel-palm biodiesel-bioethanol, diesel-palm biodiesel-2 propanol, diesel-palm biodiesel-iso butanol, diesel-palm biodiesel-pentanol, diesel-palm biodiesel-1 hexanol blends. Neat diesel and 20% (by vol.) palm biodiesel blended with neat diesel are taken as the baseline fuels as 20% biodiesel blend gives the best performance (Arbab et al., 2013). Therefore, the idea of this study is to identify the best alcohol which improves the physicochemical properties, performance and emission characteristics when used in a ternary blend compared to the neat diesel and 20% blend of diesel-palm biodiesel blend.

Characterization of the physicochemical properties like kinematic viscosity, density, calorific value, flash point, cloud point, pour point, and acid value (AV) of the base fuels (diesel, palm, coconut, mustard, calophyllum, soybean, bioethanol, 2-propanol, iso-butanol, pentanol and 1-hexanol) and the modified blends have been evaluated according to the ASTM D6751, ASTM D7467 and EN 14214 standards. Additionally, fatty acid compositions of the biodiesels are having also been studied. Engine test has been conducted to investigate the performance and emission characteristics of the test fuels. Engine test condition is variable speed (1000-2400 RPM) at constant load full throttle open.

1.6 Organization of thesis

This dissertation consists of five chapters. The organization of the chapters are given below:

Chapter 1 comprises a short overview of the present study as well as the specific scope and goals to be achieved. Highlighting the present scarcity of conventional energy sources, this section emphasizes the necessity of alternative fuel sources such as, biodiesels.

Chapter 2 presents brief description of the biodiesels and alcohols. Accumulation of the previous works associated to this study have been presented and reasoning of the outcomes have been given in way that can form a strong basis of understanding of the common trends. Critical findings from the literature have been sorted out to shape the goals of this study.

Chapter 3 discusses the methodology and the experimental techniques elaborately to meet the objectives of this study.

Chapter 4 presents all the obtained results and findings followed by a rigorous discussion and analysis of the facts appeared. Comparative analysis has been presented to highlight the feasibility of the oxygenated additives to be applied into the biodiesel-diesel blends.

Chapter 5 presents a conclusion of the significant outcomes of the study and highlights recommendations for the future studies

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

This chapter reviews major research findings by researchers around the world that will provide insight and understanding about the topic and related issues. This section describes about the disadvantages of using diesel-biodiesel and diesel-bioethanol blends, and the advantages of using diesel-biodiesel-bioethanol blends with their physicochemical properties, performance and emissions in diesel engines. This review will give us the concept of using bioethanol in diesel-biodiesel blend and its necessity. Later the feasibility of diesel-biodiesel-bioethanol blends compare to diesel-biodiesel-propanol, diesel-biodiesel-butanol, diesel-biodiesel-pentanol and diesel-biodiesel-hexanol ternary blends has been investigated. In this work feasibility is the usability of disel-biodiesel-bioethanol blend as a fuel for diesel engine. In this review all types of biodiesel have been considered to completely understand the effect of using bioethanol in a diesel-biodiesel binary blend.

2.2 Diesel-biodiesel-bioethanol blends

Biodiesel is mainly methyl ester of triglycerides prepared from animal fat and virgin or used vegetable oils (both non-edible and edible) (Agarwal, 2007). It can be used in diesel engines as a single fuel or as a diesel-biodiesel blend. These require little or no engine modifications (Agarwal, 2007; Magín Lapuerta, Armas, & Rodríguez-Fernández, 2008). Ethanol is also an attractive renewable fuel. But it cannot be used as a single fuel in diesel engines thus it is blended with diesel which results in an oxygenated fuel. This blend of ethanol and diesel is also known as diesohol/e-diesel. Diesohol has several advantages (R. L. McCormick & Parish; Shahir et al., 2014). It is already known that adding ethanol/bioethanol to the fossil diesel fuel increases the ignition delay, increases the rate of premixed combustion, increases the thermal efficiency and reduces the smoke exhaust. The solubility of ethanol/bioethanol in the diesel fuel is mainly affected by hydrocarbon composition of diesel, temperature and water content of the blend (M. n. Lapuerta, García-Contreras, Campos-Fernández, & Dorado, 2010; Reyes, Aranda, Santander, Cavado, & Belchior, 2009; Torres-Jimenez et al., 2009). However, there are some technical barriers in the direct use of diesel-ethanol blends in the CI engine. Many researchers have tested these blends with different additives (emulsifiers) but all of the blends contained small quantity of ethanol as the additives can only improve the solubility but other properties of the blend are not affected (Can, Çelikten, & Usta, 2004; Chandan Kumar, M. Athawe, Y. V. Aghav, M. K. Gajendra Babu, & Das, 2007; B.-Q. He, Shuai, Wang, & He, 2003; Magin Lapuerta, Armas, & Herreros, 2008; C. Rakopoulos, Antonopoulos, & Rakopoulos, 2007). The low flash point of this blend without biodiesel, is another critical problem, which hinders the application of this blend in the CI engine and studies have shown no effect of emulsifiers on this property (R. McCormick & Parish, 2001). When biodiesel is added to this diesel-ethanol blend then the solubility of ethanol in the diesel fuel increases over a wide range of temperature along with improving the blend's physicochemical properties (István Barabás & Todoruţ, 2011; Shahir et al., 2014). This blend is stable well below under sub-zero temperature (Fernando & Hanna, 2004; Shahir et al., 2014) and have equal or superior properties to fossil diesel fuel (M. Lapuerta et al., 2009; Shahir et al., 2014). Studies have shown that the diesel-biodiesel-ethanol/bioethanol blend has improved physicochemical properties compare to diesel-biodiesel or diesel-ethanol/bioethanol blends separately (Bhale et al., 2009; Shahir et al., 2014). This blend has better water tolerance and stability than the diesel-ethanol blend (X Shi et al., 2005). Some researchers have studied this blend with hydrous ethanol (≥95% EtOH+≤5% water) (M. Lapuerta et al., 2009) while some of them used anhydrous ethanol (≥99% EtOH+≤1% water) (István Barabás & Todoruţ, 2011; Kraipat Cheenkachorn & Fungtammasan, 2009; Guarieiro, de Souza, Torres, & de Andrade, 2009; Satgé de Caro, Mouloungui, Vaitilingom, & Berge, 2001). From previous studies it is obvious that for better physicochemical properties, anhydrous ethanol must be used in ternary blends (Shahir et al., 2014) but the quantity of ethanol in ternary blends to demonstrate best performance needs to be determined. Researchers have used up to 40% ethanol in a single ternary blend with 10% biodiesel and 50% diesel (Hulwan & Joshi, 2011) while some of them used maximum 80% biodiesel in a single ternary blend with 10% ethanol and 10% diesel (Subbaiah, Gopal, Hussain, Prasad, & Reddy, 2010). Their results showed very good performance of this ternary blend. Although many researchers have reported good performance of this blend, there are also many of them who reported very high BSFC and emissions from this blend. So, there is need to evaluate research works done on this blend to conclude about its performance. The present study reviews the literature on evaluating power, torque, fuel consumption, efficiency and emissions (soot, smoke, NOx, CO, CO_2, HC, PM, unregulated emission, sulfur dioxide and exhaust gas temperature) of this ternary blend found by many researchers around the globe.

In this review, the data from research studies conducted for evaluating diesel-biodiesel-ethanol blends are collected, summarized and compared to highlight potential of this blend as an alternative to diesel fuel.

2.2.1 Diesel-biodiesel-bioethanol blend as a diesel extender option

The strategy of adding ethanol or bioethanol to diesel is quite complex and requires dedicated solutions. The approaches are quite multifaceted and require profound solutions. Several methodologies are identified to overcome the described issues (Pidol, Lecointe, Starck, & Jeuland, 2012a).

i) Mixture of two fuels preceding injection (Elawad & Yusaf, 2004; Ghobadian G, Rahimi H, & M., February 2006; Lu, Huang, Zhang, & Li, 2005; D. C. Rakopoulos, Rakopoulos, Papagiannakis, & Kyritsis, 2011; Satgé de Caro et al., 2001; Sayin, 2010; Xing-cai, Jian-guang, Wu-gao, & Zhen, 2004a) i.e. injecting diesohol. The major weakness of this blend is its stability, which is very poor. It depends on the chemical composition of the diesel fuel used, the temperature at which the blend is used and the percentage of ethanol present in the blend.

ii) Diesel fuel can be fully substituted by ethanol (approximately 95% mass): technically this solution becomes very complex which requires major changes on the hardware of the engines to overcome ethanol's weak auto-ignition property (Haupt, Nord, Tingvall, & Ahlvik, 2004).

iii) Fumigation of ethanol i.e. ethanol addition to the intake air charge (Abu-Qudais, Haddad, & Qudaisat, 2000; Ajav EA, Singh B, & TK., 1998)

iv) Dual fuel injection; i.e. for each of the diesel and ethanol, there is a separate injection system (Noguchi, Terao, & Sakata, 1996).

Amongst all the above approaches, the first one can be selected as the most feasible way to solve the baffling issues posed by others. This approach has the following benefits:

a) No need of major technical modifications on the engine (Pidol et al., 2012a).

b) Ease of operation (Pidol et al., 2012a).

There are some very important advantages behind considering this diesohol blend as a potential fuel for the existing CI engines. They are:

a) The diesel-ethanol/bioethanol blend can significantly reduce particulate matter (PM) emissions in the motor vehicles (Ahmed, 2001; B.-Q. He et al., 2003; Xing-cai et al., 2004a; Zhang RD et al., 2004; Máté Zöldy, 2011) (approximately 15% (Beer et al., 2007)) when compared to low sulfur diesel. Adding 10% of ethanol in the diesel fuel can reduce 30-50% of this type of emission (Máté Zöldy, 2011).

c) Similar energy output can be attained compared to fossil diesel fuel (K. Cheenkachorn & Fungtammasan, 2010).

d) By adding ethanol to the diesel fuel, the cold flow properties is improved compared to fossil diesel fuel (Hulwan & Joshi, 2011).

e) The diesohol blends have high heat of vaporization compared to fossil diesel fuel (Máté Zöldy, 2011).

But as suggested in some literatures (Aakko et al., 2002; E. A. Ajav, B. Singh, & T. K. Bhattacharya, 1999; Emőd, Füle, Tánczos, & Zöldy, 2005; Emőd, Tölgyesi, & Zöldy, 2006; Pang et al., 2006; Satgé de Caro et al., 2001; Török, 2009), there are some issues which hinder the utilization of diesohol blend in the compression ignition engine.

i) CN of this blend becomes lower compared to diesel fuel. The addition of 10 v/v% of ethanol decreases CN by approximately 30%.

ii) Ethanol is not completely miscible in diesel fuel. Very small proportion (less than 5 vol. %) of ethanol shows complete miscibility in diesel fuel (Pidol et al., 2012a).

iii) Minor variations in fuel delivery system are required while using diesohol as fuel (Elawad & Yusaf, 2004; Gerdes & Suppes, 2001; Ghobadian G et al., February 2006).

iv) The density, viscosity, lubricity, energy content and the flash point of the fuel blend are affected (Pidol et al., 2012a). Due to the addition of ethanol in the diesel fuel the blend’s viscosity becomes lower. Addition of 10 v/v% of bioethanol decreases viscosity approximately by 10-25% (Máté Zöldy, 2011).

v) The swelling of T-valves fitted to bosch-type feed pumps, which results in jammed valve stems (Beer et al., 2007).

vi) The calorific value of the diesohol blend is much lower than the fossil diesel fuel (K., H., Narasingha, & J., 2004).

vii) The use of diesohol increases soot formulation (Máté Zöldy, 2011).

To solve these problems and increase the ethanol portion in the diesohol blend an emulsifier or a surfactant can be utilized (Crabbe, Nolasco-Hipolito, Kobayashi, Sonomoto, & Ishizaki, 2001; A. Hansen, Gratton, & Yuan, 2006; Alan C. Hansen, Zhang, & Lyne, 2005; Magín Lapuerta, Armas, & García-Contreras, 2007; T. M. Letcher, 1983;

Ribeiro et al., 2007; Satge de Caro, Mouloungui, Vaitilingom, & Berge, 2001; Xing-cai et al., 2004a) and maintain the blend's properties near to the fossil diesel fuel.

Different types of biodiesel can be utilized as an emulsifier or a surfactant or an amphiphile (a surface-active agent) for the long term and low temperature stability of diesohol blends (Chotwichien, Luengnaruemitchai, & Jai-In, 2009; Fernando & Hanna, 2004, 2005; A. Hansen et al., 2006; Alan C. Hansen et al., 2005; Kwanchareon, Luengnaruemitchai, & Jai-In, 2007a; M. n. Lapuerta, Armas, & García-Contreras, 2009; Rahimi, Ghobadian, Yusaf, Najafi, & Khatamifar, 2009; Randazzo & Sodré, 2011; Shi et al., 2006; X. Shi et al., 2005; Shudo, Nakajima, & Hiraga, 2009). The density of biodiesel is between 860 and 894 kg/m³ at 15° C (A. E. Atabani et al., 2012; Carraretto, Macor, Mirandola, Stoppato, & Tonon, 2004; Demirbas, 2009; Hoekman, Broch, Robbins, Ceniceros, & Natarajan, 2012; Rizwanul Fattah et al., 2013; Tate, Watts, Allen, & Wilkie, 2006a) and viscosity at 40° C is between 3.3 and 5.2 mm²/s (Carraretto et al., 2004; Demirbas, 2009; Tate, Watts, Allen, & Wilkie, 2006b). The main advantages of using biodiesel (rather than using any artificial additive synthesized in the laboratory) are as follows (Balat & Balat, 2008; Fazal, Haseeb, & Masjuki, 2011; Jain & Sharma, 2010; Jayed et al., 2011; M. Mofijur et al., 2012; Murugesan, Umarani, Subramanian, & Nedunchezhian, 2009; Ong, Mahlia, Masjuki, & Norhasyima, 2011; Rajasekar, Murugesan, Subramanian, & Nedunchezhian, 2010; Xue, Grift, & Hansen, 2011).

i) The flash point of diesohol blend is very low. When biodiesel is added to diesohol then the flash point of this ternary blend becomes high enough to store it safely.

ii) By using biodiesel, it will increase the supply of domestic renewable energy supply (Jain & Sharma, 2010).

iii) When biodiesel is added to the diesohol, the high viscosity and density of the biodiesel and the much lower viscosity and density of the diesohol are compensated by each other and these values comes within the standard diesel fuel prescribed limits.

iv) By adding biodiesel the heating value of the ternary blend comes nearer to the fossil diesel fuel (Máté Zöldy, 2011).

v) When biodiesel is added to the diesohol then the low lubricating property of diesohol blends are improved and becomes standard to use this ternary blend in the existing CI engines (K. Cheenkachorn & Fungtammasan, 2010).

vi) The high CN of biodiesel compensates the diesohol's low CN which is caused by the addition of ethanol with the diesel (Máté Zöldy, 2011).

According to Barabás and Todorut (I Barabás & Todoruţ, 2009) the diesel-biodiesel-ethanol blend is a great option as an alternative to diesel fuel for CI engines. The idea comes from the findings that, when biodiesel and ethanol/bioethanol are added to diesel fuel then the final fuel properties of this ternary blend becomes almost similar to diesel fuel alone except a few (Barabas & Todorut; Máté Zöldy, 2011). This ternary blend of diesel-biodiesel-ethanol is found to be stable even below 0° C and have some identical or superior fuel properties to regular fossil diesel fuel (Fernando & Hanna, 2004). Thus the addition of biodiesel in the diesel-ethanol blends or diesohol blends shows a favorable approach towards the formulation of a novel form of biofuels and fossil diesel fuel blend (Hulwan & Joshi, 2011).

While conducting on-field tests Raslavicius L. and Bazaras Z. (Raslavičius & Bazaras, 2009) found positive effect on dynamic and ecological characteristics of the testing vehicle fueled with a blend of 70% of diesel + 30% of biodiesel (hereinafter – B30) admixed with the dehydrated/anhydrous ethanol additive (5 v/v%). He found no reduction of power in the diesel engine, and within the boundary of the experimental error, he found a tendency of ~2% fuel economy compared to pure B30. He found a dramatic decrease in PM (40%), HC (25%) and CO (6%) emissions comparing to fossil diesel fuel while operating the vehicle at maximum power. NO_X emission from diesel-biodiesel-ethanol blends is less than (up to 4%) the B30. However, NO_X emission increases as compared to diesel fuel. Considering all these details, he concluded that a blend of 80% diesel, 15% biodiesel and 5% bioethanol is the most appropriate ratio for diesel-biodiesel-ethanol blend production, as because of the satisfactory fuel properties and reduction in emissions of the ternary blends.

2.2.2 Blend properties

Proper operation of a diesel engine depends on several fuel properties. When ethanol is added to the diesel fuel some of the key fuel properties are affected with specific reference to stability, density, viscosity, lubricity, energy content and CN of the blend. Other important factors like materials compatibility and corrosiveness are also essential to be considered (Alan C. Hansen et al., 2005). To make the selection other factors like surface tension, cold filter plugging point, flash point, carbon content, hydrogen content, heating value and finally fuel biodegradability with respect to ground water contamination etc. are also needed to be considered.

2.2.2.1 Blend stability

One of the main targets of using fuel blends in the diesel engines is to keep the engine modification minimal. A solution is a single-phase liquid system, homogeneous at the molecular level. Some diesohol formulations may be a solution of ethanol/bioethanol plus additives with diesel fuel. It was seen that such blends are technically suitable to run existing diesel engines without modifications. This ethanol-blended diesel blend yielded substantial reductions in urban emissions of carbon monoxide (CO), greenhouse gases (primarily CO_2), sulfur oxides (SOx) and particulate matter (PM). The major drawback of this diesel-ethanol blend is that, ethanol is immiscible in regular diesel fuel over a wide range of temperature. Its solubility in diesel changes with the change of ambient temperature (B.-Q. He et al., 2003; Suppes, 2000). Its miscibility in fossil diesel fuel is affected fundamentally by two factors, temperature and the blend’s water content. Presence of water in ethanol or diesel fuel can critically reduce solubility between the two portions (Lu et al., 2005; Suppes, 2000). At normal ambient temperature anhydrous/dry ethanol readily mixes with fossil diesel fuel. But below 10° C the two fuels become separate. In many regions of the world, for a long period of time during the year this temperature limit is easily surpassed. To prevent this parting of two fuels three possible ways can be considered. They are:

i) Adding an emulsifier which performs to suspend small droplets of ethanol within the diesel fuel.

ii) Adding a co-solvent that performs as a linking agent through molecular compatibility and bonding to yield homogeneous blend or

iii) Adding iso-propanol (A. Hansen et al., 2006; Alan C. Hansen et al., 2005; B.-Q. He et al., 2003; Magín Lapuerta et al., 2007; T. M. Letcher, 1983; Ribeiro et al., 2007; Satge de Caro et al., 2001; WJ, 1989; Xing-cai et al., 2004a).

To stabilize the ethanol and fossil diesel fuel blend, surface active agent i.e. an amphiphile, like Fatty Acid Methyl Ester (FAME) can also be used (Chotwichien et al., 2009; Fernando & Hanna, 2004, 2005; A. Hansen et al., 2006; Alan C. Hansen et al., 2005; Kwanchareon et al., 2007a; M. n. Lapuerta et al., 2009; Rahimi et al., 2009; Randazzo & Sodré, 2011; Shi et al., 2006; X. Shi et al., 2005; Shudo et al., 2009). To generate a blend through emulsification process usually heating and blending steps are required where on the other hand using co-solvents simplify the blending method as it permits to be “splash blended”.

The solubility of ethanol in diesel fuel is effected by its aromatic content (Gerdes & Suppes, 2001). The polar nature of ethanol induces a dipole in the aromatic molecule permitting them to interact reasonably strongly, while the aromatics stay compatible with other hydrocarbons in diesel fuel. Hence, aromatics perform as bridging agents and co-solvents to some degree. If the aromatic contents of the fossil diesel fuel are compensated, then it affects the miscibility of ethanol in the diesel fuel. Thus the quantity of the additive necessary to gain a stable blend, is affected (Alan C. Hansen et al., 2005; B.-Q. He et al., 2003; WJ, 1989).

Individually emulsifiers and co-solvents have been assessed with diesel-ethanol blend. Among the appropriate co-solvents, esters are used mostly because of their resemblance to diesel, which allows the use of diesel-ester blends in any proportion. The ester is used as a co-solvent, which permits the adding of more ethanol to the fuel blend. This develops the tolerance of the fuel blend to water, and retains the blend stable, thus for a long period the blend can be stored (Ribeiro et al., 2007; Shi et al., 2008). The percentage of required additive is dominated by the lower limit of temperature at which the blend is needed to be stable (T. Letcher, 1980). Accordingly, diesel-ethanol blend requires fewer additives in summer conditions as compared to winter. Pure Energy Corporation (PEC) of New York was the first producer to improve an additive package that allowed ethanol to be splash blended with diesel fuel using a 2-5% dosage with 15% anhydrous ethanol and proportionately less for 10% blends (Marek & Evanoff, 2001). PEC specified 5% additive for stability at temperatures well below -18 C, making it suitable for winter fuel formulation. In summer, the additive requirement drops to 2.35% with spring and fall concentrations being 3.85% by volume (Marek & Evanoff, 2001). The producer of second additive was AAE Technologies of the United Kingdom, which has been testing 7.7% and 10% diesel-ethanol blends containing 1% and 1.25% AAE proprietary additive in different states in the USA (Marek & Evanoff, 2001). The third manufacturer was GE Betz, a division of General Electric, Inc. They produced an exclusive additive derived totally from petroleum products; compared to the earlier two, which are made from renewable resources (Alan C Hansen, Hornbaker, Zhang, & Lyne, 2001; Marek & Evanoff, 2001). This additive has been utilized in many tests, exclusively with 10% diesel-ethanol blends (Alan C Hansen et al., 2001; Marek & Evanoff, 2001). Apace Research Ltd. (Beer et al., 2007; Chotwichien et al., 2009) of Australia, has also declared the successful improvement of an emulsification method by utilizing its pioneering emulsifier. Their diesel-ethanol blend consists of 84.5 vol% regular diesel fuel, 15 vol% hydrated ethanol (5% water) and their emulsifier 0.5 vol%. Tests were conducted by using diesohol on a truck and a bus and the results were compared with the results found using regular diesel fuel. It was investigated that larger amount of ethanol in the diesohol minimizes the regulated exhaust emissions (HC, CO, NOx, PM) (Kwanchareon et al., 2007a).

This study attempts to analyze the use of biodiesel as a potential amphiphile in this diesel-ethanol system. The study investigates the phase behavior of the diesel-biodiesel-ethanol ternary system in order to identify key areas within the phase diagram that are stable isotropic micro-emulsions that could be used as potential biofuels for compression-ignition engines. The instantaneous phase behavior indicated that the system formulates stable micro-emulsions over a large region of the phase triangle, depending on the concentrations of different components. The single-phase area of the three-component system was widest at higher biodiesel concentrations. The phase diagram indicated that at higher diesel concentrations, in order to formulate a stable micro-emulsion, the ratio of biodiesel to ethanol in the system should be greater than 1:1. The results of the study suggested that biodiesel could be effectively used as an amphiphile in an diesel-ethanol blend or the diesohol (Fernando & Hanna, 2005). Ludivine Pidol et al. (Pidol et al., 2012a) used a Fatty Acid Methyl Ester (FAME) to stabilize the diesel and ethanol blend. FAME stabilizes the blend by performing as a surface active agent. The investigators used Rapeseed Methyl Ester (RME) as biodiesel in this case. To raise its oxidation stability, the biodiesel was additivated with 1000 mg kg^{-1} of antioxidant (BHT- Butylated Hydroxytoluene). The miscibility of diesel-FAME-ethanol blend was studied broadly which lead to phase diagrams at different temperatures. As because the water is harmful for the blend stability, they used an anhydrous ethanol (water content is less than 0.1%). The blends were prepared in two steps:

1. First FAME was blended with the ethanol.
2. Lastly, regular diesel was added to the blend.

This process was carried out as because it allows a better blend stability.

Moses et al. (Moses, Ryan, & Likos, 1980) studied micro-emulsions by using a commercial surfactant in the blend of hydrous ethanol (containing 5% water) and fossil diesel fuel. They testified that the mixtures formed impulsively, and negligible stirring were needed. They also appeared translucent signifying that the dispersion sizes were less than a quarter of a wavelength of light and were observed as “infinitely” stable, i.e. thermodynamically steady with no parting even after some months. According to them roughly 2% surfactant was needed for each 5% hydrous ethanol addition to the fossil diesel fuel.

Letcher (T. Letcher, 1980), Meiring et al. (Meiring, Allan, & Lyne, 1981) and Letcher (T. M. Letcher, 1983) found tetrahydrofuran as an effective co-solvent, which is gained at low price from agricultural waste resources. They identified another effective co-solvent, which is named as ethyl acetate. This one can also be produced cheaply from ethanol. The relative effects of the temperature and the moisture contents on the stability of the prepared fuel blends and the required amounts of co-solvents against the increasing temperature and moisture content of the fuel blend to sustain a homogenous blend can be illustrated in a ternary liquid-liquid phase diagram. Two such ternary liquid-liquid phase diagrams are shown below under title fig. 2.1 & fig. 2.2. Letcher (T. M. Letcher, 1983) finally ended up with the conclusion that the proportion of ethyl acetate to ethanol should be consistently 1:2 to guarantee a consistent homogenous fuel blend down to 0° C.

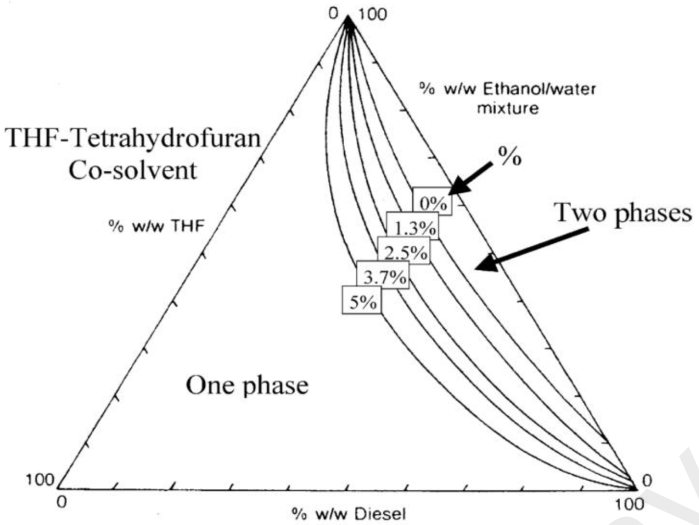


Figure 2.1: Liquid-liquid ternary phase diagram for diesel fuel, tetrahydrofuran and ethanol or ethanol water mixtures with the temperature controlled at 0° C (T. M. Letcher, 1983)

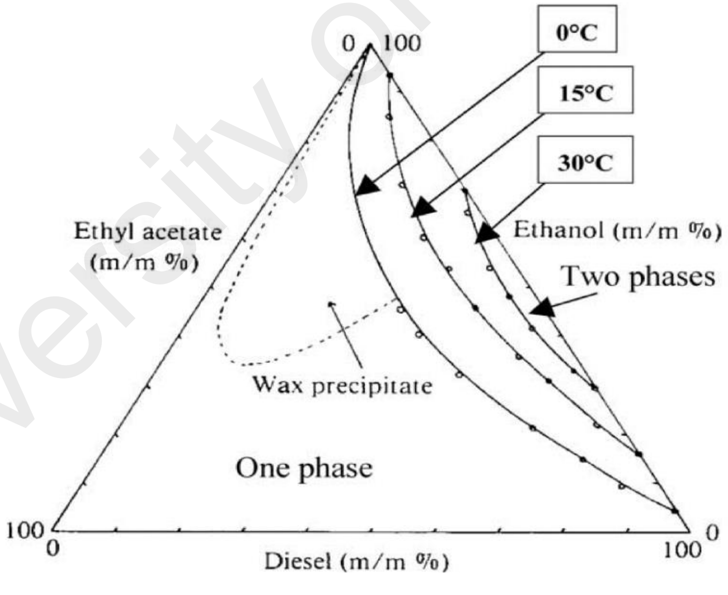


Figure 2.2: Liquid-liquid ternary phase diagram for diesel fuel, ethyl acetate and dry (anhydrous) ethanol mixtures (T. M. Letcher, 1983)

Rahimi et al. (Rahimi et al., 2009) found that the temperature of phase separation up to 4–5% bioethanol in typical diesel fuel is identical to the cloud point of the pure diesel fuel. Thus, blending up to 4–5% bioethanol places no additional temperature restrictions on these fuels (if no water is present), for example, blending bioethanol with a zero aromatic diesel increased cloud point by nearly 25° C at 5% bioethanol. Thus, the chemical properties of diesel fuel have a large effect on bioethanol solubility. They added sunflower methyl ester as biodiesel to increase the miscibility of bioethanol in diesel. Experimental results showed that at ambient temperature, 12% bioethanol could be dissolved in diesel. But when they increased the share of bioethanol in the blend or when the temperature decreased the observed phase separation. By Adding 8% biodiesel to the blend they found increased fuel stability at low temperature close to the diesel fuel pour point without any phase separation (Rahimi et al., 2009).

Kwanchareon et al. (Kwanchareon et al., 2007a) studied the phase stability of the ternary blend at room temperature by utilizing ethanol of three different concentrations (95%, 99.5%, and 99.9%). This was important as because the ethanol concentration affects the phase stability directly. Their findings are presented below by using ternary liquid-liquid phase diagrams of diesel, biodiesel and ethanol. The phase behavior of the diesel-biodiesel-ethanol (95%) system is presented below in the fig. 2.3 at room temperature.

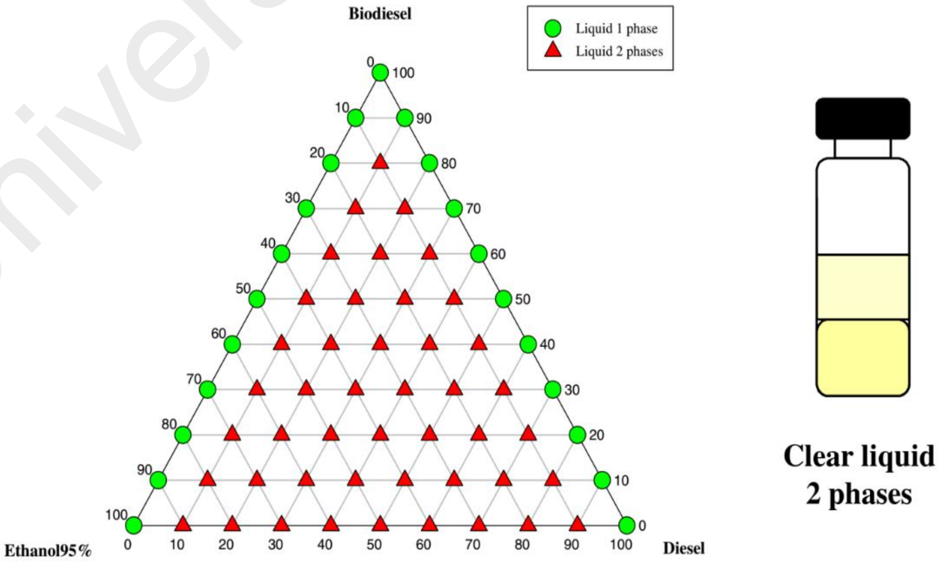


Figure 2.3: Diesel-biodiesel-ethanol 95% @ Room Temperature (Kwanchareon et al., 2007a)

As 95% ethanol contains 5% water, the investigators found the diesel and its blend insoluble. This happens because of the high polarity of water. This large portion of water in the ethanol enhances the polar part within an ethanol molecule. Thus, diesel fuel, which is a non-polar molecule, cannot be compatible with 95% pure ethanol. Biodiesel is completely soluble in 95% ethanol at all proportions which is similar to its solubility in diesel fuel. But in this case, they found that even adding biodiesel with this diesel-ethanol (95%) blend didn't increase the inter solubility of the mixture. This result of poor emulsion is due to the fact that the water in the ethanol has stronger effect than biodiesel. Thus, it is concluded that, ethanol with higher water content is not suitable for the preparation of neither diesohol nor the ternary blend of diesel-biodiesel-ethanol. On the other hand, when ethanol is used of 99.5% purity then the inter-solubility of the three liquids is not limited. These three could be used to prepare a uniform solution at any proportion as shown in the Fig. 2.4 below.

