

Title: Cold Flow Improvement of Biodiesel and Investigation
the Effect of Biodiesel Emulsification on Diesel Engine
Performance and Emissions

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Abstract

Increasing concerns over environmental issues and conventional resource depletion have heightened our motivation to use clean and alternative fuels. Biodiesel is simply derived from biomass proposed as an alternative fuel for diesel engines, which contributes to a reduction in carbon monoxide (CO), smoke intensity, and unburned hydrocarbon (HC). However, biodiesel has inferior cold flow properties and emits higher nitrogen oxides (NO_x) compared to conventional diesel. The present work aims at improving cold flow properties of biodiesel using the fractionation method combined with additives, and investigates their effects on a diesel engine's regulated emissions and performance. In addition, emulsion fuels were found to reduce both NO_x emission and smoke intensity. Experiments using urea, mixture of recovered urea and crystal, and crystal fractionation were conducted; the additives include ethanol, methanol, and diethyl ether (DEE). Results using two modern diesel engines (a light-duty and a heavy-duty) were investigated using various fuels. The heavy-duty engine was fueled with different fuel types and eight emulsion fuels at two idling conditions (1200 rpm and 1500 rpm). The light-duty engine was fueled with biodiesel blends, fractionated biodiesel blends, emulsified diesel-biodiesel, emulsified diesel-biodiesel ammonium hydroxides blends, and emulsified biodiesel at three different engine operating conditions. The conclusion was that a mixture of recovered urea and crystal fractionation provided higher production efficiency and acceptable cloud point. A significant reduction in NO_x emission was obtained from emulsified fuels compared with their bases, and emulsion biodiesel with 2.5% water revealed results that were comparable to diesel in terms of NO_x and CO emissions at all engine operating conditions.

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Nomenclature

ASTM	American Society of Testing and Materials
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
FAME	Fatty acid methyl ester
CAD	Canadian dollars
Cc	Cubic centimeter
CFP	Cold flow property
CFPP	Cold filter plugging point
CN	Cetane number
CO	Carbon monoxide
CP	Cloud point
CR	Compression ratio
cSt	Centistoke
°C	Degree Celsius
DEE	Diethyl ether
DOC	Diesel oxidation catalyst
DPF	Diesel particle filter
EGR	Exhaust gas recirculation
EB	Emulsified biodiesel
EGT	Exhaust gas temperature
FB	Fractionated Biodiesel
g/kWh	Gram per kilowatt-hour
g/L	Gram per liter
HC	Hydrocarbons
HLB	Hydrophile-Lipophile Balance
kg/m ³	Kilogram per cubic meter
kJ/kg	Kilojoule per kilogram
kW	Kilowatt
MP	Melting point
mg/m ³	Milligram per cubic meter

ml/min	Milliliter per minute
mm	Millimeter
μm	Micrometer
NO	Nitric oxide
NO ₂	Nitrogen dioxide
NO _x	Oxides of nitrogen
NSC	NO _x storage catalyst
O ₂	Oxygen
O/W	Oil-in-water
O/W/O	Oil-in-water-in-Oil
PM	Particulate matter
PP	Pour point
ppm	Part per million
rpm	Revolution per minute
Span 80	Sorbitan Monoleate
Tween 80	Polyoxyethylene Sorbitan Monoleate
W/O	Water-in-oil
W/O/W	Water-in-oil-in-water

Chapter 1: Overview

1.1 Introduction

The skyrocketing growth in the world's population over last century has heightened the demand for conventional fuel resources. Currently, the worldwide consumption of conventional petroleum products (oil and liquid fuels) is approximately 96 million barrels per day [1], [2]. Canada consumed about 1.8 million barrels per day of refined petroleum products in 2015 [3]. In that same year, the net sales of diesel and gasoline fuels were 17.989 and 44.58 million liters per year, respectively [4]. Generally, diesel is used as a fuel for compression ignition (CI) engines, while gasoline is used as a fuel for spark ignition (SI) engines. The dependency on diesel and gasoline contribute to the pollution of the environment since the main emissions exhausted from the engines that function on those fuels are carbon monoxide (CO), nitrogen oxides (NO_x), unburned hydrocarbon (HC), and particulate matters (PM). Further, increasing the demand on conventional fuel, which has an end-date, will result in it no longer being a viable option in the future.

Generally, diesel engines have advantages of high-energy conversion and economic power source over gasoline engines, especially for the same power output. Therefore, a diesel engine emits lower CO and HC [5]. Additionally, there is low maintenance required for diesel engines since they have no ignition or carburetor systems. Further, a diesel engine has more flexibility over fuel choice [6]. Thanks to these advantages, diesel engine use is wide-spread in many applications such as transportation, agricultural machines, and mining equipment. Although a diesel engine has lower emission compared to a gasoline engine, public and regulatory agencies in both developed and developing countries put more pressure on diesel engine emission control.

Extensive research has been conducted on emission reduction in diesel engines. Such potential technologies include reducing in-cylinder temperature and after-treatment of engine exhaust gases. Reducing in-cylinder temperature using exhaust gas recirculation (EGR) is an effective way to reduce NO_x emissions, which works by recirculating a portion of the exhaust gases back to the engine cylinder, thus reducing the amount of oxygen that is available for combustion in the cylinder [7]. After-treatment systems include [8]: a diesel oxidation catalyst (DOC), designed to reduce CO and HC emissions; a diesel particulate filter (DPF), designed to remove PM or soot emission; and NO_x storage catalysts (NSC) and selective catalytic reduction

(SCR), both designed to decrease NO_x emission. Despite the fact that these technologies have a significant impact on reducing diesel engine emissions, after-treatment systems are relatively expensive, and result in increased fuel consumption and operating costs [9].

Numerous studies have been conducted investigating the effects of engine variables and fuel properties on diesel engine emissions. Firstly, engine variables such as injection pressure, injection timing, and compression ratio (CR) have an influential impact on diesel engine emissions. In general, the advanced injection timing, high injection pressure, and high CR usually result in reducing CO, HC and PM emissions, while NO_x emissions show the opposite result [10]–[13]. The reason may be due to the advanced injection timing which increases ignition delay time, while the increased injection pressure results in burning more fuel and increases the CR. Hence, higher combustion temperature attributes to an increase in NO_x and a reduction in CO, HC, and PM emissions.

Secondly, fuel properties such as its cetane number (CN), latent heat of vaporization, oxygen content, and kinetic viscosity, play a major role in emission characteristics of a diesel engine. The CN of fuel affects the ignition delay time and the premixed combustion phase, which increase by reducing the CN, and decrease by raising the CN in the fuel. Therefore, fuels with a high CN cause a reduction of NO_x emission, whereas it contains high CO, HC and smoke emissions, especially at low and medium loads [14], [15]. Fuel latent heat of vaporization is the amount of heat that is required to convert fuel into gas; hence, fuel with high latent heat of vaporization contributes to less NO_x emission and higher CO emission [16]. The oxygen content of fuel has a significant effect on diesel engine emission which is, in general, fuel with high oxygen content, attributing to high combustion temperature, and thus higher NO_x and lower CO, HC, and PM emissions [17]. Viscosity also plays an important role in lubricating the fuel injection system. Therefore, fuel with higher viscosity than diesel fuel resulted in a decrease in the injection rate in power fuel atomization, and in vaporization by the injectors, consequently leading to incomplete combustion which resulted in soot emission and increased particles [18], [19].

Biodiesel is simply derived from biomass proposed as an alternative fuel in the market, and is defined as the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstocks, such as vegetable oil and animal fats [20]. Biodiesel, as a renewable fuel for diesel, offers the potential of decreasing dependence on petroleum fuels. The global shift to biodiesel

currently encompasses many different countries. The world's biodiesel consumption increased significantly over the last decade. In 2012, the biodiesel consumption in 64 countries averaged 420 thousand barrels per day; 54% of which was consumed in five countries, namely USA, Germany, Brazil, France and Spain. These countries averaged approximately 60, 48.9, 48.2, 43 and 27.4 thousand barrels per day, respectively [21]. Canada's consumption of biodiesel for the same year averaged 5 thousand barrels per day, and the consumption is expected to reach 9 thousand barrels per day by 2022 [22]. Biodiesel as an alternative fuel has many advantages over diesel fuel, but it also has a few potential downsides.

1.2 Biodiesel Advantages

1.2.1 Reduced Foreign Petroleum Oil Dependency

Biodiesel is a renewable and domestic energy source that can decrease the dependency on foreign petroleum oil since petroleum oil is not renewable, and vegetable oil could be produced worldwide. For example, USA spent approximately \$250 billion on foreign petroleum oil, consuming about 20 million barrels per day in 2007 [23]. Therefore, investing some of that money into biodiesel production would displace a considerable amount of foreign petroleum diesel.

1.2.2 Simplicity

Biodiesel can be used as a fuel in diesel engines with little modification to the engine's fuel system, and many countries have already made extensive conversions to this fuel. Additionally, a biodiesel blend of B20 (80% diesel and 20% biodiesel) or lower can be used without any modification to the engine.

1.2.3 Lubricity

Protecting an engine's moving parts from wearing out prematurely to maintain adequate performance requires lubricants in the fuels [24]. Biodiesel has been proven to be good for diesel engines, as it provides improved healthy lubrication compared to fossil diesel due to its excellent solvent properties.

1.2.4 Less Emission

Much work has been done investigating the biodiesel impact on exhaust emissions. Since biodiesel is found to reduce HC, CO, and PM [16], [17], [25], it is therefore attributed to meeting the national emission standard for atmospheric carbon reduction.

1.2.5 Higher Cetane

The CN measures the combustion quality of fuel during the compression ignition phase. Biodiesel was found to meet ASTM D6751 specification with a CN higher than 47, which is higher than conventional diesel which averages a CN of 43 [26]–[28]. A higher CN of biodiesel contributes to quieter engine operation and easier engine start-up [16].

1.3 Potential Downsides of Biodiesel

1.3.1 Lower Energy Content

The energy content of fuel is a key element in fuel economy, as well as in an engine's ability to produce power. Typically, No. 2 diesel fuel (known as summer diesel) has higher energy content than No.1 diesel (known as winter diesel) [23]. Typically, biodiesel has lower energy content than conventional diesel. For instance, canola biodiesel with a higher heating value of 40,296 kJ/kg is lower than No. 2 diesel with a higher heating value of approximately 45,000 kJ/kg, by about 10% [25].

1.3.2 Inferior Cold Flow Properties

Cloud point (CP), pour point (PP) and cold filter plugging point (CFPP) represent the cold flow properties (CFPs) of biodiesel. Typical to ASTM D2500, CP refers to the biodiesel temperature below which, which forms a cloudy appearance [29]. The PP of biodiesel is the temperature at which the liquid loses its flow characteristics (the PP standard test method is ASTM D7346-15) [30]. The CFPP is the lowest temperature at which fuel will still flow through a specific filter, usually lower than cloud point. Generally, biodiesel has inferior cold flow properties compared to conventional diesel, which is the main reason it is unusable with high percentages in colder climates such as Canada. In Canada, the biodiesel is mainly blended with a diesel, and its consumption varies from province to province due to their climate conditions. For example, the higher consumption of biodiesel in 2014 was in British Columbia, with approximately 4028 thousand cubic meter of diesel, that blended with 102 thousand cubic meter of biodiesel (about 2.4% biodiesel) [31].

1.3.3 High NO_x Emission

Although biodiesel emits lower CO, HC, and PM, biodiesel contributes to producing slightly higher NO_x emissions compared to conventional diesel due to its high oxygen content, which contributes to a higher combustion temperature [16]. NO_x emission has a negative effect

on the atmosphere because it forms smog and ozone. Additionally, dissolving NO_x in atmospheric moisture produces acid rain.

1.4 Thesis Scope

In this study, attempts will be made for improving CFPs of biodiesel to be useable in cold climate regions. In addition, controlled diesel engine emission experiments will be carried out, with the main focus on NO_x and smoke opacity emissions.

Chapter 2: Literature Review

2.1 Introduction

This chapter covers a summary of previous studies on biodiesel as a fuel for compression ignition (CI) engines. Firstly, a number of studies investigating CFPs will be briefly reviewed, followed by a selection of literature on emulsion fuels and their effect on diesel engine performance and emission. Finally, the thesis objectives will conclude the chapter.

Several studies have been conducted on improving biodiesel's CFPs. Some research focused on modifying biodiesel's fatty acid profile, while others investigated the effect of biodiesel additives and blends on biodiesel CFPs. Much work has been done on the use of biodiesel as a fuel for diesel engines, and a number of studies analyzed the effects of biodiesel on diesel engine performance and emission. According to many investigations, biodiesel has a proven substantial reduction in CO, HC, and PM emissions, whereas it emits slightly higher NO_x emission. Various experiments have been conducted investigating the effect of emulsion fuel on diesel engine performance and emission, whereby emulsion fuel was reported to improve the combustion quality and engine thermal efficiency. Additionally, some studies showed that emulsion fuel is an effective way to reduce NO_x and PM emissions.

2.2 Review on Improving Cold Flow Properties of Biodiesel (CFPs)

Biodiesel can be made from any oil feedstock that meets ASTM D6751 standards. However, biodiesel made from various crop oils contain different properties such as CN, viscosity, density, heating value, and cold flow properties due to dissimilarities in the fatty acid composition of each crop. The fatty acid composition depends on the geographical condition in which the plant grows, as well as the type and quality of the source [32]. Therefore, ASTM D6751 does not specify the biodiesel CP, but the CP must be reported to the customer. Generally, the fatty acids of biodiesel are divided into two categories (saturated fatty acids and unsaturated fatty acids); unsaturated fatty acids are divided into monounsaturated and polyunsaturated fatty acids. Table 2.2 outlines the fatty acid composition collected from different studies of several biodiesel types derived from various vegetable oils with their melting points (MP), as well as the cloud point of each biodiesel. It is clear from the table that each type of fatty acid has a different MP (see table 2.1), and that the percentage of biodiesel differs from one type to another. Therefore, biodiesel

with a higher percentage of unsaturated fatty acids shows a lower CP due to the lower MPs of unsaturated fatty acids.

Table 2.1 Melting Point of biodiesels fatty acids compositions

Fatty Acid Type	Saturated			Monounsaturated	Polyunsaturated		Ref.
Fatty Acid Composition	Myristic C14:0	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	
MP (°C)	19	30	39	-19.5	-35	-52	[33], [34]

Table 2.2 Fatty acid compositions (wt.% of different biodiesel and biodiesels CP

Type of Biodiesel	CP (°C)	Saturated Fatty Acids (wt.%)			Monounsaturated (wt.%)	Polyunsaturated (wt.%)		Ref.
		Myristic C14:0	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	
Canola	-2.6	0.1	3.9	3.1	60.2	21.1	11.1	[16], [35]
Sunflower	-1	0.1	6.6	3.1	36.2	52.9	0.6	[33], [34]
Rapeseed	-1	0.1	4.6	1.5	63.9	20.4	7.0	[36], [37]
Soybean	9	0.3	10.9	3.2	24	54.5	6.8	[36], [38]
Olive	0	0	11	3.6	75.3	9.5	0.6	[35], [36]
Palm	16	0	9.8	6.2	72.2	11.8	-	[39], [40]

Much work has been done to improve the CFPs of biodiesel. Some of the existing approaches of improving the biodiesel's CFPs was achieved by simply modifying its fatty acids profile. Other techniques were followed by blending biodiesel with fuels that have low CFPs, and some additives were proposed to improve CFPs of biodiesel. A brief review of the technologies that are used will be discussed in the following subtitles.

2.2.1 Modification of Fatty Acids Profile

The modification of fatty acids composition of biodiesel can be done mainly through chemical, physical and genetic methods. The chemical method is used in the food industry by converting the unsaturated fatty acids of oil into saturated fatty acids, which results in lower the CFPs of biodiesel [41]. On the other hand, genetic and physical methods improve the CFPs of biodiesel.

a) Genetic Engineering Method:

In this method, the genes of plant oils are modified to obtain desirable oil properties. The combination of certain genes may result in higher oil saturation level, while other genes may provide a high unsaturation level in the oil. Liu et al. [42] developed cottonseed oil with an improved oleic acid level (C18:1), which increased from 13% to 78%. Buhr et al. [43] reduced the palmitic acid level from 9% to 2.6% and increased the oleic acid from 57.7% to 89.4% by developing transgenic soybean oil. A similar composition of fatty acids reduced the oil's CP from 10°C to -1°C [44].

b) Physical Method:

The physical method of fatty acids profile modification can be accomplished using different techniques: winterisation and fractionation. Winterisation is a process whereby biodiesel is cooled, resulting in the formation of crystals. Those crystals are then filtered to obtain a high level of unsaturated fatty acids [45]. Nainwal et al. [46] achieved a 3°C reduction in biodiesel's CP through a four-stage winterisation process. Pérez et al. [47] increased the unsaturated level of peanut biodiesel from 84.45% to 88.21% using three-stage winterisation, obtaining a CP reduction of approximately 12°C. Winterisation is generally the simplest, the least expensive, and an effective way to improve biodiesel's CFPs. However, it has low separation efficiency, low yield, and requires a long time for each stage preparation (i.e., 16 hours of single-stage preparation) [48].

The second physical method of modifying the fatty acids profile is fractionation. Normally, there are two different methods of fractionation: solvent fractionation and urea fractionation. Solvent fractionation tackles winterisation's disadvantages of long preparation time and low production efficiency. Through this method, solvents such as methanol, acetone, chloroform, hexane, or isopropanol are blended with biodiesel to reduce its viscosity. The solvent fractionation process is characterized by short crystallization time and ease of filterability, leading to high separation efficiency and improved yield [49]. Urea fractionation was simply applied to alkyl ester,

mixing methanol or ethanol with urea. Through this method, the biodiesel (the mixture of solvent [methanol or ethanol] with urea) is separated into two or more portions [50], [51]. The urea fractionation method significantly improved the biodiesel's CFPs, and was reported to have the ability to lower the biodiesel's CP temperature to -30°C [48].

2.2.2 Additives

Additives are usually used for improving the biodiesel properties to reduce regulated emissions and to improve the fuel's flow properties. Although the flow improvers do not change the biodiesel's CP, they inhibit the growth of wax crystals, which in turn improves the CFPP [52], [53]. The additives used to improve biodiesel cold flow are usually known as wax crystallization modifiers. Roy et al. [17] obtained CP reduction of 5.3°C by adding 1% of wintron synergy to canola biodiesel. Using diethyl ether (DEE) as an additive of 15 vol. % to biodiesel, Roy et al. [16] improved the CFPs by approximately 3°C .

2.2.3 Biodiesel Blending

Biodiesel can be blended and used in different concentrations with petroleum diesel or kerosene (which have significant CFPs) with the required fuel properties. Blends of 5% biodiesel with winter diesel have a small influence on CFPs [40]. Ghanei [54] studied the effects of blending castor biodiesel with canola biodiesel, whereby significant improvements were obtained of the blends' CFPs with increased castor biodiesel amount. Zhao et al [55] blended biodiesel with conventional diesel, and reported that the CFPP and PP linearly decreased by increasing the diesel concentration in the blends.

2.3 Emulsion Fuel

Emulsion fuel is a mixture of polar liquid (water) and nonpolar liquid (fuel) that is blended with emulsifiers [56], [57]. It typically consists of two surfactants which have the ability to minimize surface tension between immiscible liquids [58]. Polar liquids contain somewhat of a modified charge at the extremities of the molecules, which dissolve if placed in a polar solvent. Nonpolar liquids contain the same charge at each end of their molecules, but dissolve only in nonpolar solvents. Surfactants are substances that normally contain an imbalanced concentration of polar and nonpolar molecules. "Hydrophilic" surfactants have an affinity to polar liquid, whereas a "lipophilic" surfactant tends to gravitate toward nonpolar liquids. All surfactants have a numerical value referred to as HLB (hydrophilic-lipophilic balance), which ranges between 0

and 20 [32]. HLB is the weight of the hydrophilic percentage in a surfactant. It is lipophilic when its HLB is lower than 9, and hydrophilic when it has an HLB value of 12 or higher [59]. The emulsion consists of a 2-phase emulsion (water-in-oil [W/O], or oil-in-water [O/W]) [60], and of a 3-phase emulsion (water-in-oil-in-water [W/O/W], or oil-in-water-in-oil [O/W/O]) [61]. Researchers Lin et al. [62] discovered two advantages of 2-phase emulsion over 3-phase emulsion, namely higher heating value and lower mean droplet size. Normally, emulsion fuel is made using one of the following methods: ultrasonic emulsion [63], conductive emulsion [64], or external force [65]. An ultrasonic vibrator and a homogenizer mixer were used by Lin and Chin [62] to produce diesel emulsion. They reported that the use of a vibrator made the emulsion more stable over a 7-day period.

2.4 Diesel Engine Performance and Emissions

The biodiesel properties such as oxygen content, CN, viscosity, fatty acids composition, and heating value play a major role on diesel engine performance and emission. Table 2.2 shows heating value (HHV), density, viscosity, and CN of diesel and several types of biodiesels.

Table 2.3 Prosperities of diesel and various biodiesels

Fuel Type	H.V (kJ/kg)	Density (kg/m ³)	Viscosity at 40 °C (cSt)	CN	Ref.
Diesel	45,573	830	1.86	46-50	[66]–[68]
Canola Biodiesel	40,296	881	4.2	53.7	[66], [69]
Sunflower Biodiesel	41,260	883	4.57	51.1	[70]
Rapeseed Biodiesel	41,550	857	4.6	48	[71]
Soybean Biodiesel	37,530	885	4-4.2	51	[72]
Olive Biodiesel	41,350	877.9	4.512	50	[71]
Palm Biodiesel	41,240	880	4.43	49	[40]

Engine performance is commonly measured by its brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE). The BSFC is the ratio between mass fuel consumption and brake power, while the BTE for a particular fuel is inversely proportional to thermal efficiency. Generally, the BSFC of an engine powered by any type of fuel decreases with an increase in engine load due to increased brake power, while the BTE increases with an increase in the engine load [73], [74]. Additionally, higher energy content in fuel reduces the BSFC [72]. Saleh [75] conducted an experimental investigation using biodiesel with EGR, and reported a BSFC reduction of 9.8%, as well as an increase in BTE of up to approximately 1% obtained from biodiesel compared to conventional diesel. How et al. [76] reported that a blend of bioethanol with coconut methyl ester resulted in higher BSFC compared to diesel, which they determined as a result of its lower heating value and higher viscosity than diesel. Aydin and Bayindir [77] conducted an experimental study on a diesel engine operating with a blend of cottonseed biodiesel and diesel fuel, and found that the engine power and torque decreased with the increase in biodiesel content in the blend. This occurred due to the lower heating value and higher viscosity of cottonseed biodiesel compared to conventional diesel.