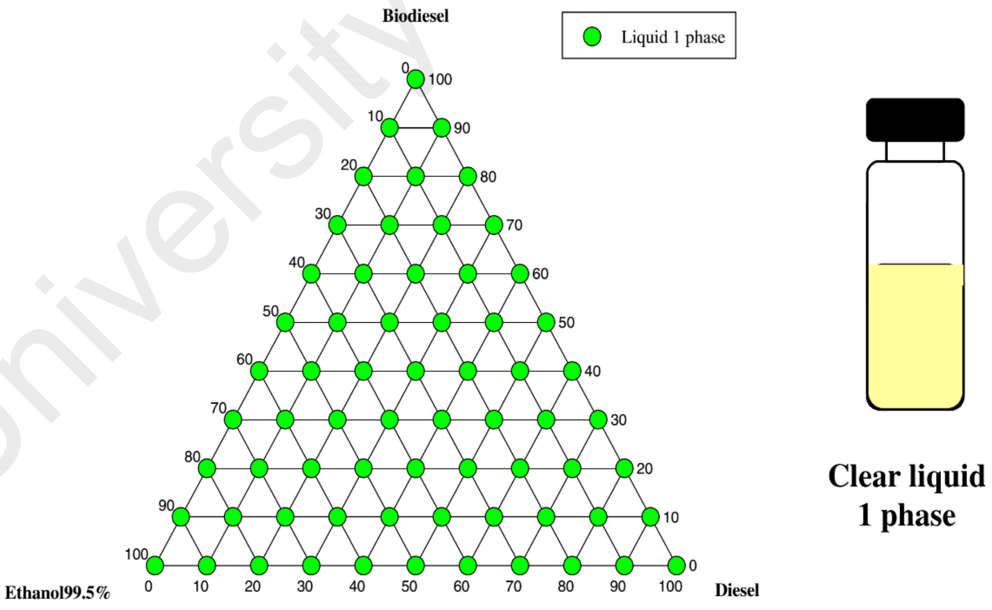


Figure 2.4: Diesel-Biodiesel-Ethanol 99.5% @ Room Temperature (Kwanchareon et al., 2007a)

This ethanol of 99.5% purity is more soluble in diesel fuel than the ethanol of 95% purity because of later ones' low water content. Although having low water content they found some blends of 99.5% ethanol and diesel were being separated into phases but the blends those contained biodiesel as an additive to the blends were still one phase liquid. This homogeneity while using biodiesel can be explained by the fact that the biodiesel turns into an amphiphile (a surface-active agent) when added to the diesel-ethanol blend and forms micelles which have polar heads and non-polar tails. These molecules are attracted to the liquid/liquid interfacial films and to each other. These micelles can act in an either way, polar or non-polar solutes. This action of biodiesel depends on the orientation of its molecules. When the diesel fuel is in the continuous phase, the polar head in a biodiesel molecule concerns itself to the ethanol while the non-polar tail concerns itself to the diesel. Depending on the physical parameters and component proportions this phenomenon hold the micelles in a thermodynamically stable state (Fernando & Hanna, 2005). The results obtained by testing ethanol of 99.9% purity are seen to be the same as the results found for 99.5% ethanol. It was seen that ethanol of 99.9% purity could also be used to prepare a homogeneous liquid solution at any proportion (Kwanchareon et al., 2007a). They also observed the phase stability at different temperatures. In the fig. 2.5 below, they found that at 10° C ethanol in the range of 20-80% by volume and diesel fuel blend is a clear liquid and in crystalline phases. Biodiesel and ethanol mixes to form a real solution, which can easily be prepared. Blends comprising of 70% to 100% biodiesel without ethanol in the blend becomes a gel. This is probably due to the presence of fatty acid in the biodiesel component.

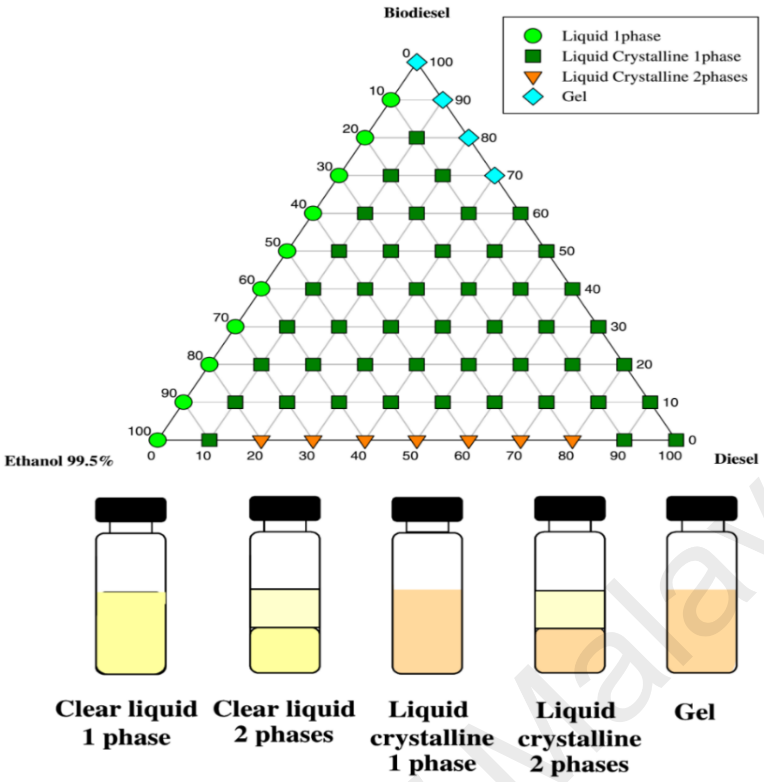


Figure 2.5: Diesel-Biodiesel-Ethanol 99.5% @ 10° C (Kwanchareon et al., 2007a)

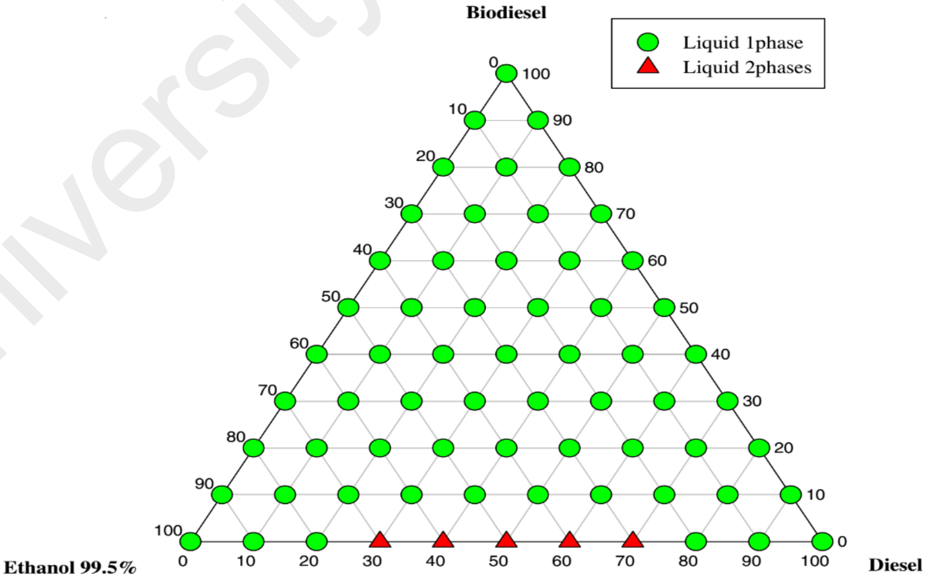


Figure 2.6: Diesel-Biodiesel-Ethanol 99.5% @ 20° C (Kwanchareon et al., 2007a)

In the Fig. 2.6, it is seen that at 20° C nearly all the blends are 1 phase liquid except for the blends having ethanol from 30-70% with diesel. In this proportions of ethanol, the mixtures are always in 2 phases in which the two components are completely immiscible with each other. Thus at 20° C, if the diesel fuel concentration is lower than 30% or greater than 70%, then the ethanol is fully miscible in diesel fuel. When the room temperature was 30° C/ 40° C they found all the blends as a single-phase liquid. At these temperatures, ethanol could be blended with diesel at any proportions. Thus, there is no problem of phase separation at 30° C and up to 40° C. These results prove that diesel-biodiesel-ethanol blends can remain stable as a single phase liquid fuel at relatively high ambient temperatures (30–40° C) (Kwanchareon et al., 2007a).

Guarieiro et al. (Guarieiro et al., 2009) also studied the phase stability of both binary (diesohol) and ternary (diesel-biodiesel-ethanol) blends at room temperature with varying ethanol concentrations. They studied the effects of both anhydrous ethanol (99.5%) and hydrous ethanol (95%). They also found that hydrous ethanol (95%) was insoluble in diesel, as because hydrated ethanol contains 5% water which means that the co-solvents investigated, did not developed the inter-solubility of the ethanol (95%) and diesel blend. On the other hand, when they added 10% anhydrous ethanol (99.5%) in the diesel fuel, they found no phase separation even after 90 days of scrutiny. But they observed that adding a greater percentage of anhydrous ethanol (15%) to the binary mixture (only diesel & ethanol/diesohol) causes phase separation on the first day. So, they prepared blends using higher percentage of anhydrous ethanol, diesel fuel and soybean biodiesel (SB), castor biodiesel (AB), residual biodiesel (RB), soybean oil (SO) and castor oil (AO) as co-solvents (at a time) and observed the stability of the ternary blends. They found some of the blends stable even after 3 months of observation while most of them were separated into phases. They described the homogeneity due to act of the co-solvents (the biodiesels and vegetable oils) they used, which act as an amphiphile (a surface-active agent) and form micelles which consists of polar heads and non-polar tails which is similar to the previous description.

Thus, the investigators selected some binary and ternary blends for further study as they were stable for 90 days' period. They selected the following blends ratios (Guarieiro et al., 2009):

a) Diesel/Ethanol – 90/10% (DE),

b) Diesel/Ethanol/SB – 80/15/5% (DESB),

c) Diesel/Ethanol/AB – 80/15/5% (DEAB),

d) Diesel/Ethanol/RB – 80/15/5% (DERB),

e) Diesel/Ethanol/SO – 90/7/3% (DESO),

f) Diesel/Ethanol/AO – 90/7/3% (DEAO).

Cheenkachorn et al. (K. Cheenkachorn & Fungtammasan, 2010) also tested several diesohol blends with different compositions of diesel and ethanol to study the homogeneity of the blends and the consequence of the emulsifiers used. Their fuel blends were little different from the others as they used hydrous and anhydrous ethanol together in most of the blends. They used palm oil biodiesel and 2-Octanol as emulsifiers. They found that the solubility of diesohol blends rises as the quantity of 2-Octanol and biodiesel increases. They also found that, greater amount of hydrous ethanol (which also contained some portion of anhydrous ethanol) in the blend obliges higher quantity of emulsifiers to stabilize the emulsions. These results agree with the earlier findings. The structural affinity between various components mixtures can be reinforced by the amphiphilic structures of the biodiesel and the 2-Octanol at the diesel/ethanol-water interface (Satgé de Caro et al., 2001). The hydrocarbon tails or oleophilic group in the biodiesels has a strong attraction with diesel fuel while the polar head or the carboxyl group represents the hydrophilic portion, which is oriented towards the ethanol-water interface (Mortier & Orszulik, 1997). The investigators also found that, if the portion of ethanol (if both hydrous and anhydrous ethanol is used together in the blend) exceeds approximately 6.4% in the diesohol blend then even biodiesel cannot prevent the blend from phase separation.

In addition to this, they summarize the use of 2-Octanol in a manner that, its proper amount can lead to lesser possibility of water separation from the blends. They also mentioned that in order to balance the hydrophilic and hydrophobic portions of the blend, the amount of 2-Octanol should be high enough. They concluded that, for the blends containing ethanol (if both hydrous and anhydrous ethanol is used together in the blend) higher than 6.6% will need a minimum amount of 4.3% 2-Octanol to avoid the phase separation. And when the percentage of ethanol (if both hydrous and anhydrous ethanol is used together in the blend) is less than 0.8% in the blend then the biodiesel can perform properly (K. Cheenkachorn & Fungtammasan, 2010).

2.2.2.2 Density

Barabas et al. (István Barabás, Todoruţ, & Băldean, 2010) tested density of several diesel-biodiesel-ethanol blends and found that the density of these ternary blends are very close to the diesel fuel density on the entire considered temperature domain (0-80° C) (István Barabás et al., 2010).

Park S. H. et al. (Park, Cha, & Lee, 2012b) tested the elementary properties of diesel-biodiesel-bioethanol (bioethanol portion in every ternary blends were kept fixed which was 20%) blends as the biodiesel portion in the blends was increased gradually. They conducted all their experiments at a blend temperature of 15° C. They found that the blend density which drops with the accumulation of bioethanol in the blend (István Barabás et al., 2010; M. n. Lapuerta et al., 2010; Park, Kim, & Lee, 2009) again escalates with the biodiesel addition. Thus, the spray momentum is recovered. Specifically a blend containing 60% diesel, 20% biodiesel and 20% bioethanol is denser than that of fossil diesel fuel (Park et al., 2012b).

Kwanchareon P. et al. (Kwanchareon et al., 2007a) prepared some ternary blends with different diesel, biodiesel and ethanol ratios for fuel property testing. They also found that the density of the blends decreases as the percentage of ethanol increases in the blends which is attributed to the fact that ethanol has a low density which lowers the final density of the blends. Again, when the percentage of biodiesel is increased in the blends, the final density of the blends increases due to the density of the biodiesel, which is greater than the former two components. However, they found density values of all the blends satisfactory and within the acceptable limits for the standard diesel engines. These outcomes match the same trend as those of earlier works (E. D. E. A. Ajav & M. O. A. Akingbehin, 2002; Kraipat Cheenkachorn & Fungtammasan, 2009; Guarieiro et al., 2009; K. et al., 2004; Kwanchareon et al., 2007a).

2.2.2.3 Viscosity and lubricity

Wrage and Goering (Wrage & Goering, 1980) created the graph shown in the fig: 2.7 below by studying the deviation of kinematic viscosity with the amount of ethanol presents in the blend.

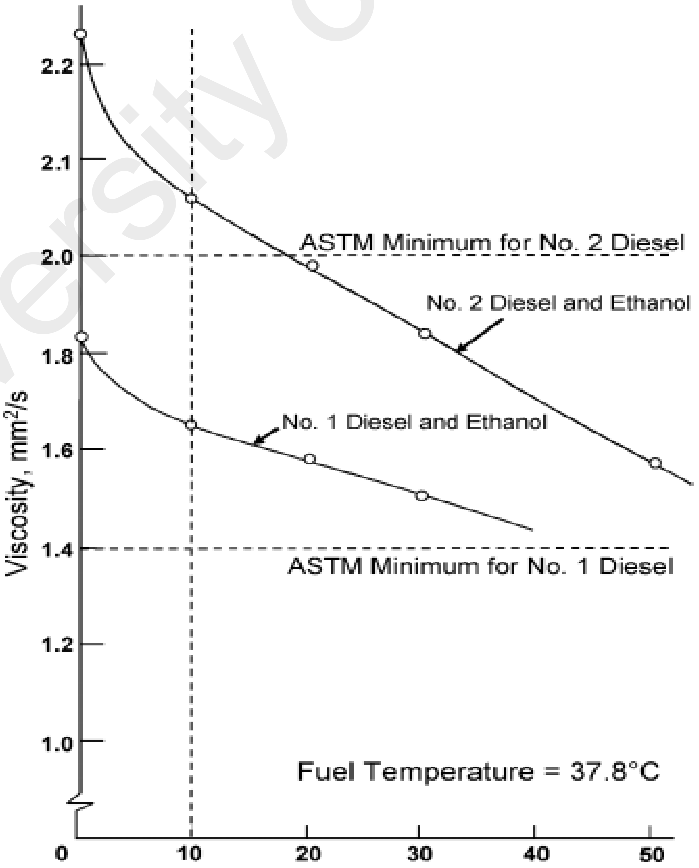


Figure 2.7: Effect of ethanol content on fuel blend viscosity (Wrage & Goering, 1980)

Barabás et al. (István Barabás et al., 2010) prepared several blends with different portions of diesel, biodiesel and ethanol. They found that the viscosity value of the blends is very near to the fossil diesel fuel and as the temperature increases the differences with diesel fuel gets lesser. This is due to the fact that the temperature of vaporization of ethanol is pretty small (approximately 78 °C). It vaporizes at the operating injector temperatures (István Barabás et al., 2010).

Park et al. (Park et al., 2012b) found that, kinematic viscosity significantly increases when biodiesel fuel is added to the diesel-ethanol blend. They kept the portion of bioethanol in the diesohol blends fixed (20% by volume) and added biodiesel in an incremental way to study its effect on the viscosity of the final blends. From the fig. 2.8 below, it is seen that, as the biodiesel content in the diesohol blends increases, the kinematic viscosity also increases. Viscosity mostly rises with the chain length of the fatty acid in a fatty aster, and biodiesel fuel comprises of fatty ester and fatty acid (Knothe & Steidley, 2005).

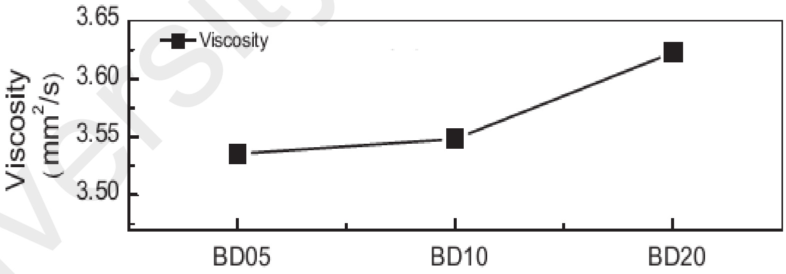


Figure 2.8: Diesel fuel viscosity results for the increase of biodiesel in diesel-bioethanol blends. The fuel temperature is 15° C (Park et al., 2012b)

Zöldy (Máté Zöldy, 2011) measured the viscosity according to EN ISO 3104:1994. He prepared several ternary blends for viscosity measurements. His results also show that, when ethanol and biodiesel are added to diesel fuel then the final viscosity of the fuel blends comes nearer to the fossil diesel fuel. He has perceived the underneath formula equation 2.1 in the field of 30-60° C for determining the viscosity of a ternary blend containing diesel, biodiesel and ethanol/bioethanol.

$$\boldsymbol{\eta_{kev} = \left(2.\,n_{e.}\eta_{e} + 3.\,n_{bd}.\,\eta_{bd} + n_{g}.\,\eta_{g} + 0.71\right).\,0.91} \qquad \textbf{2.1}$$

Where: $\eta_{\mathbf{kev}}$-The viscosity of the blend; $n_{\mathbf{i}}$ – The ratio of components (e – ethanol, bd –biodiesel, g – diesel); $\eta_{\mathbf{i}}$-The viscosity of components (e – ethanol, bd – biodiesel, g– diesel).

The author concluded from the experimental results that, from the point of view of utility, a joint blend of ethanol and biodiesel has a low decreasing effect on blend viscosity. The author suggested that the blends can be used as diesel engine fuel due to their viscosity parameters (Máté Zöldy, 2011).

2.2.2.4 Flash point

István Barabás et al. (István Barabás et al., 2010) found that all the blends having ethanol had high flammability with a flash point that is lower than the ambient temperature. This institutes an important disadvantage regarding their transportation, distribution and storage. Thus, precautions are needed to be taken in handling and transporting the fuel. Thus, special and proper ways of management are required for storage, handling and transportation of these diesel-biodiesel-ethanol blends to avoid explosions.

Prommes Kwanchareon et al. also found all the ethanol containing blends with a high flammability and a flash point temperature which was less than the ambient temperature, thus affecting the shipping and storage classifications. They also mentioned that the flash point of the diesohol blends is dominated by the portion of the fuel in the blend which has the lowest flash point among the other blend components. Thus, the storage, handling and transportation of diesohol blends require special attention compared to fossil diesel. These findings are similar to the other discussed above (E. D. E. A. Ajav & M. O. A. Akingbehin, 2002; Fernando & Hanna, 2004; K. et al., 2004; Kwanchareon et al., 2007a;

Lu et al., 2005). At standard ambient temperatures in closed vessels like storage tanks, the flammability characteristics of the diesel-ethanol blends are more or less like those of ethanol in a closed vessel thus possesses a potential threat of generating ignitable vapor above the fuel level inside the tank. As a result, there is a risk of fire or explosion which must be managed very carefully.

Due to the low flash point of ethanol, the flash point of the ternary blends also becomes very low. Barabas I. Todorut A. I. (I Barabás & Todoruţ, 2009) found the flash point of the ternary blends to be in the range of 16-18° C, which contains up to 5% ethanol. But the blends, which contains more than 5% ethanol have a flash point less than 16° C (I Barabás & Todoruţ, 2009; Rahimi et al., 2009).

Thus, it is seen that the flash point of the diesel-biodiesel-ethanol blends is dominated by the ethanol portion of the blends; whatever the type of biodiesel is used. The flash point of these ternary blends is such, that it could be classified as a Class I liquid and should be handled safely while filling a fuel tank and has to use the same infrastructures as the gasoline (Chotwichien et al., 2009).

2.2.2.5 Cetane Index (CN)

Barabas et al. (István Barabás et al., 2010) found that, due to the very low CN of the ethanol, the CN of the diesel-biodiesel-ethanol blend decreases. However, due to high CN, biodiesel can recuperate this property, thus the fuel blend can achieve the CN requirement for diesel which is 51 CN (M. Zöldy, 2006, 2007).

Rahimi et al. found through their experiments that the CN of bioethanol was extremely low (5–8) compared to the diesel fuel CN (47). Using 12% bioethanol to the diesel fuel reduces fuel blend CN to 40. But adding sunflower methyl ester to the blend the CN improves due to the higher CN of sunflower methyl ester (54) in the present case. This CN could be regarded as a suitable one to be used in diesel engines (Rahimi et al., 2009).

Kwanchareon et al. (Kwanchareon et al., 2007a) found decreasing of CN of the diesohol blend with the increasing amount of ethanol in the blend, which was due to the low CN of ethanol which is roughly 5–8. They also reported the same results as the previous study. They found the sample comprising of 80% diesel, 15% biodiesel and 5% ethanol to have maximum CN which they measured to be 48.66 (Kwanchareon et al., 2007a).

Zöldy (Máté Zöldy, 2011) studied different ternary blends for measuring CN. The investigators here also concluded that, there is a decrease in the CN of the blend with the addition of ethanol and increase again with the addition of biodiesel, which matches the other described results above. They developed a multi linear model, which can be applied for modeling the compensation factor of adding ethanol and biodiesel to diesel fuel. The model rose to be the like as displayed below for the dependency of CNs on the amount of ethanol and biodiesel. The attained formula, equation 2.2 (Máté Zöldy, 2011) shows the dependency on the components:

$$\boldsymbol{CN_{ebdg} = CN_d - 0.59n_e + 0.55n_{bd}} \qquad \mathbf{2.2}$$

where: CN_{ebdg} – the calculated CN of the blend; CN_d– the CN of diesel oil; n_e– ethanol ratio in the blend [v/v%]; n_{bd}– biodiesel ratio in the blend [v/v%].

Due to the ethanol addition a decrease of 0.6 in CN is well-compensated by adding biodiesel, which again increases the CN by an amount of 0.55. They suggested that if it is desired to hold the CN of the blend at its original value even after adding ethanol and biodiesel then these two components should be blended approximately at a 1:1 ratio with the diesel fuel (Máté Zöldy, 2011).

Park S. H. et al. (Park et al., 2012b) concluded that, increasing the biodiesel amount in the blend increases the blend CN as the biodiesel fuel has greater CN compared to both diesel fuel and ethanol. Normally, the CN of the used biodiesel is associated with the varieties of feedstock used for its making. In addition, the long fatty acid carbon chains and more saturated molecules results in a high CN (Demirbas, 2005; Knothe, Bagby, & Ryan, 1998).

2.2.3 Performance

2.2.3.1 Power and torque

Diesel-biodiesel-ethanol blends reduces engine power and torque output as the portion of oxygenated compounds (biodiesel and ethanol/bioethanol) in the blends increases (Rahimi et al., 2009). This is due to the low CN and calorific value and higher ignition delay of the blends, compared to diesel fuel (Can, Çelikten, et al., 2004). Cheenkachorn and Fungtammasan (Kraipat Cheenkachorn & Fungtammasan, 2009) found approximately 4.4-8.7% reduction in maximum power output by using diesel-biodiesel-ethanol blends compared to fossil diesel fuel.

Thus, using these blends without any additives reduce engine power and torque output. These reduced torque and power can be improved and the combustion characteristics can also be optimized by using additives with these blends (Satgé de Caro et al., 2001). If no additives are used, then the portion of the ethanol/bioethanol should be kept as low as possible.

Table 2.1: A comparative study of stability and physicochemical properties of diesel-biodiesel-bioethanol/ethanol blends with different biofuel portions at different temperatures

D:BD:EtOH; Biodiesel; Ethanol/bioethanol purity	**Miscibility & stability of blends**	**Density kg/m^3 (István Barabás et al., 2010; Barabas & Todorut; K. Cheenkachorn & Fungtammasan, 2010; Chotwichien et al., 2009; Hulwan & Joshi, 2011; Kannan, 2013; Pang et al., 2006; X. Shi et al., 2005)**	**CFPP °C (Barabas & Todorut)**	**Viscosity mm^2/s (Barabas & Todorut; K. Cheenkachorn & Fungtammasan, 2010; Chotwichien et al., 2009; Hulwan & Joshi, 2011; Kannan, 2013; Pang et al., 2006; X. Shi et al., 2005)**	**Flash point °C (Barabas & Todorut; Chotwichien et al., 2009; Hulwan & Joshi, 2011; Kannan, 2013)**	**Calorific value kJ/kg (Barabas & Todorut; K. Cheenkachorn & Fungtammasan, 2010; Chotwichien et al., 2009; Hulwan & Joshi, 2011; Kannan, 2013; Pang et al., 2006; X. Shi et al., 2005)**	**CN (Barabas & Todorut; K. Cheenkachorn & Fungtammasan, 2010; Chotwichien et al., 2009; Hulwan & Joshi, 2011; Kannan, 2013; Pang et al., 2006)**	**Pour point °C (Chotwichien et al., 2009; Hulwan & Joshi, 2011; Kannan, 2013)**	**Carbon content % by weight (Barabas & Todorut; K. Cheenkachorn & Fungtammasan, 2010; Hulwan & Joshi, 2011; Pang et al., 2006)**	**Oxygen content % by weight (Barabas & Todorut; Hulwan & Joshi, 2011; Pang et al., 2006; X. Shi et al., 2005)**
70:10:20; JBD; 99.7%		832.87 [a]	-	2.380 [c]	14	39930	50	-3	78.69	7.77
50:20:30; JBD; 99.7%		834.55 [a]	-	2.401 [c]	12.5	38965	50	-9	74.49	12.12
50:10:40; JBD; 99.7%		820.42 [a]	-	2.018 [c]	12	36338	41	-12	72.07	14.53
85:12:3; SBD; 99.7%	3 months @ NAC	840 [b]	-	3.01 [c]		41500				2.3
80:16:4; SBD; 99.7%	3 months @ NAC	840 [b]	-	3.03 [c]		41200				3.1

Table 2.1, continued

75:20:5; SBD		845 [b]	-	3.04 [b]		40900	45		83	3.9
60:30:10; WCOBD; 99.9%	1 month @ 30° C	826 [d]	-	2.44 [d]	18.5	39100	47.3	-3		
50:40:10; WCOBD; 99.9%	1 month @ 30° C	831 [d]	-	2.60 [d]	19	38700	47.2	-3		
50:30:20; WCOBD; 99.9%	1 month @ 30° C	821 [d]		2.14 [d]	15	37850	47.2	-6		
90:5:5; RSOBD; 99.3%	30hrs @ 20 & 0° C Separated in 2 phases after 30 hrs @ -8° C	843.7 [a]	-18	2.435 [c]	17.5	41707	51.04		83.22	2.20
85:10:5; RSOBD; 99.3%	30hrs @ 20 & 0° C 30 hrs @ Separated in 2 phases after 30 hrs @ -8° C	845 [a]	-17	2.421 [c]	14	41560	51.20		82.79	2.76
80:15:5; RSOBD; 99.3%	30hrs @ 20 & 0° C Clear with sediments after 30 hrs @ -8° C	847.2 [a]	-13	2.527 [c]	16	41414	51.36		82.37	3.32
75:20:5; RSOBD; 99.3%	30hrs @ 20 & 0° C Clear with sediments after 30 hrs @ -8° C	849.6 [a]	-17	2.645 [c]	17	41269	51.52		81.94	3.88

Table 2.1, continued

70:25:5; RSOBD; 99.3%	30hrs @ 20 & 0° C Homogeneous & clear after 30 hrs @ -8° C	851.9 [a]	-16	2.756 [c]	18	41124	51.68		81.52	4.43
75:15:10; RSOBD; 99.3%	30hrs @ 20 & 0° C Clear with sediments after 30 hrs @ -8° C	844.7 [a]	-4	2.374 [c]	15.5	40668	49.24		80.80	4.96
70:20:10; RSOBD; 99.3%	30hrs @ 20 & 0° C Clear with sediments after 30 hrs @ -8° C	846.8 [a]	-7	2.480 [c]	16	40524	49.41		80.38	5.52
80:15:5; POBD(PME); 99.5%	1 phase liquid after 3 months @ room temperatures	838.3 [a]		2.63 [c]	17	43800	53.2	3		
80:15:5; POBD(PEE) 99.5%	1 phase liquid after 3 months @ room temperatures	837.8 [a]		2.72 [c]	15.7	39300	-	3		
80:15:5 POBD(PBE) 99.5%	1 phase liquid after 3 months @ room temperatures	837 [a]		2.73 [c]	15	43700	-	3		
85:10:5 POBD(PME) 99.5%	1 phase liquid after 3 months @ room temperatures	836.1 [a]		2.57 [c]	15	43700	52	3		
85:10:5 POBD(PEE)	1 phase liquid after 3 months @	835.9 [a]		2.63 [c]	15	43900	-	3		

Table 2.1, continued

99.5%	room temperatures									
85:10:5 POBD(PBE) 99.5%	1 phase liquid after 3 months @ room temperatures	835.4 ^{a}		2.65 ^{c}	16	44000	-	3		
82.5:12.5:4.5:0.5(HE) POBD 99.5%	Homogenous blend after 3 months @ room temperature	829 ^{a}		2.82 ^{c}		44430	56.20			
84:11:4.75:0.25(HE) POBD 99.5%	Homogenous blend after 3 months @ room temperature	828 ^{a}		2.69 ^{c}		44560	57.91			
82.5:12.5:4.75:0.25(HE) POBD 99.5%	Homogenous blend after 3 months @ room temperature	829 ^{a}		2.78 ^{c}		44490	57.60			
80:15:4.5:0.5(HE) POBD 99.5%	Homogenous blend after 3 months @ room temperature	830 ^{a}		2.97 ^{c}		44210	56.32			

^{a}: Value taken @ 15° C; ^{b}: Value taken @ 20° C; ^{c} : Value taken @ 40° C; ^{d}: Value taken @ 27° C
NAC: Normal Ambient Condition; JBD: Jatropha Seed Biodiesel; SBD: Soybean Biodiesel; WCOBD: Waste Cooking Oil Biodiesel; RSOBD: Rapeseed Oil Biodiesel; POBD: Palm Oil Biodiesel; PME: Palm Oil Methyl Ester; PEE: Palm oil Ethyl Ester; PBE: Palm oil Butyl Ester; RME: Rapeseed Oil Methyl Ester; HE: Hydrous Ethanol

2.2.3.2 Brake specific fuel consumption (BSFC)

The BSFC of a fuel blend reflects some of the physicochemical properties like the calorific value and the density of the blend. Theoretically, BSFC of a fuel blend increases (compared to diesel fuel), as the energy content of the blend decreases. Due to the low heating value of ethanol and biodiesel, the heating value of the blend consists of these three constituents is little low compared to diesel fuel. This low heating value of the diesel-biodiesel-ethanol/bioethanol blends increase the BSFC. This increase in BSFC depends on the biofuel (ethanol and biodiesel) content of the blends. As the portion of biofuel in the blends increases, the BSFC also increases (Abdel-Rahman, 1998; E. Ajav, B. Singh, & T. Bhattacharya, 1999; István Barabás et al., 2010; Gumus, Sayin, & Canakci, 2010; Hulwan & Joshi, 2011; Rahimi et al., 2009; Subbaiah et al., 2010). But there are some researchers who investigated reduced BSFC initially but again found it increasing with increasing speeds (Rahimi et al., 2009). The difference between BSFC of diesel and diesel-biodiesel-ethanol blends is maximum when the load is small/low (István Barabás et al., 2010) and high (Subbaiah et al., 2010) on the engine. At low load condition, Barabas et al. (István Barabás et al., 2010; István Barabás & Todoruţ, 2011) found this increase to be maximum 32.4% with a 30% biofuel content. And at high load condition, Subbaiah et al. (Subbaiah et al., 2010) found maximum 40% increase but overall they encountered 26.97%, 31.33% and 35.33% increase in BSFC for B10E5, B10E10 and B10E15 blends respectively. Again there are some researchers, who found this difference negligible (X Shi et al., 2005), while some of them found decreasing BSFC with these blends (Guarieiro et al., 2009). Some researchers investigated the effect of different injection timing on the BSFC of ternary blends and found very little effect (Hulwan & Joshi, 2011).