There are upsides to using emulsions made from biodiesel-diesel blends in diesel engines (i.e., improved engine performance and fewer emissions). The percentage of water content in emulsified fuel affects both its viscosity and heating value. A diesel fuel emulsion was prepared by Ithnin et al. [78] using four percentages of water. The surfactants used were *Span 80* (Sorbitan Monoleate) and *Tween 80* (Polyoxyethylene Sorbitan Monoleate). Through their experiment, they determined that the diesel emulsion's viscosity increased, as did the water content in the emulsion. On the other hand, research done by Qi et al. [79] exposed a reduction in the heating value of the emulsified fuel and an increase in the ignition delay of diesel engines when they increased the emulsion fuel's water content. They also concluded that an engine's BTE and BSFC increased when using an emulsion fuel. Testing on engine performance was also conducted by Yang et al, whereby they investigated a diesel engine that was operated using emulsion fuel along with various nano-organic additives. These test results revealed higher BTE compared to neat diesel. Ogunkoya et al. [80] used three different types of emulsion fuel to analyze their engine's performance when fueled by diesel. The results proved that having three emulsion fuel types reduced engine efficiency and output; however there was small boost in BSFC and BTE over that of their base fuels. When investigators Baskar and Senthil Kumar [81] tested the performance of a diesel engine

powered by emulsified diesel and injected oxygen into the engine's air intake system, they discovered that the BTE was higher at all engine loads compared to the results obtained when using conventional diesel.

In terms of engine emission, biodiesel and biodiesel blends emit lower HC, CO, and PM, whereas NO_x emission is higher compared to that of conventional diesel [16], [17], [25]. Generally, biodiesel has a higher CN compared to neat diesel, and increases by increasing its saturation level, which contributes to shorter ignition delays [82], [83]. However, a lower unsaturation level in biodiesel provides higher density and lower viscosity than biodiesel with a high saturation level [84]. Therefore, higher levels of unsaturated fatty acids in biodiesel attributes to higher NO_x emission formation [85]. The HC and CO emissions are affected by the fatty acids chain length, which increases with a longer chain length due to a slightly lower oxygen content in those fatty acids [86]. Attempts have been made to reduce the combustion temperature. For example, the introduction of water into the combustion chamber, whether through direct injection as a steam-into-intake air system or as fuel emulsion of a diesel engine, is an effective technique to increase thermal efficiency and to reduce combustion temperature and engine emission [87], [88].

An effective method of reducing the flame peak temperature of diesel engine combustion is to use emulsion fuel. This is because better combustion quality results from mixing air and fuel, which is enhanced by the micro-explosion of emulsion fuel and water evaporation during the combustion process. . In addition, the reduced formation of NO_x occurred to having a lower peak flame temperature. The investigation project run by Senthil et al. [89] experimented with diesel engine emission and performance. This involved applying fuel with a blended emulsion content (20% biodiesel and diesel), along with various percentages of added water. They reported a lower BTE when using the emulsion fuel over B20 and diesel, as well as lower levels of NO_x, HC and smoke opacity. When Scarpete [90] studied the reduction of emissions on a diesel engine powered by emulsified diesel, he found that NO_x and PM emission were substantially lower when the diesel engine was fueled by emulsion fuel. Hasannuddin et al. [91] used Span 80 (1%) and two different water content levels to make emulsified diesel in order to investigate emissions on a diesel engine. During this experiment they noticed fewer PM and NO_x emissions, with an increase in CO emission at low load compared to diesel fuel.

2.5 Thesis Objective

Most of the previous studies carried out in improving the biodiesels' CFPs involved the modification of biodiesel fatty acids composition and their saturation levels, as well as investigating the effect of biodiesel blends and additives on diesel CFPs. A number of studies were carried out investigating the impact of biodiesel fatty acids profile, additives, and blends on diesel engine performance and regulated emissions. Several studies were also carried out investigating the effect of emulsion diesel and emulsion B20 on diesel engine emission and performance at limited operating conditions. To date, both winterisation and fractionated biodiesel represent lower production efficiency. Additionally, no significant correlation has been made between the biodiesel and water increment in an emulsion and its comparability with diesel in terms of engine emission and performance. In the present work, improving the production efficiency of improved biodiesel CFPs are investigated using a novel method of fractionation biodiesel. Moreover, DEE and ethanol additives to biodiesel are suggested to improve its CFPs and to control the regulated emission. Furthermore, a two-phase emulsion of diesel, biodiesel-diesel blends up to 40 (in increments of 10) using three different levels of water concentration (5%, 10%, and 15%) with Span 80 and Tween 80 are explored, with a focus on emulsion characteristics, engine performance, and engine emission at various engine operating conditions. Finally, emulsion of diesel-biodiesel blends up to B30 with two different ammonium hydroxide (NH_3) concentrations (2.5% and 5%), with 10% water concentration in emulsion, are used as fuel for a diesel engine and examined in terms of engine emission and performance.

Chapter 3: Methodology

3.1 Introduction

This chapter will include a list of all materials used, as well as an explanation of the preparation of biodiesel and emulsion fuel, urea fractionation, and crystal fractionation. We will also describe the engines that were tested, the measurement apertures, and the engine testing procedure.

Firstly, canola oil will be used to produce biodiesel via the transesterification method. Secondly, fractionated biodiesel using urea fractionation will be prepared, and the by-product will be collected and used in producing biodiesel via the crystal fractionation method. Thereafter, the emulsion preparation method will be explained, followed by a description of the engine that was tested, the apparatus used, and a brief summary of the engine testing procedure.

3.2 Biodiesel Production

Running diesel engines with 100% vegetable oil or animal fats as a fuel resulted in several operational issues, such as incomplete combustion, engine deposits, and an increase in lubricant viscosity due to the high viscosity of those oils. Therefore, attempts were made to reduce the oil viscosity using four different approaches: pyrolysis, dilution, micro-emulsification, and transesterification [92], [93]. Transesterification is simply a chemical reaction of oil and alcohol with the help of a catalyst, which accelerates the reaction to produce biodiesel [94]. Among the mentioned methods of reducing oil viscosity, transesterification has advantages of effortlessness and comparatively low cost [25]. To produce one batch of biodiesel via transesterification method, the following materials are required: 3gm of sodium hydroxide (catalyst), 200ml of methanol (alcohol), 1000ml of canola oil, and a blender. The biodiesel production procedure has been described in the following steps:

- Dissolve 3.5gm of sodium hydroxide in 200ml of methanol.
- Heat 1000ml of biodiesel up to 65°C.
- Place oil with methanol and catalyst in a blender.
- Activate the blender for approximately 45 minutes.

- Pour the solution into a 2-liter bottle, and let it stand for one day. (After 24 hours, glycerine is formed and settles at the bottom of the bottle, as seen in Figure 3.1).



Figure 3.1 Glycerine formation with dark color

- Separate the glycerine and wash the remaining biodiesel by adding 50% water to obtain a 2-to-1 biodiesel-to-water mixture (e.g., 100ml biodiesel and 50ml water). After 24 hours, repeat this process with the remaining biodiesel.
- Heat the final product (biodiesel) to 70°C to ensure that there is no remaining methanol in the biodiesel.

The volumetric collection efficiency of biodiesel was calculated to be approximately 80%, and its quality under ASTM6751 can be found in Table 3.1.

Table 3.1 Properties of canola biodiesel.

Test Name	Test Method	ASTM limit	Results
Free Glycerin (mass%)	ASTM D6584	Max. 0.02	0
Total Glycerin (mass%)	ASTM D6584	Max. 0.24	0.112
Flash Point, Closed Cup (°C)	ASTM D93	Min. 130	169
Water & Sediment (vol.%)	ASTM D2709	Max. 0.050	0
TAN (mg KOH/g)	ASTM D664	Max. 0.5	0.14
Sim. Dist., 50% Recovery (°C)	ASTM D2887	N/A	359.8
Cetane Index	ASTM D976 (2 variables formula)	N/A	50
Copper Corrosion, 3h @ 50°C (rating)	ASTM D130	Max. 3a	1a

3.3 Fractionation

3.3.1 Urea Fractionation Process

Generally, urea fractionation is applied to biodiesel using solvents such as methanol and ethanol in order to improve its CFPs. Through this method, the saturated fatty acids get extracted by the urea inclusion compound that is formed by adding guest molecules (biodiesel) to the urea and solvent mixture [48]. The materials used in this study include pure urea (44gm), methanol (150ml), and canola biodiesel (50ml). The preparation procedure is as follows:

1. Mix the urea with FAME and methanol or ethanol.
2. Heat mixture to form a heterogeneous solution.
3. Cool the mixture to between 15°C and 30°C.
4. Separate the solid crystals from the liquid using a Buchner funnel aspirator (refer to Figure 3.2)

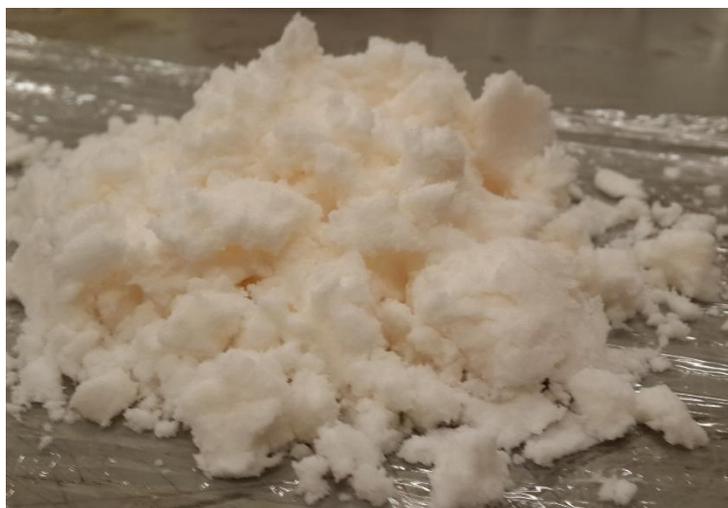


Figure 3.2 Solid crystals

5. Collect the solid crystals.
6. Heat the mixture until two distinct layers are formed (two-liquid phase), as shown in Figure 3.3.



Figure 3.3 Two-liquid phase

7. Cool the mixture to between 15°C and 30°C.
8. Separate the solids (recovered urea) from the liquid using a Buchner funnel aspirator (see Figure 3.4a).
9. Collect the recovered urea (refer to Figure 3.4b).

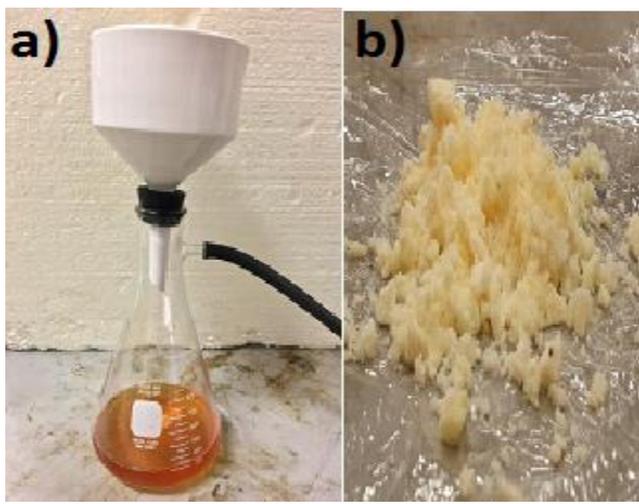


Figure 3.4 a) Buchner funnel aspirator; b) Recovered urea

10. Heat the remaining liquid (biodiesel) up to 150°C to decompose the urea. Although this method resulted in a significant reduction in the biodiesel's CP, which reached about -30°C, it also caused lower production efficiency (approximately 33% for canola biodiesel). We can therefore predict that the composition of fatty acids in the fractionated biodiesel, as was revealed in table 2.2 were Linoleic (C18:2) and Linolenic (C18:3).

3.3.2 Crystal Fractionation Process

In this study, the by-product (solid crystals and recovered urea) of urea fractionation is used to produce fractionated biodiesel. The preparation steps are exactly the same as the urea fractionation steps, while the material compositions differentiate. This method is referred to as crystal fractionation, and the materials composition is listed in Table 3.2.

Table 3.2 Material composition of crystal fractionation.

Solid crystals (gm)	Recovered urea (gm)	Methanol (ml)	Biodiesel (ml)
22.5	22.5	150	50
22.5	22.5	0	50
50	-	150	75
50	-	150	100
50	-	150	125
50	-	150	150
66	-	150	200
88	-	150	50

3.4 Emulsion Fuel Preparation Process

Emulsified fuel was prepared using the external force method. In total, 16 emulsion diesel, biodiesel, and diesel-biodiesel blends were prepared. The materials used were Span 80, Tween 80, canola biodiesel, distilled water, and a blender. The preparation process is explained in the following steps:

1. Blend Span 80 and Tween 80 in portions that produce HLB of 8.25, using the following formula [59]:

$$Tween\ 80\ \% = \frac{100 (X - HLB_{Span\ 80})}{HLB_{Tween\ 80} - HLB_{Span\ 80}} \quad (1)$$

$$Span\ 80\ \% = 100 - Tween\ 80\ \% \quad (2)$$

Where,

X= required HLB value (8.25),

$HLB_{Tween\ 80}$ is given for Tween 80 to be 15 [95],

$HLB_{Span\ 80}$ is given for Span 80 to be 4.3 [96].

2. Pour the fuel into the blender; turn on the blender.
3. Add the distilled water in the blender (different water levels of 5%, 10%, and 15% of the total emulsion volume) were investigated.
4. Add the Span 80 and Tween 80 mixture in the blender (2% of the total volume).
5. Run the blender for 15 minutes.

The results were milky emulsified fuels. The fuels used were diesel and biodiesel-diesel blends, namely B0, B10, B20, B30, and B40, with three different levels of water concentration (5%, 10% and 15%). Kerosene and a kerosene-biodiesel blend were emulsified in a similar way (using diesel and diesel-biodiesel blends with 10% and 15% water), namely EK100 and EK70. Additionally, B100 was emulsified with 2.5% water in the emulsion, and the emulsifier's HLB was 11. B0, B10, B20 and B30 were emulsified with 10% water, while adding two different concentrations of ammonium hydroxide to the water. The fuel series and properties can be seen in Table 3.3.

Table 3.3 Emulsion fuel proprieties.

Fuels	Fuel composition	H.V (kJ/kg)	Density (kg/m ³)	Viscosity (cSt @ 40°C)
B0	Diesel	44,775	832	1.92
EB0W5%	Emulsion of diesel with 5% water	42,534	861	2.68
EB0W10%	Emulsion of diesel with 10% water	40,296	869	2.80
EB0W15%	Emulsion of diesel with 15% water	38,058	878	3.05
B10	10% biodiesel in biodiesel-diesel blend	44,331	837	2.18
EB10W5%	Emulsion of B10 with 5% water	42,086	866	2.76
EB10W10%	Emulsion of B10 with 10% water	39,849	874	2.87
EB10W15%	Emulsion of B10 with 15% water	37,615	883	3.19
B20	20% biodiesel in biodiesel-diesel blend	43,878	842	2.40
EB20W5%	Emulsion of B20 with 5% water	41,638	871	3.09
EB20W10%	Emulsion of B20 with 10% water	39,397	879	3.15
EB20W15%	Emulsion of B20 with 15% water	37,159	887	3.56
B30	30% biodiesel in biodiesel-diesel blend	43,437	846	2.60
EB30W5%	Emulsion of B30 with 5% water	41,193	875	3.20
EB30W10%	Emulsion of B30 with 10% water	38,954	884	3.65
EB30W15%	Emulsion of B30 with 15% water	36,715	892	4.31
B40	40% biodiesel in biodiesel-diesel blend	42,988	851	2.91
EB40W5%	Emulsion of B40 with 5% water	40,739	861	4.01
EB40W10%	Emulsion of B40 with 10% water	38,504	869	4.35
EB40W15%	Emulsion of B40 with 15% water	36,264	878	4.66
B100	100% biodiesel	40,286	886	4.32
K100	Kerosene	46,250	790	1.02
EK100W10	Emulsion of kerosene with 10% water	41,732	821	2.01

EK100W15	Emulsion of kerosene with 15% water	39,814	835	2.78
K70	30% biodiesel in biodiesel-kerosene blend	44,292	799	1.52
EK70W10%	Emulsion of K30 with 10% water	39,809	837	2.47
EK70W15%	Emulsion of K30 with 15% water	37,761	851	3.16
EB100W2.5%	Emulsion of B100 with 2.5% water	39,279	889	5.63
EB0W10A2.5	Emulsion of diesel with 10% water and 2.5% NH ₄ OH	39,759	870	2.79
EB0W10A5	Emulsion of diesel with 10% water and 2.5% NH ₄ OH	39,211	871	2.93
EB10W10A2.5	Emulsion of B10 with 10% water and 2.5% NH ₄ OH	39,323	874	2.89
EB10W10A5	Emulsion of B10 with 10% water and 5% NH ₄ OH	38,797	875	3.01
EB20W10A2.5	Emulsion of B10 with 10% water and 2.5% NH ₄ OH	38,883	879	3.21
EB20W10A5	Emulsion of B10 with 10% water and 5% NH ₄ OH	38,378	881	3.42
EB30WA2.5	Emulsion of B10 with 10% water and 2.5% NH ₄ OH	38,470	883	3.56
EB30WA5	Emulsion of B10 with 10% water and 5% NH ₄ OH	37,997	885	3.62

3.5 Droplet-Size Distributions of Emulsion Fuel

The *Malvern Mastersizer Hydro 2000* was used for measuring the droplet-size distribution of the emulsion fuel particle. This device works on the software called v.5.54, and has an attachment called wet cell 2000S, which operates using a laser light [97]. Refractive index is the main concern in this process, and it is taken for biodiesel-diesel blend as 1.4565 [98]. Droplets of the emulsion fuel sample were added to distilled water until the obscuration level reached 10%-15%, after which time the measurements were taken.

3.6 Fuel Additives

Methanol, ethanol and DEE (in quantities of 10% and 15%) were added to the biodiesel and fractionated biodiesel, as well as to their blends with diesel. The fuel properties with the additives are outlined in Table 3.4.

Table 3.4 Blend properties of fuels and fuel additives.

Fuels	Fuel composition	H.V (kJ/kg)	Density (kg/m ³)	Viscosity (cSt @ 40°C)
B20	20% biodiesel in biodiesel-diesel blend	44509	842	2.40
B40	40% biodiesel in biodiesel-diesel blend	43462	851	2.91

B60	60% biodiesel in biodiesel-diesel blend	42464	864	3.37
B80	80% biodiesel in biodiesel-diesel blend	41343	875	3.96
B100	100% biodiesel	40,286	886	4.32
DEE	Diethyl ether	36,892	710	0.23
E	Ethanol	29,700	801	0.8
M	Methanol	23,000	792	0.45
n-Heptane	Normal-heptane	46,720	679.5	0.386
B100 DEE5%	5% DEE in B100	40,126	873	3.85
B100DEE10%	10% DEE in B100	39895	861	3.01
B100E5%	5% ethanol in B100	39866	883	4.15
B100E10%	10% ethanol in B100	38997	879	3.91
B100M5%	5% methanol in B100	39432	880	3.97
B100M10%	10% methanol in B100	38564	876	3.21
FB20	20% fractionated biodiesel in biodiesel-diesel blend	44612	845	2.37
FB40	40% fractionated biodiesel in biodiesel-diesel blend	43587	855	3.31
FB60	60% fractionated biodiesel in biodiesel-diesel blend	42638	867	3.26
FB80	80% fractionated biodiesel in biodiesel-diesel blend	41497	879	3.84
FB100	100% fractionated biodiesel	40441	899	4.23
FB100DEE5%	5% DEE in FB100	40256	875	3.69
FB100DEE10%	10% DEE in FB100	40007	864	2.98
FB100E5%	5% ethanol in FB100	40098	884	3.99
FB100E10%	10% ethanol in FB100	39204	879	3.82
FB100M5%	5% methanol in FB100	39571	883	3.79
FB100M10%	10% methanol in FB100	38779	880	3.11

3.7 Engines under Study

In this study, two compression ignition diesel engines were tested (a heavy-duty and a light-duty).

3.7.1 Heavy-Duty Diesel Engine

The heavy-duty engine is a Cummins Tier 4 Final QSB4.5 inline 4-cylinder, turbocharged, water-cooled diesel engine. This type of engine is commonly used in agricultural and mining equipment, and is displayed in Figure 3.5.



Figure 3.5 Heavy-duty diesel engine

The engine is designed with a high pressure common rail injection system, and a diesel particulate filter. A dual tank fuel system was installed for ease of switching between various test fuels. The engine specifications can be found in Table 3.5.

Table 3.5 Heavy-duty engine specifications.

Engine Make and Model	Cummins QSB 4.5 T4I
Engine Type	Inline 4-Cylinder
Number of Cylinders	Four
Bore * Stroke	102mm * 138mm
Swept Volume	4.5 l
Compressions Ratio	17.3:1
Rated Power	97KW @ 2300 RPM

3.7.2 Light-Duty Diesel Engine

The light-duty diesel engine (Figure 3.6) is an air-cooled, 2-cylinder, 4-stroke (HATZ 2G40) diesel engine with a direct fuel injection system. This engine is mainly used in passenger vehicles and in other small applications. A graduated cylinder was used as a fuel tank to measure fuel consumption. Figure 3.7 depicts the engine's schematic diagram; its specifications are outlined in Table 3.6.



Figure 3.6 Light-duty diesel engine

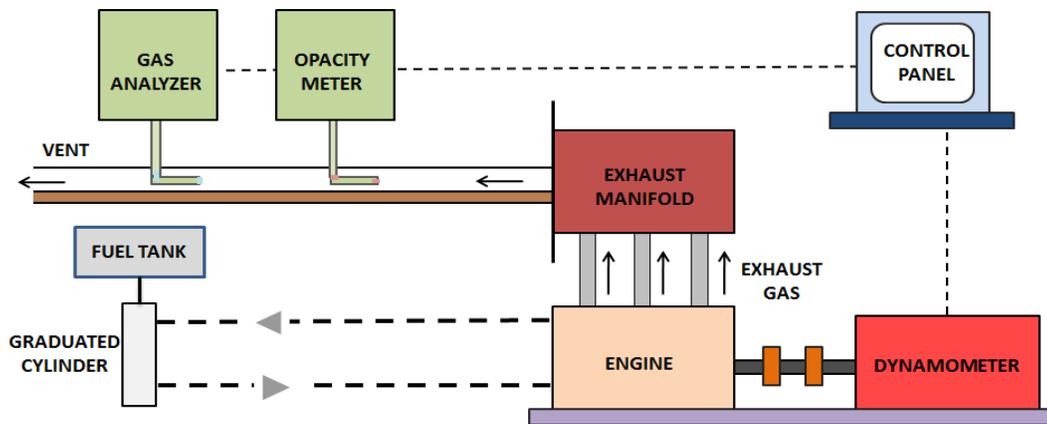


Figure 3.7 Schematic diagram of the light-duty diesel engine setup

Table 3.6 Light-duty diesel engine specifications

Engine make and model	Hatz 2G40
Engine type	4-stroke, Air-cooled
Number of cylinders	Two
Bore × Stroke	92 mm × 75 mm
Swept volume	997 cc
Compressions ratio	20.5:1
Fuel injection timing	8° BTDC (≤ 2250 rpm); 10° BTDC (≥ 2300 rpm)
Fuel injection pressure	26 MPa
Continuous max. rated power	13.7 kW @ 3000 rpm

3.8 Measurement Apparatus

3.8.1 Emissions Measurement

For emission testing, several devices were used including a Nova 7466 PK, which measures six different exhaust gases (NO, NO₂, CO, CO₂, HC and O₂), and a DWYER 1205A analyzer for measuring CO emissions. Finally, a Smart 1500 opacity meter was used to measure the amount of smoke produced. This device has a software that can be installed on a PC that uses Windows software. The specifications of emission measurement devices are described in Table 3.7.

Table 3.7 Specifications of emission measurement devices

Method of Detection	Species	Measured Unit	Range	Resolution	Accuracy
NovaGas 7466 PK					
Infrared Detector	CO	%	0-10%	0.01%	±1%
Infrared Detector	CO ₂	%	0-20%	0.10%	±1%
Electro Chemical	NO	ppm	0-5000 ppm	1 ppm	±1%
Electro Chemical	NO ₂	ppm	0-800 ppm	1 ppm	±1%
Electro Chemical	O ₂	%	0-25%	0.10%	±1%
Infrared Detector	HC	ppm x 10	0-20000 ppm	10 ppm	±1%
Dwyer 1205A					
Electro Chemical	CO	ppm	0-2000	1 ppm	±5%
ExTech EA10	Temp	0.1 °C	(-)200 ⁰ C to 1360 ⁰ C	0.1 ⁰ C	±0.3%
Smart 1500	Opacity	%	0-100%	0.1%	±2%
	Soot Density	mg/m ³	0-10 mg/m ³	0.00001	±2%

3.9 Performance Measurement

A dyno-meter is installed on the engine. It has a capacity of 15 to 800, torque of between 2 lb/ft and over 5000 lb/ft, and rpm ranging from 1000 to over 10000. Water-brake load valves control the engine load. It is equipped with a software option called DYNO-MAX, which can be installed on a Windows-run PC. Its features include a real-time trace graph display, adjustable voice/color limit warnings, push-button controls, and user-configurable analog and digital gauge ranges. Publication-quality color graphs and detailed reports are available for printing. The engine load can be controlled either manually or automatically using the computer. Several parameters can be obtained from the software including engine rpm, exhaust gas temperature, ambient temperature, engine load, engine torque, and operation time. Moreover, the software automatically

records up to 1000 readings per second. The following formulas are used for calculating the engine BSFC and BTE:

$$BSFC = \frac{\dot{m}_f}{B_p} \left(\frac{g}{kWh} \right) \quad (3)$$

$$BTE = \frac{3600}{BSFC * HHV} \text{ , } (\%) \quad (4)$$

Where,

\dot{m}_f = fuel consumption (g/h),

B_p = brake power (kW).

3.10 Engine Test Procedure

3.10.1 Heavy-Duty Engine

This engine was tested at two idling conditions: 1200rpm and 1500rpm, with no engine load. The engine was tested for 30 minutes, starting from a cold start for each test. CO, CO₂, NO_x, HC, and exhaust temperature readings were taken at 0, 2, 4, 6, 8, 10, 15, 20, 25 and 30-minute intervals, respectively. The engine was tested outdoors, with an ambient temperature ranging from 5°C to 25°C. The fuels tested in this engine were diesel, kerosene, biodiesel, n-Heptane, EB0W10%, EB0W15%, EB30W10%, EB30W15%, EK100W10%, EK100W15%, EK70W10%, and EK70W15%.

3.11 Light-Duty Engine

The light-duty diesel engine was tested at three different loads (low: 20%, medium: 50%, and high: 100%) at three different speeds (1000rpm, 2100rpm, and 3000rpm). The engine was warmed up for approximately 10 minutes. The test duration for all engine operating conditions/fuels was about 45 minutes. More than 60 fuels were tested in this engine; all are described in Table 3.3 and Table 3.4. The engine was tested indoors, at a consistent ambient temperature of 25°C.

Chapter 4: Results and Discussion

4.1 Introduction

In this chapter, we examine the results obtained throughout the study. Firstly, the cloud point of the fractionated biodiesel will be discussed. Secondly, the emulsion fuel characteristics will be reviewed. The effect of fractionated biodiesel, fractionated biodiesel-diesel blends, fractionated biodiesel with additives, and emulsified fuels on a diesel engine's performance and emission under various operating conditions will be described. We will then provide an overview of the benefits and cost analysis of using emulsion fuel. Finally, emission of the heavy-duty diesel engine powered by various fuels at two idling conditions will be investigated.

4.2 Fractionated Biodiesel Cloud Point

Ten fuel samples were sent to Intertek Laboratory in Hamilton, Ontario to determine cold flow properties using ASTM D5773 standards, the results of which are listed in Table 4.1. The urea fractionation exhibited the lowest cloud point among all fractionated biodiesel investigated; it was lower than normal biodiesel by 28.4°C.

Table 4.1 Cloud point and production efficiency of fractionated biodiesel prepared using different methods.

Material compositions				CP (°C)	Production efficiency (vol.%)	
Biodiesel				-2.6	80	
44 gm of urea + 150ml methanol + 50ml biodiesel				-31	33	
Recovered urea and crystal fractionation						
Solid crystals (gm)	Recovered urea (gm)	Methanol (ml)	Biodiesel (ml)	CP (°C)	PP (°C)	Production efficiency (vol.%)
22.5	22.5	150	50	-18	-24	100
22.5	22.5	0	50	-9	-	87
50	-	150	75	-13.8	-	90
50	-	150	100	-11.1	-	92
50	-	150	125	-7.9	-	91
50	-	150	150	-9	-	95
66	-	150	200	-8.5	-	90
88	-	150	50	-14.8	-	95

However, urea fractionation exhibited inferior production efficiency compared to all other fractionated biodiesels. This is due to the ability of urea and methanol solution to extract the fatty acids, which had lower CFPs with solid crystals throughout the preparation process. From the fatty acids composition of biodiesel shown in table 2.2, the oleic fatty acid (monounsaturated fatty acid) content in canola biodiesel is approximately 60.2 wt.%, and this type of fatty acid has a melting point of -19.5°C . The saturated fatty acid content in canola biodiesel is approximately 7.1 wt.%, which has CFPs higher than 10°C . The remaining fatty acids content in biodiesel are polyunsaturated fatty acids with weight percentage of 32.2, which have a melting point lower than -35°C . From the previous analysis of canola biodiesel, it is clear that the fatty acid composition of canola biodiesel produced through the urea fractionation method are polyunsaturated fatty acids. Biodiesel with a higher content of polyunsaturated fatty acids revealed worse oxidative stability [99]. Oxidative stability of biodiesel is an important factor to determine biodiesel's self-life. High unsaturation fatty acid chains are responsible for their interaction with oxygen when exposed to air. It has been reported that the degree of unsaturation, location, and number of fatty acids that have a double-bond affect the biodiesel rate of auto-oxidation [52], [100].

Using the by-products of urea fractionation (solid crystals and solid crystals recovered urea mixture) for fractionated biodiesel resulted in significant improvements in production efficiency. Using 22.5mg of solid crystals and 22.5gm of recovered urea, with 150ml of methanol for fractionated biodiesel (50ml canola), resulted in overall higher production efficiency, which reached 100 vol.%, CP of -18°C , and -24°C PP, as seen in Table 4.1. The higher production efficiency could be due to the fact that some of unsaturated fatty acids extracted by urea fractionation with the by-products were recovered when the solid crystals and recovered urea were used for fractionated biodiesel. Different compositions of crystal fractionation material used had different CPs and production efficiency. The most interesting results from using solid crystals and recovered urea without adding methanol was a CP of -9°C , and 87 vol.% production efficiency. Generally, the solid crystal and recovered urea produced biodiesel with acceptable CFPs to be used in the coldest countries such as Canada. For example, the Thunder Bay, Ontario weather report for 2015 [101] outlines the lowest temperature reached in each month, as listed in figure 4.1. The lowest temperatures in the city of Thunder Bay over the 12-month period were in February with -35°C , and in January with -30°C . In the remaining months, the minimum temperature reached was -17°C . Therefore, fractionated biodiesel using 22.5gm of solid crystals, 22.5gm of recovered urea with methanol, and 150ml and 50ml of biodiesel respectively, could be used in diesel engines from March to December, while it could be used in January and February if blended with winter diesel or kerosene. Further, recovered urea and

solids crystal without methanol provided biodiesel's CP of -9°C , which means that it could be used in May, June, July, August, September and October.

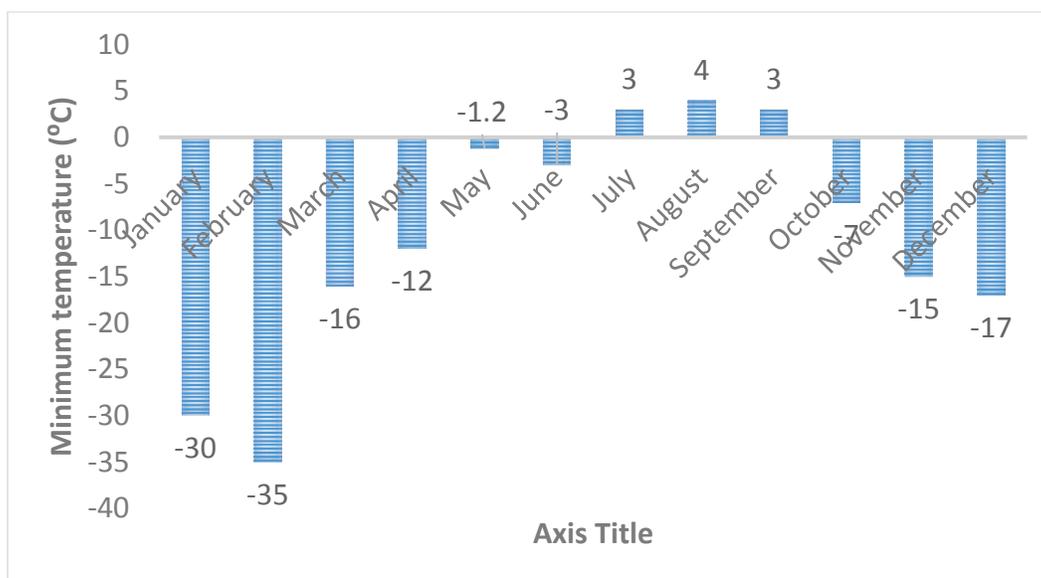


Figure 4.1 Temperature for Thunder Bay, ON (2015)

4.3 Emulsion Fuel Characteristics

4.3.1 Droplet Size of Emulsion

This process involved using various emulsion fuels and water concentration levels ranging from 5% to 15%. Using a polarizing microscope, we took photos to capture the fuel particles' composition. We then acquired diagrams from the *Malvern Mastersizer Hydro 2000* (particle size analyzer). Figure 4.2 details the emulsion diesel fuel, which had the smallest droplet size as were visible in the microscopic photos. The droplets grew constantly with the continual gradual supply of biodiesel in biodiesel-diesel blends, and additional water content. The trend was that the heavier the molecules and the higher the water levels, the larger the droplet size. EB0W5, EB0W10, and EB0W15 had mean particle size distributions of $4.5\ \mu\text{m}$, $6.3\ \mu\text{m}$, and $7.8\ \mu\text{m}$, respectively. EB20, EB30, and EB40 had a similar distribution of particle size (ranging from approximately $0.15\ \mu\text{m}$ to $45\ \mu\text{m}$), however variations in the concentration of particle size existed. The concentration of smaller particles (ranging between $0.15\ \mu\text{m}$ and $8\ \mu\text{m}$) was higher in fuel emulsions that contained less water and biodiesel, resulting in a lower mean particle size. Figure 4.3 outlines the mean particle size of all emulsion fuels.

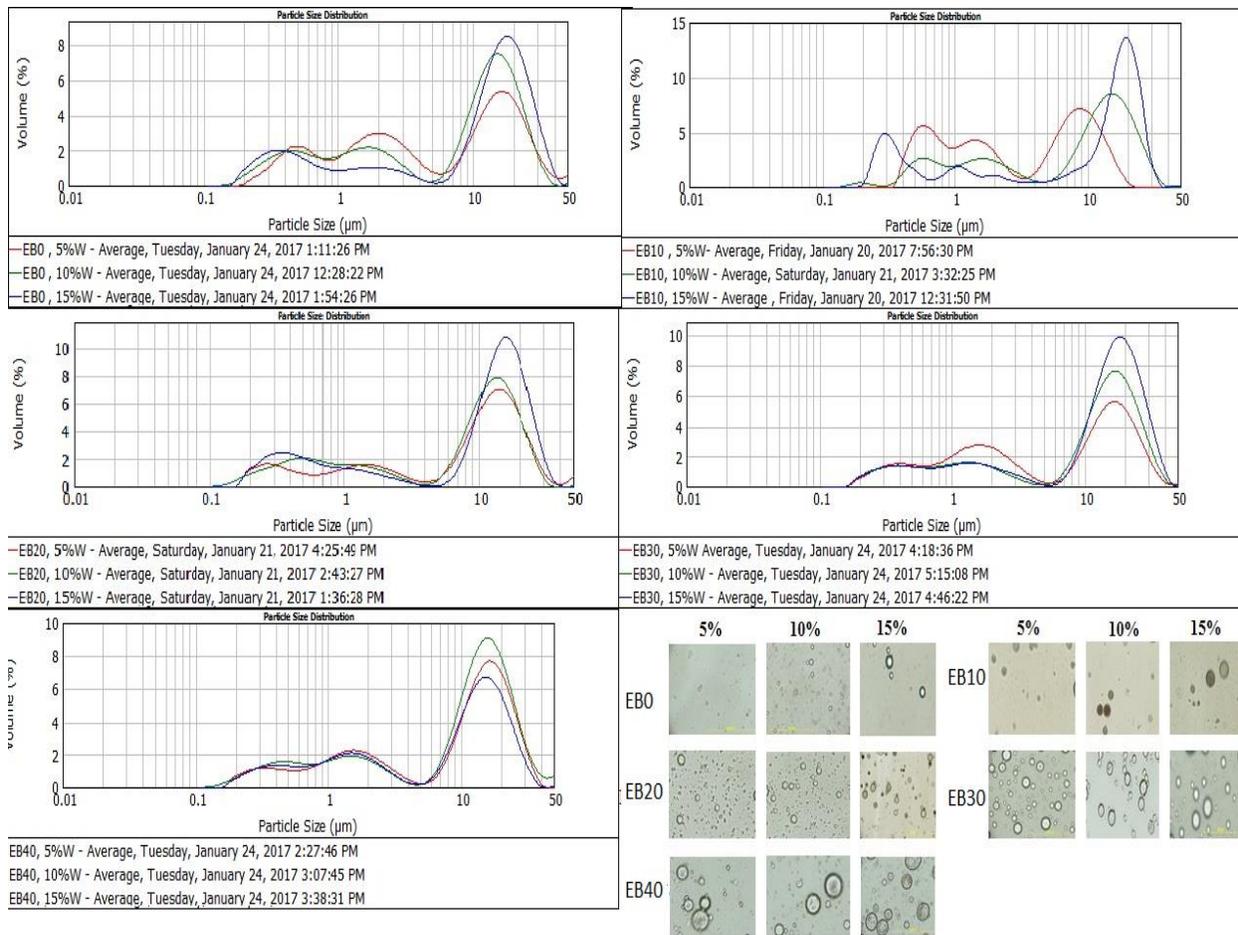


Figure 4.2 Graphs and microscopic photos for emulsion fuels particle size distribution [ref.102]

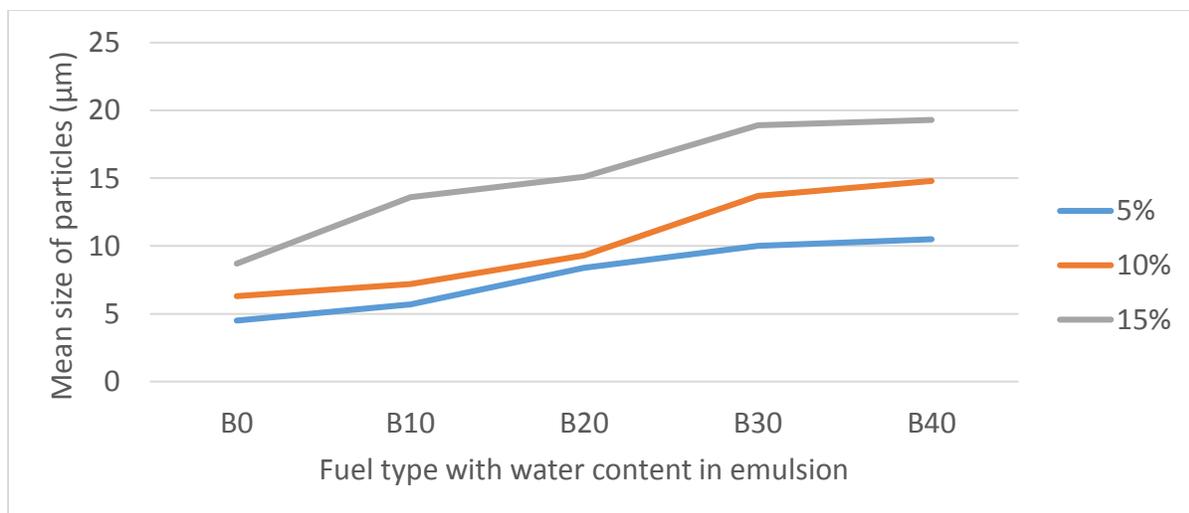


Figure 4.3 Mean particle size of emulsion diesel-blends with three water levels [ref.102]

4.3.2 Emulsion Fuel Viscosity

The relationship between water content in emulsion fuel and viscosity marginally increased with the additional water content in all emulsion fuels investigated (refer to Figure 4.4). The various distribution sizes of the particles and surface contact in the emulsion influenced enlargement of the particles' surface contact [83].

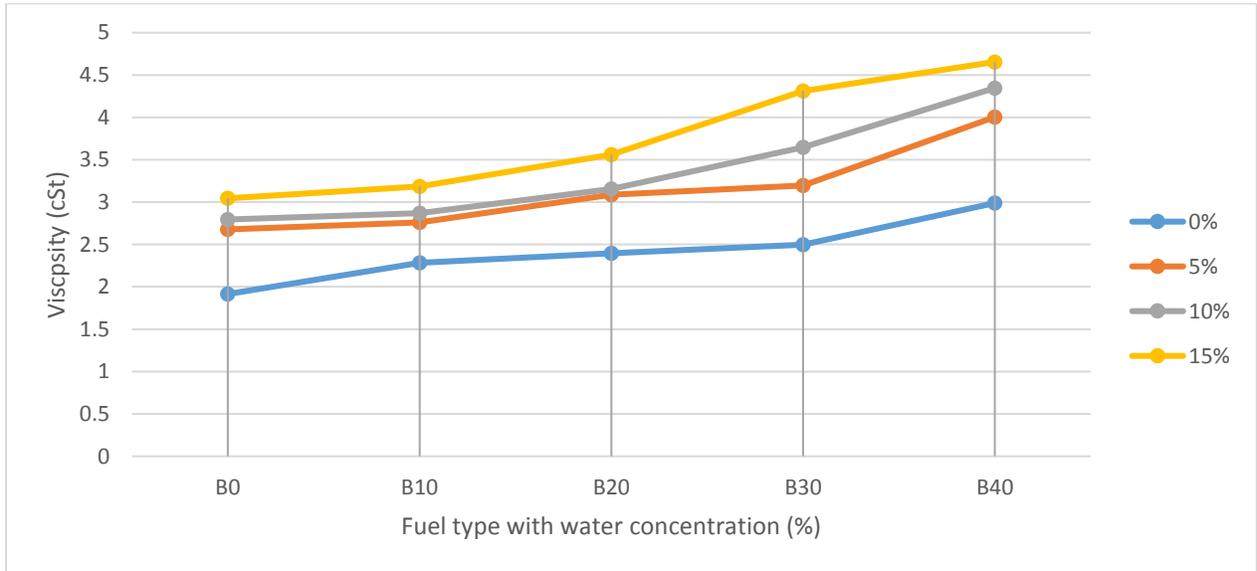


Figure 4.4 Viscosity of different fuels vs water concentration [ref.102]

4.3.3 Emulsion Stability

At the point when separation could no longer be detected, the emulsion was considered to have stabilized [103]. Our research investigated the stability at room temperature (measured in days), during which we concluded that emulsions containing 5% water demonstrated better stability compared to emulsions containing 10% and 15% water. Emulsion diesel had the longest period of stability among all emulsion fuels investigated. Emulsion fuel with lower particle size distribution showed improved stability. Figure 4.5 outlines the stability statistics for EB0W5, EB0W10, and EB0W15, which were 87, 81, and 74 days respectively.

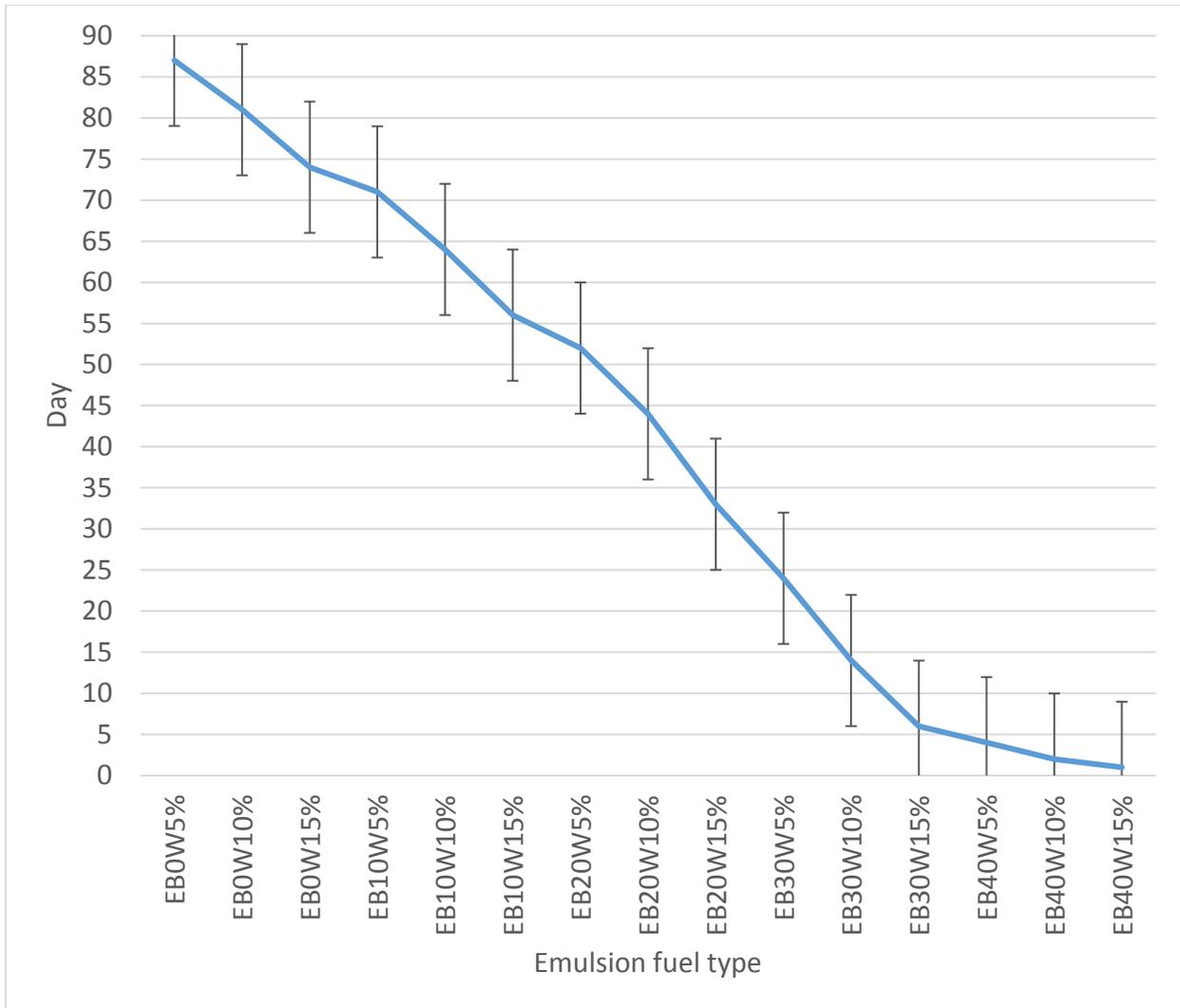


Figure 4.5 Emulsion fuel stability

4.4 Light Duty Diesel Engine Performance

Engine performance was tested under three different speeds and loads. The engine speeds were 1000 rpm, 2100 rpm and 3000 rpm; the engine loads were set at 20%, 50% and 80%. Several fuels and fuel series were used in this study.