Instead of diesel, when Pidol et al. (Pidol et al., 2012a) tested Fischer Tropsch fuel in the diesel-biodiesel-ethanol blend they also found a 6% and 11% increase in BSFC at 1500 and 2500 rpm. And when they used fossil diesel and iso-pentane as an additive, they reported BSFC even higher, which is near to 50%. This increase in BSFC was due to incomplete and inefficient combustion. And even when they increased the EGR rate, they discovered more deteriorated combustion leading to misfiring.

Table 2.2: BSFC of different ternary blends

Diesel:Biodiesel:Ethanol	Conditions	Comparison with Diesel performance
1. D85B10E5	Low Load	↑29-30%^{cg} (István Barabás & Todoruţ, 2011); ↑5-10%^{cg} (Subbaiah et al., 2010)
	Medium load	↑7.5-8.5%^{cg} (István Barabás & Todoruţ, 2011); ↑2-3%^{cg} (M. Al-Hassan, 2012); ↑24-28%^{cg} (Subbaiah et al., 2010)
	High Load	↑4-5%^{cg} (István Barabás & Todoruţ, 2011);↑28-33%^{cg} (Subbaiah et al., 2010)
2. D80B15E5	Low load	↑30-32%^{cg} (István Barabás & Todoruţ, 2011)
	Medium load	↑8-9%^{cg} (István Barabás & Todoruţ, 2011)
	High Load	↑4-5%^{cg} (István Barabás & Todoruţ, 2011)
3. D70B25E5	Low load	↑ 32.4% (István Barabás & Todoruţ, 2011)
	Medium load	↑ 8-10%^{cg} (István Barabás & Todoruţ, 2011)
	High Load	↑ 10-15.8%^{cg} (István Barabás & Todoruţ, 2011)
4. D80B10E10	Low Load	↑7-10%^{cg} (Subbaiah et al., 2010)
	Medium Load	↑ 5-6%^{cg} (M. Al-Hassan, 2012); ↑24-28%^{cg} (Subbaiah et al., 2010)
	High Load	↑30-35%^{cg} (Subbaiah et al., 2010)
5. D75B10E15	Low Load	↑10-15%^{cg} (Subbaiah et al., 2010)
	Medium Load	↑13-14%^{cg} (M. Al-Hassan, 2012); ↑24-28%^{cg} (Subbaiah et al., 2010)
	High Load	↑36-40%^{cg} (Subbaiah et al., 2010)
6. D70B10E20	Medium Load	↑22-23%^{cg} (M. Al-Hassan, 2012)
7. D85B12E3	High Load	↑4-5%^{cg} (X Shi et al., 2005)
8. D80B16E4	High Load	↑3-5%^{cg} (X Shi et al., 2005)
9. D94.95B2.05E3	High Load	↑1.5-3%$^{cg, avg}$ (Rahimi et al., 2009)
10. D89.90B4.1E6	High Load	↑3-6%$^{cg, avg}$ (Rahimi et al., 2009)
11. D84.85B6.15E9	High Load	↑5-10%$^{cg, avg}$ (Rahimi et al., 2009)
12. D79.80B8.2E12	High Load	↑9-14%$^{cg, avg}$ (Rahimi et al., 2009)
13. D75B20E5	Constant Speed Variable Load	↑7-11%$^{tbl, avg}$ (Pang et al., 2006)
	Constant Load Variable Speed	↑2-5%$^{tbl, avg}$ (Pang et al., 2006)

$^{cg:}$ Calculated from graph; $^{avg:}$ Average Value

Table 2.2 shows that, at low load, medium load and high load conditions the maximum rise in BSFC could be 32.4%, 33% and 40% respectively. It can be observed that the overall BSFC of an engine running on blends, is higher than running on diesel fuel. Thus, the portion of biofuel (biodiesel and ethanol) in the ternary blends must be kept as low as possible, especially ethanol as they govern the BSFC of the engine.

2.2.4 Emissions

2.2.4.1 Soot and smoke

Among the particulate matter components, soot is acknowledged as the main reason behind smoke opacity. Oxygenates have remarkable effects on the reduction of smoke, when is added to diesel fuel. Thus, high amount of ethanol and biodiesel addition to diesel fuel reduces smoke. Its formation mainly takes place in the fuel rich zone where the temperature and pressure are high and air deficiency is extreme which is in the core region of each fuel spray. It strongly depends on the engine load and as the load on the engine increases, the air-fuel ratio decreases due to the high rate of fuel injection which results in higher smoke (Can, Celikten, & Usta, 2004). It is normally observed that; smoke emission is reduced compared to diesel fuel when diesel-biodiesel-ethanol/bioethanol blends are used. This is owing to the atomic bond of oxygen in ethanol which satisfies positive chemical control over soot formation (Boruff, Schwab, Goering, & Pryde, 1982; Xiao, Ladommatos, & Zhao, 2000). In-cylinder photography of combustion reveals lower luminous flames while using ethanol blends which is the indication of low soot formation (Chen, Shi-Jin, & Jian-Xin, 2007; Xingcai, Zhen, Wugao, & Degang, 2004). Almost every researcher and investigator found this true. When smoke emission from diesel-biodiesel-ethanol/bioethanol blends are compared with smoke emission from diesel, some of the researchers marked small reduction (Rahimi et al., 2009; Subbaiah et al., 2010), while others reported a significant reduction with these blends (István Barabás et al., 2010; Park et al., 2012b; Pidol et al., 2012a; Shi et al., 2008; X Shi et al., 2005) even when the blend contained only 10% diesel (Bhale et al., 2009). With 16% biodiesel and 4% ethanol, Shi et al. (Shi et al., 2008; X Shi et al., 2005) found this emission to be 47% and 90% lower at full load and full speed respectively while Barabas et al. (István Barabás et al., 2010) found smoke emission to be decreased as much as 50% for fuel blends at all loads, especially at medium and small loads. They found minimum of 27.6% decrease and maximum of 50.3% decrease at higher loads.

Hulwan and Joshi (Hulwan & Joshi, 2011) studied the soot and smoke emission from diesel-biodiesel-ethanol blends by changing the injection timings. They found smoke emission to be almost constant and negligible at small loads, but slowly increases with increasing loads by using diesel-biodiesel-ethanol blends. They found this true for all blends even with the blend containing 50% biofuel. They observed this scenario of smoke emission at all injection timings and speeds. Although they observed that, the smoke emission increases with the increasing load, they found its emission to be always lower than the diesel fuel. At an injection timing of 13°, they observed excessive smoke for a blend containing 20% ethanol and 10% biodiesel. This happened due to insufficient time for soot oxidation. They also noticed that, smoke is significantly reduced when injection timing is advanced at higher loads. Advanced injection timing leads to greater cylinder pressure, thus the soot particles get more time to be oxidized before exhaust valve opens (Can, Celikten, et al., 2004). Due to excess oxygen content and better mixing ability, the blends can utilize the additional time more effectively than the diesel fuel (Hulwan & Joshi, 2011).

Table 2.3: Smoke emissions from different ternary blends

Diesel:Biodiesel:Ethanol	Conditions	Comparison with Diesel performance
1. D85B12E3	High Load	↓15%[cg] (X Shi et al., 2005)
2. D80B16E4	High Load	↓47% (X Shi et al., 2005)
3. D85B10E5	Low Load	Not much difference[cg] (Subbaiah et al., 2010)
	Medium Load	Not much difference[cg] (Subbaiah et al., 2010)
	High Load	↑0-2%[cg] (Subbaiah et al., 2010)
4. D80B10E10	Low Load	Not much difference[cg] (Subbaiah et al., 2010)
	Medium Load	Not much difference[cg] (Subbaiah et al., 2010)
	High Load	↓0-2%[cg] (Subbaiah et al., 2010)
5. D75B10E15	Low Load	Not much difference[cg] (Subbaiah et al., 2010)
	Medium Load	Not much difference[cg] (Subbaiah et al., 2010)
	High Load	↓2-5%[cg] (Subbaiah et al., 2010)
6. D10B80E10	Low Load	↓27-32%[cg] (Bhale et al., 2009)
	Medium Load	↓18-22%[cg] (Bhale et al., 2009)
	High Load	↓10-15%[cg] (Bhale et al., 2009)

[cg]: Calculated from graph

Thus, it is obvious that soot and smoke emission is reduced remarkably when ternary blends are used. There are some researchers who reported no reduction in soot and smoke emission, but they observed its emission almost identical to diesel fuel. But if the EGR rate is increased (Pidol et al., 2012a) or the injection timing is advanced (Park et al., 2012b) then soot and smoke emission increases. After all the discussions (see table. 2.3) it can be concluded that, maximum of 60%-80% soot and smoke emission can be reduced when ternary blends are used.

2.2.4.2 Nitrogen oxides (NOx)

The most troublesome emission from CI engine is NOx. The oxides of nitrogen in the exhaust emissions contain nitric oxide (NO) and nitrogen dioxide (NO_2). NOx formation highly depends on the temperature inside the cylinder, the concentration of oxygen, the residence time for the reaction to take place and the equivalence ratio (Ajav EA et al., 1998; Challen & Baranescu. R, 1999). Any of the fuel density or the CN or the aromatic fuel composition or they can jointly influence NOx formation. The air-fuel equivalence ratio might be shifted by the oxygenated fuels to the level that yields lower NOx emission (Kraipat Cheenkachorn & Fungtammasan, 2009). Another possibility of lower NOx emission from ethanol added fuel may be its cooling effect of evaporation, which leads to a reduced flame temperature (Kraipat Cheenkachorn & Fungtammasan, 2009). On the other hand, the decrease of CN due to the addition of oxygenated fuel to the fossil fuel, leads to an increased ignition delay which results in higher NOx emissions (Xing-cai, Jian-Guang, Wu-Gao, & Zhen, 2004b). Another reason studied for the increase of NOx emission from biodiesel is the higher bulk modulus of compressibility of biodiesel which results in small advance in injection timing (James P. Szybist & Boehman, 2003). It is suggested that, retarding injection timing can reduce NOx in (W. G. Wang et al., 1997). Thus, the effect of biofuel blends/oxygenated fuel blends on the NOx emission is complex and not conclusive. The real fact is that; the result of NOx emission is found to be variable by different researchers. Some of them reported increased NOx emission for using biofuel blends (Ali, Hanna, & Leviticus, 1995; Can, Celikten, et al., 2004; Graboski, McCormick, Alleman, & Herring, 2003; Kwanchareon, Luengnaruemitchai, & Jai-In, 2007b; Magin Lapuerta et al., 2008; R. McCormick & Parish, 2001; R. L. McCormick, Graboski, Alleman, Herring, & Tyson, 2001; Shi et al., 2006; X Shi et al., 2005; W. Wang, Lyons, Clark, Gautam, & Norton, 2000), while others reported it to be lower than diesel fuel (E. Ajav et al., 1999; B.-Q. He et al., 2003; Li, Zhen, Xingcai, Wu-gao, & Jian-guang, 2005; Park et al., 2012b; C. Rakopoulos et al., 2007). There are also some researchers who found NOx emission from ternary blends identical to diesel fuel (Bhale et al., 2009). Randazzo and Sodre (Randazzo & Sodré, 2011) found increasing NOx emission as the amount of biodiesel is increased in the blend. But when ethanol is added to this blend, they again found decreasing NOx with the increasing amount of ethanol in the blend. This is because of the low heating value of ethanol which results in more required fuel for producing the power demand from the engine, thus escalating fuel vaporization and reducing the attained temperature in the combustion chamber. As the peak temperature is reduced, the NOx formation rate is reduced. This is also observed by He et al. (B.-Q. He et al., 2003), Agarwal (Agarwal, 2007) and Guarieiro et al. (Guarieiro et al., 2009). Guarieiro et al. (Guarieiro et al., 2009) found little decrease in NOx emission using fuel blends. At 1800 and 2000 rpm, they discovered 30%-84% reduction in NOx emission by adding 10% bioethanol to diesel fuel. This tendency was also observed by adding vegetable oil and biodiesel. They found best results with castor oil and residual biodiesel than others. Regarding ternary fuel blends, their observation showed a decrease in NOx emission at 1800 and 2000 rpm in the range of 6.9-75% and 4-84% respectively. Opposite results are also observed by Shi et al. (X Shi et al., 2005) and Barabas et al. (István Barabás et al., 2010). Shi et al. (X Shi et al., 2005) observed the positive effect of ethanol in the increase of NOx formation. They observed its highest emissions with 4% ethanol in the blend. It was an increase of 19% at full load and 30% at full torque operating condition. While Barabas et al. (István Barabás et al., 2010) also found less influence of oxygenated components of the fuel blends in the NOx formation at smaller loads. But at medium and high engine load conditions, the NOx emission is increased by 10-26% compared to diesel fuel. This is because of the higher combustion temperature which is due to the oxygen content of the biodiesel and bioethanol and the reduced CN of the blend (Kwanchareon et al., 2007b; X. Shi et al., 2005).

When researchers studied ternary blends in different load conditions, then Kwanchareon et al. (Kwanchareon et al., 2007b) found higher NOx emission from the diesel-biodiesel-ethanol blends at low, medium and high loads compared to diesel fuel. Especially at full load condition, the increase was significant. But Subbaiah et al. (Subbaiah et al., 2010) marked the NOx emission from the diesel-biodiesel-ethanol blends lower at lower loads and higher at medium and high loads compared to diesel fuel. Their results also indicate that the NOx emission increases with the increasing portion of ethanol in the blends. And when Shi et al. (Shi et al., 2006) studied NOx emission from diesel-biodiesel-ethanol blends at varying load-constant speed condition then they found its emission 11.4% higher than diesel fuel and at varying speed-constant load condition, then it was 5.6 % higher. This increased NOx emission can be controlled by increasing the EGR rate (Pidol et al., 2012a) which is an advantage of using ethanol in ternary blends. And to understand the effect of diesel-biodiesel-ethanol/bioethanol blends in a real life, Cheenkachorn and Fungtammasan (Kraipat Cheenkachorn & Fungtammasan, 2009) tested the blends in a vehicle mounted on a chassis dynamometer and tested the blends in 3 phases. They found NOx emission to be increased rapidly during an acceleration period of gear shift. Their study is showing less NOx emission from diesel-biodiesel-ethanol blends than the conventional fossil diesel.

Hulwan and Joshi (Hulwan & Joshi, 2011) studied in details the effect of injection timings on the NOx emission from diesel-biodiesel-ethanol/bioethanol blends. They found decreased emission of NOx for blends at low load and all injection timings. They also identified that, at high load NOx emission increases as the ethanol blended fuels are used replacing diesel fuel. But when the RPM is 1600 and the injection timing is 21° or 13° the NOx emission is less than the diesel fuel. They found that NOx emission increases considerably high when injection timing is advanced for blends and as well as for diesel. Their results are almost the same as found by Cenk et al. (Sayin, Uslu, & Canakci, 2008). They found NOx emission as becoming almost double when the injection timing is advanced from 13° to 21° at all load condition for both diesel fuel and blends. They found decreased NOx emission for all the blends and no effect of ethanol content due to residence time available for reaction and decreased combustion temperature with increased speeds. Their results are similar as found by the authors in (Xing-cai et al., 2004b).

To lower the NOx emission from the diesel engine some selective catalytic reduction is attractive technology. He and Yu (H. He & Yu, 2005) studied that Ag/Al_2O_3-ethanol NOx catalytic converter satisfied the NOx emission requirements of the Euro III standard using European Economic Community's 13-mode test cycle. The combination of diesel-biodiesel-ethanol and Ag/Al_2O_3-ethanol system in CI engine may reduce the PM emission and NOx emission simultaneously (Shi et al., 2006). Shi et al. (Shi et al., 2008) also found the same result with different catalyst assemblies. They used 3 types of catalyst for emission reduction. They also observed approximately 5.5% increase in NOx emission from diesel-biodiesel-ethanol blend without any catalyst assembly. But when they used Ag/Al_2O_3 catalyst, the NOx reduced by 73%. Again, when the exhaust was passed through the $Ag/Al_2O_3+Cu/TiO_2$ catalyst and $Ag/Al_2O_3+Cu/TiO_2$+Pt-supported catalysts, the reduction was 71% and 61% respectively.

Table 2.4: NOx emissions from different ternary blends

Diesel:Biodiesel:Ethanol	Conditions	Comparison with Diesel performance
1. D85B12E3	High Load	↑12-14%^{cg} (X Shi et al., 2005)
2. D80B16E4	High Load	↑19% (X Shi et al., 2005)
3. D80B5E15 (SOYBEAN BD)	Low Load	↓10-70%^{cg} (Guarieiro et al., 2009)
	Medium Load	↓40-50%^{cg} (Guarieiro et al., 2009)
	High Load	↓70-75%^{cg} (Guarieiro et al., 2009)
4. D80B5E15 (CASTOR BD)	Low Load	↓0-40%^{cg} (Guarieiro et al., 2009)
	Medium Load	↓0-30%^{cg} (Guarieiro et al., 2009)
	High Load	↓5-10%^{cg} (Guarieiro et al., 2009)
5. D80B5E15 (RESIDUAL BD)	Low Load	↓10%^{cg} (Guarieiro et al., 2009)
	Medium Load	↓20-50%^{cg} (Guarieiro et al., 2009)
	High Load	↓50%^{cg} (Guarieiro et al., 2009)
6. D90B5E5	Low Load	Not much difference (Kwanchareon et al., 2007b)
	Medium Load	↑24-28%^{cg} (Kwanchareon et al., 2007b)
	High Load	↑192-196%^{cg} (Kwanchareon et al., 2007b)
7. D85B10E5	Low Load	Not much difference (Kwanchareon et al., 2007b); ↑5-9%^{cg} (Subbaiah et al., 2010);

Table 2.4, continued

		Not much difference (István Barabás & Todoruţ, 2011)
	Medium Load	↑40-45%^{cg} (Kwanchareon et al., 2007b); ↑4-8%^{cg} (Subbaiah et al., 2010); ↑10-15%^{cg} (István Barabás & Todoruţ, 2011)
	High Load	↑175-180%^{cg} (Kwanchareon et al., 2007b); ↑95-100%^{cg} (Subbaiah et al., 2010); ↑3-6%^{cg} (István Barabás & Todoruţ, 2011)
8. D85B5E10	Low Load	Not much difference (Kwanchareon et al., 2007b)
	Medium Load	↑38-42%^{cg} (Kwanchareon et al., 2007b)
	High Load	↑185-190%^{cg} (Kwanchareon et al., 2007b)
9. D80B15E5	Low Load	↑28-32%^{cg} (Kwanchareon et al., 2007b); Not much difference (István Barabás & Todoruţ, 2011)
	Medium Load	↑42-46%^{cg} (Kwanchareon et al., 2007b); ↑22-26%^{cg} (István Barabás & Todoruţ, 2011)
	High Load	↑180-185%^{cg} (Kwanchareon et al., 2007b); ↑2-5%^{cg} (István Barabás & Todoruţ, 2011)
10. D80B10E10	Low Load	↑22-26%^{cg} (Kwanchareon et al., 2007b); ↑13-17%^{cg} (Subbaiah et al., 2010)
	Medium Load	↑41-45%^{cg} (Kwanchareon et al., 2007b); ↑15-20%^{cg} (Subbaiah et al., 2010)
	High Load	↑180-185%^{cg} (Kwanchareon et al., 2007b); ↑111-116%^{cg} (Subbaiah et al., 2010)
11. D80B5E15 (PALM BD)	Low Load	↑20-24%^{cg} (Kwanchareon et al., 2007b)
	Medium Load	↑34-38%^{cg} (Kwanchareon et al., 2007b)
	High Load	↑180-185%^{cg} (Kwanchareon et al., 2007b)
12. D75B10E15	Low Load	↑17-22%^{cg} (Subbaiah et al., 2010)
	Medium Load	↑14-19%^{cg} (Subbaiah et al., 2010)
	High Load	↑128-133%^{cg} (Subbaiah et al., 2010)
13. D75B20E5	Constant Speed Variable Load	↑11.4% (Shi et al., 2006); ↑9-14%$^{tbl, avg}$ (Pang et al., 2006)
	Constant Load Variable Speed	↑5.6% (Shi et al., 2006); ↑15-20%$^{tbl, avg}$ (Pang et al., 2006)
14. D70B25E5	Low Load	↑7-12%^{cg} (István Barabás & Todoruţ, 2011)

Table 2.4, continued

	Medium Load	↑14-20%^{cg} (István Barabás & Todoruţ, 2011)
	High Load	↑7-12%^{cg} (István Barabás & Todoruţ, 2011)

$^{cg:}$ Calculated from graph; $^{avg:}$ Average Value; $^{tbl:}$ Calculated from Table

Thus it can be said that the emission of NOx by burning oxygenated fuels in the conventional diesel engine is not conclusive (Kowalewicz, 2005; Kwanchareon et al., 2007b; W. G. Wang et al., 1997) and it depends on the specific engine and its operating conditions (Corkwell KC). At low load condition, the NOx emission is reduced in most cases, but sometimes it is reported to increase slightly. Most of the researchers found NOx emission to increase significantly at medium and high load conditions. But overall NOx emissions from diesel-biodiesel-ethanol/bioethanol blends are little high from that of fossil diesel fuel. By using catalyst assembly this emission can be reduced significantly.

2.2.4.3 Carbon monoxide (CO)

The fuel-rich combustion is the reason behind the formation of CO and it increases nearly linearly with deviation from stoichiometry (Heywood & J.B., 1988; Sayin et al., 2008). The addition of biodiesel and ethanol/bioethanol with the fossil diesel fuel might solve this problem as the portion of these two biofuels are increased in the ternary blends, the oxygen content of the blends also increases which in return helps to increase the oxygen-to-fuel ratio in the fuel rich regions which leads to complete combustion and thus reducing CO emission (Ajav EA et al., 1998; Can, Celikten, et al., 2004; Li et al., 2005; Rahimi et al., 2009). But the low heating value and the evaporative cooling effect/high latent heat of ethanol result in low combustion temperature and burning velocity (W. G. Wang et al., 1997) which lead to incomplete combustion and higher CO emission (Guarieiro et al., 2009; Randazzo & Sodré, 2011; W. G. Wang et al., 1997; Xing-cai et al., 2004b). Another reason behind high CO emission might be the ignition delay developed due to the oxygenated fuel (Can, Çelikten, et al., 2004). Although some investigations observed reduced CO emission by using diesel-biodiesel-ethanol/bioethanol blends (Bhale et al., 2009; Durbin, Collins, Norbeck, & Smith, 2000; Durbin & Norbeck, 2002; Li et al., 2005; X Shi et al., 2005; W. Wang et al., 2000; Zhang et al., 2004), opposite results are also observed (B.-Q. He et al., 2003; Xing-cai et al., 2004b).

While investigating CO emission from diesel-biodiesel-ethanol/bioethanol blends, researchers found different results depending on their blend compositions, biodiesel type and the test conditions. Some researchers marked that, as the biodiesel and ethanol portion in the ternary blends increases, the CO emission decreases alongside (Rahimi et al., 2009; Subbaiah et al., 2010) but Randazzo and Sodre (Randazzo & Sodré, 2011) found no significant effect of adding biodiesel to diesel fuel in CO emission, but when ethanol is added to this blend of diesel and biodiesel, the CO emission increases proportionally with the amount of ethanol in the blend. When researchers tested the ternary blends in low load condition, Hulwan and Joshi (Hulwan & Joshi, 2011) found its emission higher than the diesel fuel. They described this increase due to the low cylinder gas temperature and delayed combustion process but Barabas et al. (István Barabás et al., 2010) found the lowest CO emission at low and medium load condition with 10% biodiesel and 10% bioethanol in the ternary blends. On the other hand, Kwanchareon et al. (Kwanchareon et al., 2007b) and Pang et al. (Pang et al., 2006) found no major difference in CO emission from diesel-biodiesel-ethanol blends compared to fossil diesel fuel at low and medium load (0%, 30% and 60%). Again, when tested at high load conditions, Kwanchareon et al. (Kwanchareon et al., 2007b), Pang et al. (Pang et al., 2006), Hulwan and Joshi (Hulwan & Joshi, 2011), Guarieiro et al. (Guarieiro et al., 2009) and Subbaiah et al.(Subbaiah et al., 2010) found reduced CO emission from ternary blends compared to fossil diesel fuel. At this load, Kwanchareon et al. (Kwanchareon et al., 2007b) found lowest CO emission (~0.6-0.8 vol%) with 15% biodiesel and 5% ethanol while Subbaiah et al.(Subbaiah et al., 2010) found the lowest CO emission (0.44% vol) with 10% biodiesel and 15% ethanol in ternary blends. But at high load some researchers reported increased CO emission (István Barabás et al., 2010). They also reported that, this increase in CO emission at higher loads from ternary blends is very much lower than its increase with the diesel fuel which can be lower as much as 59%. At this high load, it was observed by Hulwan and Joshi (Hulwan & Joshi, 2011) that the CO emission from ternary blends is not affected by injection timing and speed. But regarding overall CO emission, Park et al. (Park et al., 2012b) reported that, it is mainly governed by ignition delay and injection timing rather than premixed combustion phasing (CA50). They investigated the CO emission with respect to the CA50, injection timing and the ignition delay which helps to understand the behavior of CO emission from the diesel-biodiesel-ethanol blend more clearly. Their blends reduced CO in the emission slightly at the advanced injection timing regions (25° BTDC, 30° BTDC). In the advanced injection timing region, the higher percentage of CO emission is the result of fuel-rich combustion. But as the fossil diesel is partially substituted, the fuel-rich combustion is reduced which slightly reduce the CO emission in that region. They also found no CO emission when the ignition delay was between 5° and 10° irrespective of the biodiesel blend. Moreover, the effect of blending biodiesel on CO emission appeared at advanced injection timing regions such as 30° BTDC near the squish area region. And when this ternary blends were tested in conditions like constant speed-varying load and varying speed-constant load, then researchers Shi et al. (Shi et al., 2006) found varying results. When they tested the blends in constant speed-varying load condition, then they observed higher CO emission but when the condition was varying speed-constant load (full load), then CO emission was high initially at low speeds but again decreased at high speeds.

There are also some researchers who tested ternary blends with additives, some of them tried to find out the effect of different catalyst assemblies while some of them tested diesel-biodiesel-ethanol/bioethanol blends in a vehicle on a chassis dynamometer for real time experiment to study CO emission. Pidol et al. (Pidol et al., 2012a) used iso-pentane as additive and Fischer Tropsch diesel in ternary blends but even then they found a huge increase in CO emission which was a 100% increase. This increase was due to the very slow combustion which matches the observations in (Ali Mohammadi, Takuji Ishiyama, Hiroshi Kawanabe, & Horibe, 2004; Xing-cai et al., 2004b). But when Kwanchareon et al. (Kwanchareon et al., 2007b) used oxygenates in the ternary blends then the CO emission resulted in a small reduction at low and medium loads but significant reduction at high load conditions which also matches the results in (Li et al., 2005). Again when Shi et al. (Shi et al., 2008) used the catalyst assemblies, they observed positive results in most cases. Initially when they tested the ternary blends without any catalyst assembly, they found no difference in CO emission from the blends compared to fossil diesel fuel but when they used Ag/Al_2O_3 catalyst, its emission increased by 13 times. When they used the other 2 catalyst assembly, $Ag/Al_2O_3+Cu/TiO_2$ catalyst and $Ag/Al_2O_3+Cu/TiO_2+$Pt-supported catalyst assembly, the CO emission decreased by 50% and 70% compared to the Ag/Al_2O_3 catalyst assembly. In chassis dynamometer test, Cheenkachorn and Fungtammasan (Kraipat Cheenkachorn & Fungtammasan, 2009) tested the fuel blends in 3 phases with different speed, distance and time travel in each phase. They found the diesel-biodiesel-ethanol blends to be emitting less CO than the fossil diesel in the first 2 phases. But in the last phase of testing, which consists of the long distance traveled and high speed, the CO emission from the fuel blends is slightly higher than the fossil diesel fuel. This is because of the excess oxygen content of the fuel blend which gives rise to an improper fuel-air equivalence ratio.

Table 2.5: CO emissions from different ternary blends

Diesel:Biodiesel:Ethanol	Conditions	Comparison with Diesel performance
1. D80B16E4	High Load	↓19% (X Shi et al., 2005)
2. D80B5E15 (SOYBEAN BD)	Low Load	↑50-140%^{cg} (Guarieiro et al., 2009)
	Medium Load	↑30-60%^{cg} (Guarieiro et al., 2009)
	High Load	↓0-10%^{cg} (Guarieiro et al., 2009)
3. D80B5E15 (CASTOR BD)	Low Load	↑90-220%^{cg} (Guarieiro et al., 2009)
	Medium Load	↑50-90%^{cg} (Guarieiro et al., 2009)
	High Load	↓0-20%^{cg} (Guarieiro et al., 2009)
4. D80B5E15 (RESIDUAL BD)	Low Load	↑60-180%^{cg} (Guarieiro et al., 2009)
	Medium Load	↑40-80%^{cg} (Guarieiro et al., 2009)
	High Load	↑10-30%^{cg} (Guarieiro et al., 2009)
5. D90B5E5	Low Load	Not much difference (Kwanchareon et al., 2007b)
	Medium Load	Not much difference (Kwanchareon et al., 2007b)
	High Load	↓40-46%^{cg} (Kwanchareon et al., 2007b)
6. D85B10E5	Low Load	Not much difference (Kwanchareon et al., 2007b); ↓1-4%^{cg} (Subbaiah et al., 2010); ↓13-19%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	Medium Load	Not much difference (Kwanchareon et al., 2007b); Not much difference ^{cg} (Subbaiah et al., 2010); ↓45-50%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	High Load	20-25%^{cg} (Kwanchareon et al., 2007b), ↓45-50%^{cg} (Subbaiah et al., 2010); ↓57-63%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
7. D85B5E10	Low Load	Not much difference (Kwanchareon et al., 2007b)
	Medium Load	Not much difference (Kwanchareon et al., 2007b)
	High Load	↓45-50%^{cg} (Kwanchareon et al., 2007b)
8. D80B15E5	Low Load	Not much difference (Kwanchareon et al., 2007b); ↓10-15%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	Medium Load	Not much difference (Kwanchareon et al., 2007b); ↓45-50%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	High Load	62-67%^{cg} (Kwanchareon et al., 2007b); ↓52-58%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
9. D80B10E10	Low Load	Not much difference (Kwanchareon et al., 2007b); ↓1-4%^{cg} (Subbaiah et al., 2010)
	Medium Load	Not much difference (Kwanchareon et al., 2007b); Not much difference ^{cg} (Subbaiah et al., 2010)
	High Load	↓55-60%^{cg} (Kwanchareon et al., 2007b); ↓50-55%^{cg} (Subbaiah et al., 2010)
10. D80B5E15 (PALM BD)	Low Load	Not much difference (Kwanchareon et al., 2007b)
	Medium Load	Not much difference (Kwanchareon et al., 2007b)
	High Load	↓58-62%^{cg} (Kwanchareon et al., 2007b)
11. D75B10E15	Low Load	↓1-4%^{cg} (Subbaiah et al., 2010)
	Medium Load	Not much difference ^{cg} (Subbaiah et al., 2010)
	High Load	↓52-58%^{cg} (Subbaiah et al., 2010)
12. D75B20E5	High Load	↓20-30%^{cg} (Shi et al., 2006)
13. D70B25E5	Low Load	↓10-15%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)

Table 2.5, continued

	Medium Load	↓42-48%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	High Load	↓33-38%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
14. D10B80E10	Low Load	↓34-39%$^{cg, avg}$ (Bhale et al., 2009)
	Medium Load	↓39-43%$^{cg, avg}$ (Bhale et al., 2009)
	High Load	↓35-40%$^{cg, avg}$ (Bhale et al., 2009)

$^{cg:}$ Calculated from graph; $^{avg:}$ Average Value; $^{tbl:}$ Calculated from Table

Thus, the CO emission from diesel-biodiesel-ethanol/bioethanol blends depends on the operating conditions. Some of the researchers found greater CO emission from ternary blends (compare to diesel) while others found, either no major difference or reduced emission. From table. 2.5 and table 2.9 highest emission is recorded with Fischer Tropsch diesel which is a 100% increase, while with regular diesel fuel maximum CO emission is found to be 220% at low load. But increased CO emission is recorded by only few researchers who investigated ternary blends with high percentage of ethanol/bioethanol (>15%). When overall CO emission is considered, then reduced or little difference is found compared to diesel. Thus, the portion of ethanol in ternary blends should be kept low to control the CO emission.

2.2.4.4 Carbon dioxide (CO_2)

When a hydro-carbon fuel is burnt, the most common by-product is CO_2 and water. The oxygenated fuels result in slightly less CO_2 emission as the biodiesel has less carbon in its molecules and combustion of ethanol products contain less CO_2 and more H_2O (Kowalewicz, 2005). However at high engine speed and load when more fuel is burnt without more excess air, this effect is not visible which results in high CO_2 emission (Kraipat Cheenkachorn & Fungtammasan, 2009). Some researchers reported this high percentage of CO_2 emission from diesel-biodiesel-ethanol/bioethanol blends compared to diesel (István Barabás et al., 2010; Shi et al., 2006; Subbaiah et al., 2010), while some of them found CO_2 emission from ternary blends almost similar to diesel fuel (Pang et al., 2006). There are also many investigators who reported decreased CO_2 emission (Guarieiro et al., 2009; Randazzo & Sodré, 2011). Subbaiah et al. (Subbaiah et al., 2010) marked increasing CO_2 emission from ternary blends as the ethanol portion in the blends increases while He et al. (B.-Q. He et al., 2003) observed that by increasing the proportion of ethanol in the blends, CO_2 emission decreases. This phenomenon can be explained by the low carbon-to-hydrogen ratio in the ethanol molecule.

Hulwan and Joshi (Hulwan & Joshi, 2011) found similar CO_2 emission from diesel-biodiesel-ethanol blends compared to diesel fuel except at low loads. At the low load conditions; due to lower combustion characteristics of the blends, the fuel consumption increases to meet the same power as diesel fuel which increases the CO_2 emission. They found no effect of advancing injection timing on the CO_2 emission. But when they advanced the injection timing up-to 40%, they found considerable increase in CO_2 for every 3° crank angle advance injection timing but this advancing the injection timing also results in decreased CO emissions.

Table 2.6: CO_2 emissions from different ternary blends

Diesel:Biodiesel:Ethanol	Conditions	Comparison with Diesel performance
1. D80B5E15 (SOYBEAN BD)	Low Load	↑10%^{cg} (Guarieiro et al., 2009)
	Medium Load	↓2-6%^{cg} (Guarieiro et al., 2009)
	High Load	↓8-28%^{cg} (Guarieiro et al., 2009)
2. D80B5E15 (CASTOR BD)	Low Load	↓0-1%^{cg} (Guarieiro et al., 2009)
	Medium Load	↑3-7%^{cg} (Guarieiro et al., 2009)
	High Load	↑0-2%^{cg} (Guarieiro et al., 2009)
3. D80B5E15 (RESIDUAL BD)	Low Load	↓0-10%^{cg} (Guarieiro et al., 2009)
	Medium Load	↓0-10%^{cg} (Guarieiro et al., 2009)
	High Load	↓8-15%^{cg} (Guarieiro et al., 2009)
4. D85B10E5	Constant Speed Variable Load	↑1.03%^{avg} (Subbaiah et al., 2010)
	Low Load	↑22-26%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	Medium Load	↑37-42%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	High Load	↑20-25%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
5. D80B10E10	Constant Speed Variable Load	↑1.91%^{avg} (Subbaiah et al., 2010)
6. D75B10E15	Constant Speed Variable Load	↑2.94%^{avg} (Subbaiah et al., 2010)
7. D75B20E5	Constant Speed Variable Load	↑5-10%^{cg} (Shi et al., 2006)
	Constant Load Variable Speed	↑1-5%^{cg} (Shi et al., 2006)
8. D80B15E5	Low Load	↑22-26%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	Medium Load	↑38-44%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	High Load	↑18-23%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
9. D70B25E5	Low Load	↑37-43%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	Medium Load	↑57-63%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	High Load	↑32-38%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)

$^{cg:}$ Calculated from graph; $^{avg:}$ Average Value

In the end it can be conclude that, with lower percentage of ethanol in ternary blends, CO emission decreases but CO_2 emission increases (see table 2.6 and table 2.9 also). Thus, it can be said that as the portion of ethanol in the blend increases, the CO_2 emission decreases. When diesel-biodiesel-ethanol blend is used in the real life cycle test assembly, the CO_2 emission is found to be reduced compared to diesel fuel although this reduction is very small (Kraipat Cheenkachorn & Fungtammasan, 2009).

2.2.4.5 Hydrocarbon (HC)

THC or the total hydrocarbon emission is the emission of unburned hydrocarbon and is an indicator of efficiency of combustion or completeness (Kraipat Cheenkachorn & Fungtammasan, 2009). Fuel blend of diesel and ethanol are reported by some investigators to increase THC but adding biodiesel with this blend are found to reduce THC compared to diesel (Canakci, 2007; Durbin et al., 2000; B.-Q. He et al., 2003; Kegl, 2008; Qi et al., 2009; Satge de Caro et al., 2001; W. Wang et al., 2000; Xing-cai et al., 2004b). The biodiesel with high CN causes shorter ignition delay and improves efficiency of the combustion which in return reduces unburned hydrocarbon. In addition to this, the presence of oxygen in the molecules of biodiesel intensifies the post flame oxidation process of unburned hydrocarbons in the combustion chamber (Randazzo & Sodré, 2011). Many researchers found significant reduction in THC emission from diesel-biodiesel-ethanol/bioethanol blends compared to diesel fuel (István Barabás et al., 2010; Bhale et al., 2009; Kraipat Cheenkachorn & Fungtammasan, 2009; Kwanchareon et al., 2007b; Pang et al., 2006; Park et al., 2012b; Rahimi et al., 2009; Randazzo & Sodré, 2011; Shi et al., 2008) while some of them found moderate decrease (Pang et al., 2006; Shi et al., 2006). This moderate reduction from ternary blends could be 10.3% (Pang et al., 2006) and 4.2% (Shi et al., 2006) at constant speed/varying load condition or 8.8% (Pang et al., 2006) and 5.3% (Shi et al., 2006) at constant load/varying speed condition, depending on the biodiesel and ethanol content and quality in the blend. With only 3% bioethanol and 2% biodiesel in ternary blends, this reduction could be 60 ppm for some speeds (Rahimi et al., 2009) while with 5% bioethanol, this reduction could be 50% at high loads (István Barabás et al., 2010). Even a few researchers (Bhale et al., 2009) added only 10% diesel with 80% biodiesel and 10% ethanol to prepare ternary blend which also showed lower

HC emission at lower loads compared to diesel. But as the load increases, the emission becomes identical to diesel fuel HC emission. And at high load, the HC emission again becomes smaller than the diesel fuel emission. There are some researchers (Subbaiah et al., 2010) who also marked that the HC emission from ternary blends at higher load become lower than the diesel fuel. But they marked its emission higher at low and medium loads. In terms of injection timing, Park et al. (Park et al., 2012b) found the lowest HC emission at 20° BTDC. During this period, the utilization of oxygen is relatively high, and the fuel is directly sprayed towards the piston bowl.

Along with these regular tests, some researchers tested diesel-biodiesel-ethanol/bioethanol blends in a vehicle on a chassis dynamometer for real time experiment (Kraipat Cheenkachorn & Fungtammasan, 2009) while some of them used catalyst assemblies to test the ternary blends HC emission (Shi et al., 2008). In the chassis dynamometer test, the investigators found THC emission to be at its highest level during an acceleration period of gear shift. They reported consistently less THC emission by burning diesel-biodiesel-ethanol compared to fossil diesel at an average of 29.6%. This was due to the high oxygen content of the blend which shifted the air-fuel ratio in favor of less THC emission. On the other hand the catalyst assemblies had no positive effect on the HC reduction in the emissions (Shi et al., 2008). When they used Ag/Al_2O_3 catalyst, the HC emission increased greatly. The increase was about 7 times the normal emission without any catalyst. This was due to the ethanol addition that remained after the ethanol-selective catalytic reduction (SCR) process. And when $Ag/Al_2O_3+Cu/TiO_2$ catalyst assembly and $Ag/Al_2O_3+Cu/TiO_2+$Pt-supported catalyst assembly were used, the HC emission reduced by 60% and 80% respectively compared to the Ag/Al_2O_3 catalyst process. Although after all these catalyst assembly process, the HC emission was larger than the original engine emitted exhaust using diesel-biodiesel-ethanol blends.

There are some researchers who found higher HC emission from diesel-biodiesel-ethanol/bioethanol blends compared to diesel fuel (Randazzo & Sodré, 2011; X Shi et al., 2005). This might be due to the ethanol in the blends which causes greater ignition delay for the ternary blends, causing incomplete combustion which in return increases the HC emission (Randazzo & Sodré, 2011). Another factor could be the effect of slow vaporization of rate of ethanol and by the difficulty to produce a homogenous blend with diesel fuel, thus contributes to the formation of ultra-lean mixtures in some regions of the combustion chamber (B.-Q. He et al., 2003).

Table 2.7: HC emissions from different ternary blends

Diesel:Biodiesel:Ethanol	Conditions	Comparison with Diesel performance
1. D85B12E3	High Load	↑51-55%^{cg} (X Shi et al., 2005)
2. D80B16E4	High Load	↑44-47%^{cg} (X Shi et al., 2005)
3. D90B5E5	Low Load	↑148-152%^{cg} (Kwanchareon et al., 2007b)
	Medium Load	↑248-252%^{cg} (Kwanchareon et al., 2007b)
	High Load	↓67-72%^{cg} (Kwanchareon et al., 2007b)
4. D85B10E5	Low Load	↑188-192%^{cg} (Kwanchareon et al., 2007b); ↑185-190%^{cg} (Subbaiah et al., 2010); ↓46-51%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	Medium Load	↑98-102%^{cg} (Kwanchareon et al., 2007b); ↑48-52%^{cg} (Subbaiah et al., 2010); ↓46-51%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	High Load	↓55-58%^{cg} (Kwanchareon et al., 2007b); ↓46-52%^{cg} (Subbaiah et al., 2010); ↓43-49%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
5. D85B5E10	Low Load	↑278-282%^{cg} (Kwanchareon et al., 2007b)
	Medium Load	↑228-232%^{cg} (Kwanchareon et al., 2007b)
	High Load	↓60-65%^{cg} (Kwanchareon et al., 2007b)
6. D80B15E5	Low Load	↑170-175%^{cg} (Kwanchareon et al., 2007b); ↓33-39%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	Medium Load	↑138-145%^{cg} (Kwanchareon et al., 2007b); ↓15-20%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	High Load	↓72-78%^{cg} (Kwanchareon et al., 2007b); ↓42-47%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
7. D80B10E10	Low Load	↑370-375%^{cg} (Kwanchareon et al., 2007b); ↑218-224%^{cg} (Subbaiah et al., 2010)

Table 2.7, continued

	Medium Load	↑358-363%^{cg} (Kwanchareon et al., 2007b); ↑298-302%^{cg} (Subbaiah et al., 2010)
	High Load	↓43-47%^{cg} (Kwanchareon et al., 2007b); ↓32-37%^{cg} (Subbaiah et al., 2010)
8. D80B5E15 (PALM BD)	Low Load	↑370-375%^{cg} (Kwanchareon et al., 2007b)
	Medium Load	↑308-313%^{cg} (Kwanchareon et al., 2007b)
	High Load	↓58-63%^{cg} (Kwanchareon et al., 2007b)
9. D75B10E15	Low Load	↑279-283%^{cg} (Subbaiah et al., 2010)
	Medium Load	↑368-372%^{cg} (Subbaiah et al., 2010)
	High Load	↓37-42%^{cg} (Subbaiah et al., 2010)
10. D75B20E5	Constant Speed Variable Load	↓4.2%^{avg} (Shi et al., 2006); ↓10.3%^{avg} (Pang et al., 2006)
	Constant Load Variable Speed	↓5.3%^{avg} (Shi et al., 2006); ↓8.8%^{avg} (Pang et al., 2006)
11. D70B25E5	Low Load	↓50-55%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	Medium Load	↓34-39%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)
	High Load	↓44-50%$^{cg, avg}$ (István Barabás & Todoruţ, 2011)

$^{cg:}$ Calculated from graph; $^{avg:}$ Average Value

Thus, it is confirmed after all the review that the HC emission by using diesel-biodiesel-ethanol/bioethanol blends directly depends on the ethanol/bioethanol and biodiesel content of the blends. As the ethanol portion increases in the blend, the HC emission increases proportionally, while HC emission decreases as the biodiesel portion in the blends increases (István Barabás et al., 2010; Kwanchareon et al., 2007b; Park et al., 2012b; Subbaiah et al., 2010). So, to prevent increased HC emission from ternary blends the ethanol and biodiesel portion should be balanced; if high amount of ethanol is used then high amount of biodiesel also must be used in the ternary blends to control HC emission. From table 2.7 and table 2.9 it can be concluded that, although HC emission from ternary blend increases at low and medium load conditions, its overall emission is lower than the fossil diesel fuel or almost like it.

2.2.4.6 Particulate matter (PM)

The emission of particulate matters (PM) is the primary concern of diesel engines. Diesel PM is a complex mixture of elemental carbon, a variety of HCs, sulfur compounds and other species (Burtscher, 2005). It is a mixture of solid and liquid and mainly consists of carbonaceous material known as soot, some absorbed organic compound and sulfates. PM emission from IC engines might be caused by fuel or lubricant. But fuel has got the greater effect on PM emission rather than the lubricant (W. G. Wang et al., 1997). For reducing PM emissions, oxygenated fuels can be used, although some investigators found it increasing with oxygenated fuels. Due to the oxygen present in the fuel blend, it is delivered to the pyrolysis zone of the burning diesel spray which results in reduced PM formation (R. L. McCormick et al., 2001; W. Wang et al., 2000). The mechanism of reduced PM emission by burning oxygenated fuels is not yet clearly known. The reduction of PM emission by burning biodiesel in diesel engines had been widely studied (X. Shi et al., 2005; W. G. Wang et al., 1997). It is also reported in (W. G. Wang et al., 1997), that the low carbon to hydrogen (C:H) ratio and complex structure of any fuel shows a tendency to form smoke precursors due to pyrolysis and combustion. Compared to fossil diesel, the biodiesel has got a lower C:H ratio and the structure of ethanol is less complex. These two factors might contribute to the lower PM emission from diesel-biodiesel-ethanol/bioethanol blends (Kraipat Cheenkachorn & Fungtammasan, 2009). Some authors have suggested that the effect of fuel on PM emission varies from vehicle to vehicle (Durbin et al., 2000; Park, Cha, & Lee, 2010; W. Wang et al., 2000). But overall most of the investigators have reported reduced PM emission from diesel-biodiesel-ethanol/bioethanol blends compared to diesel fuel, irrespective of the operating conditions (Kraipat Cheenkachorn & Fungtammasan, 2009; Pang et al., 2006; Randazzo & Sodré, 2011; Shi et al., 2006; X Shi et al., 2005). This reduction could be maximum 52% (Kraipat Cheenkachorn & Fungtammasan, 2009). This high reduction is due to the fact that, through the formation of hydroxyl radical (◦OH), the oxygen component consumes the soot precursors which results in a lower soot formation (Chen et al., 2007; Song et al., 2002). Other investigators also found this reduction to be 22-40% (Pang et al., 2006), 21-39% (Shi et al., 2006) and 48% at full speed while 34% at full torque condition (X Shi et al., 2005). In (X Shi et al., 2005), Shi et al. used 4% ethanol and 16% biodiesel with the diesel fuel to get the highest reduction. They also prepared a blend with 3% ethanol and 12% biodiesel from which they marked maximum 34% reduced PM emission at the highest speed while it was 17% at the highest torque.

There are also some researchers who marked high PM emission from diesel-biodiesel-ethanol/bioethanol blends compared to fossil diesel (Shi et al., 2008). They found 16% increased PM emission from diesel-biodiesel-ethanol blends compared to fossil diesel fuel. In this study they fractioned the PM in 3 terms: soluble organic fractions (SOF) (which consists of mainly volatile organic materials, which are easily oxidized (Hosoya & Shimoda, 1996; Stein, 1996), dry soot (DS) and sulfate/water. The sum of these three components is equal to total PM. When the investigators used no catalyst assembly, they found decreased DS portion but increased SOF by 42% and the sulfate/water portion very little which results in a total increase in PM emission. This increase in SOF might be due to the unburned ester condensed on the particulates because of the low volatility of the methyl soyate. Stein and Hosoya (Stein, 1996) and Shimoda (Hosoya & Shimoda, 1996) suggested that, oxidation catalyst might reduce PM emissions. In this study the investigators found that to be true when their catalyst assembly reduced the PM emission significantly. They found the $Ag/Al_2O_3+Cu/TiO_2$ catalyst assembly reducing about 46% of PM emissions. While the other $Ag/Al_2O_3+Cu/TiO_2+Pt$-supported catalyst assembly increased the PM emissions by 4% compared to value (from diesel-biodiesel-ethanol blends) without any catalyst.

Table 2.8: PM emissions from different ternary blends

Diesel:Biodiesel:Ethanol	Conditions	Comparison with Diesel performance
1. D85B12E3	High Load	↓34% (X Shi et al., 2005)
2. D80B16E4	High Load	↓48% (X Shi et al., 2005)
3. D75B20E5	High Load	↓21-39%^{avg} (Shi et al., 2006); ↓22-40%^{avg} (Pang et al., 2006)

$^{avg:}$ Average Value

Table 2.8 shows that diesel-biodiesel-ethanol blends reduce PM emission significantly. Some investigators even found it decreasing as much as 52%, depending on the operating conditions. But this decrease can be maintained if the portion of biodiesel in the blend is kept as high as possible while the portion of ethanol in the blend is kept as low as possible. This low PM emission from high biodiesel and low ethanol content ternary blends is due to the high CN of biodiesels and low CN of ethanol (Canakci, 2007; Randazzo & Sodré, 2011). Some researchers have found PM emission from ternary blends higher than diesel fuel. Their results vary from other many researchers. This might be due to their biodiesel quality and the purity of ethanol.

Table 2.9: Performance and emission of different diesel-biodiesel-bioethanol/ethanol blends compared to fossil diesel fuel

Blend Name	**% Volume of each part in the blend** **Diesel: Biodiesel: Ethanol**	**Biodiesel feedstock & Ethanol purity**	**Test equipment specifications**	**Adjustments and/or modifications and operating condition**	**Comparison with diesel fuel performance (% change) in exhaust gas and emissions**						**Ref.**
					Soot and smoke	**NOx**	**CO**	**CO₂**	**HC**	**Brake Specific Fuel Consumption** **BSFC**	
D70B10E20 D50B20E30 D50B10E40	70:10:20 50:20:30 50:10:40	Jatropha Oil 99.7%	3 cyl 3300 cc CR: 18:1	Varying Speed (1200 & 1600 RPM) Constant injection pressure Varying IT(13°, 18° & 21° CA BTDC)	Condition: Injection timing advanced. ↓52% max for blend D70B10E20 Condition: at all injection timings & speeds. Almost constant and negligible @ small loads but ↓ as the load increases ↓ Maximum 60%-70% with high ethanol content.	↓@ low loads @ both speeds and all injection timings ↑ @ other loads except 1600 RPM of 21° & 13° injection timing	↑ @ low loads ↓slightly @ high loads ↓when the injection timing is advanced to 33° from 21°	Same as diesel fuel @ all loads except low loads. ↑@ low loads When the injection timing is advanced up-to 40% ↑ considerably for every 3° crank angle		Very little effect of injection timing @ all loads	(Hulwan & Joshi, 2011)
D94.95B2.05E3 D89.9B4.1E6 D84.85B6.15E9 D79.8B8.2E12	94.95:2.05:3 89.90:4.1:6 84.85:6.15:9 79.8:8.2:12	Sunflower Oil 95%	2 cyl B: 95 mm S: 85 mm 1205 cc	Variable speed @ full load	↓relatively as the biodiesel used		↓as the portion of the biofuel increases		↓ Largely Maximum 60 ppm ↓ @ some speeds	↓Initially but again ↑ with speeds ↑As the biofuel portion increases	(Rahimi et al., 2009)

Table 2.9, continued

D85B10E5 D80B15E5 D70B25E5	85:10:5 80:15:5 70:25:5	Rapeseed Oil 99.3%	4 cyl, B: 110mm, S: 130mm, CR: 17:1, RP: 46.5kW @ 1800RPM, RT: 285Nm @ 1200RPM	Constant speed Variable load	↓Maximum of 50%. ↓ Is observed @ all loads.	Less influence of oxygenated fuels @ lower loads ↑ 10%-26% @ medium & high loads	↓ @ All loads Lowest with the blend D80B15E5 Max ↓ of 59% @ high loads with D85B10E5	↑As the load increases	↓At all loads But ↑ as the ethanol portion increases & ↓ as the BD portion increases @ all loads Highest ↓ could be 50%	↑32.4% max @ small loads ↑6.2-15.8% @ Medium and high loads	(István Barabás & Todoruţ, 2011)
DESB (soybean BD) DEAB (castor BD) DERB (residual BD)	80:5:15 80:5:15 80:5:15	Soybean Oil Castor Oil Residual Oil 99.5%	2 cyl, B: 90mm, S: 100mm, CR: 18:1, 1272cc, RT: 7daNm @ 2500RPM	Constant speed Variable load		↓ @ all engine speeds and operating conditions Soybean BD showed highest reduction	↑@ Low and medium loads ↓@ High loads	↓ 27% Maximum with soybean BD		↓@ High loads	(Guarieiro et al., 2009)
BE-diesel	75:20:5		4 cyl CR: 17.5:1 3.92 L	Constant load (full load) varying speed Constant speed (1800 RPM) varying load		↑ Slightly	No major difference	No major difference	↓ 8.8% @ constant load & ↓ 10.3% @ constant speed		(Pang et al., 2006)
Fuel B Fuel C Fuel D	40(FT):40:20 40:40:20 40(FT): 40:20 + iso-pentane	Rapeseed Oil 99.9%	4 cyl, CR: 18:1, 1.6L, B: 75mm, S: 88.3mm, RP: 66kW	1500 rpm & 3 bar of BMEP 2500 rpm & 6 bar of BMEP 4000 rpm-full load	↓ @ All speed ↑ When EGR rate is increased	↓ When EGR rate is increased	Huge increase even after adding additive ↑ 100%		↑ % Depends on the operation	↑ 6% & 11% @ 1500 rpm & 2500 rpm with FT. ↑ 50% with fossil diesel & iso-pentane	(Pidol et al., 2012a)

Table 2.9, continued

Total 6 fuel blends with 10% increment in each blend of every component	90:5:5 85:10:5 85:5:10 80:15:5 80:10:10 80:5:15	Palm Oil 99.5%	1 cyl	Variable load		↑ @ All loads	No significant difference @ low and medium loads ↓ Significantly @ high loads		↓ @ High load ↑ @ Low and medium loads		(Kwanchareon et al., 2007b)
BD05 BD10 BD20	75:05:20 70:10:20 60:20:20	Soybean Oil	1 cyl B: 75 mm S: 84.5 mm CR: 17.8:1	1200 rpm Injection Pressure: 120 MPa Injection Timing: 30° BTDC - TDC	↓ @ All ignition delay, injection timing and CA50 except @ advanced injection timing condition (fuel-rich combustion)	↓ @ Long ignition delay and retardation of CA50	↓ Slightly in advanced injection timing region		↓ As the biodiesel content increases		(Park et al., 2012b)
Several blends	5, 10, 15, 20% vol with D:E ratio of 95:5 10, 15, 20, 25% vol for D:E ratio of 90:10 and 85:15	Palm Oil derived biodiesel 99.5%	4 cyl B: 93 mm S: 92 mm 2.499 L CR: 17.7:1 RP: 58 kW @ 3900 RPM RT: 176 Nm @ 1800 RPM	Chassis dynamometer test: P: 1# d: 3.51km, t: 823s, v: 10-20km/hr, av: 14.61km/hr P: 2# d: 9.70 km, t: 730s, v: 40-60km/hr, av: 46.77km/hr P: 3# d: 14.84km, t: 724s, v: 60-80km/hr, av: 72.64km/hr		↓ compared to fossil diesel	↓ @ P1 and P2 ↑ @ P3	↓ slightly	↓ consistently at an average of 29.6%	↑ insignificantly	(Kraipat Cheenkachorn & Fungtammasan, 2009)

Table 2.9, continued

B20E2 B20E5	78:20:2 75:20:5	Soybean Oil Anhydrous ethanol	4 cyl, 1.248L, CR: 17.6:1, RP: 62.6kW @ 4000RPM, RT: 200.1Nm @1750RPM	Vehicle placed over a chassis dynamometer according to NEDC cycle		↓ As the amount of ethanol increases in the blend	↑ Proportionally with ethanol content	↓ Significantly	↑ With the amount of ethanol added		(Randazzo & Sodré, 2011)
BE-diesel	75:20:5	Soybean Oil 99.7%	4 cyl, 3.92L, CR: 17.5:1, B: 102mm, S:120mm, RP:76kW @ 2800 RPM, RT: 245Nm @ 1600RPM	Constant load (full load) varying speed Constant speed (1800 RPM) varying load		↑ 11.4% @ varying load & 5.6% @ varying speed	↑ @ Constant speed In full load condition ↑ @ low speed and ↓ @ high speeds	↑ By an average of 3.5%	↓ 4.2% @ varying load & 5.3% @ varying speed		(Shi et al., 2006)
BE-diesel	75:20:5	Soybean Oil	4 cyl 5.12 L B: 102 mm S: 120 mm CR: 17.5:1 RP: 132 kW @ 2300 RPM RT: 660 Nm @ 1300-1500 RPM	Steady state 13-mode test cycle of the European Stationary Cycle (ESC)	↓ 60%-80% depending on test mode	↑ 5.5% with no catalyst ↓ 73% with Ag/Al_2O_3 catalysts ↓ 71% with Ag/Al_2O_3+ Cu/TiO_2 catalysts ↓ 61% with Ag/Al_2O_3+ Cu/TiO_2+Pt -supported catalysts	Same as the diesel with no catalyst ↑ 13 times with Ag/Al_2O_3 catalysts ↓ 50% with Ag/Al_2O_3+Cu/TiO_2 catalysts compared to Ag/Al_2O_3 catalysts ↓ 70% with Ag/Al_2O_3+Cu/TiO_2+Pt-supported catalyst compared to Ag/Al_2O_3 catalysts		↓ Compared to diesel ↑ 7 times when Ag/Al_2O_3 catalysts used ↓ 60% with Ag/Al_2O_3+Cu/TiO_2 catalysts compared to Ag/Al_2O_3 catalysts ↓ 80% with Ag/Al_2O_3+Cu/TiO_2+Pt-supported catalyst compared to Ag/Al_2O_3 catalysts		(Shi et al., 2008)

Table 2.9, continued

							By using the later one it finally matches the raw exhaust emission		But it was still larger than the original exhaust		
BE15 BE20	85:12:3 80:16:4	Soybean Oil 99.7%	4 cyl, 2.8L, B: 94.4mm, S: 100mm, CR: 18.5:1, RP: 76kW @ 3600 RPM, RT: 245 Nm @ 1900 RPM	Constant load (full load) varying speed Constant speed (1900RPM) varying load	Max ↓ 47% @ full load & 90% @ full speed	↑ Maximum with 4% ethanol ↑ 19% @ full load & 30% @ full speed	↓ 19% @ full load & ↓ 20% @ full speed		↑ Significantly @ all operating conditions	↑ Slightly	(X Shi et al., 2005)
MME E10 D10	10:80:10	Mahua Oil	1 cyl, 661cc, B: 87.5mm, S: 110mm, CR: 17.5:1, RP: 5.2 kW @ 1500 RPM	Constant speed (1500 RPM) varying load (varying BMEP from 0-650 kPa)	Reduced considerably	Identical to diesel fuel.	↓ Significantly		↓ @ Low load As the load increases the emission becomes identical ↓ @ high load		(Bhale et al., 2009)
B10E5 B10E10 B10E15	85:10:5 80:10:10 75:10:15	Rice bran Oil 99.5%	1 cyl, CR: 16.5:1, B: 80mm, S: 110mm, RP: 3.72kW, Maximum Speed: 1500rpm	Fixed Speed: 1500 rpm Variable load Date obtained from 0%-100% with 20% increment	↑ 2.55% with B10E5 ↓ 1.7% with B10E10 ↓ 5.11% with B10E15	↓ @ Low load & ↑ @ Medium & high load ↑ With the increasing % of ethanol	No difference @ low & medium load ↓ 46.39% with B10E5 ↓ 51.54% with B10E10 ↓ 54.63% with B10E15	↑ 1.03% with B10E5 ↑ 1.91% with B10E10 ↑ 2.94% with B10E15	↑ @ Low & medium load ↓ 48.8% with B10E5 ↓ 34.3% with B10E10 ↓ 40.0% with B10E15 @ Full load condition	↑ As the ethanol in the blend increases ↑ 26.97% for B10E5 ↑ 31.33% for B10E10 ↑ 35.33% for B10E15	(Subbaiah et al., 2010)

↓: Decreasing; ↑: Increasing; cyl: Cylinders; CR: Compression Ratio; B: Bore; S: Stroke; RP: Rated Power; RPM: Rotation per Minute; RT: Rated Torque; Max: Maximum; FT: Fischer-Tropsch; vol: Volume; p: Phase; d: Distance; t: Time; v: Velocity; av: Average Velocity; NEDC: New European Driving Cycl

2.3 Density and viscosity calculation models for diesel-biodiesel-bioethanol blends

By using ternary blend, many problems can be solved, which are integrated with biodiesel and diesel-biodiesel blends use in unmodified internal combustion engines, especially the high density and viscosity. Among the physicochemical properties of biofuels, density and viscosity are the most important parameters as they directly affect the performance, combustion and emission characteristics and also influence the air/fuel mass ratio, engine deposits formation and engine behavior in cold weather conditions (Alptekin & Canakci, 2008; Ismail et al., 2012; Nita, Geacai, & Iulian, 2011; Tesfa, Mishra, Gu, & Powles, 2010; Veny et al., 2009b). Again, properties like cetane number and heating values are partially related to density (Tat & Van Gerpen, 2000). Density influences every step related to fuels of internal combustion engines, like the design of manufacturing and distribution of the fuel (Pratas et al., 2011; Yaws, 2008), reactors, distillation units and separation process, storage tanks and process pipes (Noureddini, Teoh, & Davis Clements, 1992; Veny et al., 2009a). To provide proper combustion, density must be known as the injection systems, pumps and injectors have to deliver a precise amount of fuel for this purpose (Dzida & Prusakiewicz, 2008). Boudy and Seers (Boudy & Seers, 2009) and Baroutian et al. (Baroutian, Aroua, Raman, & Sulaiman, 2008) showed that the main physicochemical property that influences the amount of mass injected is the density of the fuel. The viscosity is not only required for the design of fittings, pipes and equipment to be used in the industry of fuel and oil (Gonçalves, Ceriani, Rabelo, Maffia, & Meirelles, 2007), but also for monitoring the quality of the fuel to be used in the diesel engines. A poor atomization, which is the first step of combustion, is the result of a viscous fuel, is responsible for a poor fuel combustion (Boudy & Seers, 2009; C. E. Ejim, B. A. Fleck, & A. Amirfazli, 2007).