4.4.1 Biodiesel and Fractionated Biodiesel

The biodiesel-diesel was blended with diesel at different volume percentages (20-100 vol.%) in increments of 20. The blends were named B0, B20, B40, B60, B80 and B100. In addition, the methanol, ethanol and diethyl ether were added to B100 in amounts of 5% and 10%, and were named B100M5, B100M10, B100E5, B100E10, B100DEE5, and B100DEE10. The same fuel

series were used with fractionated biodiesel. The fuels blend were named B0, FB20, FB40, FB60, FB80, FB100, FB100M5, FB100M10, FB100E5, FB100E10, FB100DEE5, and FB100DEE10.

a) Brake-Specific Fuel Consumption (BSFC)

The variation of BSFC for all tested fuel with engine load and speed is shown in Figure 4.6. As can be observed, the BSFC of all fuels at low speed and low load is higher than that at medium and high loads. It also decreases with the engine load set at a faster speed, which signifies higher burning efficiency. Due to lower heat content in biodiesel compared to conventional diesel, the BSFC value increased with a higher biodiesel content in the blend; the increase for B100 was found to be higher by 11.98%, 10.353%, and 11.537% at low load, and speeds of 1000 rpm, 2100 rpm, and 3000 rpm, respectively. Similarly, the methanol and ethanol additives resulted in decreased heat content of the biodiesel, which led to an increase in the BSFC by increasing the amount of additive in the biodiesel. Generally, B100M10 had higher BSFC among all fuels that were tested at all engine operating conditions, while B100E10 produced slightly higher BSFC than B100. At low speed and low load operating conditions, the BSFC of B100 was 272.838 (g/kWh), while it was 277.011 (g/kWh) and 276.941(g/kWh), respectively for B100M10 and B100E10 at the same operating conditions. Although DEE resulted in decreased biodiesel heating value, the BSFC of B100DEE10 was found to be lower than B100 at all engine operating conditions. The higher CN of DEE could be a reason of this reduction, which resulted in lowering the ignition delay period and earlier charge combustion near the TDC [104]. The BSFC reduction of B100DEE10 at engine conditions of high load and high speed was approximately 0.7% compared to that obtained from B100.

The fractionated biodiesel series tested depicted a similar BSFC trend to the normal biodiesel series (see figure 4.7). However, fractionated biodiesel blends provided slightly lower BSFC than normal biodiesel blends, due to the fact that fractionated biodiesel had slightly lower viscosity but higher heat content and density [77], [105], [106] (see table 3.1). For instance, the BSFC of FB100 was higher than B100 by 0.824%, 1.278% and 1.252% respectively at the following engine operating conditions: speed (1000 rpm) and three different loads (low, medium, and high).

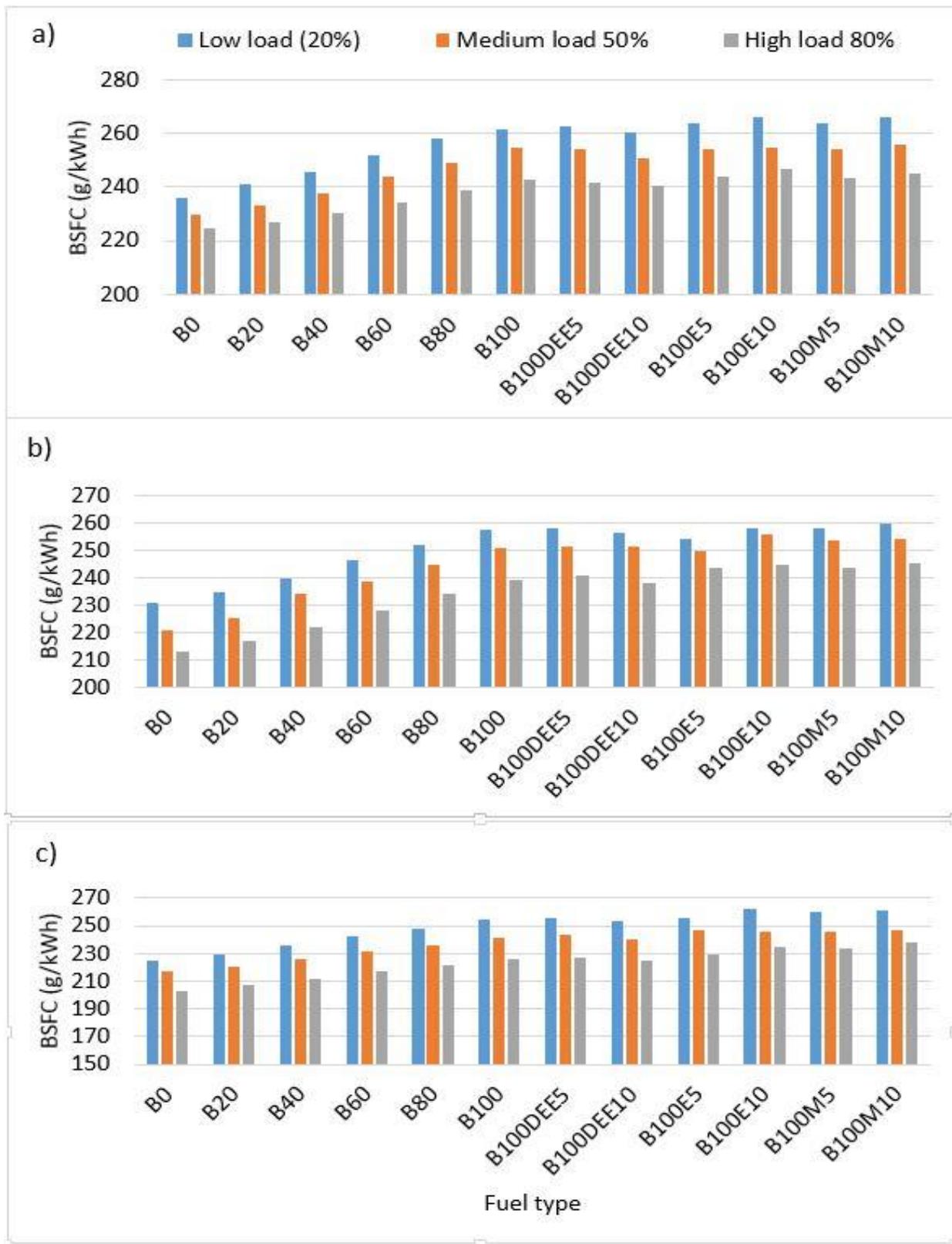


Figure 4.6 BSFC of different biodiesel-diesel blends at various engine loads at a) 1000 rpm, b) 2100 rpm and c) 3000 rpm

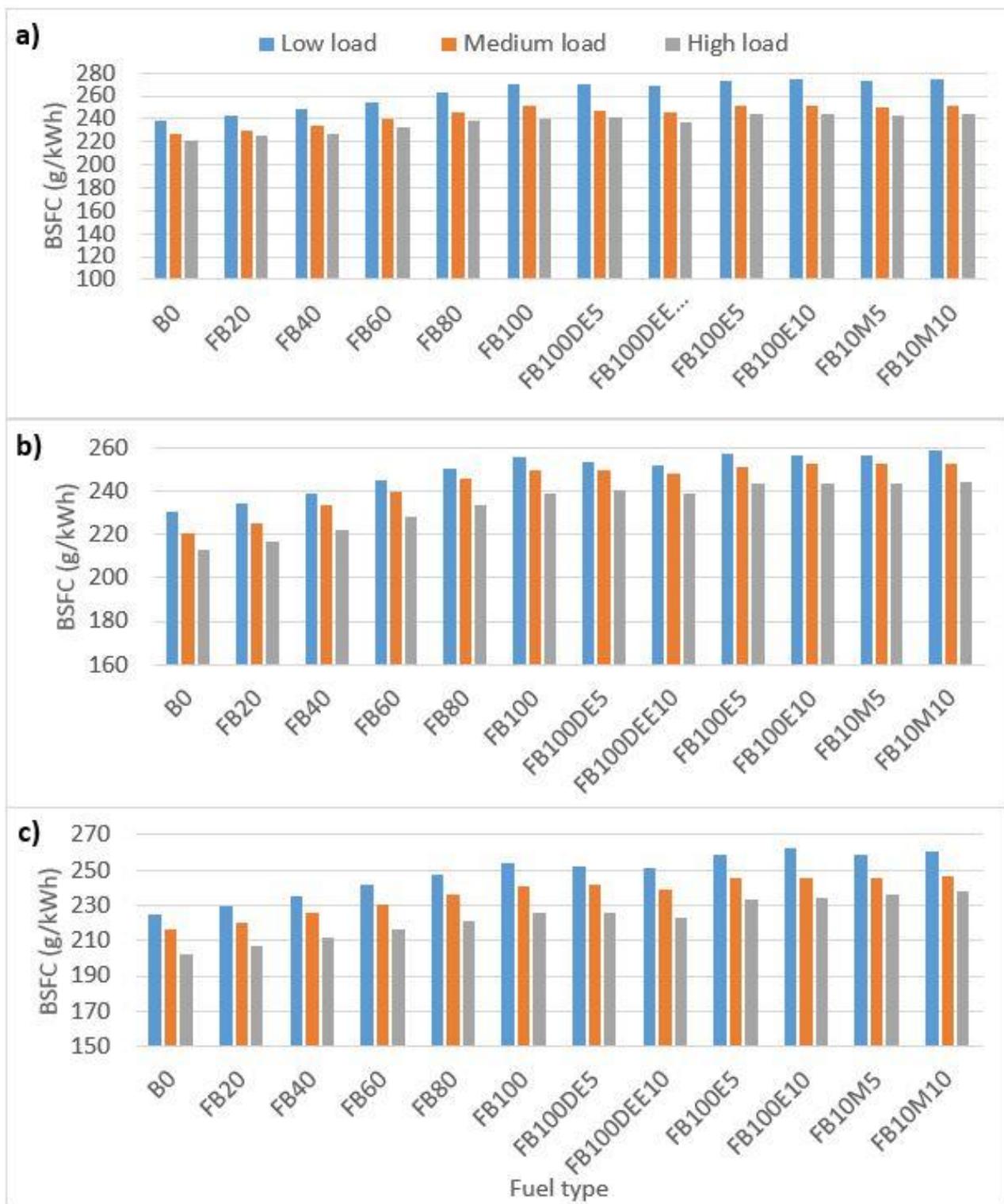


Figure 4.7 BSFC of different fractionated biodiesel blends at various engine loads at a) 1000 rpm, b) 2100 rpm and c) 3000 rpm

b) Brake Thermal Efficiency (BTE)

BTE indicates the combustion's ability to accept the experimental fuel, and how efficiently the fuel is converted into mechanical output. Figure 4.8 depicts the BTE of different biodiesel-diesel blends from B0 to B100 in increments of 20, with variations in engine speed and load. The biodiesel has low heat content compared to diesel, but the BTE was found to increase with an increase in biodiesel content in the blend because the oxygen content in biodiesel provides higher burning efficiency. From the figure, we concluded that BTE rises with an increase in engine load and speed. The BTE of B100 compared to B0 increased by 2.98%, 2.66%, and 2.64% at engine operating conditions of medium load and three different speeds (1000 rpm, 2100 rpm, and 3000 rpm, respectively). The BTE was also found to increase with an increase in DEE content in the biodiesel due to the fact that the oxygen presence in the DEE, as well as its volatility, helped to improve the fuel-air mixing prior to combustion. This in turn attributed to the improvement of combustion efficiency, and to fully burn the fuel [107]. The B100DEE10 at engine operating conditions of medium load and speed of 2100 rpm provided higher BTE by 0.38% and 3.029% compared to B100 and B0, respectively. B100E10 and B100M10 presented higher BTE compared to both B100 and B0 at all engine operating conditions, which may be due to the fact that both methanol and ethanol have lower CN, resulting in longer ignition delay. Because longer ignition delay leads to lengthier air and fuel mixing time, more fuel is combusted in the premixed phase, resulting in higher maximum heat release rate; hence a higher BTE. B100E10 and B100M10 provided an average of BTE 2.62% and 3.03%, respectively, higher than B100 and B0, at operating conditions of high load and speed of 2100 rpm.

The fractionated fuel blends series revealed a similar trend to that of the normal biodiesel blend series, however the fractionated biodiesel blend series provided higher BTE compared to the normal biodiesel blend series, as shown in figure 4.9. The reason is that fractionated biodiesel has slightly higher heat content and density, while its viscosity was slightly lower than normal biodiesel. The BTE of FB100 increase was higher than that of B100 by about 0.03%, 0.11% and 0.13% at engine operating conditions of 3000 rpm speed and low, medium and high loads respectively. At the same operating condition, FB100 provided higher BTE than B0 by approximately 1.41%, 1.6% and 1.45%, respectively.

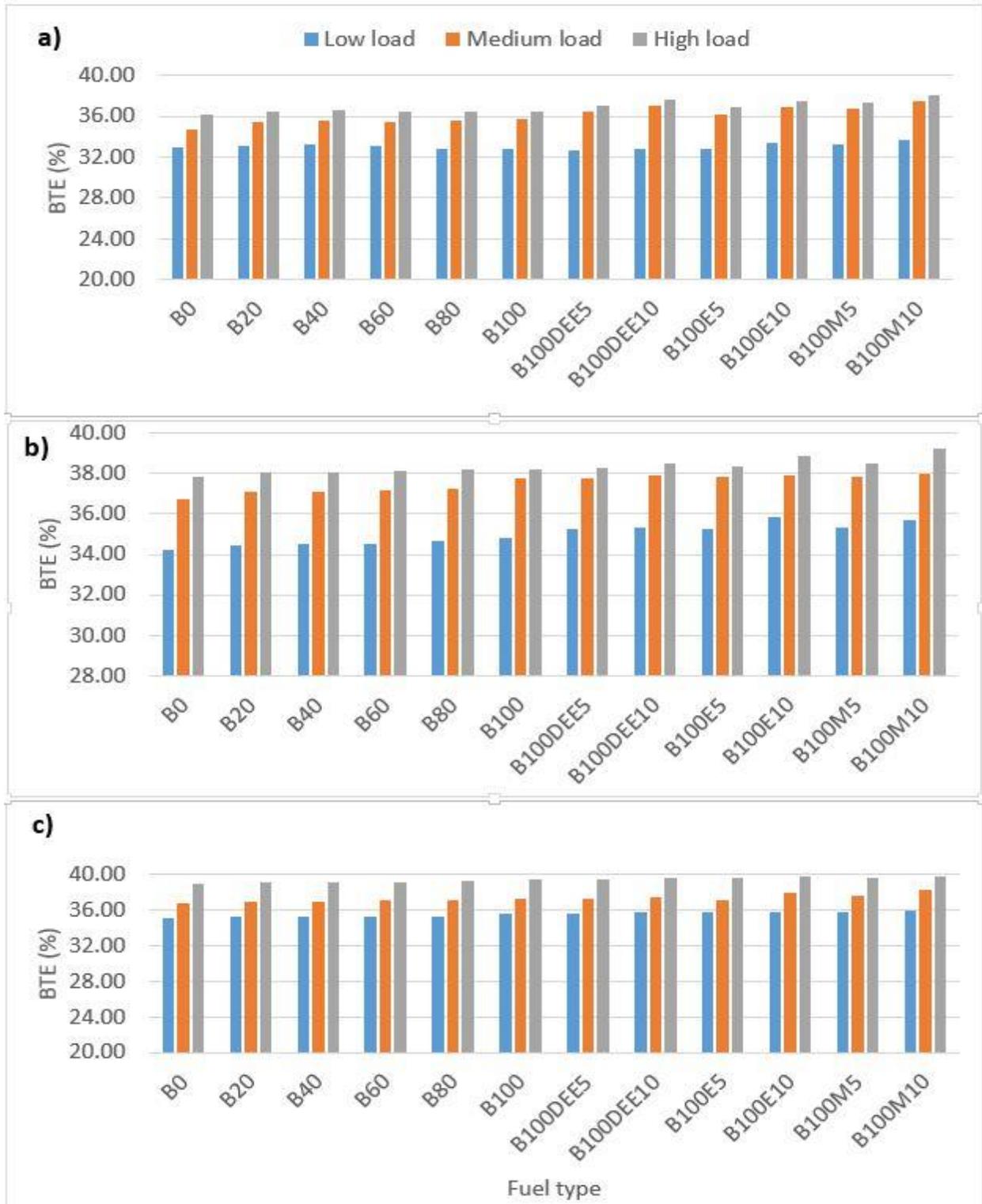


Figure 4.8 BTE of different biodiesel-diesel blends at various engine loads at a) 1000 rpm, b) 2100 rpm and c) 3000 rpm

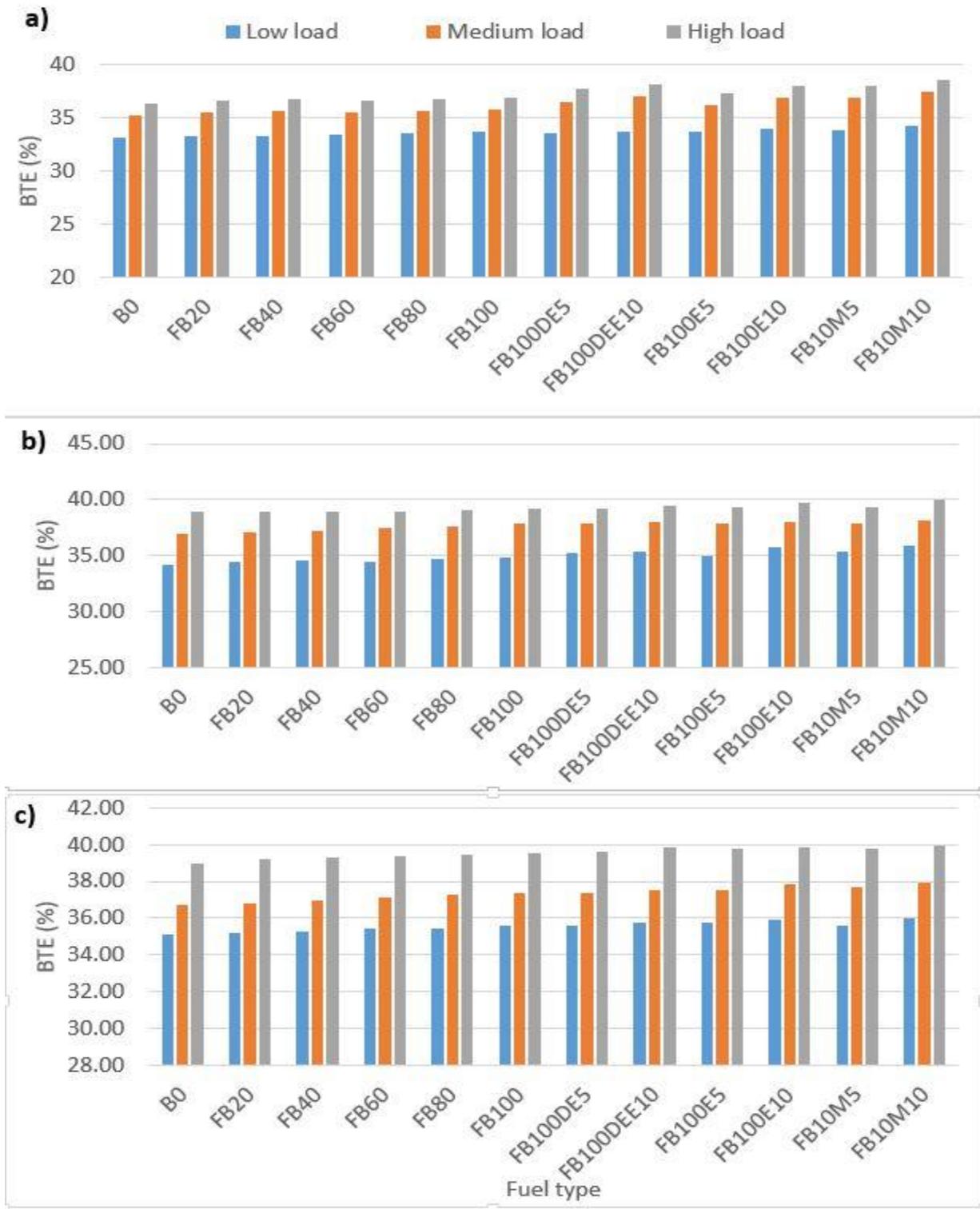


Figure 4.9 BTE of different fractionated biodiesel blends at various engine loads at a) 1000 rpm, b) 2100 rpm and c) 3000 rpm

4.4.2 Emulsion Fuel

The following combinations of emulsified fuels were used: biodiesel-diesel blends, biodiesel, and biodiesel-diesel ammonium hydroxide blends. The biodiesel-diesel blends from 0 to 40 (in increments of 10) were emulsified using three percentages of water (5%, 10% and 15%). The biodiesel was emulsified using 2.5% water. The biodiesel-diesel blends from 10 to 30 (in increments of 10) were emulsified using 10% water, with ammonium hydroxide concentrations of 5% and 10% (refer to Table 3.3 for the list of emulsion fuel series). We applied engine speeds of low: 1000 rpm; medium: 2100 rpm (for maximum torque); and high: 3000 rpm (for maximum power). At each speed, we operated at three engine loads: (low: 20%; medium: 50%; and high: 80%). Since all fuels investigated demonstrated parallel trends of engine performance with load variation at each engine speed, the results of B0, B20, B40, B30W10A2.5, B30W10A5 and B100 operated at 2100 rpm are the main focus in the attached figures. The complete list of results is outlined in appendix C and D tables.

a) Brake-Specific Fuel Consumption

Figure 4.7 illustrates BSFC of different fuels and their emulsions at various engine loads at a speed of 2100 rpm. At low load, the BSFCs of B0, B20 and B40 fuels were 230.9, 232.7, and 234.5 g/kWh, respectively. All emulsion fuels consisting of 15% water had higher BSFC than those with 5% and 10% water, with their base fuels at constant operating conditions. This is due to the lower heat of emulsion fuels that contained more water. As is evident in the figure, the BSFC for all fuel types decreased with the increase in engine load, which signifies higher burning efficiency.