It is very important to know the correlation between diesel, biodiesel and bioethanol portion and their individual density and viscosity against the final density and viscosity of the blends before blending these 3 components to test in an engine. The physicochemical properties of these 3 components are completely different from each other. Diesel is made up of different types of hydrocarbon and biodiesel is a mixture of different types of fatty acid methyl or ethyl esters while bioethanol is the only pure substance. Thus, it becomes very difficult to predict the density and viscosity of these ternary fuel blends (diesel-biodiesel-bioethanol blend) as the components are of three different natures. In case of biodiesel and diesel-biodiesel binary blends, a lot of prediction models are available to calculate their density and viscosity at different temperatures (Alptekin & Canakci, 2008; Ramírez-Verduzco, García-Flores, Rodríguez-Rodríguez, & del Rayo Jaramillo-Jacob, 2011; Tat & Van Gerpen, 2000), but a very few for diesel-biodiesel-bioethanol blends with low biofuel contents. To the best of our knowledge there are no available calculation models to calculate density and viscosity of ternary blends with high biofuel contents. Thus, if it is possible to predict the density and viscosity of diesel-biodiesel-bioethanol blends through calculation, then it will be easier for the researchers to predict the engine performance, combustion characteristics and exhaust emissions using ternary blends.

2.3 Critical findings from the literature

The following points can be summarized from the review of the literatures.

- Bioethanol is immiscible in neat diesel over a wide range of temperature. its solubility in neat diesel changes with change of temperature. An effective way to prevent the phase separation is adding biodiesel to this binary blend of diesel and bioethanol. Besides, in this way the biofuel content of the blend could be improved and the use of biodiesel (amount) blend with diesel could be increased.
- The flash point of any diesel-biodiesel-alcohol blend is dominated by the alcohol portion of the blend.

- The alcohol part of the ternary blend governs the engine brake specific fuel consumption (BSFC).
- Particulate matter (PM) is significantly reduced by using ternary blend of diesel-biodiesel-bioethanol blends. This high reduction can be maintained by keeping the portion of biodiesel in the blend as high as possible. This might also be true for other ternary blends of diesel, biodiesel and alcohol.
- Hydrocarbon emission depends on the portion of biodiesel and bioethanol in the blend. As the portion of biodiesel in the blend increases the its emission decreases.
- Carbon monoxide emission using diesel-biodiesel-bioethanol blend depends on the operating conditions.
- Smoke emission is reduced greatly when ternary blend of diesel-bio-bioethanol is used.
- Diesel-biodiesel-bioethanol blend is a promising diesel extender option. By using this ternary blend, many problems can be solved, which are integrated with other biofuel blends use in unmodified internal combustion engines, especially the high density and viscosity. Thus, density and viscosity calculation models would be very useful which will help to calculate the properties of newly developed ternary blends.

CHAPTER 3 : RESEARCH METHODOLOGY

3.1 Introduction

This chapter contains the methodology of the research work. The procedure and apparatus used for the characterization of the neat fuels and their blends are discussed initially. This is followed by the procedure of the engine testing which includes engine performance and emission data collection and analysis. Later, the methods used for developing density and viscosity models are discussed.

3.2 Neat diesel, biodiesel feedstocks and alcohols

Neat diesel was obtained from PETRONAS, Malaysia and used as the base fuel. The palm oil, coconut oil, mustard oil, calophyllum oil and soybean oil were supplied by the local suppliers. The bioethanol was purchased from Chemical Industries (Malaya) Sdn. Bhd., Malaysia and other alcohols from QREC Chemical Company, Thailand.

3.3 Biodiesel production

Producing biodiesel from crude oil requires 2 processes. If the acid value of the oil is below 4 then only the transesterification process is enough for producing biodiesel from the very oil. But if the acid value of an oil is above 4, then both the esterification and transesterification processes are required. Due to low acid value, palm oil biodiesel, soybean oil biodiesel and mustard oil biodiesel were produced only through transesterification process. But the high acid value of coconut oil and calophyllum oil required both the esterification and transesterification processes. In the esterification process, 70% (v/v) methanol and 1% H_2SO_4 were added to the crude oils in the reactor at a temperature of 60°C with 900 RPM steering speed for 3 hours as shown in the figure 3.1 below.

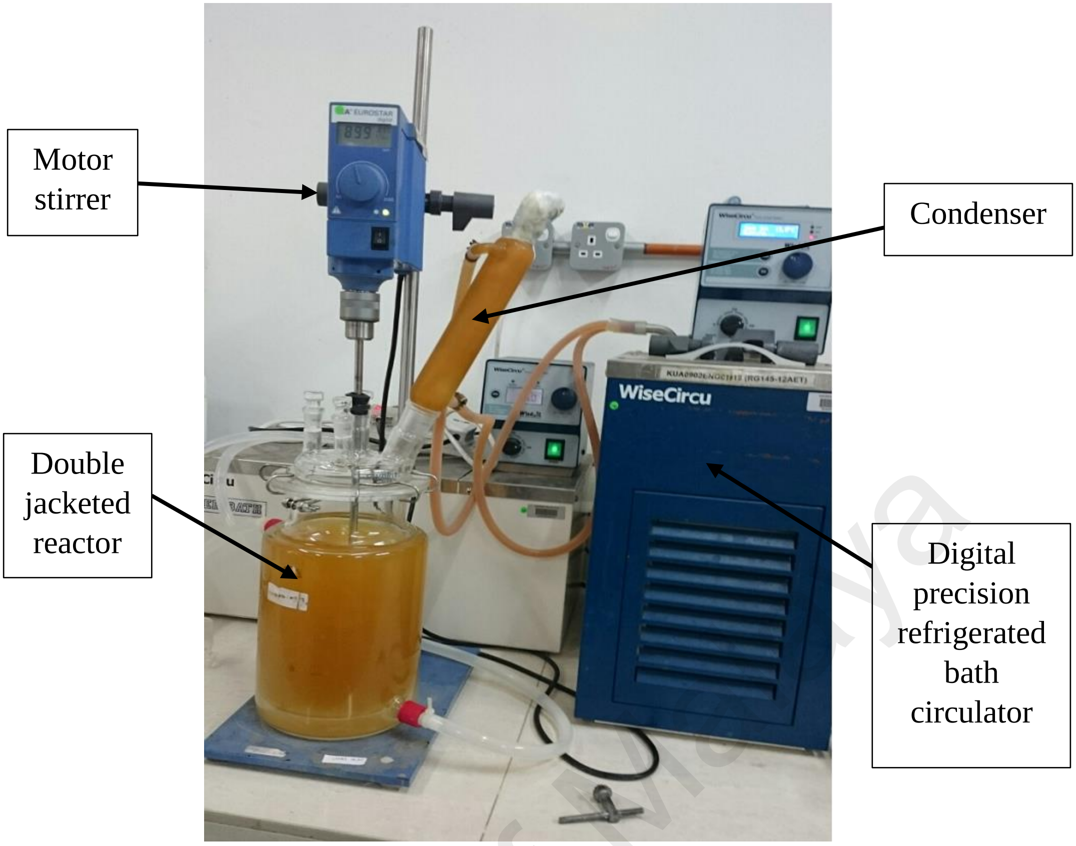


Figure 3.1: Reactor and condenser used in esterification and transesterification process.

After this process, the excess alcohol, sulfuric acid and the impurities were separated, and the esterified oil was then transesterified. In the transesterification process, the oils were again reacted with 25% (v/v) methanol and 1% (w/w) potassium hydroxide (KOH) in the reactor for 2 hours at 60°C with 900 RPM steering speed (similar set up as shown in above figure 3.1). Later, the glycerol was removed by separation funnel technique. Finally, after washing the biodiesel produced, it was dried in a rotary evaporator as shown in figure 3.2, for removing excess methanol and water.

Figure 3.2: Rotary evaporator (IKA RV 10)

Finally, the biodiesels were again dried with Na_2SO_4 and filtered. Finally, the acid value of each biodiesel was again measured to assure the quality. Acid value is an important physicochemical property as this can affect the density and viscosity of the biodiesel. Pure biodiesel is not acidic, but some residual acid could increase the acid number of the biodiesel which could influence other properties like density and viscosity if high in value. To avoid this influence, all the 5 biodiesels were produced in a controlled environment. This includes, every time washing the oil with water heated at 60°C until filtration, measuring the amount of oil, methanol, KOH and H_2SO_4 using same scale, volumetric flask and burette.

3.4 Equipment and fuel property characterization

First step to analyze the feasibility of any fuel for use in internal combustion engines included assessing its physicochemical properties which directly effects the performance and emission of the engine. These properties include density, viscosity, calorific value, cloud point (CP), pour point (PP), cold filter lugging point (CFPP), flash point, acid value, oxidation stability etc. Again, in case of biodiesel, these properties are directly controlled by its fatty acid methyl/ethyl/butyl ester content. In this research work, methanol was used to produce biodiesel. In this section, the apparatus and standards used to measure the physicochemical properties of the neat fuels and fuel blends are discussed. Table 3.1 below represents the list of the apparatus used in this research work.

Table 3.1: Equipment used for characterization of physicochemical properties of fuels.

Property	Equipment	Manufacturer	Standard method	ASTM D6751 limit	Accuracy
Kinematic viscosity at 40 °C	SVM 3000	Anton Paar, UK	ASTM D7042	1.9–6.0	±0.35%
Density at 40 °C	SVM 3000	Anton Paar, UK	ASTM D7042	n.s.	0.0005 g/cm3
Flash point	NORMALAB NPM 440	Normalab, France	ASTM D93	130 min	±0.1 °C
Oxidation stability	873Rancimat	Metrohm, Switzerland	EN 14112	3 h	±0.01 h
Calorific value	C2000 basic calorimeter	IKA, UK	ASTM D4809	n.s.	±0.1% of reading
Cloud point	NORMALAB NTE 450	Normalab, France	ASTM D2500	Report	±0.1 °C
Pour point	NORMALAB NTE 450	Normalab, France	ASTM D97		±0.1 °C
Acid value	Mettler Toledo G20 compact titrator	Mettler Toledo, Switzerland	ASTM D664	0.5 max	±0.001 mg KOH/g

3.4.1 Gas chromatography analysis

The fatty acid ester composition of any biodiesel is unique to its kind. The fatty acid methyl ester (FAME) composition of the biodiesels used in this work were determined using an Agilent 6890 gas chromatograph (figure 3.3). Table 3.2 below, shows the GC operating conditions.

Figure 3.3: Agilent 6890 gas chromatograph

Table 3.2: GC operating conditions.

Property	Specifications
Carrier gas	Helium
Type of injector	Split and split less
Flow rate	2.0 mL min^{-1} (column flow)
Detector temperature	250.0 °C
Column dimension	Stabilwax (from Restek), 30.0 m × 0.25 µm × 0.25 mm
Injector	250.0 °C
Split ratio	50:1
Injection volume	1.00 µL
Oven Temperature	60°C, 2 min
	10°C min^{-1}, 200°C
	5°C min^{-1}, 240°C, 7 min
	Post run 255°C, 2 min

3.4.2 Density and viscosity

In this study, an Anton Paar automatic viscometer (SVM 3000) (shown in figure 3.4) was used to measure the density (kg/m^3) and kinematic viscosity (mm^2/s) of the ternary blend samples according to ASTM D7042. Before measurements, the viscometer was calibrated with the standard calibration fluid provided by the Paragon Scientific Ltd., England. The reproducibility of the density value is 0.0005 g/cm^3 within the range of 0.65 to 1.5 g/cm^3 and for kinematic viscosity value it is 0.35%. The temperature reproducibility is 0.02°C from 15 to 105 °C. The cell inside the viscometer was washed with solvent (acetone and toluene) liquid and air dried every time before measuring a blend sample or same sample at different temperatures. The measurement cell was filled with 2.5 mL of sample during each measurement. Initially, density and viscosity of all the pure fuels were measured at 40°C followed by the measuring of the same properties for the binary and ternary blends. Finally, for developing density and viscosity models for diesel-biodiesel-bioethanol blends, the density and kinematic viscosity of neat diesel and 5 biodiesels were measured from 15°C to 100°C at 5°C interval and due to lower boiling point (78.37°C) of bioethanol compared to diesel and biodiesels, it’s both properties were measured up to 75°C starting from 15°C. To obtain maximum accuracy at all levels of measurements, always 3 sets of data were obtained during each measurement and average of the values were recorded for further analysis.

Figure 3.4: SVM 3000 Viscometer

3.4.3 Oxidation stability (OS)

The oxidation of any fuel is one of the major factors that helps assess its quality. Oxidation stability is an indication of the degree of oxidation, potential reactivity with air, and can determine the need for antioxidants. Oxidation is influenced by some factors such as presence of air, heat, traces of metal, peroxides, light, or structural features of the compounds themselves, mainly the presence of double bonds. The chemical composition of crude oil fuel makes it more susceptible to oxidative degradation than fossil diesel fuel. The Rancimat method is listed as the oxidative stability specification in ASTM D6751 and EN 14214. In this work, 873 Biodiesel Rancimat from Metrohm was used as shown in figure 3.5 below by applying accelerated oxidation test according to EN 14112. Formation of volatile acids measured by a sudden increase of conductivity is the indicator of the end of the induction period (IP) during a forced oxidation of ester sample at 110°C with an airflow of 10 L/h passing through the sample.

Figure 3.5: 873 Biodiesel Rancimat from Metrohm

3.4.4 Acid value

The acid number is a measure of the amount of carboxylic acid groups in a chemical compound i.e., the fatty acid or in a mixture of compounds. Acid number can provide an indication of the level of lubricant degradation while the fuel is in service. Acid value or neutralization number is expressed as mg KOH required to neutralize 1 g of fatty acid methyl esters and is set to a maximum value of 0.5 mg KOH/g in the European standard EN14104 and ASTM D664. A Mettler Toledo G20 Compact Titrator (shown in figure 3.6) was used to measure the acid value of the fuel.

Figure 3.6: Acid value tester from Mettler Toledo

3.4.5 Cloud point and pour point

A diesel fuel’s cold-weather characteristics are measured by the two main characteristics, cloud (CP) and the pour points (PP). CP is the temperature of the fuel at which small solid crystals can be observed as the fuel cools and the PP refers to the lowest temperature at which movement of the fuel is present when the container is tipped. Compared with petroleum diesel, biodiesel tends to have near range of temperatures between the CP and the PP. Whereas a 20° difference exists between the CP and the PP of petroleum diesel and biodiesel may have a difference of only a few degrees. An automatic NTE 450 (Norma lab, France) cloud and pour point tester as shown in figure 3.7 was used to measure the cloud point and pour point of the test fuels according to the ASTM D2500 and ASTM D97 respectively.

Figure 3.7: NORMALAB NTE 450 CP and PP tester

3.4.6 Flash point

The flash point is the lowest temperature at which a liquid starts to give off sufficient vapors to form an ignitable mixture in the air near the surface of the liquid. The relationships between viscosity and flash point for vegetable oil methyl esters are considerably regular. The flash point values of biodiesel are considerably higher than those of petroleum diesel. Biodiesel has a high flash point, usually more than 150 °C whereas diesel fuel has 98 °C. On the other hand, alcohols have a low flash point. To measure the flash point of the research fuels according to the ASTM D93 standard, Normalab NPM 440 flash point analyzer was used as shown in figure 3.8. It is measured by heating the sample in a small confined chamber until the vapor ignites by a small flame which is passed over the surface of the fuel.

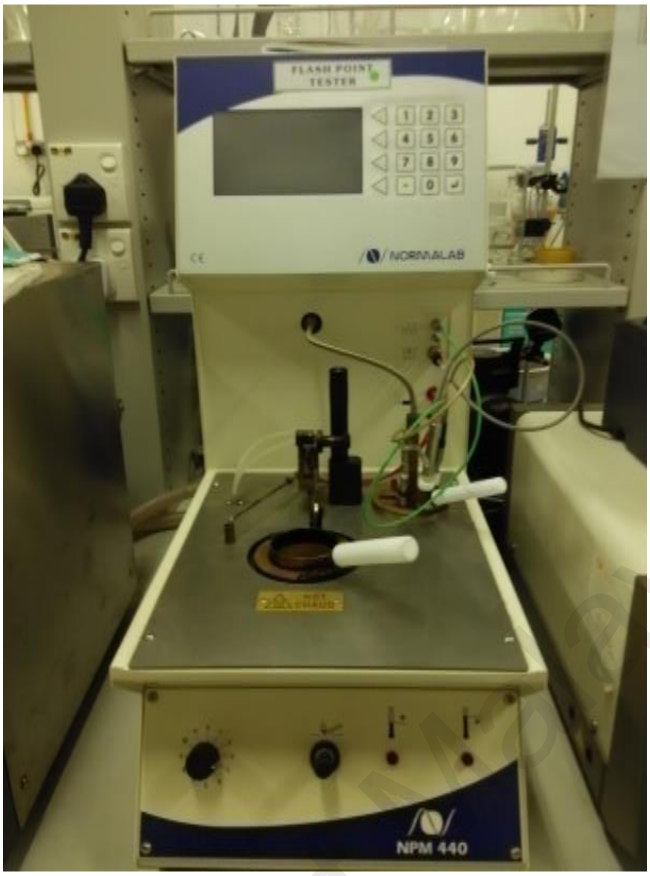


Figure 3.8: NORMALAB NPM 440 flash point tester

3.4.7 Calorific value

Calorific value or heating value is the standard measure of the energy content of any fuel. The heating value is measured by the complete combustion of a unit quantity of fuel in an oxygen-bomb calorimeter under predefined conditions. A bomb calorimeter is a constant-volume calorimeter used in obtaining the heat of combustion of a particular fuel. To measure the calorific value of the fuel samples according to ASTM D4809 standard an IKA C2000 Basic Bomb calorimeter was used as shown in the figure 3.9.

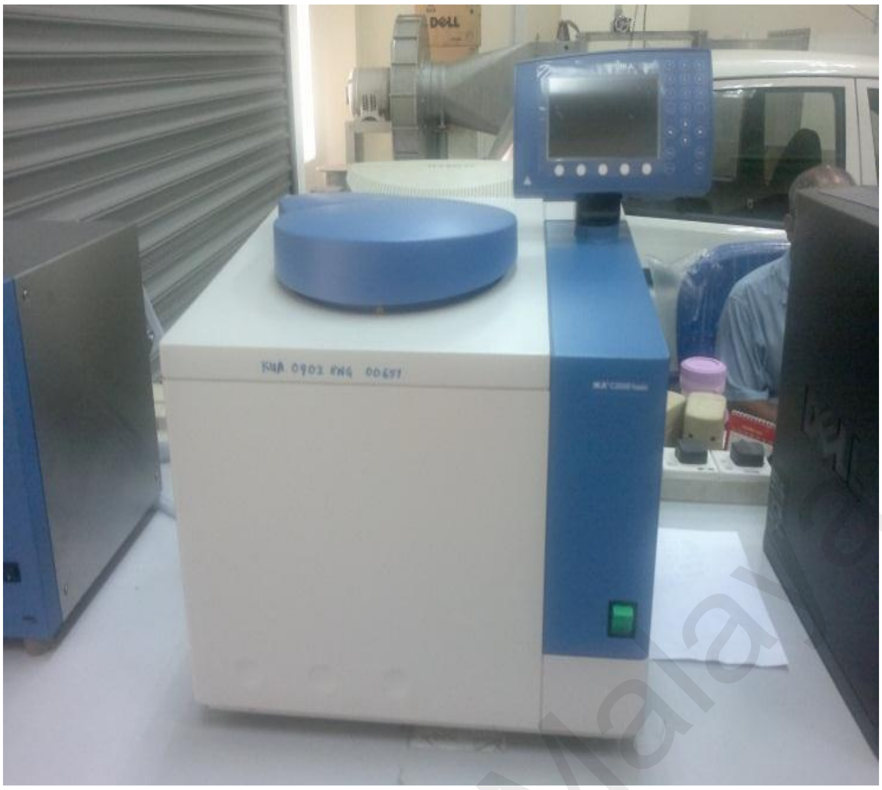


Figure 3.9: IKA C2000 Basic Bomb calorimeter

3.4.8 Iodine value (IV), saponification value (SV) and calculating cetane index (CI)

Iodine value (IV) and saponification value (SV) of the samples were measured according to EN 14111 and AOCS Cd3-25 standards. To calculate cetane index according to ASTM D4737 which is also known as “the four-variable equation” was used. This method is similar as ISO 4264. Density and distillation range (only 10%, 50% and 90% recovery temperatures) of the fuel sample are used in this equation to calculate the CI. Due to unavailability, IV, SV and the distillation tests of the samples were outsourced from ITS Testing Services (M) Sdn Bhd, Malaysia.

3.5 Engine test fuel blends

The fuel blends for engine testing were prepared at the Engine Tribology Laboratory, Department of Mechanical Engineering, University of Malaya. Total 7 fuel blends were finalized for this investigation. In the Table 3.3, the composition of the test fuels is given. Except neat diesel all the other fuel blend samples were prepared by mixing the respective constituents (as shown in table 3.3) at the exact volume using a motor stirrer at 4000 rpm for 15-20 min. 2 L of each of the test samples were prepared for physicochemical properties and engine testing.

Table 3.3: Composition of fuel blends tested

Name	Diesel	Palm biodiesel	Alcohol
D100	100%	0	0
P20	80%	20%	0
P20E10	70%	20%	10% Bioethanol
P20Pr10	70%	20%	10% Propanol
P20B10	70%	20%	10% Butanol
P20Pe10	70%	20%	10% Pentanol
P20H10	70%	20%	10% Hexanol

There are five reasons behind adding 10% of alcohol to each diesel-biodiesel blend and they are:

a) How much the ternary blends could reduce the feasibility problems associated with the 20% blend of palm biodiesel and neat diesel.

b) By keeping the portion of alcohol in the blends constant, we can assess their performance and feasibility easily and accurately.

c) Performance and feasibility of ternary blends of diesel-biodiesel-propanol, diesel-biodiesel-pentanol and diesel-biodiesel-hexanol in single cylinder diesel engine are rarely available.

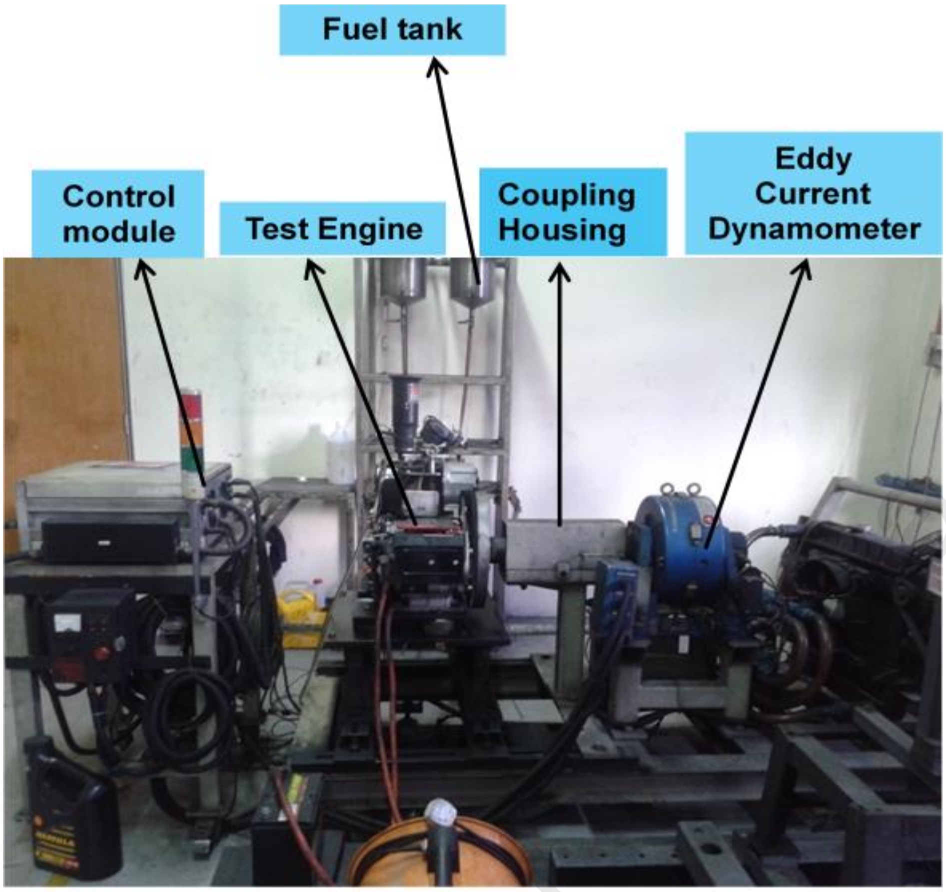
d) According to the literature review, increasing the portions of alcohol in a diesel-biodiesel-alcohol blend offsets some physicochemical properties, which are needed to be identified.

e) Additionally, there is an absence of comparative study in the literature of using bioethanol, 2-propanol, iso-butanol, pentanol and 1-hexanol in the ternary blend of diesel-biodiesel-alcohol. It has been shown earlier in the literature review section that many of the researchers have attempted to improve the neat-biodiesel and diesel-biodiesel blends performance by adding bioethanol, which indicates the potential of other alcohols in the diesel-biodiesel blends.

3.6 Engine test setup

The engine test was carried out in the Heat Engine Laboratory of the Department of Mechanical Engineering, University of Malaya, in a single cylinder, water-cooled, naturally aspirated, direct injection and four-stroke diesel engine. Schematic diagram of the engine test bed setup is shown in figure 3.10 and the detail specifications of the engine are presented in table 3.4. The engine was coupled to an eddy current dynamometer. The test bed was connected to the data acquisition system, which collects and processes signal. The data acquisition system was connected to the laptop, from where the engine was controlled, and the data were monitored and collected using DYNO-MAX 2000 software through controller.

Every time before testing any sample, the engine was run for at least 5 minutes with neat diesel to avoid emission fluctuations. After warming the engine for certain period, the engine was flush ran with the consecutive blend to be tested for at least 5 mins to remove the neat diesel from the fuel system. Engine tests were conducted from 1000 to 2400 RPM speed at 200 RPM interval at constant load and full throttle condition. In this test procedure, at every engine test speed (which was kept same for all fuels), the engine produced a certain amount of power for every unique blend as the load and throttle were constant. Therefore, it becomes easier to compare the performance of the fuel blends having different calorific values considering respective brake specific fuel consumption (BSFC). The parameters selected to evaluate the engine performance were BSFC and brake thermal efficiency (BTE). The engine performance and exhaust emission test were conducted three times at each operating point and their average results were reported in this study.



Engine on test bed coupled with a with a dynamometer

Engine front view

Engine rear view

Figure 3.10: Engine test bed setup

Table 3.4: Detail specifications of the engine

Engine type	**4 Stroke DI diesel engine**
Number of cylinders	One
Aspiration	Natural aspiration
Cylinder bore * stroke (mm)	92×96
Displacement (L)	0.638

Table 3.4, continued

Compression ratio	**17.7**
Maximum engine speed (rpm)	2400
Maximum power (kW)	7.7
Injection timing (deg.)	17^o bTDC
Injection pressure (kg/cm^2)	200
Power take off position	Flywheel side
Cooling system	Radiator cooling
Connecting rod length (mm)	149.5

3.7 Gas analyzer for engine emissions measurement

An AVL Emission Tester (Series 4000) (figure 3.11) was used for engine emissions analysis of NOx, HC and CO. Specifications of the emission analyzer are presented in table 3.5. NOx and HC in ppm volume (vol.) and CO in volume percent were measured.

In this research, exhaust emissions were measured at the same operating points where the performance of the engine for every consecutive fuel sample was measured.

Figure 3.11: AVL Emission tester (series 4000)

Table 3.5: Gas analyzer specifications

Equipment	**Method**	**Measurement**	**Measurement Range**	**Resolution**
AVL Emission Tester Series 4000	Non-dispersive infrared	CO	0-10 % vol.	0.01 % vol.
	Flame ionization detector (FID)	HC	0-20000 ppm vol.	1 ppm
	Heated vacuum type chemiluminescence detector (CLD)	NO_X	0-5000 ppm vol.	1 ppm

The tester is automatic, and microprocessor controlled. It conducts calibration before every analysis automatically. After the instrument is switched ON it takes three to five minutes to warm up and calibrate itself. Measurement is not possible during this time. During the measurements, water was found condensing in the hose connected to the probe and it was cleaned after every 9 measurements. During every test, it took 1 minute (on average) for the emission data to reach a stable condition after the engine was started. Thus, the emission data were always taken after 1 minutes of the engine starting time. Similar to the performance data, the emission data were also taken three times at every operating condition for every consecutive fuel sample. Then the average data is presented here.

3.8 Density and viscosity prediction models

Due to the availability, low price and higher prospect as economic diesel extender option, palm, coconut, mustard, calophyllum inophyllum and soybean oils were used to prepare biodiesels. This selection was done in a manner so that the fatty acid composition of the biodiesels should vary widely. This is due to the fact that the models developed using these biodiesels could be used for a wide range of diesel-biodiesel-bioethanol ternary blends. The biodiesels and bioethanol were blended with diesel fuel in different ratios. The ternary blends contain biofuels up to 55% (vol %). With each type of biodiesel, 6 different diesel-biodiesel-bioethanol blends were prepared for measurements and comparisons. In total, 30 diesel-biodiesel-bioethanol blend samples were prepared for the prediction of their density at 15°C and kinematic viscosity at 40°C. The ternary blends were prepared in a room with a temperature-controlled environment at 25°C. 250 mL of each sample was prepared using class A precision pipette by volumetric dosing. Later, the '% mass' of each component in every ternary blend is calculated and also used in the calculation along with '% volume'. The prepared blends were entitled in such a way so that it reflects the volumetric composition of the blend e.g. D92B5E3 indicates that this blend is a composition of 92% neat diesel, 5% biodiesel and 3% bioethanol.

3.8.1 Density prediction models

If any liquid is a pure substance, then it is easier to develop models to determine its density, but when the liquid is made up of different components like the diesel-biodiesel-bioethanol blends then it becomes difficult to establish one common mathematical correlation for density. Firstly, identifying proper rules for determining the density of this type of complex blends are important. In the hydrocarbon mixture industry, a common method to determine density of fuel blends by using the properties of the blends components is the Kay's mixing rule (Nita et al., 2011). To determine the final density of a fuel blend, the Kay's mixing equation for density (KED) can be described as below:

$$\boldsymbol{\rho_{blend}} = \sum_{i=1}^{n} \boldsymbol{\rho_i \, \delta_i} \qquad \textbf{Equation 3.1}$$

Where $\boldsymbol{\rho_{blend}}$ is the estimated density, $\boldsymbol{\rho_i}$ is the density of the component $\boldsymbol{i}$ and $\boldsymbol{\delta_i}$ is the volume or mass or molar fraction of the component in the blend.

Even though this rule was established to determine the density of the blends composed of components of similar physicochemical properties, this rule has been successfully used to determine density of biodiesels, compose of diverse raw materials and diesel-biodiesel blends (Alptekin & Canakci, 2008; Benjumea, Agudelo, & Agudelo, 2008; DL, 1996; C. Ejim, B. Fleck, & A. Amirfazli, 2007; Tat & Van Gerpen, 2000). In case of determining density of biodiesels based on their ester contents by using KED, researchers have tested the esters concentration expressed in molar (DL, 1996), mass (Tat & Van Gerpen, 2000) and also volume fractions (Pratas et al., 2011). Thus, this equation will also be evaluated for accuracy while using it for determining density of diesel-biodiesel-bioethanol ternary blends in this work.

3.8.2 Viscosity prediction models

Viscosity of biodiesels are higher than the fossil diesel fuel, which could be up to 1.6 times at 40°C. And when the temperature is below 25°C then the above ratio increases (Bhale et al., 2009). It is a very important property for fuels used in CI engines. It affects the fuel drop size, jet penetration, quality of atomization, spray characteristics and the combustion quality (Shahir et al., 2014). For every engine, there is a highest and a lowest limit for the viscosity of a fuel to be used in that engine. To ensure the durability of the fuel injection system and the reliability of starting the engine when it is hot, minimum viscosity and lubricity of the fuel is mandatory.

The viscosities of the diesel-biodiesel-bioethanol blends can be predicted by using popular mixing laws like the L. Grunberg & Alfred H. Nissan law proposed by Arrhenius (Grunberg & Nissan, 1949). From literature review this is the only available method which could be used to predict the viscosity of complex ternary blends. The law can be expressed in the following mathematical form:

$$ln(\eta_v) = \delta_1\, ln(\eta_1) + \delta_2\, ln(\eta_2) + \delta_3 ln(\eta_3) \qquad \textbf{Equation 3.2}$$

Where, η_v is the kinematic viscosity (mm²/s) of the blend, η_1, η_2 and η_3 are the kinematic viscosities of the components 1, 2 and 3 and δ_1, δ_2 and δ_3 are the mass or volume fraction of the components 1, 2 and 3.

Thus, it is obvious that there is a need for simple and reliable mathematical models, which can be used to calculate the densities and viscosities of the diesel-biodiesel-bioethanol blends. In this work, one model for the calculation of density and 3 models for the calculation of kinematic viscosity of the ternary blends are proposed and those models are evaluated along with the existing models for the accuracy. These models will be of great use in the engine intake, combustion and exhaust modeling.

3.8.3 Evaluation of models

To study the predictive ability and accuracy of the density and viscosity models studied in this work, the following statistical indicators have been used: Absolute Percentage Error (APE)-Equation (3), Mean Absolute Percentage Error (MAPE)-Equation (4), Standard Deviation, SD-Equation (5), Coefficient of Correlation, R^2-Equation (6).

$$\textbf{APE (\%)} = \frac{|x_{calc} - x_{expt}|}{x_{expt}} \times 100 \qquad \textbf{Equation 3.3}$$

$$\textbf{MAPE (\%)} = \sum_{i=1}^{N} \frac{|x_{calc_i} - x_{expt_i}|}{x_{expt_i}} \times \frac{100}{N} \qquad \textbf{Equation 3.4}$$

$$\textbf{SD} = \sqrt{\frac{\sum_{i=1}^{N}(x_{calc_i} - x_{expt_i})^2}{N-2}} \qquad \textbf{Equation 3.5}$$

$$\mathbf{R^2} = \frac{\sum_{i=1}^{N}(x_{calc_i} - \bar{x}_{expt})^2}{\sum_{i=1}^{N}(x_{expt_i} - \bar{x}_{expt})^2} \qquad \textbf{Equation 3.6}$$

Where x_{expt} and x_{calc} are the experimental and calculated values of densities and viscosities, $\bar{x}_{expt}$ is the average value of the measured densities and viscosities and N is the total number of observations.

CHAPTER 4 : RESULTS AND DISCUSSION

4.1 Introduction

The findings and analysis of all the results of this research work are presented in this chapter. At first, the fatty acid compositions of palm, coconut, soybean, mustard and calophyllum biodiesels are discussed which is followed by the analysis of the physicochemical properties of the above-mentioned biodiesels, neat diesel and bioethanol, 2-propanol, iso-butanol, pentanol and 1-hexanol. After neat components, the physicochemical properties of the 6 research fuel blends and their effects on a single cylinder diesel engine's performance and emissions are discussed. Finally, the experimental and statistical analysis of the 30 diesel-biodiesel-bioethanol blends are presented with critical analysis.

4.2 Research fuels characterizations

Physicochemical properties of any fuel give an indication of its quality and feasibility as a fuel for IC engines. These properties of biodiesels vary with the feedstock's properties, production process, storage and handling whereas these properties of alcohols vary with their water content and production process.

4.2.1 Fatty acid methyl ester composition of biodiesels

A fatty acid containing only single bonds then they are known as saturated fatty acids. When any of them contains one double bond or more than one double bond then they are known as monounsaturated and polyunsaturated fatty acids. Fatty acid methyl ester (FAME) compositions with their saturation levels of 5 different biodiesels are presented in table 4.1 below. FAMEs analysis of biodiesels shows that palm biodiesel is mainly composed of 44.51% saturated and 42.43% monounsaturated fatty acids while coconut biodiesel is 87.5% saturated with traces of unsaturation and mustard biodiesel is 74.3% monounsaturated.

Table 4.1: Fatty acid methyl ester composition of biodiesels

Common Name	**Structure**	**Molecular mass g/mol**	**Chemical Structure**	**Palm BD (% wt.)**	**Coconut BD (% wt.)**	**Mustard BD (% wt.)**	**Calophyllum BD (% wt.)**	**Soybean BD (% wt.)**
Methyl Caproate	C6:0	130.18	$CH_3(CH_2)_4COOCH_3$	-	0.3	-	-	0.1
Methyl Caprylate	C8:0	158.24	$CH_3(CH_2)_6COOCH_3$	-	6.5	-	-	0.1
Methyl Caprate	C10:0	186.29	$CH_3(CH_2)_8COOCH_3$	-	6	-	-	0.1
Methyl Laurate	C12:0	214.34	$CH_3(CH_2)_{10}COOCH_3$	0.14	42.1	-	-	0.1
Methyl Myristate	C14:0	242.40	$CH_3(CH_2)_{12}COOCH_3$	1.05	17.4	-	0.1	0.1
Methyl Palmitate	C16:0	270.45	$CH_3(CH_2)_{14}COOCH_3$	38.84	11.3	1.9	14.9	10.5
Methyl Palmitoleate	C16:1	268.43	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOCH_3$	0.22	0.2	0.2	0.2	0.1
Methyl Stearate	C18:0	298.5	$CH_3(CH_2)_{16}COOCH_3$	4.08	3.8	1.2	17.2	4.3
Methyl Oleate	C18:1	296.49	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$	42.21	9.2	12.7	38.2	25.0
Methyl Linoleate	C18:2	294.47	$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7COOCH_3$	12.81	3	12.3	27.6	51.5
Methyl Linolenate	C18:3	292.46	$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOCH_3$	0.25	<0.1	7.2	0.3	6.8
Methyl Arachidate	C20:0	326.56	$CH_3(CH_2)_{18}COOCH_3$	0.4	0.2	1.0	0.9	0.4
Methyl Eicosenoate	C20:1	324.54	$CH_3(CH_2)_{16}CH{=}CHCOOCH_3$	-	<0.1	6.4	0.2	0.2
Methyl Eicosadienoate	C20:2	322.53	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_9COOCH_3$	-	-	0.4	-	-
Methyl Eicosatrienoate	C20:3	320.51	$C_{21}H_{36}O_2$	-	-	0.1	-	-
Methyl Behenate	C22:0	354.61	$CH_3(CH_2)_{20}COOCH_3$	-	<0.1	0.9	0.3	0.4
Methyl Erucate	C22:1	352.59	$C_{23}H_{44}O_2$	-	<0.1	53.7	-	0.1
Methyl Docosadienoate	C22:2	350.58	$C_{23}H_{42}O_2$	-	-	0.8	-	-
Methyl Lignocerate	C24:0	382.66	$CH_3(CH_2)_{22}COOCH_3$	-	<0.1	-	0.1	0.2
Methyl Nervonate	C24:1	380.65	$C_{25}H_{48}O_2$	-	-	1.3	-	-
Saturated				44.51	87.5	5	33.5	16.3
Monounsaturated				42.43	9.45	74.3	38.6	25.4
Polyunsaturated				13.06	3.05	20.7	27.9	56.3
Total				100	100	100	100	100

Besides these, soybean biodiesel is more than 50% polyunsaturated and calophyllum biodiesel is comprised of equal portions of saturated, monounsaturated and polyunsaturated fatty acid methyl esters.

4.2.2 Physicochemical properties of research fuels

The physicochemical properties of the research fuels are presented in table 4.2 below. High acid value represents residual acid in the biodiesel which may alter the physicochemical properties of the respective biodiesel. The 5 biodiesels used in this work have acid value within the ASTM D6751 and EN 14214 standards and range between 0.20-0.30 mg KOH/g. There are two biodiesels which could be differentiated from the others a lot, i.e. coconut and mustard biodiesels. Mustard methyl ester (MME) is the lowest saturated with highest viscosity, oxygen stability and CN. MME also shows very good cold flow properties and is the best among the used 5 biodiesels. On the other hand, coconut methyl ester (CME) is the highest saturated with lowest viscosity, iodine value and calorific value. Among other 3 biodiesels used, Palm methyl ester (PME) and calophyllum methyl ester (CaME) have medium level saturation while soybean methyl ester (SME) is less saturated compare to highly saturated CME. In case of monounsaturation and polyunsaturation, Mustard ME is the most monounsaturated while Soybean is the most polyunsaturated which might be the reason behind its high iodine value. In case of CaME, it is composed of almost equal portions of saturated, monounsaturated and polyunsaturated fatty acids. From the result it can be concluded that the highly saturated MEs excel in flash point and iodine value but exhibits poor cold flow properties. As it cannot be concluded regarding the choice of best biodiesel in terms of properties, production and performance thus the selection of biodiesel for this study was performed in a manner so that the MEs would have different fatty acid ME compositions and the results could be used for a wide range of biodiesels types in terms of composition and properties.

4.2.2.1 Density and viscosity

Density and viscosity are 2 very important properties of any fuel which effects the engine performance characteristics directly (V & A, Matrix Rom 2007). Other properties like CN and heating value are also associated to them. Fuel drop size, jet penetration, quality of atomization, spray characteristics and combustion characteristics are directly influenced by the fuel’s density and viscosity (Alptekin & Canakci, 2009; V & A, Matrix Rom 2007). Injection system used for diesel fuel, measure the fuel by volume thus the variation of the fuel density will affect the output power of the engine due to an altered mass of injected fuel. Generally higher density causes greater fuel flow resistance which results in higher viscosity which may lead to inferior fuel injection. At low temperatures, when the fluidity of the fuel is reduced, the operation of the fuel injection system is directly affected by the fuel’s viscosity (István Barabás et al., 2010). For every engine there is a highest and a lowest limit for viscosity of a fuel to be used in that engine. If very low viscous fuel is used, it could cause the fuel system leakage. It typically results in smaller sauter mean droplet diameters, thereby increasing the surface area of the fuel droplets and significantly influences the evaporation characteristics time (Desantes, Arregle, Pastor, & Delage, 1998; Heywood & J.B., 1988). On the other hand, high viscosity of the fuel can cause the followings:

1. Poor fuel atomization and incomplete combustion.
2. Increasing the engine deposits.
3. Requiring more energy to pump the fuel.
4. And causing more problems in cold weather as because the viscosity increases as the temperature decreases, i.e. the fluidity of the fuel is reduced at low temperature conditions.

Thus, the viscosity of any fuel should be low enough to flow freely at its lowest functioning temperature. Fuel pump lubrication & injectors are also affected by the fuel viscosity (V & A, Matrix Rom 2007), especially those incorporated with rotary distributor injection pumps which rely completely on the fuel for lubrication within the high pressure pumping mechanism. In the case of common rail accumulator fuel-injection system, the fuel delivered to the rail by the high-pressure pump also depends on the fuel for lubrication. There is less dependence on the fuel for lubrication in the case of in-line pumps and unit injectors; but still there are few metal interfaces like the interface between the plunger and barrel require lubrication by the fuel. Injector lubrication, particularly at the needle guide-nozzle body interface is also affected (Alan C. Hansen et al., 2005). Among the engine test fuels, density of palm biodiesel is 2.74% higher whereas the density of alcohols is 3.70%-7.94% lower than that of neat diesel. Similarly, palm biodiesel has a 22.22% higher and the alcohols have a 0.80-69.94% lower viscosity than that of neat diesel. Among the alcohols, propanol has the lowest density while hexanol has the highest among them. Although bioethanol has a density lower than propanol, its viscosity is higher compare to the later one and the lowest among all the alcohols. In this scenario, where one component (biodiesel) of the ternary blend has a higher density and viscosity and another component (alcohol) has a lower density and viscosity compare to the neat diesel then the final density and viscosity of the ternary blend will depend on the portion of the components in the blend.

Table 4.2: Physicochemical properties of neat diesel, biodiesels and bioethanol

Properties	**Measuring standard**	**Diesel**	**Palm**	**Coconut**	**Mustard**	**Calophyllum**	**Soybean**	**Bioethanol**	**2-Propanol**	**Iso-butanol**	**Pentanol**	**1-Hexanol**
Density @ 40°C (kg/m³)	ASTM D7042	835.2	858.1	855.8	861.9	871.2	867	775.9	768.9	786.4	793.7	804.3
Viscosity @ 40°C (mm²/s)	ASTM D7042	3.68	4.49	2.75	5.82	5.05	4.15	1.11	1.67	2.69	2.99	3.65
Flash Point (°C)	ASTM D93	77.5	182.5	166.5	149.5	172.5	158.2	12	22	35	43	68
Cloud Point (°C)	ASTM D2500	8	13	1	5	10	3	-	-	-	-	-
Pour Point (°C)	ASTM D97	7	15	-3	-18	8	-3	-114	-126	-89	-75	-70
Acid Value (mg KOH/g)	ASTM D664	0.13	0.25	0.27	0.29	0.24	0.21	-	-	-	-	-
Iodine Value (g I/100g)	EN 14111	-	61	15.76	102	82.1	129.8	-	-	-	-	-
Saponification Value (mg KOH/g)	AOCS Cd3-25	-	206	262.78	179	191.6	198.9	-	-	-	-	-
Calorific Value (MJ/kg)	ASTM D4809	45.46	39.91	38.29	40.71	39.91	39.88	28.85	29.7	32.8	34.5	35.8
Oxygen stability (h)	EN 14112	59.1	3.92	8.14	15.92	3.18	3	1.5	1	2	1.85	1.3
Cetane Index	ASTM D4737	48	61	63.52	76	56.3	51	8	12	17	20	42

To ensure the durability of the fuel injection system and the reliability of starting the engine when it is hot, minimum viscosity and lubricity of the fuel blends are mandatory (Alan C. Hansen et al., 2005). When ethanol or any alcohol is blended with diesel fuel in high proportions, it yields an overall viscosity of the blend lower than the ASTM minimum. This decreased viscosity of the diesel-alcohol blends significantly affects the fuel injection system's lubrication. Again when biodiesel is added to this blends, its high lubricity compensates the low lubricity of the diesel-alcohol blends (Pidol et al., 2012a).

4.2.2.2 Flash point

Flash point of any fuel describes its flammability. Flammability limits can be described as the maximum and minimum concentrations of combustible vapor in the air and the temperatures at which the vapor occurs, that will propagate a flame after sufficient ignition energy is provided. While handling and storage of an alternative fuel using existing facilities come into consideration then the property of the fuel which is needed to be considered is its flammability limits. During refueling or when damage or leaks occur in any fuel system components, then flammable conditions might occur in the partially filled fuel tanks by the vapor produced through the evaporation of the fuel. At ambient temperature, fossil diesel fuel generates inadequate vapor to reach its lower flammability limit whereas the upper flammability limit of gasoline is exceeded by the vapor concentration. With a flash point of approximately 11-14°C, ethanol/bioethanol falls between the gasoline and fossil diesel fuel in terms of flammability temperature limits and flash point. Thus, bioethanol can produce ignitable vapor at normal ambient temperature above the fuel level. The flash point of many diesel-bioethanol blends or diesohol blends were measured and found that whatever the ethanol ratio was, the two fuel mixture characteristically reaches to a flash point value (measured between 12 and 15° C) which is close to the value of pure ethanol (Pidol et al., 2012a). And in the case of diesel-biodiesel blends, the flash point increases as the biodiesel content in the blends increases (Alptekin & Canakci, 2009). The flash point of all the biodiesels and diesel used for study meet the ASTM D6751, EN 14214 and EN 590 standards respectively. Among these, palm biodiesel has a 135% higher and the alcohols have 84.52-12.25% lower flash point compare to neat diesel. Among the alcohols, 1-hexanol is observed to have a flash point close to that of neat diesel which is measured to be 68°C.

4.2.2.3 Calorific value

Heat of combustion or the calorific value of a fuel blend is another very important property to determine its suitability as an alternative to diesel fuel. Lower heating value or the net calorific value of a fuel blend influences the power output of an engine directly. The calorific value of both the biodiesel and the alcohols are less than the diesel fuel. Thus, their addition to the diesel fuel lowers the calorific value of the final blend which is lower than the diesel fuel individually. As the amount (%vol or %wt) of biofuels (biodiesel and alcohol) are increased in the ternary blends, the calorific value of the final blends decreases (E. Ajav & O. Akingbehin, 2002; Kraipat Cheenkachorn & Fungtammasan, 2009; Chotwichien et al., 2009; Fernando & Hanna, 2004; Kannan, 2013; Park, Cha, & Lee, 2012a; Pidol, Lecointe, Starck, & Jeuland, 2012b). This is the result of the lower calorific value of alcohols and biodiesel. Biodiesels and alcohols contains less amount of carbon, hydrogen and oxygen compare to neat diesel, thus this decrease in calorific value is obvious (Abdelaziz E Atabani et al., 2012). However, the blends containing bioethanol, lower than 10% are seemed to have heating value nearer to fossil diesel fuel (Kwanchareon et al., 2007a). In this study mustard biodiesel and hexanol are found to have highest calorific value among biodiesels and alcohols respectively. Calorific value of palm biodiesel is only 1.97% and 12.21% lower than mustard and neat diesel respectively.

4.2.2.4 Cetane Index (CI)

Cetane index of a CI engine fuel can be defined as the measurement of the combustion quality of a fuel during compression ignition. The measurements those determine the overall fuel quality, CI (CI) is a significant one among them. The requirements of minimum CI depend on the engine design, size, nature of speed and load variations, as well as starting and atmospheric conditions. Using fuels of CI higher than the requirement does not materially increase the performance of the engine. Accordingly, to ensure the maximum fuel availability, the specified CI should be up to a certain limit. Again, using fuels with low CI than the actual requirements could cause rough operation of the engine. Problem like difficult starting, especially in the cold weather or at high altitudes are faced by using this type of fuels. Formation of lube oil sludge is also accelerated by using this type of fuel. Besides, low CI fuels are the cause of larger engine deposits which results in extra smoke than usual, increased exhaust emissions and greater engine wear. Based on the CI of the constituents and the mass composition of the blend, the CI of that specific blend is assessed (Bamgboye & Hansen, 2008; Barabas & Todorut). Lower CI means longer ignition delays, allowing more time for fuel to vaporize before combustion starts. Initial burn rates are higher causing more heat release at constant volume, which is a more efficient conversion process of heat to work. Nevertheless it is preferable to add an ignition improver to raise the CI of diesel-ethanol blends so that they fall within an acceptable range equivalent to that expected of No. 2 diesel fuel (Alan C. Hansen et al., 2005). As specified by the ASTM Standard D 975-02 the minimum CI for No. 2 diesel should be 40. Typically, the CI for No. 2 diesel fuels varies from 45 to 50. Normally, the CI of the biodiesels are less than the neat diesel due to the long chain hydrocarbon groups without any branching or hydrocarbon structures (Hoekman et al., 2012). In this study it has been observed that MME has the highest CI which is 58.33% higher than the neat diesel. Among the tested biodiesels, although PME has a medium CI it is still 27.08% higher than that of neat diesel. In case of alcohols, all their CIs are seen to be lower than diesel. It is seen from the results that, as the number of carbons in the atom increases, the CI of the alcohol increases. Following this pattern, the hexanol is seen to have a CI near to that of neat diesel. Bioethanol, propanol, butanol, pentanol and hexanol have an 83.33%, 75%, 64.58%, 58.33% and 12.50% lower CI compare to diesel fuel. So, it is obvious that, if any alcohol is added to a diesel-biodiesel blend then the final CI of the ternary blend will decrease. Thus, the diesel-PME blend is expected to have a shorter ignition delay and advanced start of combustion due to their higher CI than neat diesel and diesel-PME-alcohol blends.

4.2.2.5 Cloud point (CP) and pour point (PP)

Cloud point and pour point are two very important fuel properties when the fuel is used in cold climatic conditions. CP is the temperature below which wax in the fuel forms a cloudy appearance. This solidified wax thickens the oil and clogs the fuel filters and injectors. Whereas PP is the lowest temperature at which a liquid can flow. As the temperature of a fuel approaches to its PP it becomes cloudy due to the formation of crystals and finally the crystals solidify. This causes major operability problems (Knothe, 2005). All the biodiesels, only PME and CaME have CP and PP higher than neat diesel whereas CME, MME and SME have PP and CP lower than neat diesel. On the other side, due to the absence of wax, the alcohols only have PP which are well below neat diesel. Due to the very low PP of the alcohols, when any of them are added to diesel-biodiesel blend then the PP of the final blend decreases which is a major advantage of using ternary blends.

4.2.2.6 Oxygen stability, acid value, iodine value

Oxygen stability is another important fuel property when the long-term storage of any fuel comes into consideration. As the biodiesels and alcohols are oxygenated fuels, their oxygen stability is measured to be lower than that of neat diesel. The acid value of all the biodiesels meets the ASTM D6751 and EN 14214 which are maximum 0.8 mg KOH/g and 0.5mg KOH/g respectively. In case of iodine value, except SME, all the other biodiesels meet the EN 14214 standard which limit the biodiesels to have an iodine value of maximum 120 g I/100g. The research biodiesel, PME has an iodine value well below the standard limit.

4.2.3 Physicochemical properties of engine test fuels

Table 4.3 represents the physicochemical properties of the fuels tested in the engine for its performance and emission. The density and viscosity of PME is 2.74% and 22.22% higher than neat diesel respectively (from table 4.2). Thus when 20% (v/v) of PME is blended with neat diesel then we find the density and viscosity of the final blend (P20 in table 4.3) to be increased by 0.25% and 9.50% respectively compare to neat diesel. On average, the densities and viscosities of the alcohols are 5.82% and 35.37% (respectively) lower than that of neat diesel and 7.93% and 47.12% (respectively) lower than that of PME respectively. Thus, when diesel, biodiesel and any alcohol are blended together the resultant density and viscosity of the final blend comes closer to neat diesel. From table 4.3 we can observe that the densities and viscosities of the ternary blends are very much closer to neat diesel. The density and viscosity of the blend of diesel, biodiesel and hexanol are closest to neat diesel. Even, the viscosity of this blend is greater than neat diesel. This might be due to its high viscosity, which gives a rise to the final viscosity of the blend.

The oxygen stability of the ternary blends is found to be 79.70%-82.74% less than neat diesel and 60.26%-66.23% lower than PME. Although the oxidation stability of the ternary blends is lower than neat diesel and biodiesel, they meet the EN 14241 standard for biodiesel, which means that the existing storage and supply systems for FAME/biodiesels can be used for the ternary blends of diesel, biodiesel and alcohol. The flash point of the ternary blends is found to be 70.32%-78.06% and 76.65%-82.74% lower than neat diesel and P20 respectively. the cold flow properties of the ternary blends are found to be very good compare to neat diesel and P20 blend. In terms of cold flow properties, P20Pr10 is found to be the best fuel to be used in a cold climatic condition. Although this cold flow property of the fuels is of limited concern in the hot and tropical areas of Asia and Africa, but it is very important to consider in countries where the weather is cold.

Table 4.3: Physicochemical properties of engine test fuels

Research fuel blends	**Density at 40°C (kg/m^3)**	**Kinematic viscosity at 40°C (mm^2/s)**	**Oxygen stability (h)**	**Flash point (°C)**	**Pour point (°C)**	**Calorific value (MJ/kg)**	**Cetane Index CI**
D100	835.2	3.6765	59.1	77.5	7	45.46	48
P20	837.3	4.0256	30.2	98.5	8	44.35	50.6
P20E10	830.0	3.1802	11.1	17.0	-3	42.69	46.6
P20Pr10	829.2	3.3049	10.2	18.0	-5	42.77	47
P20B10	831.3	3.5160	12.0	20.0	-1	43.08	47.5
P20Pe10	832.6	3.5803	11.58	21.5	1	43.25	47.8
P20H10	833.8	3.9119	10.73	23.0	1	43.38	50

The calorific value of the ternary blends and P20 are found to be lower than neat diesel as expected. The calorific value of P20E10 is found to be 6.09% lower than neat diesel and the lowest among the engine test fuels. The calorific value of P20Pr10, P20B10, P20Pe10 and P20H10 are 5.92%, 5.24%, 4.86% and 4.58% lower than neat diesel respectively. Thus, it is needed to investigate the amount of power which is lost due to the addition of biodiesel and alcohol with neat diesel.

The lesser the CI, the shoddier will be the ignition property. Engine performance, its start-up and combustion are effected by the CI of the fuel being used (István Barabás et al., 2010). As the CI of the alcohols are very low compare to neat diesel, their addition to the neat diesel brings down the CI of the final binary (diesel-alcohol) blend. Again, due to the high CI of the FAME/biodiesels, their addition to the blend of diesel-alcohol offsets the reduced CI. Thus, the engine ignition is improved (Ribeiro et al., 2007; Shi et al., 2008). All the research fuel blends have been found to have cetane index (CI) similar to that of neat diesel. Among tested blends, P20 and P20H10 are found to have CI more than the neat diesel.

4.3 Engine performance analysis

Analysis of the engine performance running on the engine test fuels is discussed in this section. Two engine performance parameters are selected to evaluate the engine performance. These are brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE).

4.3.1 Brake specific fuel consumption (BSFC)

Brake specific fuel consumption (BSFC) of any engine in any condition is the ratio of the fuel consumption and the brake power output in that condition. BSFC of all the engine test fuels is presented in figure 4.1. The effect of diesel-palm biodiesel-alcohol blends on the engine BSFC with respect to engine speed is shown in figures 4.1. BSFC of all the engine test fuels decreases as the engine speed increases from 1000 RPM to 2000 RPM. This decrease in BSFC is due to the higher automization ratio whereas the increase in BSFC after 2000 RPM can be attributed to the decreased volumetric efficiency at high speeds. All the fuel blends showed higher BSFC compare to neat diesel. Among the blends, P20 showed highest BSFC which is 11.62% higher than D100 on average. This increase in BSFC might be due to high density and viscosity but a low calorific value of the blend compare to neat diesel. Due to the high density, more mass of fuel is injected , which increases the BSFC. Although all the ternary blends showed higher BSFC than neat diesel, their BSFC are foud to be less than that of P20 blend. P20E10, P20Pr10, P20B10, P20Pe10 and P20H10 ternary blends exhibited 6.37%, 6.57%, 8.49%, 4.72% and 7.45% higher BSFC compare to D100. This increase is due to the low calorific value of the ternary blends which gives a rise to the fuel consumption for producing the same amount of power as neat diesel produced at the same operating condition. This result is also found by other researchers (István Barabás & Todoruţ, 2011; Pang et al., 2006; Rahimi et al., 2009; Subbaiah et al., 2010).

It can be observed that, as the number of the carbon atom in the alcohol molecule increases, the BSFC also increases, but in case of P20Pe10 blend, the BSFC suddenly drops and comes closer to D100. Its BSFC is only 4.72% higher than neat diesel and 6.16% lower than P20 blend. After diesel-biodiesel-pentanol blend, the BSFC of the diesel-biodiesel-hexanol blend again increases. This low BSFC of P20Pe10 might be due to the viscosity and cetane index, which are found almost identical to neat diesel. In spite of these two important properties, the BSFC of the blend is still higher due to its calorific value, which is lower than neat diesel. Besides P20Pe10, other ternary blends have also shown potential as their BSFCs are lower than P20.

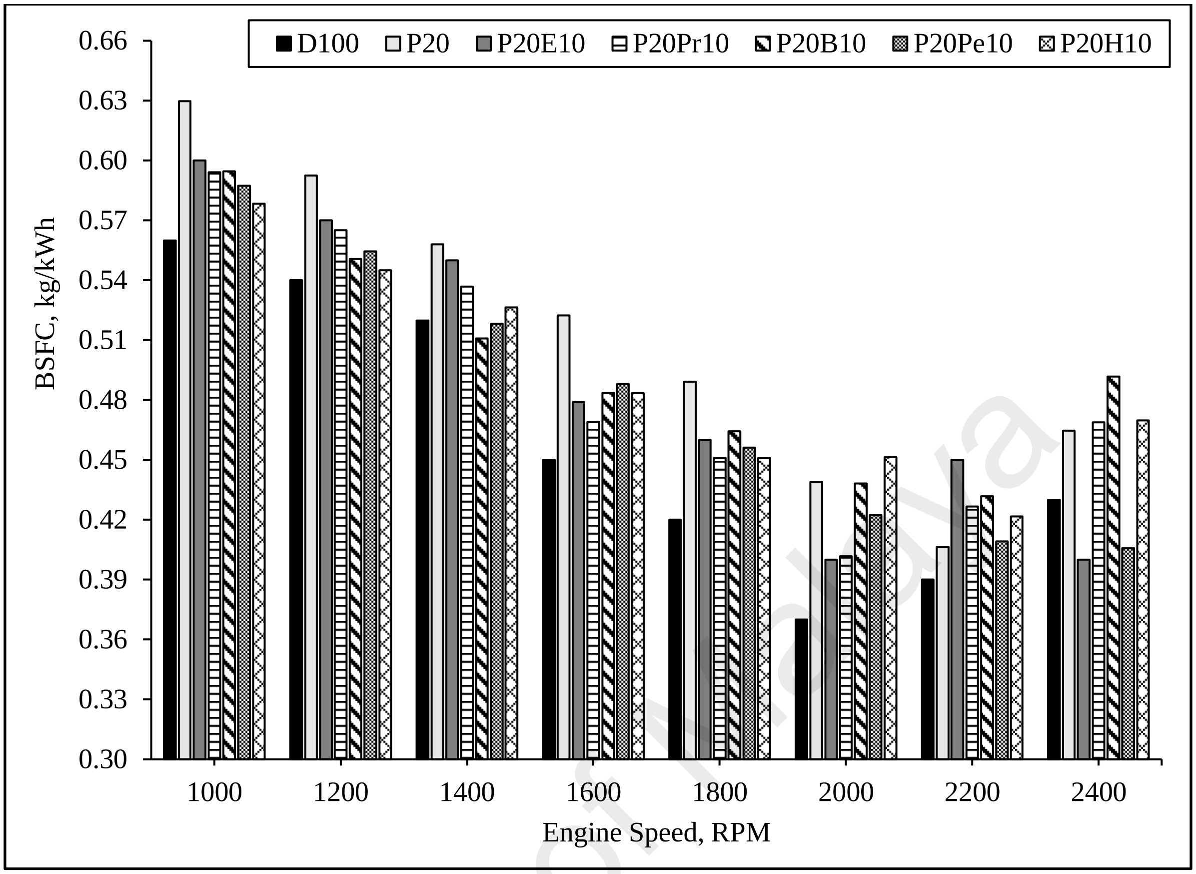


Figure 4.1: Variation of brake specific fuel consumption with engine speed for 100% load condition.

4.3.2 Brake thermal efficiency (BTE)

Brake thermal efficiency (BTE) is another important parameter to measure engine performance. The results of BTE for all the engine test fuels are presented in figure 4.2 below. BTE of an engine indicates its efficiency of converting the chemical energy of the fuel into useful work. It is calculated using the BSFC and the calorific value of the consecutive fuel used. Normally BTE increases with the decrease of BSFC.