Figure 4.8 depicts BSFC of B30 and its emulsion with 10% water and two ammonium hydroxide levels (2.5% and 10%). The BSFC of the emulsion fuel increased with higher ammonium hydroxide in the emulsion, which was lower at low load than at higher loads, which might be due to the lower heating value of ammonium hydroxide. The BSFC of B30W10A5 was higher by 5.81% and 2.37% than B30W0A0 and B30W10A0, respectively, at high load, while at low load the BSFC of B30W10A5 was higher by 5.134% and 0.85% than B30W0A0 and B30W10A0.

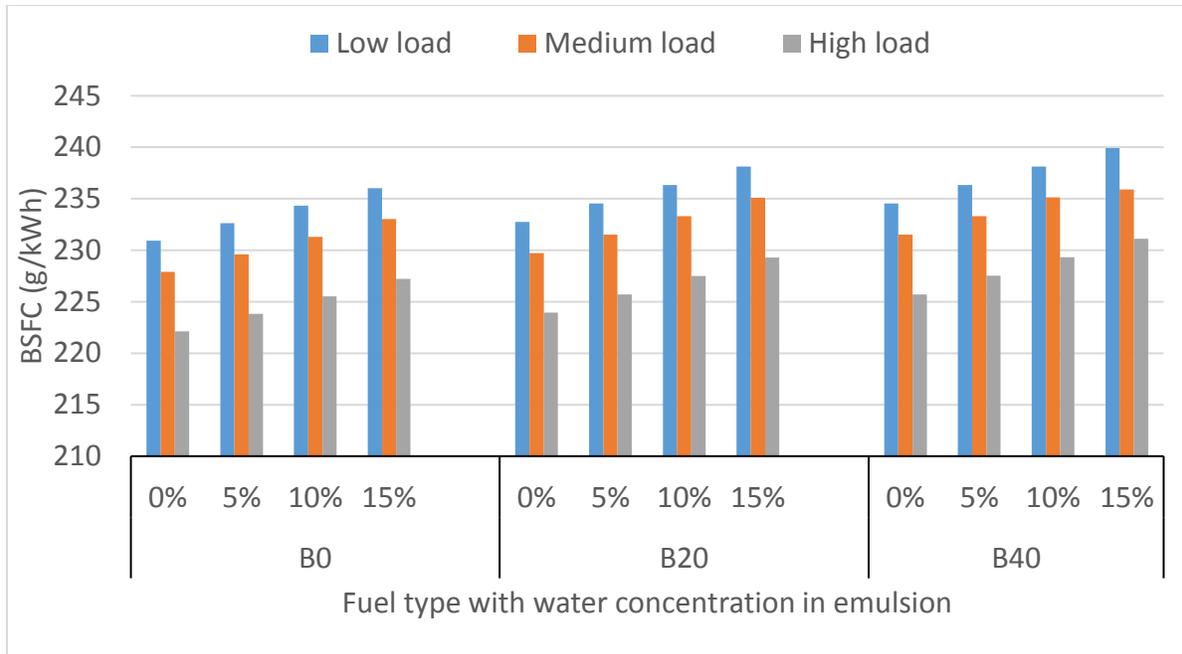


Figure 4.10 BSFC of different fuel blends with three different water levels in emulsion at various engine loads at 2100 rpm speed [ref.102]

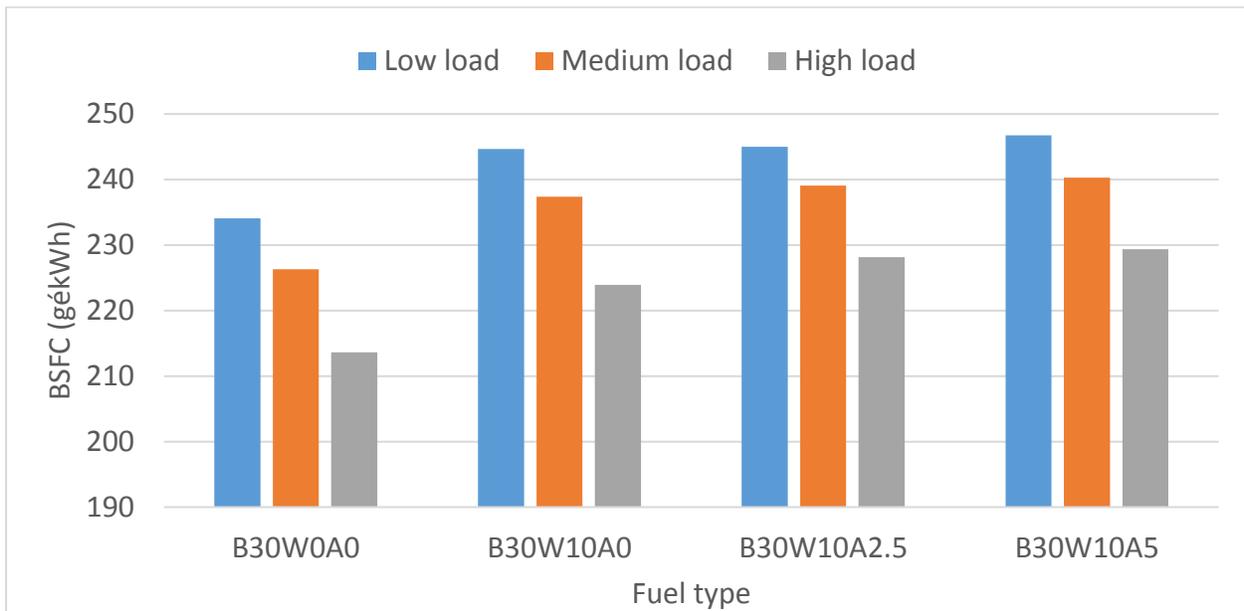


Figure 4.7 BSFC of B30 with three different ammonium hydroxide levels in emulsion with water content of 10% at various engine loads at 2100 rpm speed

Figure 4.12 shows the BSFC of B100 and its emulsion containing 2.5% water at various loads compared to B0. B100W2.5 represented BSFC of 5.6%, 7.38% and 8% higher than B0 at low load, medium load, and high load, respectively. At the same operating conditions, the BSFC of B100W2.5 was higher than B100 by 0.95%, 1.411% and 2.35%, respectively. Generally, the

higher the biodiesel content in the emulsion, the higher the BSFC, because these fuels are cooler than than fuels with base and lower biodiesel content.

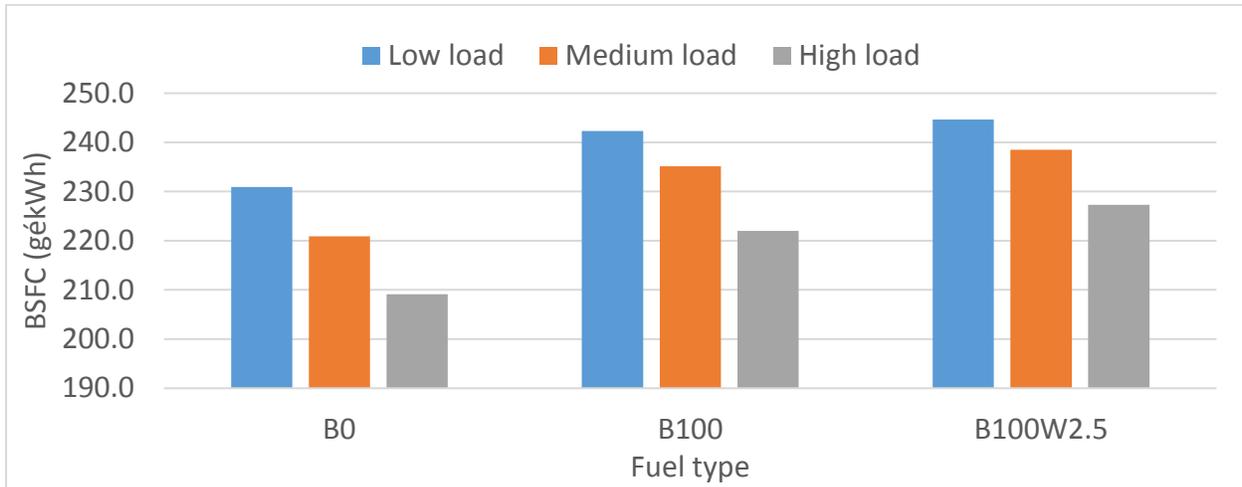


Figure 4.8 BSFC of B0, B100 and B100W2.5 at various engine loads and 2100 rpm speed.

b) Brake Thermal Efficiency

Figure 4.13 demonstrates BTE of B0, B20, and B40 with their emulsions at various engine loads. The BTE rises with an increased engine load. Although biodiesel-diesel blends have a lower heating value than pure diesel, the oxygen content in biodiesel fosters burning efficiency. Therefore, biodiesel-diesel blends have slightly higher BTE compared to diesel at all engine conditions. Correspondingly, emulsion fuels significantly improved the engine's BTE, which increased with the additional water and biodiesel content in the emulsion. The BTE of EB40W15 increased by 5.85% and 6.75% compared to B40 and B0, respectively, at high load. Similar results were obtained from the study conducted by Lin and Wang [108], which investigated engine performance using different water concentration levels in the emulsion. In general, 15% water in the emulsions of diesel and biodiesel-diesel blends could substitute neat diesel fuel for improved BTE in diesel engines.

The amount of ammonium hydroxide in the emulsion slightly increased the BTE compared to the base fuel emulsion containing 10% water, as can be seen in figure 4.14. The BTE increased with an increase in engine load, which signifies higher burning efficiency. B30W10A0 had 0.55% and 1.27% lower BTE compared to B30W10A2.5 and B30W10A5 at medium load.

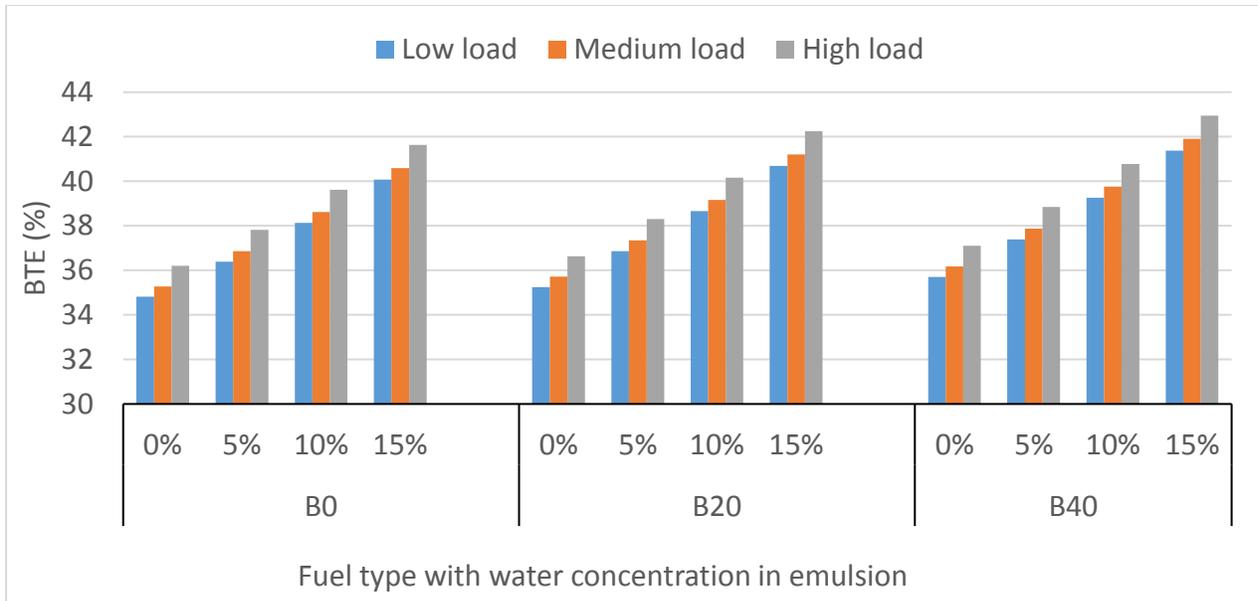


Figure 4.9 BTE of different fuels and their emulsions at various engine loads and 2100 rpm speed [ref.102]

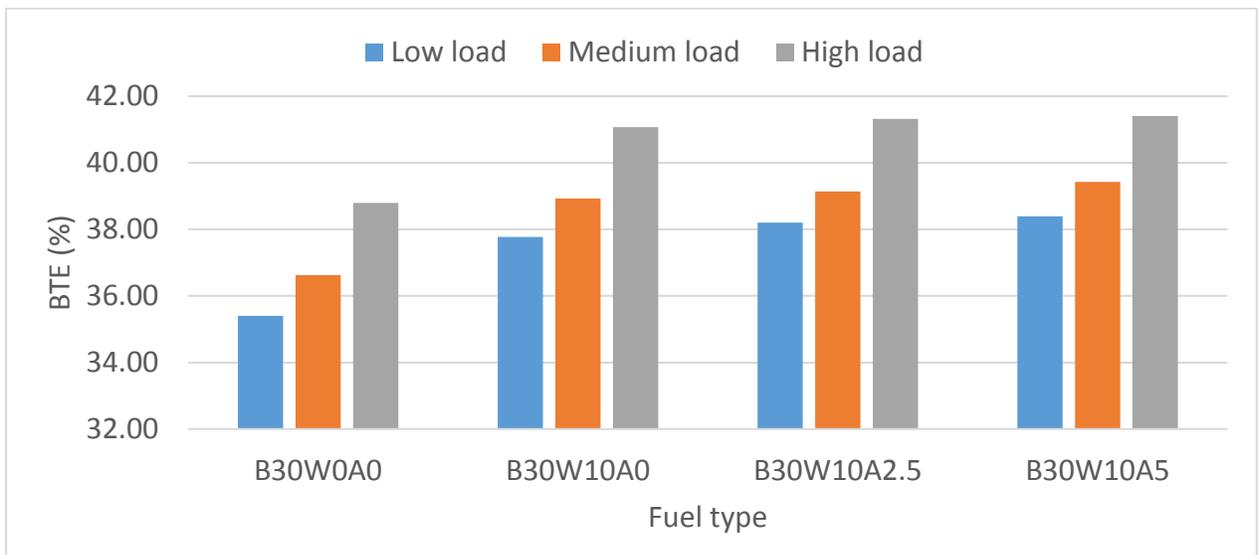


Figure 4.14 BTE of B30 with three different ammonium hydroxide levels in emulsion with water content of 10% at various engine loads and 2100 rpm speed.

Figure 4.15 shows the BTE of B0, B100 and B100W2.5 at various engine loads. From the figure, it is clear that B100W2.5 had higher BTE compared to B0 and B100 at all load conditions. At high load, the BTE increase rate was higher than at both low and medium loads. The BTE increase for B100W2.5 at high load was 5.45% and 1.89% higher than B0 and B100, respectively. Indeed, all emulsion fuels investigated with higher biodiesel and water content provided higher

BTE compared to their bases or emulsion with lower biodiesel and water content. However, B40 with 15% water had higher BTE than B100W2.5 at all engine operating conditions, which might be attributed to the fact that micro-explosion of emulsion fuel and water evaporation during combustion enhances air-fuel mixing process, hence leading to improved combustion efficiency.

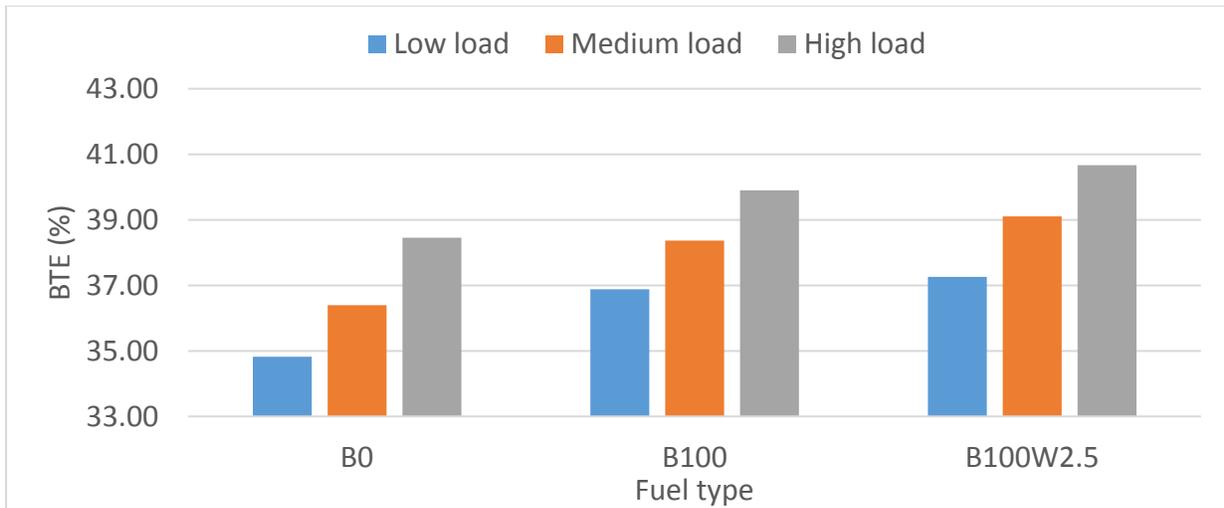


Figure 4.15 BTE of B0, B100 and B100W2.5 at various engine loads and 2100 rpm speed

4.5 Light Duty Diesel Engine Emissions

We investigated emissions of a diesel engine than ran on both diesel and biodiesel-diesel blends, with their emulsions, operating at different operating conditions. For this experiment, the engines were operated at three different speeds: low (1000 rpm); medium (2100 rpm) for maximum torque; and high (3000 rpm) for utmost power. At each speed, we used three engine loads: low (20%), medium (50%), and high (80%). Because the engine emissions from all fuels investigated demonstrated similar trends with load variation at each engine speed, we targeted the results in our figures at 2100 rpm. (For a complete list of results, refer to Appendix A, B, C and D tables).

4.5.1 Biodiesel and Fractionated Biodiesel

The same fuel series of biodiesel blends and fractionated biodiesel blends, which were investigated to understand their effect on engine performance, were also used to test the engine's NO_x, smoke, CO, and HC emissions.

a) NO_x Emission:

Figure 4.16 illustrates NO_x emission of biodiesel-diesel blends and additives at various engine loads. It is clear that NO_x emission increased with an increase in engine load due to the additional fuel supply, resulting in higher combustion temperature, attributing to extra NO_x formation. However, the NO_x emission decreased slightly with an increase in engine speed. The shorter ignition delay was due to an increase in both volumetric efficiency and inlet air motion, which enhanced air-fuel mixing at a higher speed; this could be a reason for NO_x emission reduction. In addition, for each engine cycle, the reaction time decreased with an increase in engine speed, resulting in a decrease in the residence time of fuel-air mixture within the cylinder at a high temperature; hence lower NO_x emission [109], [110]. NO_x emissions increased with an increase in biodiesel content in the emulsion due to its higher oxygen content. B100 emitted more NO_x by 9.64%, 12.68%, and 12.55% than that of B0 at low, medium and high engine loads, respectively. The DDE contains very high CN (125), therefore increasing its amount in the fuel led to an increase in the fuel's CN, thus resulting in a lower ignition delay period and lower NO_x emission. The fuel with higher DEE content provided a noticeable reduction in NO_x emission. The NO_x reduction of B100DEE10 averaged approximately 9.9% at all engine loads, while the NO_x reduction of B100DEE5 averaged only 1.7% at the same operating conditions compared to B100. Ethanol and methanol both have lower CN (5-6), as well as a high oxygen content (34.3% for ethanol, and 50% for methanol) [111]. However, the result of biodiesel with ethanol and methanol content was lower NO_x emission, due to the fact that both methanol and ethanol have high latent heat of vaporization, which reached 846 kJ/kg and 1100 kJ/kg, respectively[16]. Latent heat of vaporization is the energy required to change the state from liquid to vapor at a constant temperature. The high latent heat of vaporization is mainly responsible for the reduction of a cylinder's peak flame temperature and NO_x emission. The B100E10 presented lower NO_x emission by about 0.64% than that of B100 at high engine load. Similarly, B100M10 provided lower NO_x emission than B100 by 5.5% at high load. B100DEE10 showed slightly lower NO_x emission compared to both B100M10 and B100E10 at all operating conditions.

With respect to DEE addition to fractionated biodiesel, the fractionated biodiesel fuel series had a similar NO_x emission trend as the biodiesel fuel series (see figure 4.17). However, all fractionated biodiesel blends provided higher NO_x emission than biodiesel blends at all engine operating conditions, which could be due to higher density of fractionated biodiesel than biodiesel,

and therefore more kilograms of fuel were burned in the cylinder for the same volume. Additionally, as previously discovered, biodiesel with a higher level of unsaturated fatty acids contains lower CN than biodiesel with a higher level of saturated fatty acids [112]. FB100 had higher NO_x emission by approximately 6.1% than B100 at high load. With the same content of additives, 10% of DEE in FB100 revealed a noticeable reduction when compared to 10% methanol and ethanol at all engine operating conditions than those of normal biodiesel. The reason is that DEE improves the fractionated biodiesel's CN, while the methanol and methanol further decreased it.