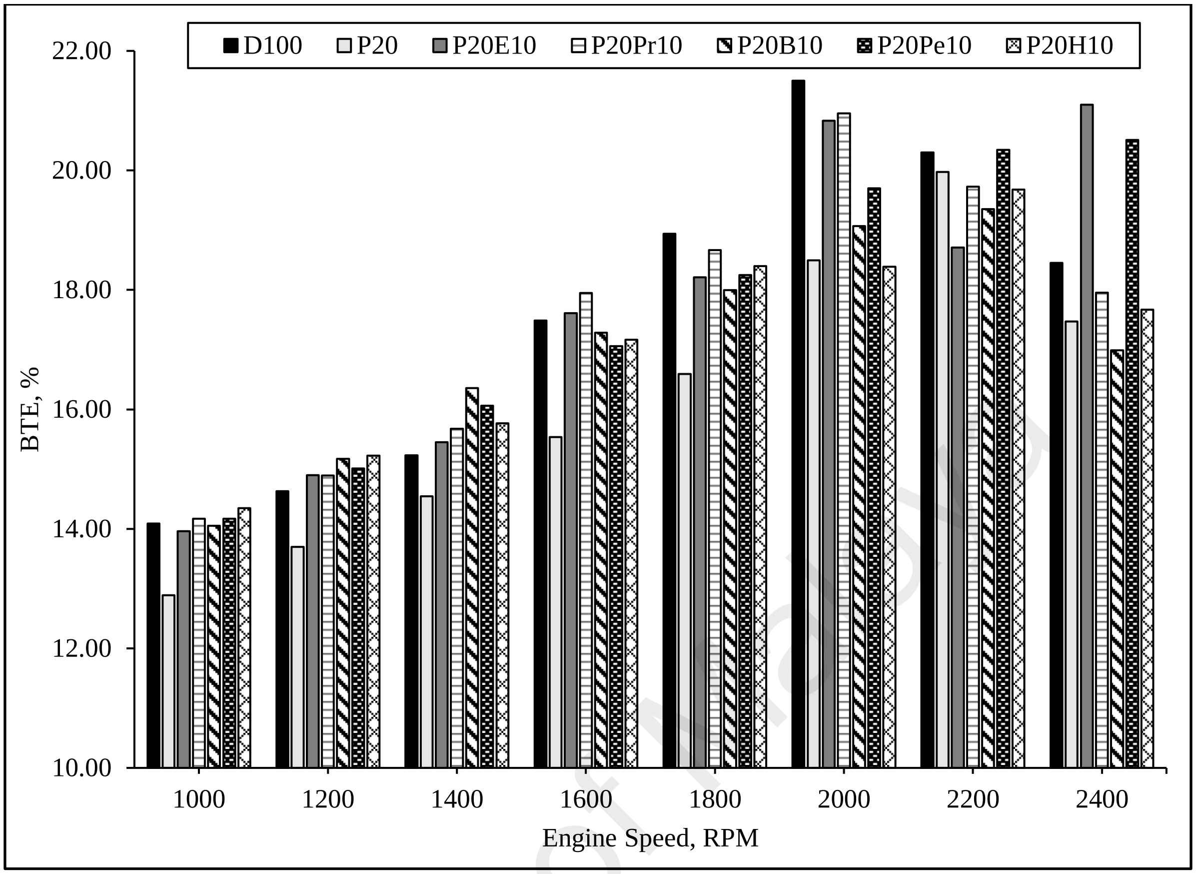


Figure 4.2: Variation of brake thermal efficiency with engine speed for 100% load condition.

From figure 4.2 it can be observed that the engine exhibited lowest BTE while running on P20 binary blend among all the engine test fuels. On average, the engine produced power 16.15% efficiently while running on P20 blend of diesel and palm biodiesel. On the contrary, the engine produced power more efficiently while running on the ternary blends of diesel, biodiesel and alcohol. BTE of the engine running on P20E10, P20Pr10, P20B10, P20Pe10 and P20H10 ternary blends are found to be 17.60%, 17.50%, 17.04%, 17.64% and 17.08% on average respectively and 17.58% while running on neat diesel. Thus, it is seen that only the ternary blends containing bioethanol and pentanol can produce usable power more efficiently than neat diesel. On average, the BTE of the engine is increased by 0.33% and 0.69% when diesel-palm biodiesel-bioethanol and diesel-palm biodiesel-pentanol ternary blends are used as fuel respectively rather than neat diesel. This better BTE is associated with the calorific value and low BSFC of the blends. In case of ternary blends containing bioethanol, this better BTE might be due to low density, viscosity and flash point which favor a leaner combustion and extended ignition delay (Subbaiah et al., 2010). All the other ternary blends produce power less efficiently than neat diesel as we can observe in the figure above.

4.4 Exhaust gas emission

In order to examine emission characteristics of all fuel samples, a portable BOSCH exhaust gas analyzer (model BEA-350) was used to measure the concentration of the exhaust gases of the test engine. This section describes the effect of different fuel properties on different engine emission parameters. Emission parameters include nitrogen oxides (NO_X), hydrocarbon (HC) and carbon monoxide (CO). Emission analysis was carried out at all engine speed ranged from 1000-2400 rpm at every 200 rpm interval at 100% load conditions by inserting probe into the tail pipe. The exhaust gases emission of NO_X and HC was measured in ppm while CO in volume percentage.

4.4.1 Nitrogen oxides (NO_X) emission

The most troublesome emission from CI engine is NOx. The oxides of nitrogen in the exhaust emissions contain nitric oxide (NO) and nitrogen dioxide (NO2). NOx formation highly depends on the temperature inside the cylinder, the concentration of oxygen, the residence time for the reaction to take place and the equivalence ratio (Ajav EA et al., 1998; Challen & Baranescu. R, 1999). Any of the fuel density or the cetane number or the aromatic fuel composition or they can jointly influence NOx formation The air–fuel equivalence ratio might be shifted by the oxygenated fuels to the level that yields lower NOx emission (Kraipat Cheenkachorn & Fungtammasan, 2009). The results of NO_X emission for all ternary fuel blends are presented in figure 4.3. It can be observed that P20, P20E10, P20Pr10 and P20B10 produced 10.29%, 44.03%, 17.85% and 28.03% lower NOx than diesel fuel respectively. Whereas P20Pe10 and P20H10 produced 17.50% and 15.88% higher NOx than diesel fuel respectively. The NOx emission values are higher when higher alcohols are used in the blend.

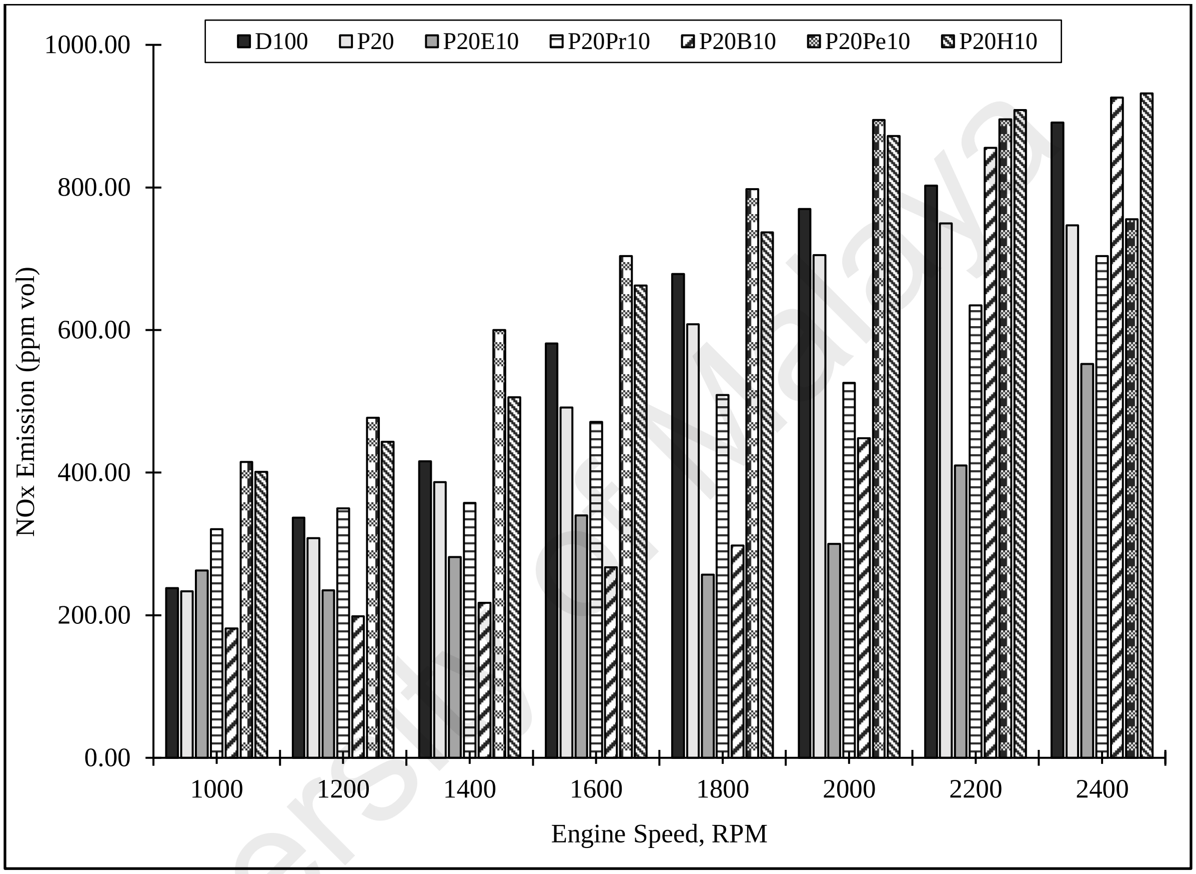


Figure 4.3: Variation of NO_X emission for the test fuels with speed at 100% load

The reason of increasing NOx can be explained in terms of adiabatic flame temperature. Biodiesel fuel contains higher percentages of unsaturated fatty acids that have higher adiabatic flame temperature which causes higher NOx emission. But when low carbon alcohols or bioethanol, propanol and butanol are used in the blend then the NOx emission decreases. Another possibility of lower NOx emission from these alcohols might be the cooling effect of evaporation, which leads to a reduced flame temperature (Kraipat Cheenkachorn & Fungtammasan, 2009). Other researchers had also found similar results (E.

Ajav et al., 1999; B.-Q. He et al., 2003; Li et al., 2005; Park et al., 2012b; C. Rakopoulos et al., 2007). On the contrary, higher oxygen content results in higher combustion temperature which leads to higher NO_X emission which might be the reason behind higher NO_X emission from blends containing pentanol and hexanol (Kwanchareon et al., 2007b; X. Shi et al., 2005).

4.4.2 Hydrocarbon (HC) emission

Hydrocarbon (HC) or the total hydrocarbon emission is the emission of unburned hydrocarbon and is an indicator of efficiency of combustion or completeness (Kraipat Cheenkachorn & Fungtammasan, 2009). This emission in the diesel engine is due to the mixture of fuel which is leaner than the lean combustion limit during the delay period. During air−fuel interactions, particularly in the fuel-rich region, the oxygen content of biodiesel and alcohols provides advantageous conditions (post flame oxidation, high flame speed etc.) that enhance the oxidation of unburned HC (Ramos, Fernández, Casas, Rodríguez, & Pérez, 2009). Figure 4.4 shows the variation of HC emission (in ppm) for all the research fuel blends at various engine speeds. As seen in the figure, HC emission decreases with increasing engine speed. This result can be attributed to the high in-cylinder temperature due to the high in-cylinder pressure at high speeds.

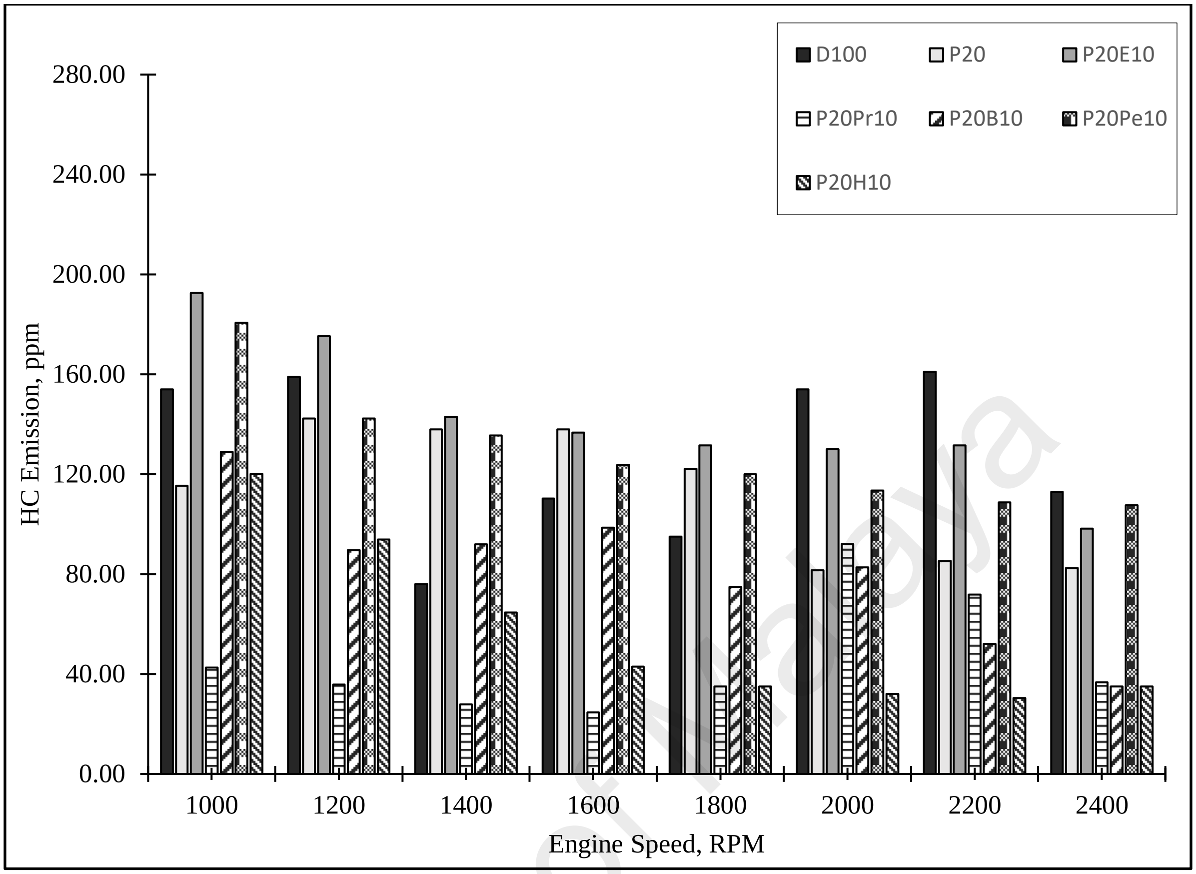


Figure 4.4: Variation of HC emission for the test fuels with speed at 100% load

The highest HC emission is recorded at 1000 rpm, with HC emission levels of 154, 120.13, 180.69, 129, 42.60, 192.60 and 115.40 ppm for diesel, P20, P20E10, P20Pr10, P20B10, P20Pe10 and P20H10 respectively. The overall average HC emission for P20, P20Pr10, P20B10 and P20H10 ternary blends reduced by 55.57%, 36.04%, 64.17% and 11.45% respectively, whereas P20E10 and P20Pe10 ternary blends show an increased HC emission by 0.94% and 11.39% respectively, compare to that of neat diesel. This result matches the findings of other researchers also (Randazzo & Sodré, 2011; X. Shi et al., 2005). This might be due to the bioethanol in the blends which causes greater ignition delay for the ternary blends, causing incomplete combustion which in return increases the HC emission (Randazzo & Sodré, 2011). Another factor could be the effect of slow vaporization rate of bioethanol and by the difficulty to produce a homogenous blend with diesel fuel, thus contributes to the formation of ultra-lean mixtures in some regions of the combustion chamber (B.-Q. He et al., 2003).

4.4.3 Carbon monoxide (CO) emission

In general, carbon monoxide (CO) is a result of partial combustion which lacks sufficient oxygen to produce CO_2. It is a product of the imperfect combustion of hydrocarbon fuels and is affected by engine speed, air−fuel ratio, fuel pressure, fuel type and injection timing (Palash et al., 2013). Figure 4.5 shows the variation in CO emissions for the different tested fuels at different engine speeds. The figure shows that CO emission decreases with increasing engine speed. This result can be attributed to the high in-cylinder temperature due to the high in-cylinder pressure at the tested speeds. The reduction in CO emission can also be attributed to the complete combustion as the flame front approached the crevice volume; in other words, excess air helped the conversion of CO to CO_2. At 1000 RPM, the highest CO emissions for diesel, P20, P20E10, P20Pr10, P20B10, P20Pe10 and P20H10 are 7.50, 8.19, 4.83, 6.33, 3.49, 8.83 and 6.92 vol %, respectively. Thus, the CO emissions for P20E10, P20Pr10, P20B10 and P20H10 reduced by 35.67%, 15.60%, 53.41% and 7.76%, respectively whereas P20 and P20Pe10 increased by 9.16% and 17.73% respectively. The presence of higher oxygen content in all tested ternary blends allowed complete combustion, which ensured that less CO was formed in the fuel blends than in diesel fuel. P20B10 had the lowest CO emission among the tested fuels. This result can be ascribed to the higher oxygen content. A high oxygen content of a fuel blend enhances combustion. A high oxygen content ensures a high in-cylinder combustion temperature, which promotes the complete combustion of fuels.

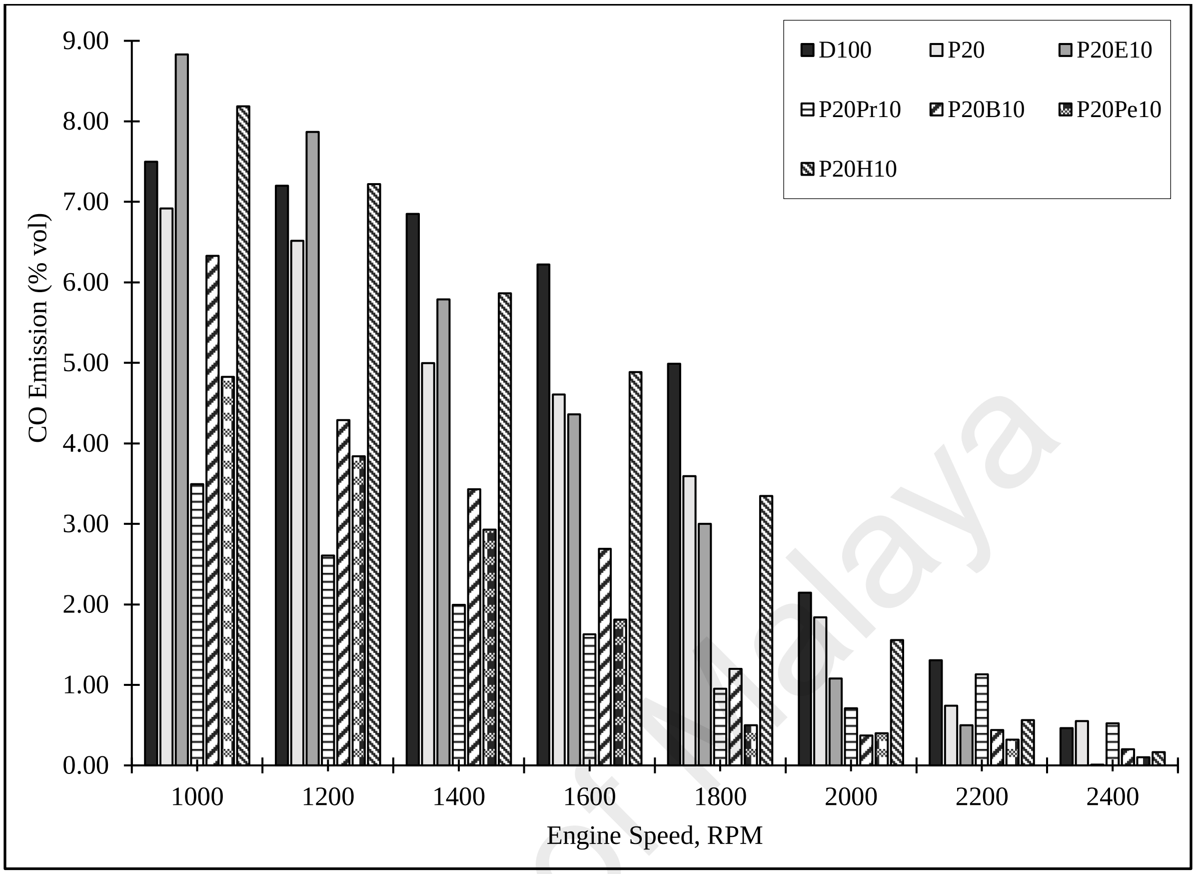


Figure 4.5: Variation of CO emission for the test fuels with speed at 100% load

4.5 Density and viscosity models for components

4.5.1 Density model for components

The density variation against temperature of the fuels is presented below in figure 4.6. The densities of diesel and bioethanol at 15°C are 852.6 kg/m³ and 797.7 kg/m³ respectively. At any temperature, the maximum density is observed for calophyllum inophyllum biodiesel while the minimum density is observed for coconut biodiesel among the 5 biodiesels. At 15°C, the density of calophyllum inophyllum and coconut biodiesels are 888.9 kg/m³ and 875.4 kg/m³ respectively. The density of calophyllum biodiesel is 4.26% and 11.43% higher than neat diesel and bioethanol respectively while the density of coconut biodiesel is only 2.67% higher than neat diesel and 9.74% higher than bioethanol. As the temperature increases, the density of all the components decreases linearly as shown in the figure 4.6.

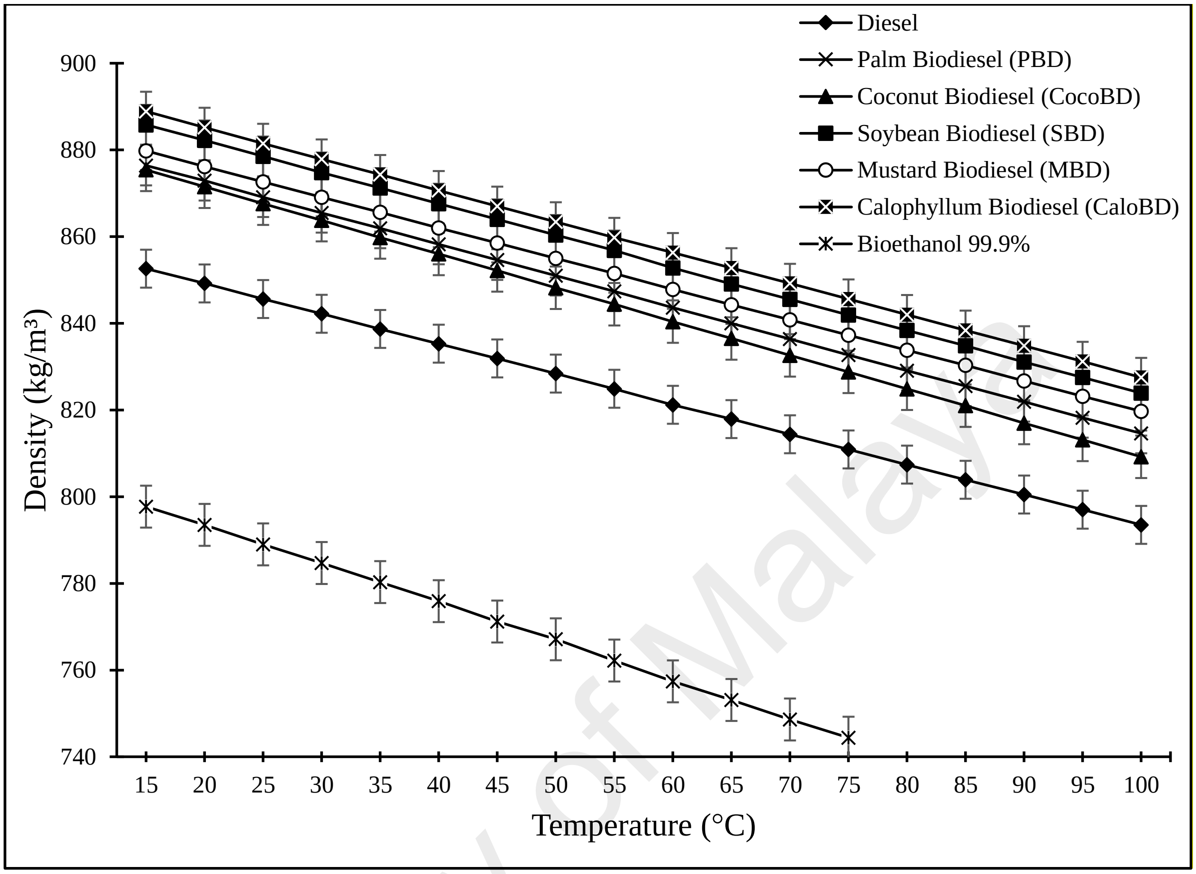


Figure 4.6: Variation of the density of diesel, biodiesel and bioethanol fuels with temperature

Equations 4.1-4.6 for neat diesel, palm, coconut, soybean, mustard and calophyllum biodiesels and equation 4.7 for anhydrous bioethanol are proposed for calculating density at temperatures ranging from 15°C-100°C and 15°C-75°C respectively. These equations have high coefficient of determinations and can be used for calculating the density of the respective biodiesel's high accuracy.

$$\rho_{D100} = -0.696T + 863.08 \qquad R^2 = 0.9999 \qquad \text{Equation 4.1}$$

$$\rho_{PBD100} = -0.728T + 887.35 \qquad R^2 = 0.9999 \qquad \text{Equation 4.2}$$

$$\rho_{CocoBD100} = -0.778T + 887.12 \qquad R^2 = 0.9999 \qquad \text{Equation 4.3}$$

$$\rho_{SBD100} = -0.730T + 896.74 \qquad R^2 = 0.9999 \qquad \text{Equation 4.4}$$

$$\rho_{MBD100} = -0.707T + 890.31 \qquad R^2 = 0.9999 \qquad \text{Equation 4.5}$$

$$\rho_{CaloBD100} = -0.719T + 899.50 \qquad R^2 = 0.9999 \qquad \text{Equation 4.6}$$

$$\rho_{EtOH_{99.9\%}} = -0.895T + 811.45 \qquad R^2 = 0.9998 \qquad \text{Equation 4.7}$$

4.5.2 Effect of biodiesel and bioethanol portions on density

When biodiesel is blended with diesel fuel, the density of the blend increases than the density of the diesel previously. Again, if bioethanol is blended with this binary mixture of diesel and biodiesel, then the density of the final ternary blend decreases. This decrease in density of ternary blends depends on the amount of biodiesel and bioethanol in the corresponding blend (Shahir et al., 2014). By mixing suitable amount of biodiesel and bioethanol with neat diesel, the problems associated with high density of fuels of CI engines can be resolved. Table 4.4 shows the density of the 30 different diesel-biodiesel-bioethanol blends measured and calculated in different ways.

Column 5 in table 4.4 shows the density of the test sample blends measured by using the viscometer. The density values (column 5 in table 4.4) of the blends are near to each other. Equation 4.8 below, is proposed for calculating density of diesel-biodiesel-bioethanol blends at 15°C, where the bioethanol must be anhydrous.

$$\rho_{blend} = \beta_1 D + \beta_2 BD + \beta_3 \rho_{BD} + \beta_0 \qquad \text{Equation 4.8}$$

Where ρ_{blend} is the density of diesel-biodiesel-bioethanol blend, D is the fraction (%) of diesel, BD is the fraction (%) of biodiesel in the ternary blend and ρ_{BD} is the density of the respective biodiesel used in the ternary blend at 15°C.

Table 4.4: Density of diesel-biodiesel-bioethanol blends by experimental method, mixing equation 3.1 and correlation equation 4.9 at 15°C

1	2	3	4	5	6	7	8	9
Type of biodiesel used	Portion of biodiesel in blend (% vol/ % mass)	Portion of bioethanol in blend (% vol/ % mass)	Density of biodiesel by using viscometer kg/m^3	Density of blend by using viscometer kg/m^3	Calculated Density, kg/m^3			
					Using KED/ equation 3.1 with % vol	Using KED/ equation 3.1 with % mass	Using correlation equation 4.9 with % vol	Using correlation equation 4.9 with % mass
Palm biodiesel	5/5.14	3/2.81	876.4	851.6	852.14	852.28	851.24	851.40
	10/10.29	6/5.62		850.9	851.69	851.96	850.69	851.02
	15/15.44	9/8.43		850.3	851.23	851.65	850.15	850.64
	20/20.60	12/11.25		849.7	850.77	851.33	849.6	850.26
	30/30.88	15/14.05		850.4	851.51	852.23	850.48	851.35
	40/41.05	15/14.01		852.4	853.89	854.68	853.32	854.27
Coconut biodiesel	10/10.25	2/1.87	875.4	853.2	853.78	853.91	853.19	853.35
	10/10.27	5/4.68		851.2	852.14	852.37	851.23	851.52
	10/10.29	8/7.50		849.2	850.49	850.83	849.26	849.67
	10/10.32	12/11.28		846.8	848.29	848.76	846.64	847.20
	10/10.34	15/14.13		844.9	846.65	847.20	844.67	845.34
	25/25.66	10/9.35		851.3	852.81	853.32	852.22	852.83
Soybean biodiesel	20/20.66	3/2.79	885.8	856.5	857.59	857.93	856.61	856.93
	20/20.68	5/4.66		855.4	856.5	856.91	855.3	855.72
	20/20.75	10/9.34		852.3	853.75	854.36	852.02	852.67
	20/20.78	12/11.23		851.1	852.65	853.33	850.71	851.44
	20/20.82	15/14.06		849.3	851.01	851.79	848.74	849.59
	35/35.99	5/4.63		860.3	861.48	862.01	859.56	860.09
Mustard biodiesel	20/20.64	10/9.36	879.8	851.2	852.55	853.08	851.31	851.92
	30/30.76	5/4.65		857	858.02	858.42	857.43	857.88
	30/30.82	8/7.45		855.3	856.37	856.89	855.47	856.06
	30/30.86	10/9.33		854.1	855.27	855.87	854.16	854.84
	30/30.90	12/11.21		852.9	854.17	854.85	852.85	853.62
	30/30.96	15/14.04		851	852.53	853.32	850.88	851.78
Calophyllum biodiesel	5/5.24	10/9.40	888.9	847	848.93	849.34	848.12	848.59
	10/10.45	10/9.38		848.7	850.74	851.25	849.54	850.08
	15/15.64	10/9.36		850.5	852.56	853.14	850.97	851.57
	20/20.81	10/9.34		852.3	854.37	855.03	852.39	853.05
	25/25.96	10/9.32		854.1	856.19	856.91	853.81	854.53
	20/20.94	20/18.79		846.2	848.88	849.88	845.83	846.89

To develop the equation 4.9, only the major contributor in the final density of the ternary blends; which are neat diesel and biodiesel, are used. The constants in the equations are determined using regression analysis with high coefficients of determinations and standard deviations. This equation can be used to calculate density of ternary blends at 15°C.

$$\boldsymbol{\rho_{blend} = 0.6554D + 0.9397BD + 0.1180\rho_{BD} + 682.825} \qquad \textbf{Equation 4.9}$$

$$\boldsymbol{R^2 = 0.9823} \qquad \textbf{SD=0.4535}$$

In equation 4.9, both ‘% volume’ and ‘% mass’ of the components can be used. But, using volume fraction and mass fraction in this equation will not give same accuracy. Densities calculated using the correlation equation of all the blends are shown in the table 4.4. The APEs using volume and mass fraction are presented in the figure 4.8. The KED is also tested with both ‘% volume’ and ‘% mass’. To determine the most accurate model, APEs are calculated between each of the values obtained from the KED and experimental method and between the proposed density model and the experimental method. The values obtained using % vol in KED have a MAPE of 0.16% but using % mass gives a MAPE of 0.23%. On the contrary, using % vol and % mass in the correlation equation 4.9 give MAPE of only 0.04% and 0.08% respectively. For better understanding and to observe the calculative accuracy of the two models described, APEs are calculated and presented in figure 4.8. In case of both the models, using ‘% volume’ of components gives lower APE compare to using ‘% mass’. And in all the cases, the proposed correlation equation gives the best calculative density of any ternary blend. This result is only valid with low bioethanol content. Density of blends containing up to 15% bioethanol and 30% biodiesel can be calculated precisely using ‘% volume’ in the equation 4.9.