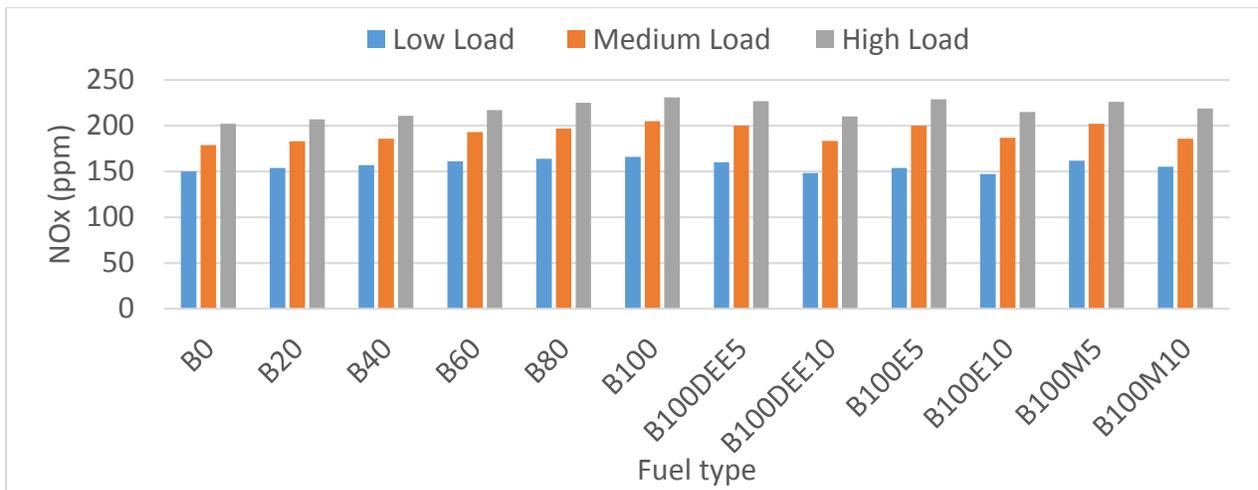


Figure 4.10 NO_x emission of biodiesel-diesel blends at various engine loads and 2100 rpm speed

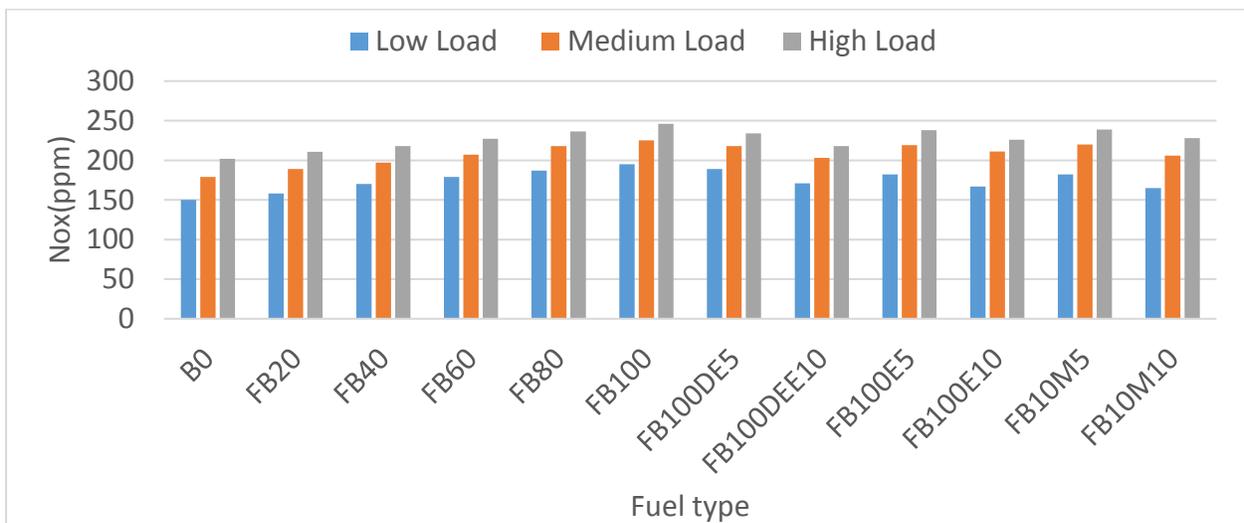


Figure 4.11 NO_x emission of fractionated biodiesel-diesel blends at various engine loads and 2100 rpm speed

b) Smoke Opacity:

Smoke opacity increased when increasing the biodiesel content in the fuel blends due to the higher viscosity of the fuels; it also increased with an increase in engine load (see figure 4.18). This may have increased the injection pressure, causing over-penetration of the fuel, which could have resulted in wall-quenching. The biodiesel additives contained lower smoke opacity due to the fact that additives reduce fuel viscosity and enhance combustion quality. The smoke opacity of B0 at low load condition was 2.7%, while it was 8.3% for B100 at the same load. B100DEE10 reduced the smoke by 22.77% at high load condition compared to B100. Smoke opacity in both B100E10 and B100M10 decreased by an average of approximately 26.5% at high load condition compared to that obtained from B100.

Fractionated biodiesel blends, with a variation in engine loads, represented a trend similar to biodiesel blends, as outlined in figure 4.19. Nevertheless, we discovered that smoke opacity values were significantly lower for fractionated biodiesel blends than that of biodiesel blends at all engine operating conditions. Smoke is comprised mainly of carbon soot particles and volatile organic compounds, the latter of which was found to reduce with an increase in unsaturated fatty acids level in biodiesel, therefore leading to reduced smoke opacity [19]. When comparing FB100 to B100 in terms of smoke opacity at high load engine conditions, FB100 exhibited a 25.8% reduction. For all fuel series at the same load conditions, the average reduction was approximately 19.75% compared to the biodiesel blends fuel series.

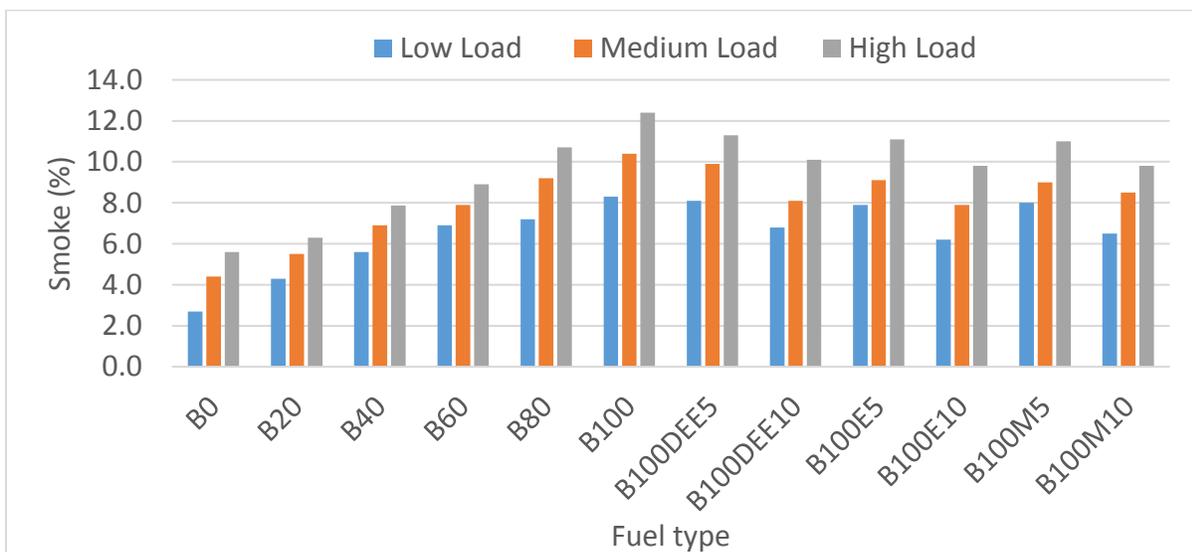


Figure 4.12 Smoke opacity of biodiesel blends at various engine loads and 2100 rpm speed.

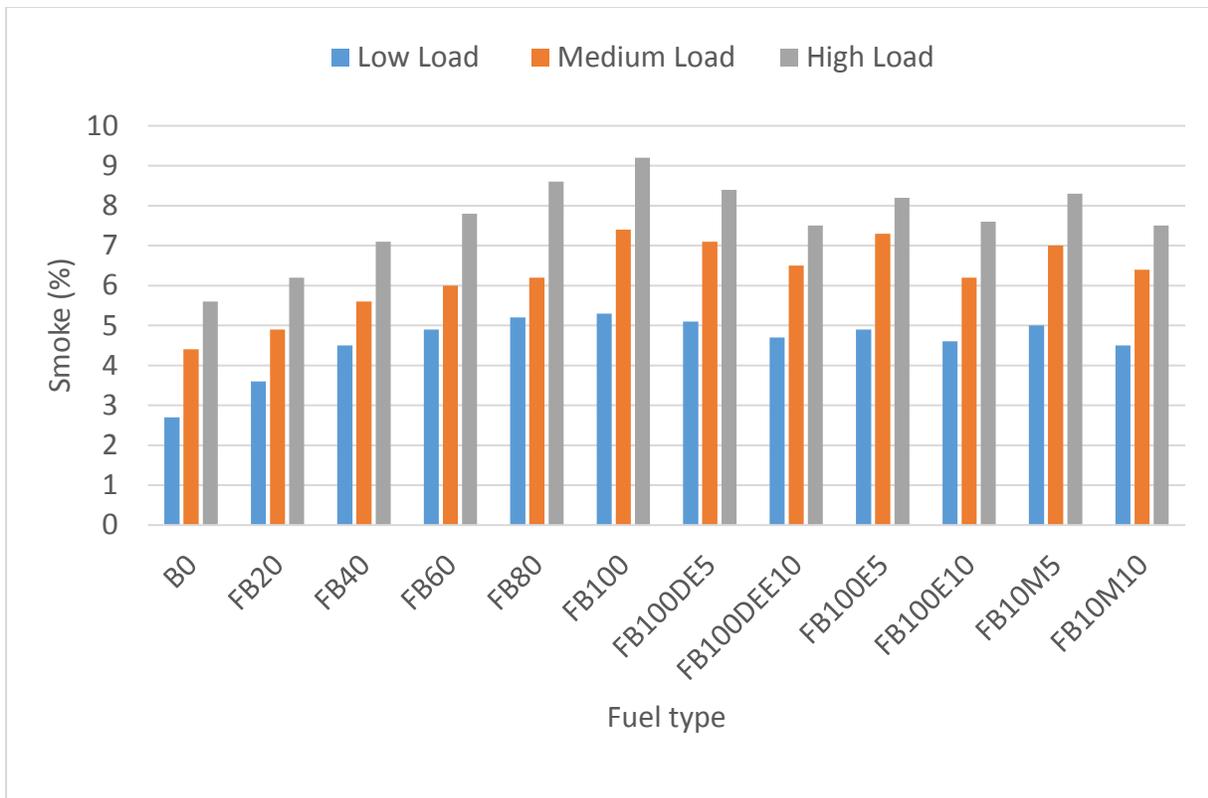


Figure 4.13 Smoke opacity of fractionated biodiesel blends at various engine loads and 2100 rpm speed

c) CO Emission

CO emission is one component of incomplete combustion. Many factors affect CO emissions such as engine speed, engine load, and fuel type. Increased engine load and speed results in decreased CO emissions due to the fact that combustion temperature increases with an increase in both engine load and speed, leading to oxygenated CO forming CO₂ emissions [20]. Refer to figure 4.20, which reveals the CO emission of biodiesel with a variation in engine loads. It was found that CO emissions decreased by increasing the biodiesel percentage in the blends. This reduction is attributed to the higher oxygen content, which leads to more complete combustion. CO emission of B100 was lower than B0 by approximately 26% at load medium engine load. Adding DEE to biodiesel resulted in a reduction of CO emissions, which was more noticeable with a higher percentage of DEE content in the biodiesel. The reason is that DEE has a very high CN, which is mainly responsible for reducing the ignition delay and improving the combustion quality. At high load, B100DEE10 had a CO reduction of 8.13% higher than B100. However, alcohol additives (methanol and ethanol) have high latent heat of vaporization, which leads to a reduction in the combustion temperature, hence higher CO emission. B100E10 and B100M10 had higher

CO emission by 19.6% and 10.87%, respectively, than that of B100 at high load condition, however they emitted lower CO than B0 at all engine operating conditions. The CO reduction of B100M10 and B100E10 were 10.87% lower than B0 at high load operating conditions.

Fractionated biodiesel showed slightly lower CO emission than normal biodiesel, which could be attributed to its lower CN and high oxygen content. All fractionated biodiesel-diesel blends, as well as the biodiesel's alcohol additives, had a similar trend as that obtained from normal biodiesel blends and additives (as seen in figure 4.21). However, the DEE additives in the biodiesel exposed an opposite trend to normal biodiesel, whereby its CO emission increased slightly over that of FB100. This might be because fractionated biodiesel has a low CN, and the DEE improves the CN of the blend; however it might not reach a CN high enough to provide improved combustion quality. The CO of FB100 decreased by 11.38% compared to that obtained from B100 at low load conditions. With FB100DEE10, we discovered a slight increase in CO emissions compared to FB100, i.e., 15 ppm higher at high load engine operating condition.

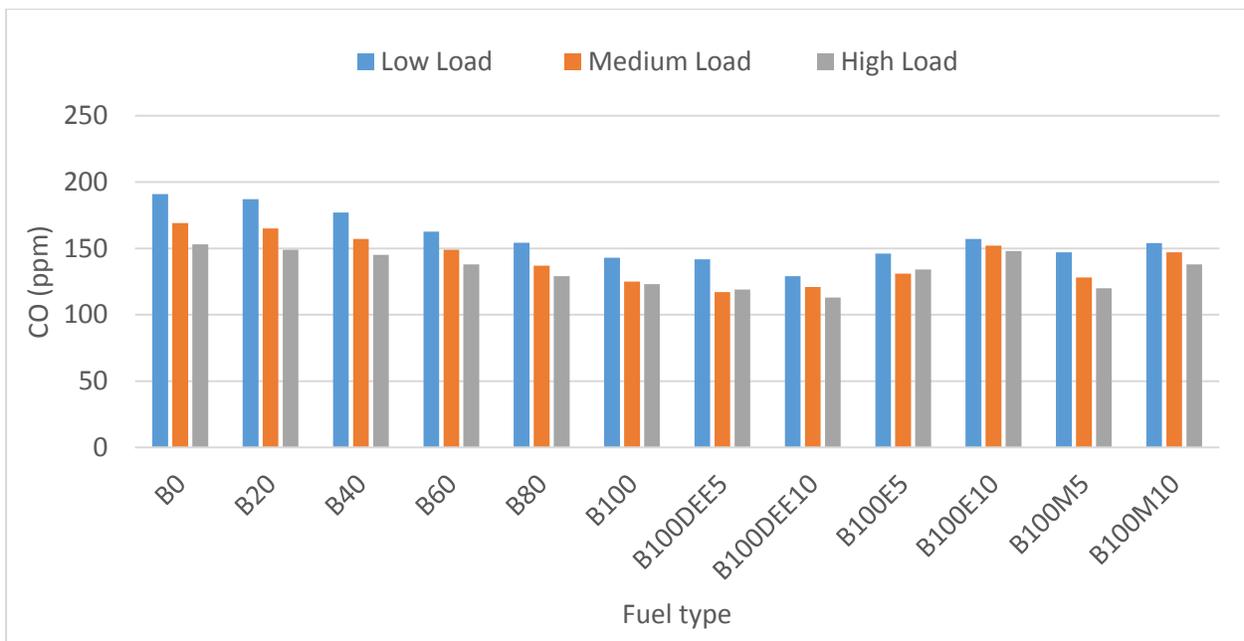


Figure 4.14 CO emission of biodiesel-diesel blends at various engine loads and 2100 rpm speed

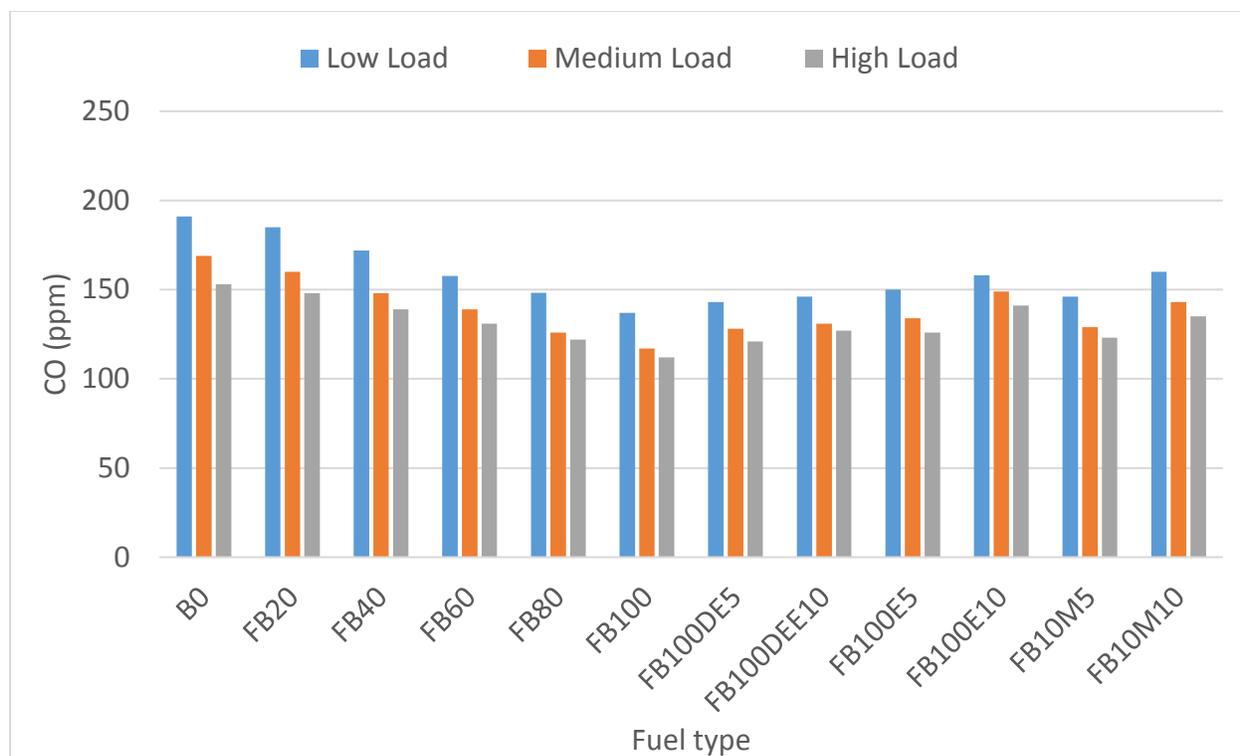


Figure 4.15 Fractionated biodiesel blends at various engine loads and 2100 rpm speed.

d) HC Emission

Low temperature bulk quenching of oxidation reactions, locally over-lean or over-rich mixture, liquid wall films for excessive spray impingement, and incomplete fuel combustion are the main causes of HC emission [113]. The HC emission was found to decrease with an increase engine load and speed, due to an increase in the combustion temperature, as shown in figure 4.22. The oxygen content in biodiesel enhances combustion quality, thus producing lower HC emission. Therefore, HC emission is reduced by increasing the biodiesel content in the blend. B100 exposed the highest HC reduction among all biodiesel-diesel blends with 7.5 ppm. Generally, the biodiesel additives led to a slight reduction in HC emission when compared to B100, and the reduction was significant when compared to B0. This reduction was obtained because of the effect of the additives on reducing fuel density (see table 3.1). The lowest HC reduction among all fuels investigated was obtained from B100E10 at all engine operating conditions. B100E10 at a high engine load revealed a HC reduction in excess of 70% compared to B0, and approximately 50% lower emission than B100.

Fractionated biodiesel blends revealed a similar trend of HC emission as that obtained from biodiesel, but they had slightly higher HC emissions than (see figure 4.23). The higher density, as well as the lower viscosity and CN, could be reason for this HC increase (see table 3.1). HC emission of FB100 increased by 16.67% at a high engine load compared to B100.

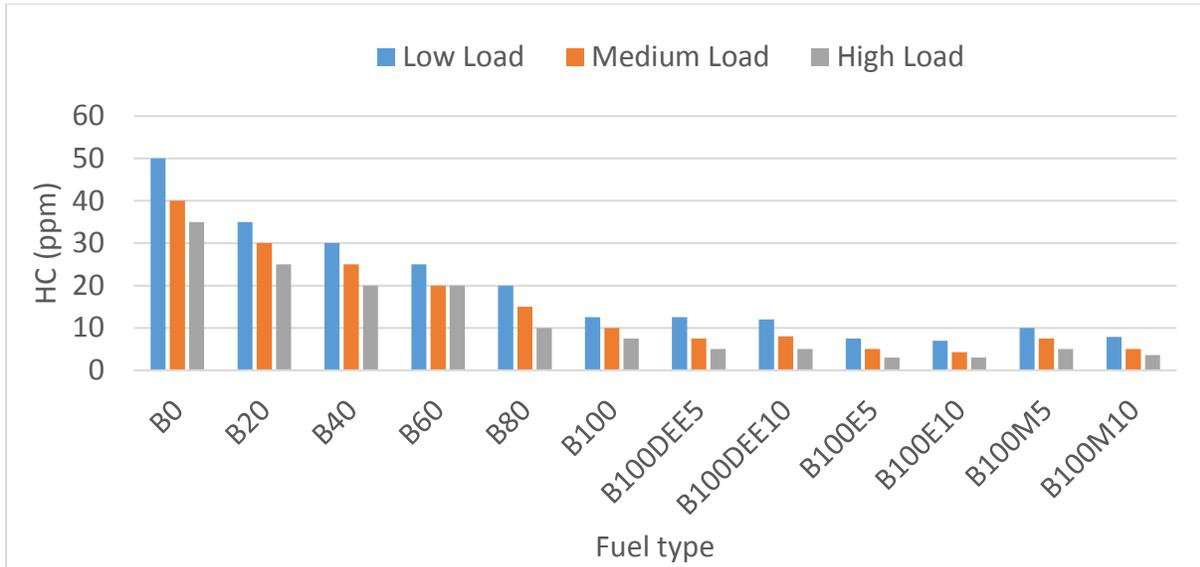


Figure 4.16 HC emission of biodiesel-diesel blends at various engine loads and 2100 rpm speed

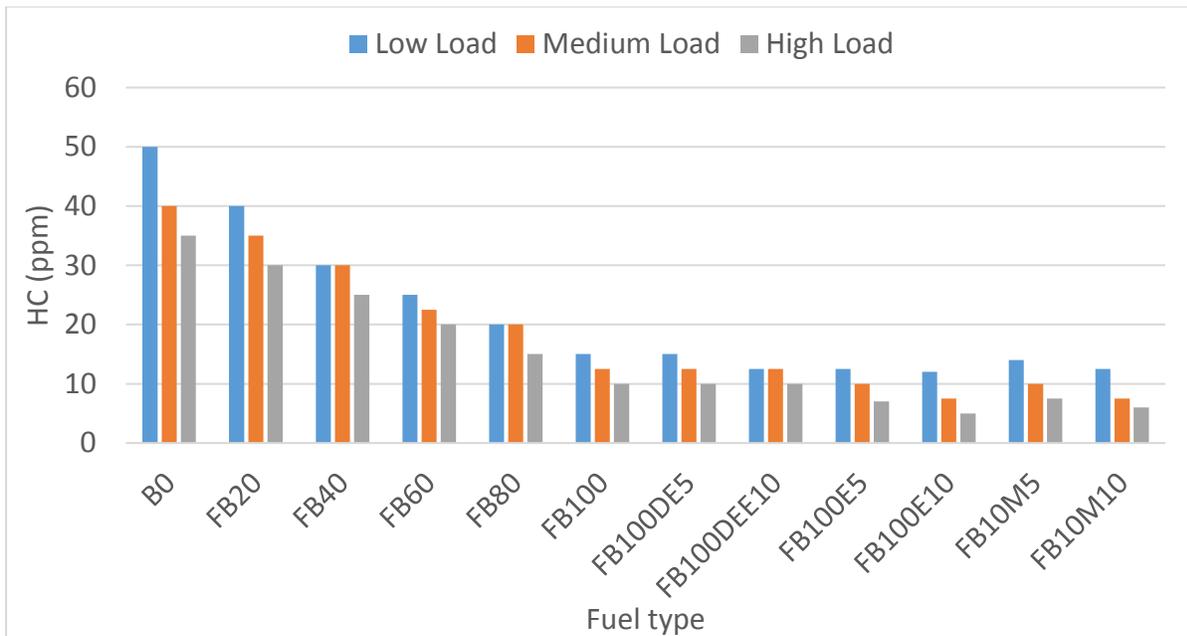


Figure 4.17 HC emission of fractionated biodiesel-diesel blends at various engine loads and 2100 rpm speed

4.5.2 Emulsion Fuel

In this section, B0, B20, B40, B30W10A2.5, B30W10A5 and B100 constitute the main focus of the presented figures. The complete list of results will be presented in the various tables.

a) NO_x Emission

NO_x emission rose at an increased load at a constant engine speed for all fuels investigated (refer to figure 4.24). This is because the higher combustion temperature that resulted from the added fuel supply contributed to extra NO_x formation. Figure 4.24 shows a considerable reduction in NO_x emission with the use of emulsion fuel, as well as water concentration of 15%, presented lower NO_x emission compared to 5% and 10% water concentration. The NO_x reduction percentages for emulsions fuel with 15% of B0, B20, and B40 at low load were found to be 34%, 32.7% and 33.74% compared with their bases. The heat energy absorption by the water introduced in the emulsion led to a reduction in peak flame temperature, hence fewer NO_x emissions.