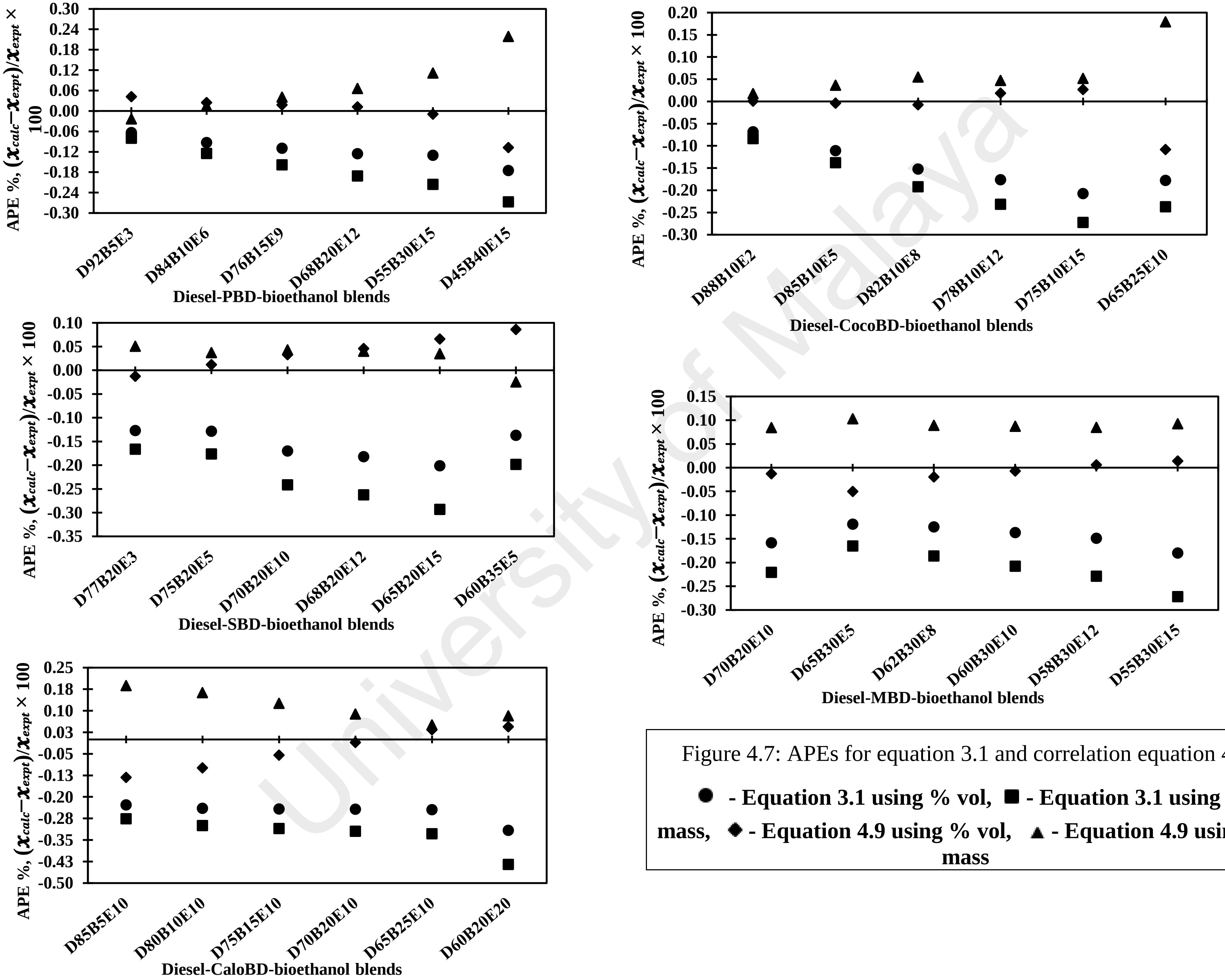


Figure 4.7: APEs for equation 3.1 and correlation equation 4.9

● - Equation 3.1 using % vol, ■ - Equation 3.1 using % mass, ◆ - Equation 4.9 using % vol, ▲ - Equation 4.9 using % mass

4.5.3 Viscosity models for components

Kinematic viscosities of neat diesel, 5 biodiesels and bioethanol are presented in figure 4.8. At 40°C, the maximum viscosity is observed for mustard biodiesel, which is 5.8097 mm^2/s and the lowest is observed for coconut biodiesel which is 2.7675 mm^2/s. The viscosity of soybean biodiesel is found to be closest to the neat diesel viscosity (3.6490 mm^2/s) which is 4.1837 mm^2/s. At low temperatures, the viscosity of the fuels differs from each other a lot, but as the temperature increases, the differences decrease and at higher temperature like 100°C, the viscosity of the fuels comes closer to each other. The viscosity pattern as the temperature increases; of all the 7 components used in this work is not linear like their density pattern, which is a linear decrease with the temperature increase. To handle these non-linear data series, they must be transformed for more accurate models.

The natural log of all the viscosity values are calculated and then equations 4.10-4.16 are developed for kinematic viscosity calculations of neat diesel, palm, coconut, soybean, mustard, calophyllum inophyllum biodiesels and anhydrous bioethanol from 5-100°C. In all cases, the coefficient of determination was very high, which indicates that the models are very good fits.

$$\boldsymbol{ln\,\eta_{D100} = -0.019T + 2.092} \qquad \boldsymbol{R^2 = 0.9833} \qquad \textbf{Equation 4.10}$$

$$\boldsymbol{ln\,\eta_{PBD100} = -0.018T + 2.279} \qquad \boldsymbol{R^2 = 0.9846} \qquad \textbf{Equation 4.11}$$

$$\boldsymbol{ln\,\eta_{CocoBD100} = -0.016T + 1.702} \qquad \boldsymbol{R^2 = 0.9862} \qquad \textbf{Equation 4.12}$$

$$\boldsymbol{ln\,\eta_{SBD100} = -0.017T + 2.166} \qquad \boldsymbol{R^2 = 0.9858} \qquad \textbf{Equation 4.13}$$

$$\boldsymbol{ln\,\eta_{MBD100} = -0.019T + 2.573} \qquad \boldsymbol{R^2 = 0.9847} \qquad \textbf{Equation 4.14}$$

$$\boldsymbol{ln\,\eta_{CaloBD100} = -0.019T + 2.422} \qquad \boldsymbol{R^2 = 0.9844} \qquad \textbf{Equation 4.15}$$

$$\boldsymbol{ln\,\eta_{EtOH_{99.9\%}} = -0.018T + 0.809} \qquad \boldsymbol{R^2 = 0.9980} \qquad \textbf{Equation 4.16}$$

Where $\boldsymbol{T}$ is the temperature in °C and $\boldsymbol{\eta}$ is the kinematic viscosity at corresponding temperature in mm^2/s.

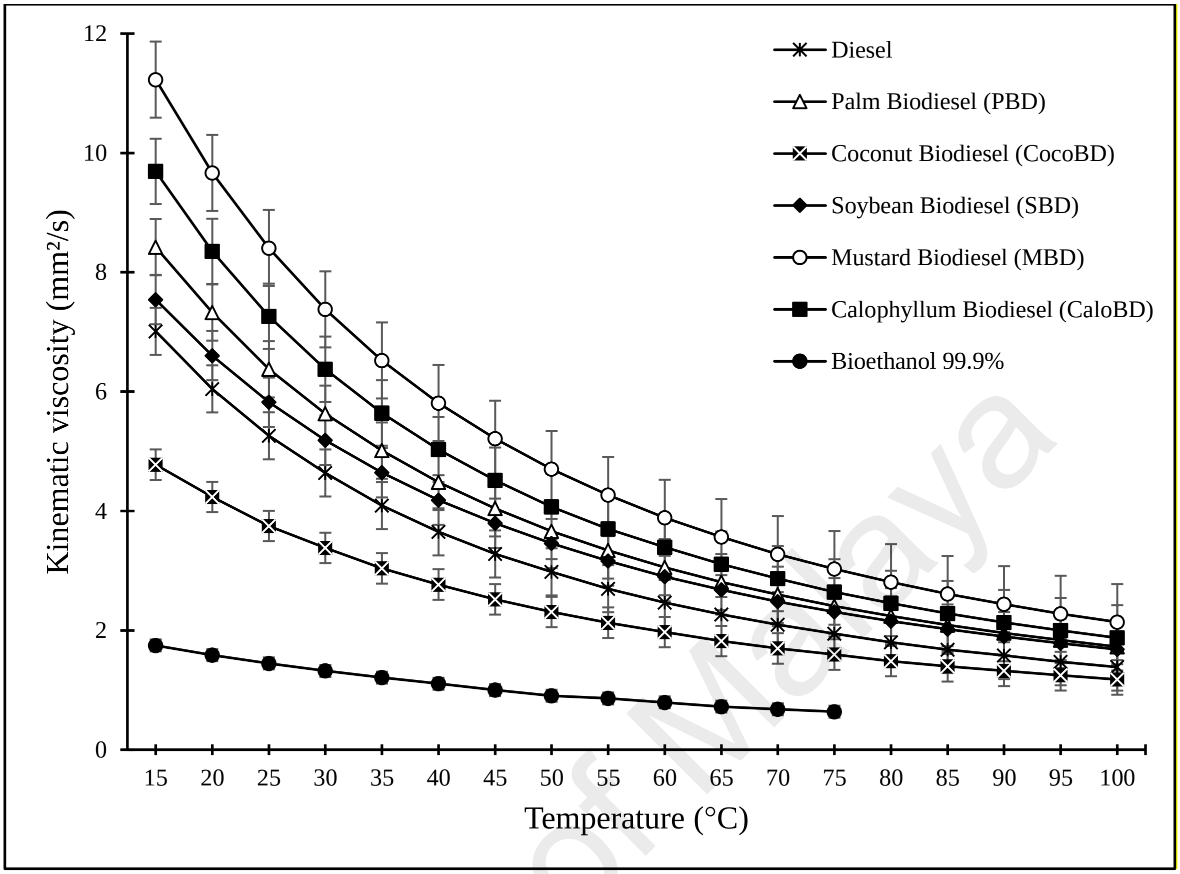


Figure 4.8: Variation of the kinematic viscosity of diesel, biodiesel and bioethanol fuels with temperature

4.5.4 Effect of biodiesel and bioethanol fraction on kinematic viscosity

Kinematic viscosity of diesel-biodiesel-bioethanol blends is also governed by the portion of biodiesel and bioethanol in the blends (Shahir et al., 2014). As the biodiesel portion in any blend increases, the viscosity of the blend increases, again when bioethanol portion in the blend increases, the viscosity decreases proportionally. Kinematic viscosity all the sample blends at 40°C is presented in table 4.5. Using the '% volume' and '% mass' and the kinematic viscosities of the components in the only available mixing equation 2, the final viscosity of each blend is calculated and presented in column 6 and 7 in table 4.5.

Table 4.5: Kinematic viscosity of diesel-biodiesel-bioethanol blends by experimental methods, mixing equation and correlation equations at 40°C

1	2	3	4	5	6	7	8	9	10	11	12	13
Type of biodiesel used	Portion of biodiesel in blend (% vol/ % mass)	Portion of bioethanol in blend (% vol/ % mass)	Kinematic viscosity of biodiesel by using viscometer mm²/s	Kinematic viscosity of blend by using viscometer mm²/s	Calculated viscosity, mm²/s							
					Using mixing equation 3.2 with % vol	Using mixing equation 3.2 with % mass	Using correlation equation 4.18 with % vol	Using correlation equation 4.18 with % mass	Using correlation equation 4.19 with % vol	Using correlation equation 4.19 with % mass	Using correlation equation 4.20 with % vol	Using correlation equation 4.20 with % mass
Palm biodiesel	5/5.14	3/2.79	4.4844	3.3299	3.5570	3.5671	3.3747	3.4112	3.3282	3.3411	3.2705	3.2872
	10/10.29	6/5.58		3.1770	3.4674	3.4868	3.1661	3.2003	3.1919	3.2166	3.0876	3.1032
	15/15.45	9/8.38		3.0383	3.3800	3.4083	3.0427	3.0755	3.0612	3.0965	2.9742	2.9891
	20/20.61	12/11.18		2.9286	3.2948	3.3314	2.9518	2.9836	2.9359	2.9808	2.8862	2.9004
	30/30.90	15/13.97		2.8612	3.2451	3.2914	2.8879	2.9190	2.8426	2.8982	2.8821	2.8965
	40/41.08	15/13.93		2.8957	3.3127	3.3628	2.8949	2.9264	2.8971	2.9567	2.9956	3.0112
Coconut biodiesel	10/10.24	2/1.86	2.7675	3.2644	3.4657	3.4694	3.3145	3.3502	3.1534	3.1627	3.2701	3.2894
	10/10.26	5/4.65		3.0447	3.3437	3.3553	2.9370	2.9684	2.9958	3.0152	3.1113	3.1291
	10/10.28	8/7.46		2.8573	3.2260	3.2446	2.7577	2.7871	2.8459	2.8741	2.9592	2.9756
	10/10.31	12/11.21		2.6883	3.0755	3.1018	2.6093	2.6368	2.6578	2.6953	2.7863	2.8010
	10/10.33	15/14.05		2.5924	2.9673	2.9984	2.5296	2.5560	2.5249	2.5679	2.6560	2.6696
	25/25.64	10/9.30		2.6483	3.0219	3.0419	2.7576	2.7871	2.8298	2.8675	2.9705	2.9875
Soybean biodiesel	20/20.66	3/2.77	4.1837	3.3860	3.6182	3.6313	3.5072	3.5477	3.3764	3.3939	3.4088	3.4256
	20/20.69	5/4.63		3.2482	3.5328	3.5520	3.2774	3.3151	3.2629	3.2882	3.3178	3.3337
	20/20.76	10/9.28		2.9747	3.3280	3.3601	2.9842	3.0182	2.9955	3.0368	3.0718	3.0856
	20/20.79	12/11.16		2.8735	3.2494	3.2859	2.9099	2.9429	2.8948	2.9413	2.9813	2.9943
	20/20.83	15/13.97		2.7446	3.1350	3.1773	2.8201	2.8518	2.7500	2.8031	2.8504	2.8623
	35/35.99	5/4.60		3.2983	3.6060	3.6282	3.3218	3.3606	3.3572	3.3867	3.6517	3.6710

Table 4.5, continued

Mustard biodiesel	20/20.65	10/9.30	5.8097	3.1757	3.5538	3.5948	3.1931	3.2283	3.2329	3.2761	2.9931	3.0071
	30/30.77	5/4.62		3.6522	3.9521	3.9846	3.5445	3.5844	3.5890	3.6179	3.3908	3.4085
	30/30.84	8/7.40		3.4604	3.8130	3.8554	3.3262	3.3634	3.4095	3.4501	3.2518	3.2682
	30/30.88	10/9.27		3.3429	3.7230	3.7712	3.2256	3.2615	3.2949	3.3421	3.1567	3.1723
	30/30.93	12/11.13		3.2385	3.6351	3.6887	3.1445	3.1794	3.1841	3.2373	3.0643	3.0791
	30/30.99	15/13.95		3.0865	3.5072	3.5679	3.0461	3.0797	3.0249	3.0856	2.9231	2.9366
Calophyllum biodiesel	5/5.24	10/9.34	5.0296	2.9346	3.2906	3.3193	2.9426	2.9760	3.0292	3.0652	2.9006	2.9116
	10/10.45	10/9.32		2.9851	3.3438	3.3761	3.0258	3.0604	3.0581	3.0967	2.9091	2.9207
	15/15.65	10/9.30		3.0429	3.3979	3.4337	3.0709	3.1062	3.0873	3.1285	2.9769	2.9893
	20/20.82	10/9.28		3.0834	3.4528	3.4919	3.0996	3.1354	3.1167	3.1604	3.0683	3.0816
	25/25.97	10/9.26		3.1209	3.5087	3.5509	3.1187	3.1550	3.1465	3.1926	3.1751	3.1894
	20/20.97	20/18.69		2.6594	3.0641	3.1222	2.8099	2.8417	2.6269	2.6915	2.6346	2.6444

When the viscosity values calculated using equation 2 are compared to the measured values (obtained using viscometer, column 5 in table 4.5), the MAPE is found to be 11.55% (with % vol) and 12.64% (with % mass), which are very high. For better accuracy, here in this work 3 mathematical models for calculating kinematic viscosity at 40°C are proposed.

These models are developed keeping 2 cases in considerations: a) the '% volume/mass' of all the components in a blend are known along with their individual kinematic viscosities at 40°C and b) the fractions are known but the components viscosity values are unavailable while only density values are available.

Case 'a': To calculate kinematic viscosity at 40°C of any ternary blend consists of diesel, biodiesel and bioethanol, a correlation model, equation 4.17 is proposed.

$$\boldsymbol{ln\ (\eta_{blend}) = ln\,\alpha + \beta_0\, ln(D) + \beta_1 ln\ (BD) + \beta_2 ln\ (\eta_{BD}) + \beta_3 ln\ (EtOH)}$$

Equation 4.17

Where, $\boldsymbol{\eta_{blend}}$ is the final viscosity, $\boldsymbol{\alpha, \beta_0, \beta_1, \beta_2}$ and $\boldsymbol{\beta_3}$ are constants, $\boldsymbol{D}$ is the fraction of diesel in the blend, $\boldsymbol{BD}$ is the fraction of biodiesel in the blend, $\boldsymbol{EtOH}$ is the fraction of bioethanol in the blend and $\boldsymbol{\eta_{BD}}$ is the kinematic viscosity of the corresponding biodiesel at 40°C. Both the '% volume' and the '% mass' of the components could be used in this equation.

The value of the constants is calculated using the slope and coefficients from the regression analysis. Here the effect of the portions of each component and the viscosity of the biodiesel is obvious. This model has a very high R square/$\boldsymbol{R^2}$ value which indicates that it is a very good fit for viscosity calculation.

$$\boldsymbol{ln\,(\eta_{blend}) = 0.0521 \times ln(D) + 0.0448 \times ln\ (BD) + 0.2060 \times ln\ (\eta_{BD}) - 0.13 \times ln\ (EtOH) + 0.7423}$$

Equation 4.18

R^2=0.9202 ***SD= 0.0738***

In search for more accuracy, exponential regression analysis is found to be a good fit, which gives one of the simplest kinematic viscosity models at 40°C for ternary blends. Using this method, the equation 4.19 is developed, which has got a high coefficient of determination along with a very low standard deviation.

$$\boldsymbol{ln(\eta_{blend}) = 0.0171 \times (D) + 0.0190 \times (BD) + 0.0469 \times ln(\eta_{BD}) - 0.6761}$$

Equation 4.19

R^2=0.9468 ***SD= 0.0589***

Where, $\boldsymbol{\eta_{blend}}$ is the final viscosity, $\boldsymbol{D}$ is the fraction of diesel in the blend, $\boldsymbol{BD}$ is the fraction of biodiesel in the blend and $\boldsymbol{\eta_{BD}}$ is the kinematic viscosity of the corresponding biodiesel at 40°C. Both the '% volume' and the '% mass' of the components could be used in this equation.

Another advantage of this model is that, it uses only 3 variables (portion of diesel and biodiesel in the blend and the natural log of the kinematic viscosity value of the respective biodiesel used) for final viscosity calculation.

Case 'b': To meet this condition and for more convenience and less effort, the variables are changed and analyzed to find an optimum model for viscosity prediction. Here the variables like the portions of the individual components were kept as same as before but the variables like the viscosity of each component are changed to density of each components and the final density of the ternary blend. After analysis the best model is identified based on the R square value and standard deviation. This model is described by the following equation 4.20.

$$\boldsymbol{ln(\eta_{blend}) = -0.0246 \times ln\,(D) - 0.0610 \times ln\,(BD) + 0.0006 \times ln(EtOH) - 0.3268 \times ln(\rho_{BD}) + 21.8024 \times ln(\rho_{blend}) - 143.4953}$$

Equation 4.20

R^2* = 0.7207** ***SD= 0.1433

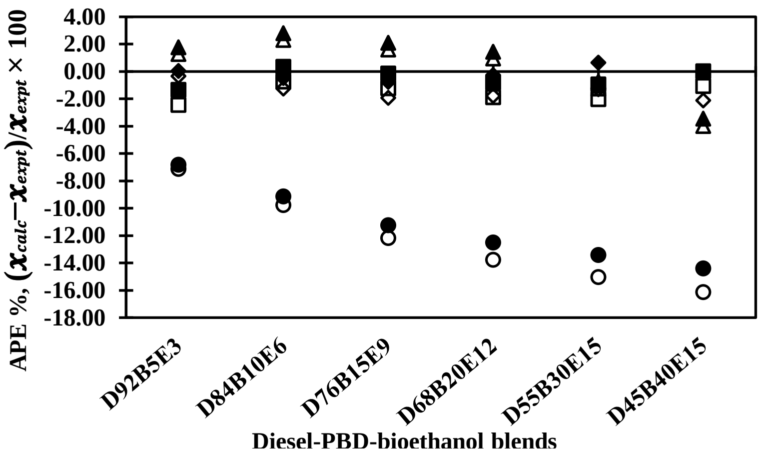
Where, $\boldsymbol{\eta_{blend}}$ is the final viscosity, $\boldsymbol{D}$ is the fraction of diesel in the blend, $\boldsymbol{BD}$ is the fraction of biodiesel in the blend, $\boldsymbol{EtOH}$ is the fraction of bioethanol in the blend, $\boldsymbol{\rho_{BD}}$ is the density of the biodiesel and $\boldsymbol{\rho_{blend}}$ is the density of the blend at 40°C.

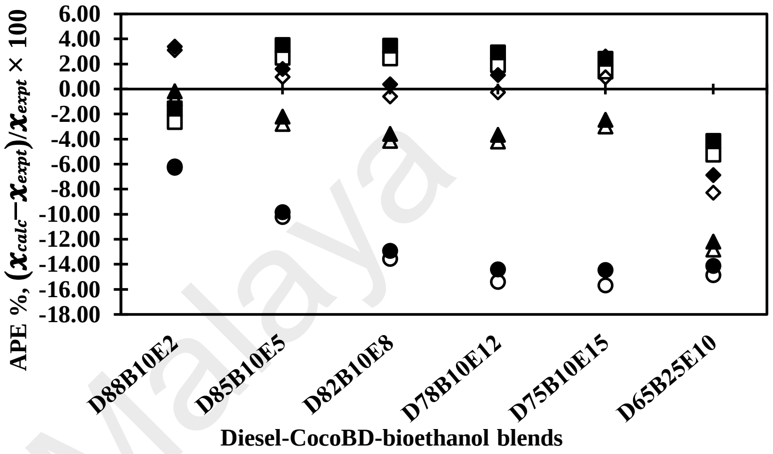
This mathematical model is based on log-log regression analysis. This equation can be used to calculate the viscosity of any ternary blend using only the components portions in the respective blend and the density of the blend and biodiesel at 40°C.

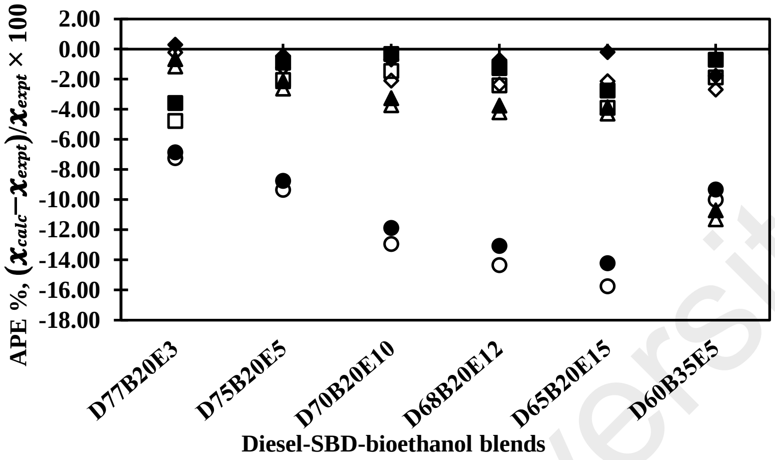
The developed models were tested with the blends produced for density and viscosity measurements. Kinematic viscosity of all the 30 blends at 40°C are calculated using the three correlation equations and shown in the table 4.5 in columns 8-13.

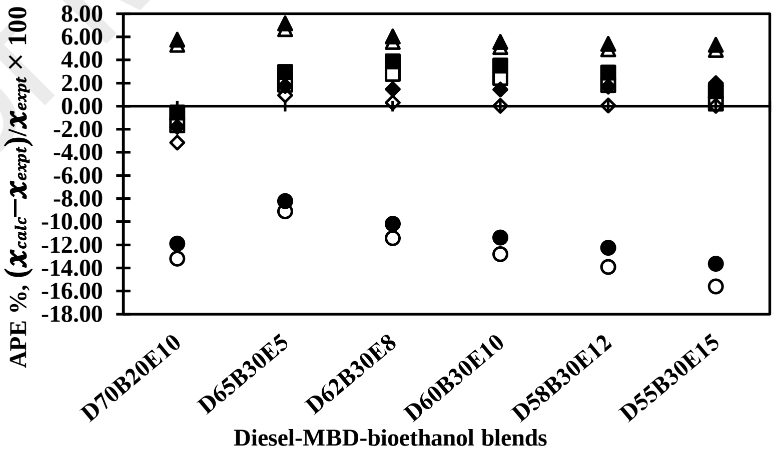
To test the proposed viscosity models, each value obtained using the equations 2, 4.18, 4.19 and 4.20 are compared with the measured value using viscometer to determine the MAPE and shown in figure 4.9. MAPE obtained using three correlation equations 4.18, 4.19 and 4.20 are 1.84%, 1.42% and 3.50% respectively using volume fraction while it is 2.28%, 1.84% and 3.54% respectively using mass fraction. From MAPE value it is obvious that the equation 4.19 is the best fitted model while using volume fraction.

In figure 4.9, the viscosities obtained using mixing equation is not even closer to the actual values. The other three correlation equations are quite good enough for viscosity calculation. From the figures, it is also confirmed that the equation 4.19 can be used precisely for palm, coconut, soybean and mustard biodiesel blends but in case of calophyllum biodiesel blends this equation will not be the most perfect. In case of diesel-CaloBD-bioethanol blends, the best equation to calculate the kinematic viscosity is the equation 4.18.









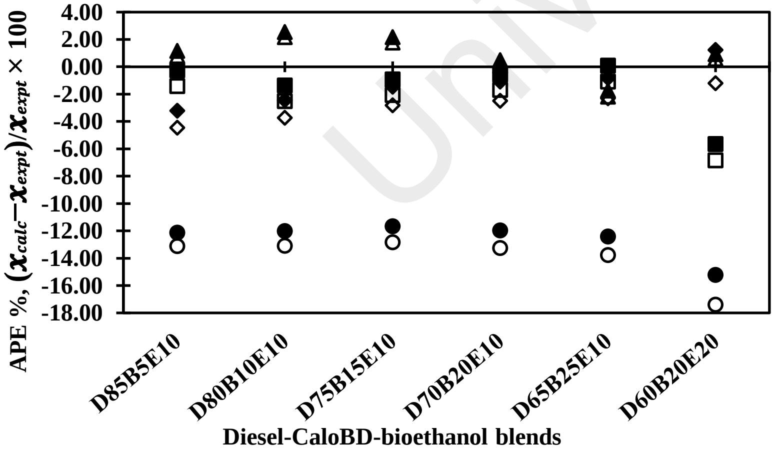


Figure 4.9: APEs using mixing equation 2 and correlation equations 4.18, 4.19 & 4.20

●- Mixing Equation 3.2 using % vol, ○ - Mixing Equation 3.2 using % mass, ■ - Equation 4.18 using % vol □ - Equation □ - Equation 4.18 using % mass, ◆- Equation 4.19 using % vol, ◇ - Equation 4.19 using % mass, ▲ - Equation 4.20 using % vol, △- Equation 4.20 using % mass.

CHAPTER 5 : CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Biodiesel is a potential biofuel which can replace at least some portion of neat diesel efficiently. In Malaysia the energy demand is growing rapidly, and some biodiesel feedstocks grow abundantly here. Among the biodiesel feedstocks, palm oil has the highest production rate which was 19.20 million tonnes in 2015. At present it is compulsory to add 5% palm biodiesel to neat diesel in Malaysia, but some physicochemical properties of the biodiesel restrict its portion in the diesel-palm biodiesel blend. The properties which hinders the use of higher amount of palm biodiesel are its higher density, viscosity and cetane number. To make palm biodiesel more feasible for diesel engines and increase its portion in diesel-biodiesel blends, a third fuel or additive is required, which will not only improve the physicochemical properties of the blend but will also improve the performance, emission and combustion characteristics. This third fuel or additive could be an alcohol which will also increase the oxygen content of the final fuel blend. Many researchers have tested diesel-biodiesel-bioethanol in diesel engines and found no difficulty in using it, which matches this work results. Beside bioethanol, there are some other alcohols which have also potential to be used in diesel-biodiesel blend.

In this research work a comprehensive investigation has been performed to evaluate and compare the performance and harmful exhaust emissions characteristics between diesel-palm biodiesel (P20), diesel-palm biodiesel-bioethanol, diesel-palm biodiesel-2 propanol, diesel-palm biodiesel-iso butanol, diesel-palm biodiesel-pentanol and diesel-palm biodiesel-1 hexanol blends. Thus, the following conclusions are drawn:

- The viscosities of all the ternary blends are within the acceptable limit of ASTM D6751 (standard for pure biodiesel and biodiesel blends for use in unmodified diesel engine), EN 590 and ASTM D975 (standard for neat/pure diesel for use in unmodified engine) standards. According to ASTM D975 standard, all the ternary blends used for engine testing falls within the limit for “Low Sulfur No. 2 Diesel”.

- The cetane number of all the ternary blends are within the acceptable limit of EN 590 and ASTM D975 standard and is near to the diesel one.
- The calorific values of the ternary blends are very near to neat diesel.
- Engine performance results show that, P20 and all the ternary blends showed higher BSFC than neat diesel because of the lower calorific value and inferior atomization quality. Among the ternary blends, P20Pe10 has the lowest BSFC. Second lowest BSFC is exhibited by P20E10.
- Among the ternary blends, only P10E10 and P20Pe10 blends exhibited higher BTE compare to neat diesel. These two blends showed 17.60% and 17.64% BTE respectively.
- All the engine test fuels exhibited lower NO_X except P20Pe10 and P20H10 compare to neat diesel. P20Pe10 gave a 17.50% rise in NO_X emission whereas P20E10 gave 44.03% lower NO_X emission compare to neat diesel.
- All the engine test fuels were investigated to lower the HC emission except the P20E10 and P20Pe10. P20B10 ternary blend gave the lowest HC emission. And P20E0 gave 91.75% lower HC emission compare to P20Pe10.
- In case of CO emission, only P20 and P20Pe10 are found to increase its emission. All the other engine test fuels gave a lower CO emission compare to neat diesel.

Therefore, it can be observed that, among all the test fuels P20E10 and P20Pe10 have shown good overall performance and emission characteristics except for high HC and CO emission of P20Pe10. These discussions indicate that from the point of view of fuel properties (e.g. flash point, pour point, cetane number, viscosity, density) with a small increase in HC emission and fuel consumption penalty (which is equal to the decrease of energy content), P20E10 blend can be suggested for unmodified diesel engines. This result gives us an opportunity to increase the portion of biodiesel in diesel-biodiesel blend. Using 10% bioethanol the portion of biodiesel can be increased by 20% in diesel-biodiesel blend. Thus 30% neat diesel can be replaced by biofuels effectively.

The proposed density and viscosity models can be used for all types of biodiesels as the models use only the components density and viscosity and their portions in the blend. These models can be used at temperatures ranging from 15°C to 75°C. Calculating density and kinematic viscosity of diesel-biodiesel-bioethanol blends outside the specified temperature range could be possible but the accuracy will drop, as above 78°C, the bioethanol starts to evaporate. The constants and parameters of the proposed models have been developed and evaluated using the fuels used in this research work. As the physicochemical properties of diesel and biodiesel and the concentration of the bioethanol depends on the nature and quality of the raw materials and processes used to produce them, thus the differences of the physicochemical properties of other fuels should be considered while using the equations for determining their density and viscosity. The models of this research work will provide important information before mixing the 3 components for fuel respecting the density and viscosity standards. In case of density calculation, using equation 4.9, '% mass' will give the most accurate result. The proposed density model has high accuracy rate and in case of viscosity models, the correlation equation 4.18 is suggested to use for designing and other sophisticated purposes, where high accuracy is needed.

5.2 Recommendations

This research finds the 70% diesel-20% palm biodiesel-10% bioethanol blend to be the best option to increase biofuel portion in diesel-palm biodiesel blend based on performance and emission characteristics of a single cylinder diesel engine.

Based on the conclusions, the following recommendations for future works are suggested:

- To make this blend commercially viable it needs to be tested on real life engines and need to understand its combustion characteristics.
- Engine materials compatibility to this ternary blend need to be investigated.
- Calorific value, flash point and cetane number calculation models can be developed for design purposes.

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APPENDIX 1: PUBLICATIONS

Journal papers

S.A. Shahir, H.H. Masjuki, M.A. Kalam, A. Imran, I.M. Rizwanul Fattah. A. Sanjid. Feasibility of diesel–biodiesel–ethanol/bioethanol blend as existing CI engine fuel: An assessment of properties, material compatibility, safety and combustion.
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