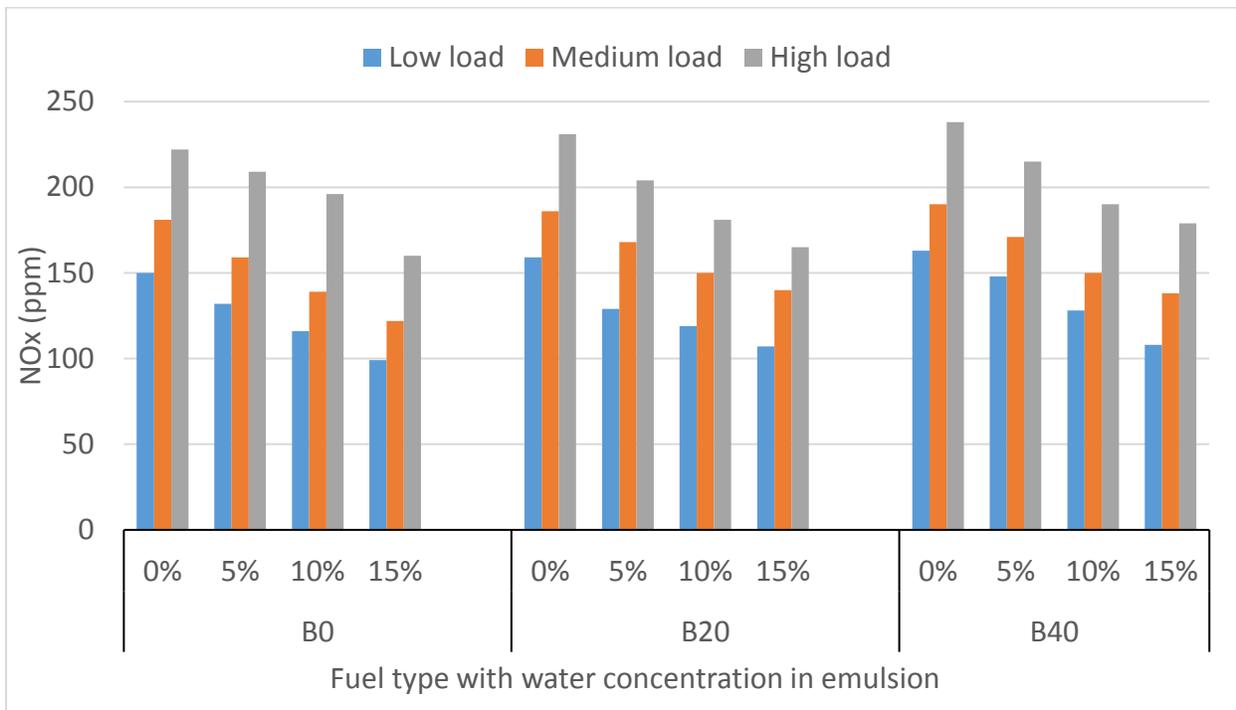


Figure 4.18 NO_x emission of biodiesel-diesel blends and their emulsions at various engine loads and 2100 rpm speed [ref.102]

Figure 4.25 depicts the NO_x emissions of B30 with emulsions of three different levels of ammonium hydroxide with 10% water content at various engine loads. The NO_x emission for all fuels investigated increased with an increased engine load, which varied from one fuel to another. For example, the B30 emulsion with ammonium hydroxide increased considerably at high load

engine condition compared to medium load, however this was not the case for the other types of fuel. The reason is that ammonium hydroxide contains a substantial amount of nitrogen, and operating the engine at high load resulted in a higher combustion temperature, therefore leading to more NOx formation. At high load condition, B30W10A5 provided NOx emission that were 24.7% higher than that obtained at medium load, while the increase for B30W10A0 at same engine conditions was 16.2%. However, B30W10A5 is still showing lower NOx emission than B30W0A0 at high load engine conditions, with a reduction of 0.8% less than B30W0A0. At low and medium engine loads, the emulsion's ammonium hydroxide level slightly increase when compared to B30W10A0.

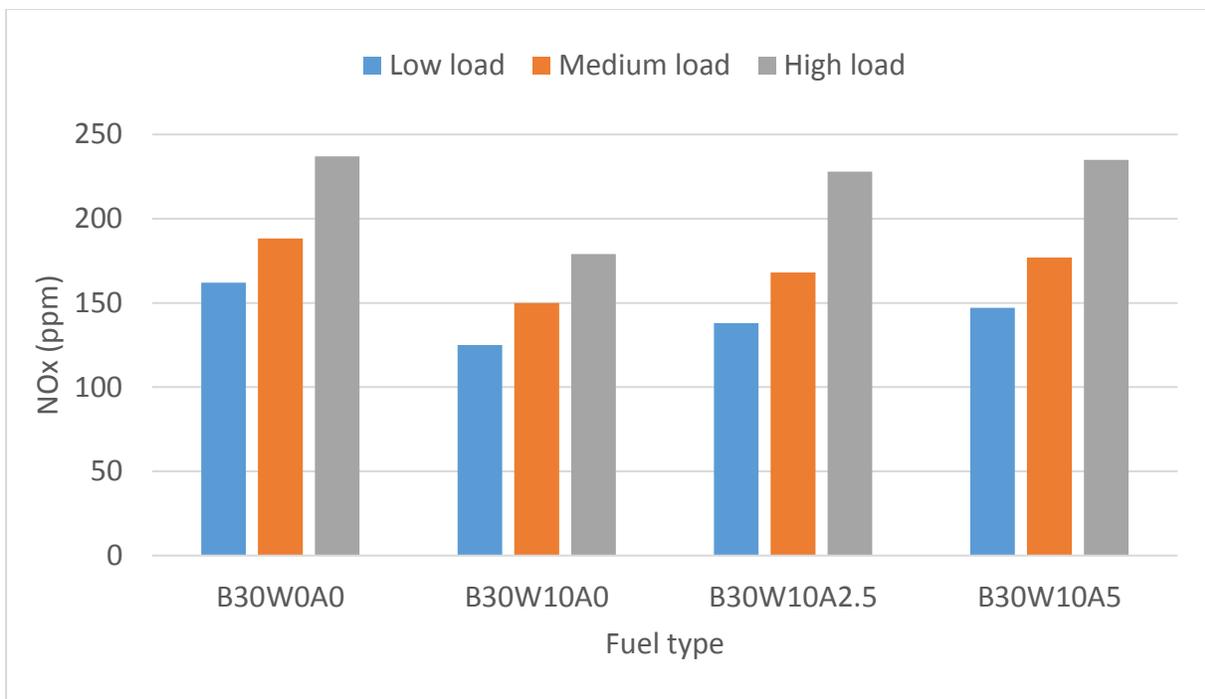


Figure 4.19 NOx emission of B30 with three different ammonium hydroxide levels in emulsion with water content of 10% at various engine loads and 2100 rpm speed.

Figure 4.26 shows a variation in NOx emissions, with load, from biodiesel and emulsion of biodiesel with 2.5% water content, compared to conventional diesel. It was found that B100W2.5 had comparable NOx emissions as B0, and was definitely lower than B100 due to the reduction of peak flame temperature caused by the water content in the emulsion at all engine operating conditions. At high load, the difference in NOx emission between B100W2.5 and B0 was 9 ppm (B100W2.5 was higher). The NOx emission reduction for B100W2.5 at medium load was 9.76% more than B100.

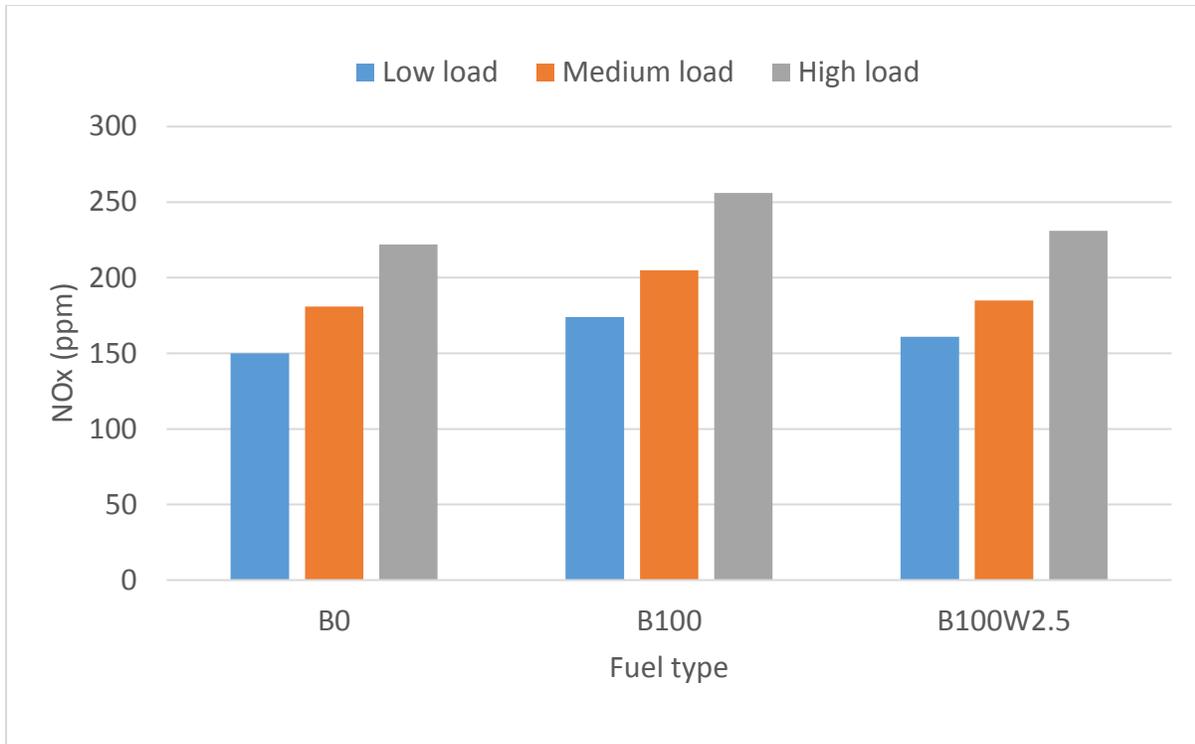


Figure 4.20 NOx emission of B0, B100 and B100W2.5 at various engine loads and 2100 rpm speed

b) Smoke Opacity

Figure 4.27 outlines the smoke opacity emission of diesel, DB10, DB20, DB30, and DB40, as well as their emulsion with 3 different concentrations of water (5%, 10% and 15%) at various engine load conditions. It is clear that smoke intensity in the exhaust gas is higher for those with a higher content of biodiesel in diesel-biodiesel blends, which is perhaps due to higher viscosity. This may increase injection pressure, resulting in over-penetration of the fuel, which could cause quenching. Micro-explosion of emulsion fuel due to improved fuel mixing, better fuel atomization, and vaporization by the injectors contributed to a reduction in smoke intensity, which could explain the smoke reduction with the increased levels of water concentration. Smoke opacity reduction at 15% water concentration for all emulsion fuels averaged approximately 25% compared to their fuel bases at the same engine load.

Similarly, B100W2.5 revealed smoke reduction at all engine operating conditions when compared to B100 (refer to figure 4.28). This reduction was found to be 6.5% less than B100 at high load. Nevertheless, B100W2.5 had higher NOX emissions than B0 at all engine operating conditions, and was found to be 66% higher at medium engine load.

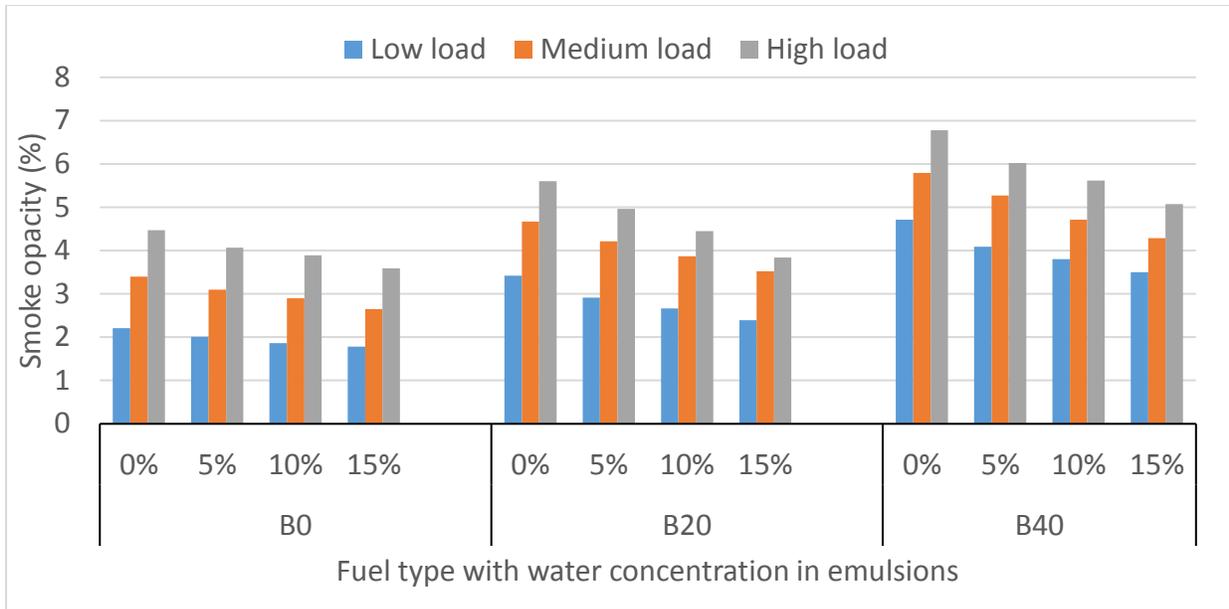


Figure 4.21 Smoke opacity of diesel and diesel-biodiesel blends with their emulsions at various engine loads and 2100 rpm speed [ref.102]

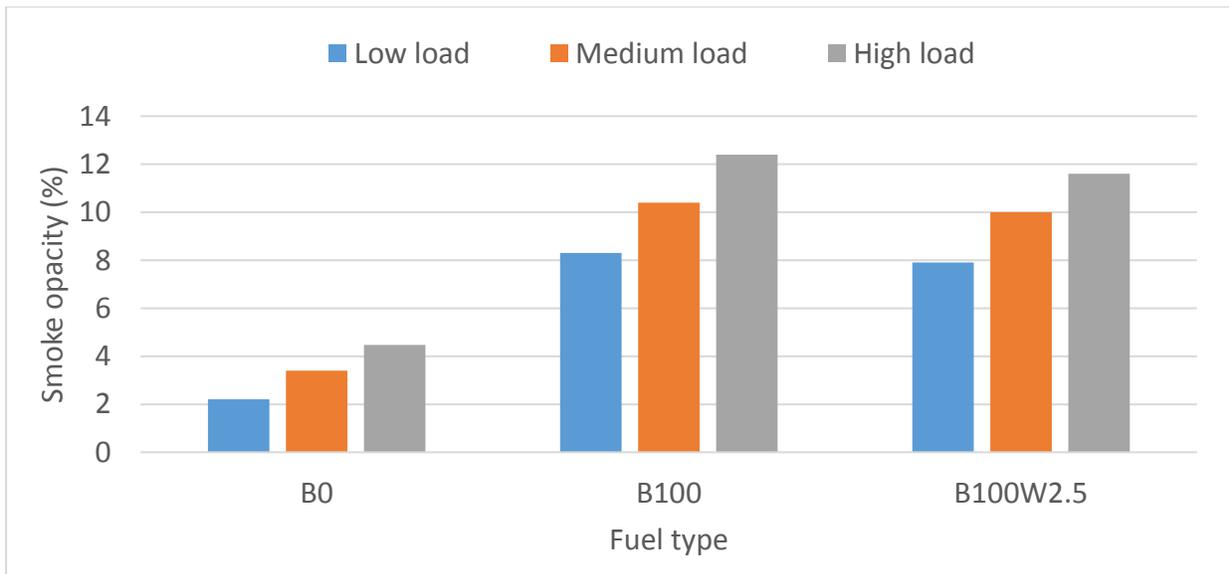


Figure 4.22 Smoke opacity of biodiesel and biodiesel emulsion at various engine loads and 2100 rpm speed

The ammonium hydroxide increase in the emulsion resulted in a higher smoke intensity reduction, as revealed in figure 4.29. B30W10A5 at low load, had 11.2%, 15% and 33.8% smoke reduction than did B30WA2.5, B30W10A0 and B30W0A0, respectively.

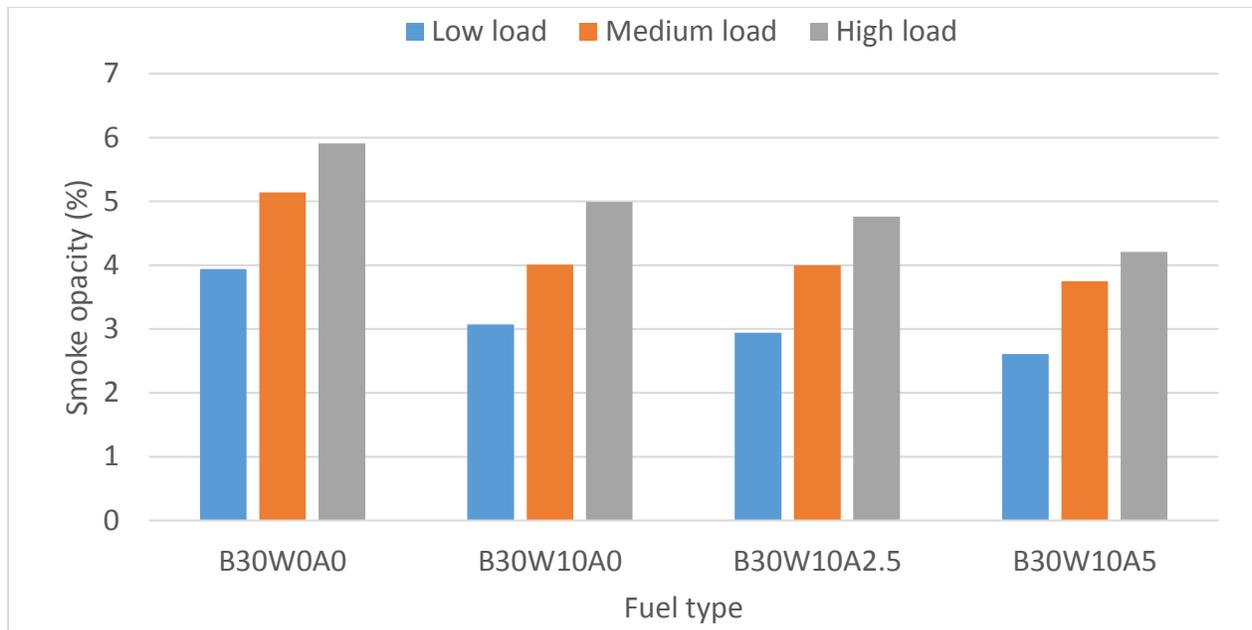


Figure 4.23 Smoke opacity of B30 with three different ammonium hydroxide levels in emulsion with water content of 10% at various engine loads and 2100 rpm speed

c) CO Emission

CO is formed mainly during the combustion of air-fuel mixture, whereas insufficient oxygen oxidizes the fuel to form CO₂. In addition, CO can be formed as a result of incomplete propagation of flame through mixture and fuel pyrolysis with partial oxidation. Therefore, the diesel-biodiesel blends led to reduced CO emission compared to pure diesel at all engine conditions investigated, as shown in figure 4.30, whereas B100 showed lower CO emission (see figure 4.31). It is clear from the figures that load increase led to an adequate turbulence and increment of the EGT, which resulted in more CO reacting with the air to form CO₂ emission. This can explain the CO reduction with the increase in CO₂ emission at higher loads for all fuel types. Fuel emulsion contributes to increased CO emission, and increases with a higher percentage of water. This rise could be due to the lower combustion temperature introduced by the water in the emulsions. However, the increase in the biodiesel amount in the emulsion reduces the CO emission compared to the emulsion fuel that contains less biodiesel. Figure 4.30 demonstrates that B40W5 has lower CO emission compared to all emulsion diesel-biodiesel investigated with the same amount of water. Emulsion B100W2.5 revealed a CO emission result very similar to pure diesel at all engine conditions (see results in figure 4.31). However B100W2.5 provided higher CO emission than B100, i.e., 27.38% higher than B100 at high load.

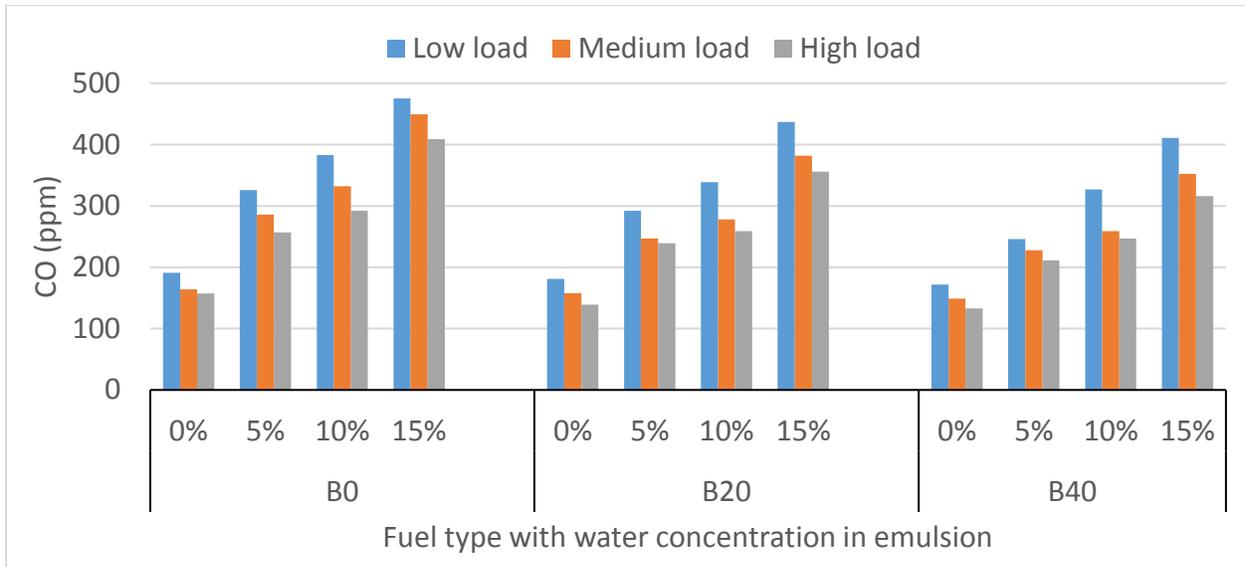


Figure 4.24 CO emission of diesel and diesel-biodiesel blends with their emulsions at various engine loads and 2100 rpm speed [ref.102]

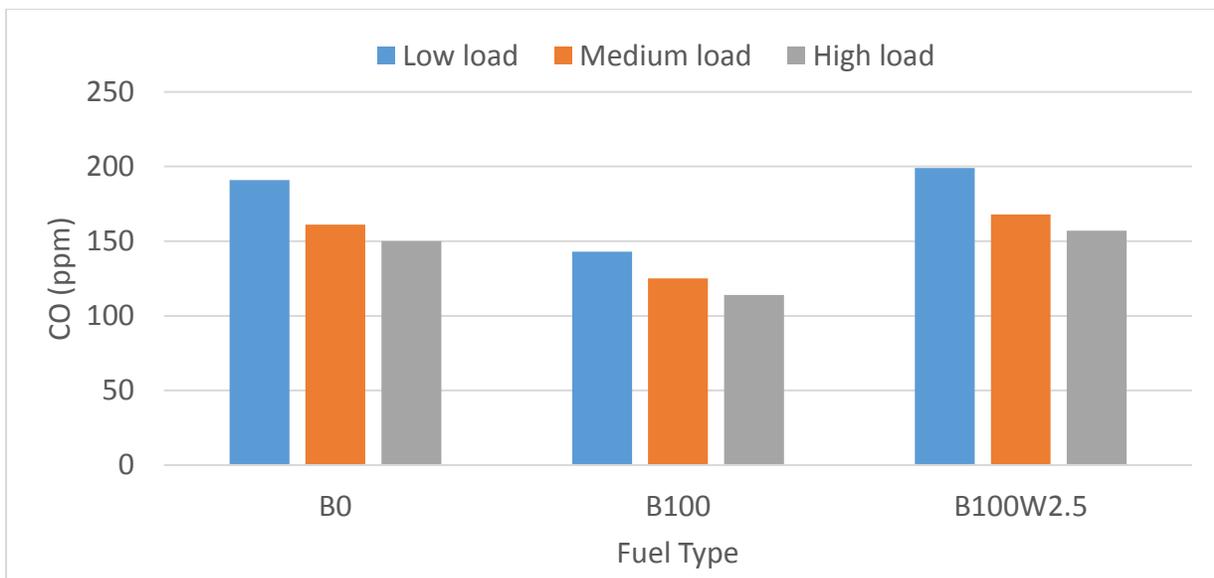


Figure 4.25 CO emission of biodiesel and biodiesel emulsion at various engine loads and 2100 rpm speed

Emulsion B30 with water and ammonium hydroxide contributed to reduced CO emission compared to B30W10A0 (see figure 4.32). This might be attributed to a higher amount of oxygen, which reacted with nitrogen to form NO_x emission. B30W10A5 provided CO emission of 27.5% lower than B30W10A0 at high load. However, B30W10A5 still emitted higher CO when

compared to B30W0A0 and B0 at all engine operating conditions. B30W0A0 had 33.5% fewer emissions than B30W10A5 at a high load engine condition.

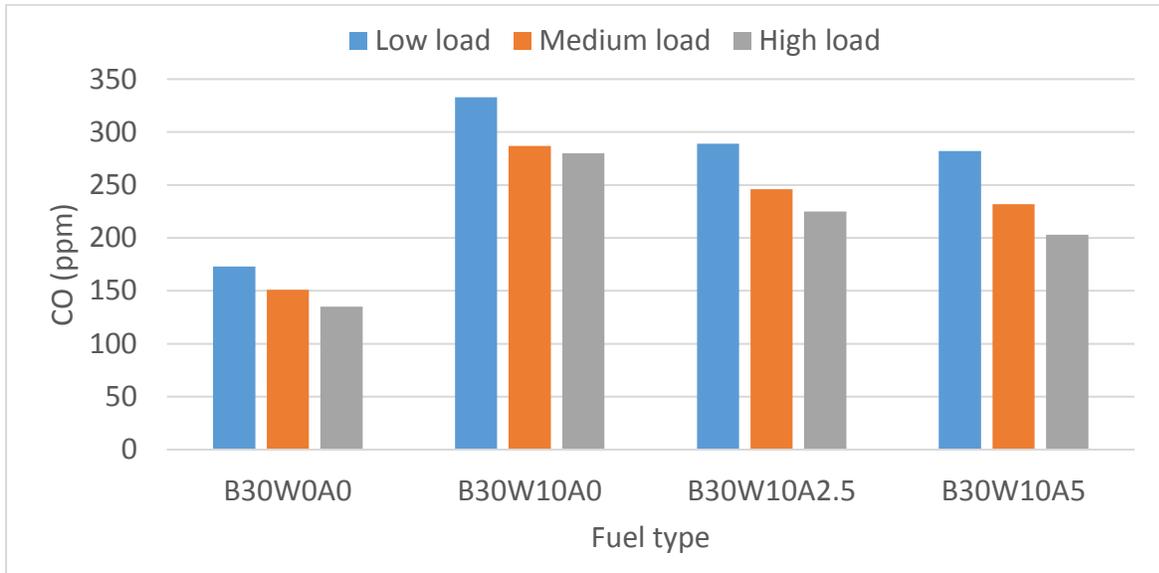


Figure 4.26 CO emission of B30 with three different ammonium hydroxide levels in emulsion with water content of 10% at various engine loads and 2100 rpm speed

d) HC Emission

Unstable engine speed, the change in fuel injection, and excessive volumes of nozzle cavity are some reasons for HC emission[114]. Figure 4.33 depicts the HC emission of diesel, and biodiesel-diesel blends with their emulsions. It is clear that HC emissions reduce with an increase in engine load. This might be due to the lean air-fuel mixing at low load, and the possibility that the flame speeds may be too low to complete the combustion. Biodiesel had higher combustion efficiency due to its high oxygen content (12%), leading to reduced hydrocarbon emission. B40 showed in excess of 50% HC emission reduction than B0 at all engine operating conditions. Although emulsion fuels reduce the combustion temperature, they show a very slight increase in HC emission. The reason is that atomization can occur twice inside the engine cylinder, whereas in diesel fuel, atomization can happen only once. In other words, atomization first occurs through the injector nozzle, and occurs the second time by evaporating the water, which leads to minute fuel species that are smaller than normal fuels.

Similarly, B100W2.5 provided slightly higher HC emission than B100, whereas a significant reduction was obtained when compared to B0 at all engine operating conditions. The HC reduction of B100W2.5 was approximately 64.7% lower than B0.

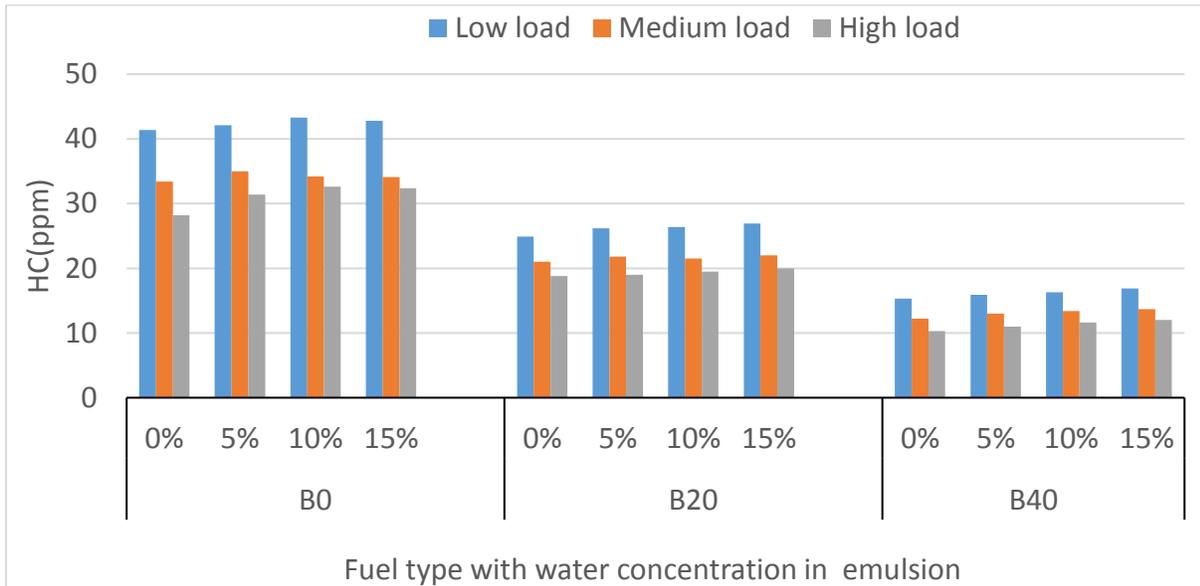


Figure 4.27 HC emission of diesel and diesel-biodiesel blends with their emulsions at various engine loads and 2100 rpm speed [ref.102]

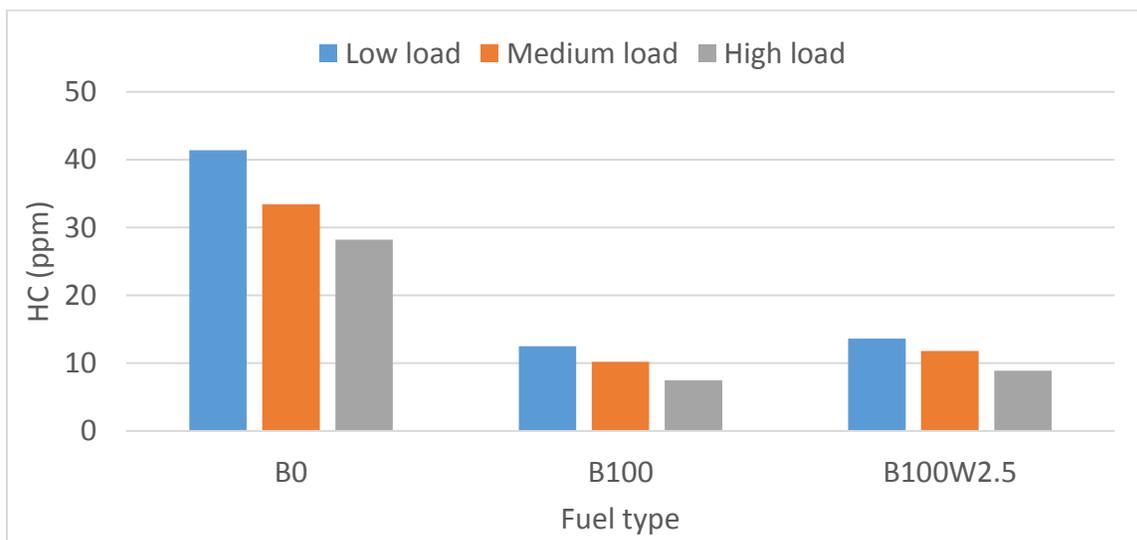


Figure 4.28 HC emission of biodiesel and biodiesel emulsion at various engine loads and 2100 rpm speed.

Figure 4.35 shows HC emission of B30 and its emulsion with water and ammonium hydroxide and a variation in engine loads. There was a very slight increase in HC emission, which may be attributed to the lower combustion temperature and increased amounts of both water and ammonium hydroxide in the emulsion. With ammonium hydroxide, atomization can occur three times due to different boiling points of ammonium hydroxide and water.

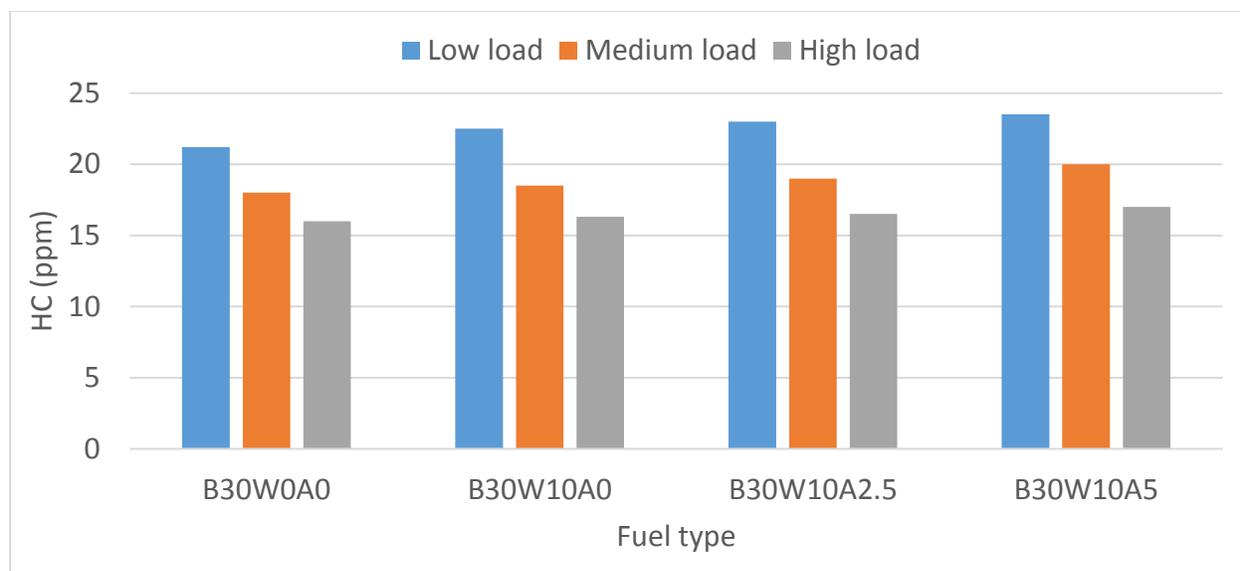


Figure 4.29 HC emission of B30 with three different ammonium hydroxide levels in emulsion with water content of 10% at various engine loads and 2100 rpm speed.

4.6 Heavy Duty Diesel Engine Emissions

The fuels investigated, which determined their effect on heavy-duty diesel engine emissions, included B0, B100, Kerosene and n-Heptane. The emulsion fuels included B0W10, B0W15, K100W0, K100W15, K70W10 and K70W15. Two engine idling speeds were investigated (1200 rpm and 1500 rpm). The exhaust emissions were NO_x, CO and HC. All fuels investigated discovered similar trends with speed variation. Therefore, the emissions at a speed of 1500 rpm will constitute the main focus in the figures presented. The complete list of results can be found in appendix E, table A.1.

4.6.1 NO_x Emission

Figure 4.36 illustrates NO_x emissions of various fuels at an engine speed of 1500 rpm. It is clear that B100 provided a higher average of NO_x emissions among all fuel types investigated due to the oxygen presence in biodiesel. K100 and n-Heptane had approximately the same average NO_x, and they both had a slightly higher average than NO_x than B0. The reason might be attributed to the lower density and viscosity of those two fuels and higher heat, which resulted in increasing combustion temperature, hence fewer NO_x emissions. All emulsion fuels provided lower NO_x emission; the lowest average NO_x was obtained from EB0W10. The reduction was 33.1%

compared to that obtained from B0. Increased biodiesel in the emulsion increased the averaged NOx. EB30W15 had incremental NOx increase of 7.6% compared to EB0W15.

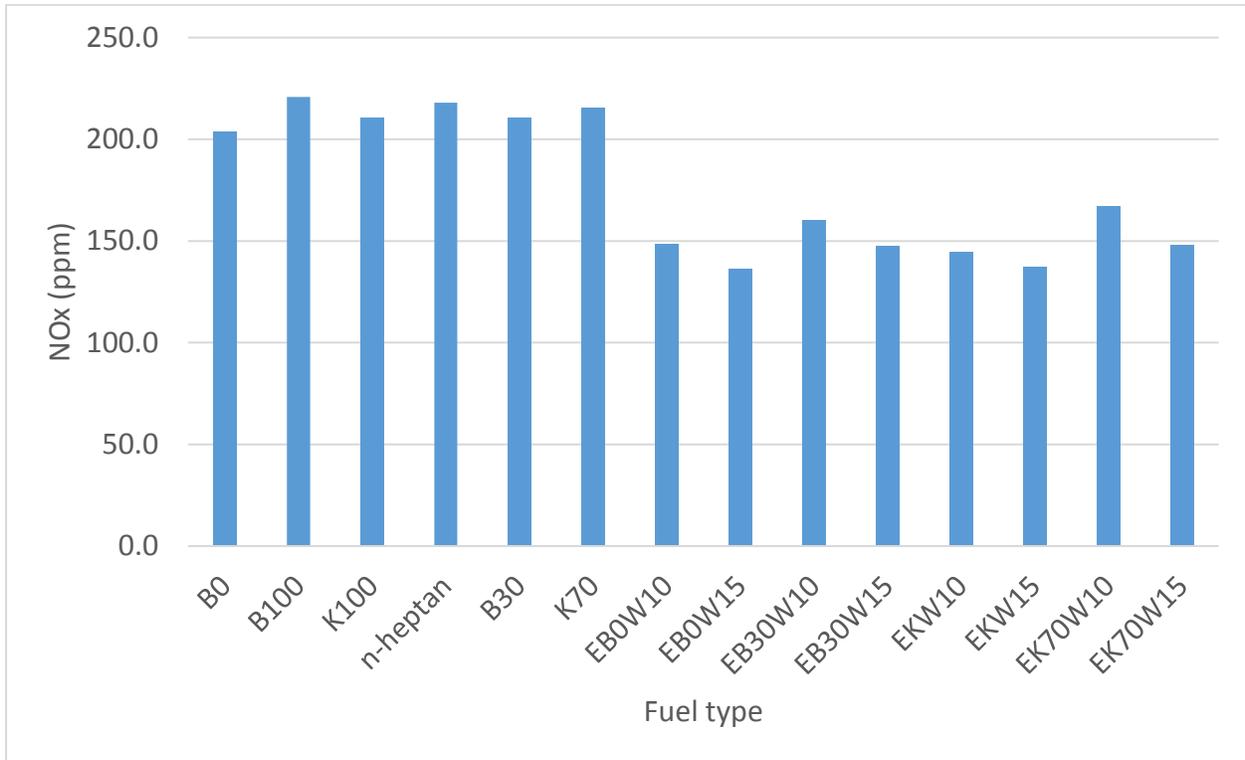


Figure 4.30 NOx emission of different fuel at 1500 rpm engine speed

4.6.2 CO Emission

Figure 4.37 shows CO emission of various fuels and emulsion fuels at speed of 1500 rpm. B100 and n-Heptane had lower average CO emission among all fuels investigated, while the results for B0 and K100 were comparable. All base fuels provided fewer average CO emissions compared to their emulsions. The reason is that fuel emulsions provide lower combustion temperature because of their water content, and therefore the temperature is not sufficient to form CO₂ in order to achieve complete combustion. A significant increase in CO emission was obtained from EK100W15, which reached 41.9% compared to K100, and 73.8% compared to B100. This significant increase is due to the fact that the engine is equipped with a cold EGR system, which leads to a larger reduction in combustion temperature.

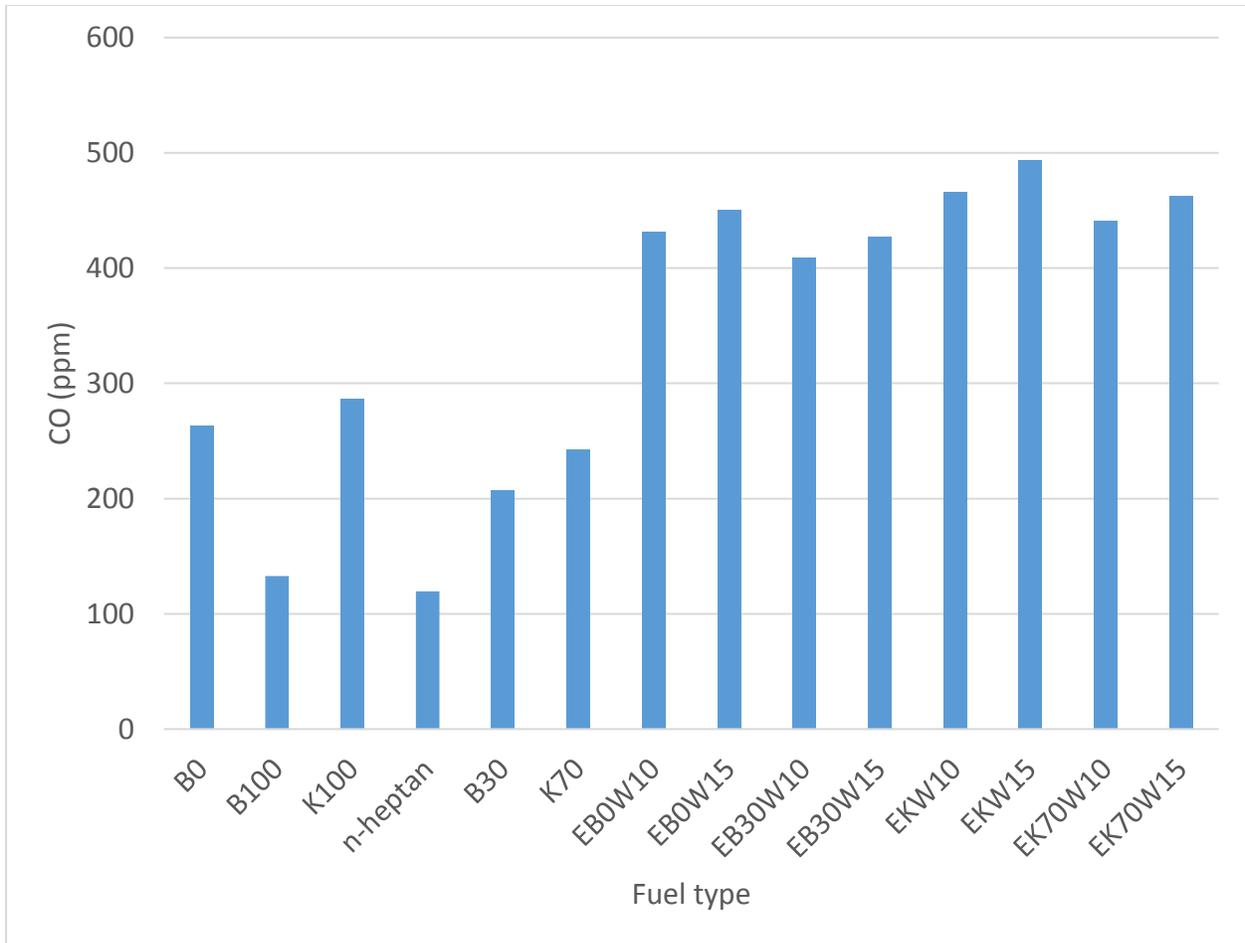


Figure 4.31 CO emission of various fuels at 1500rpm engine speed

4.6.3 HC Emission

Figure 4.38 depicts HC of various fuels and emulsion fuels at an engine speed 1500 rpm. B0 had the highest HC emission compared to n-Heptane, B100, K100, B30, and K30. Consequently, emulsion diesel had the highest average HC emission among all fuels investigated; the increase was significantly higher than B0, which reached 31.9%. The reason for this increase is because a heavy-duty engine is equipped with a cold EGR system, which is the second main component responsible for decreasing both combustion temperature and oxygen content inside the combustion chamber.

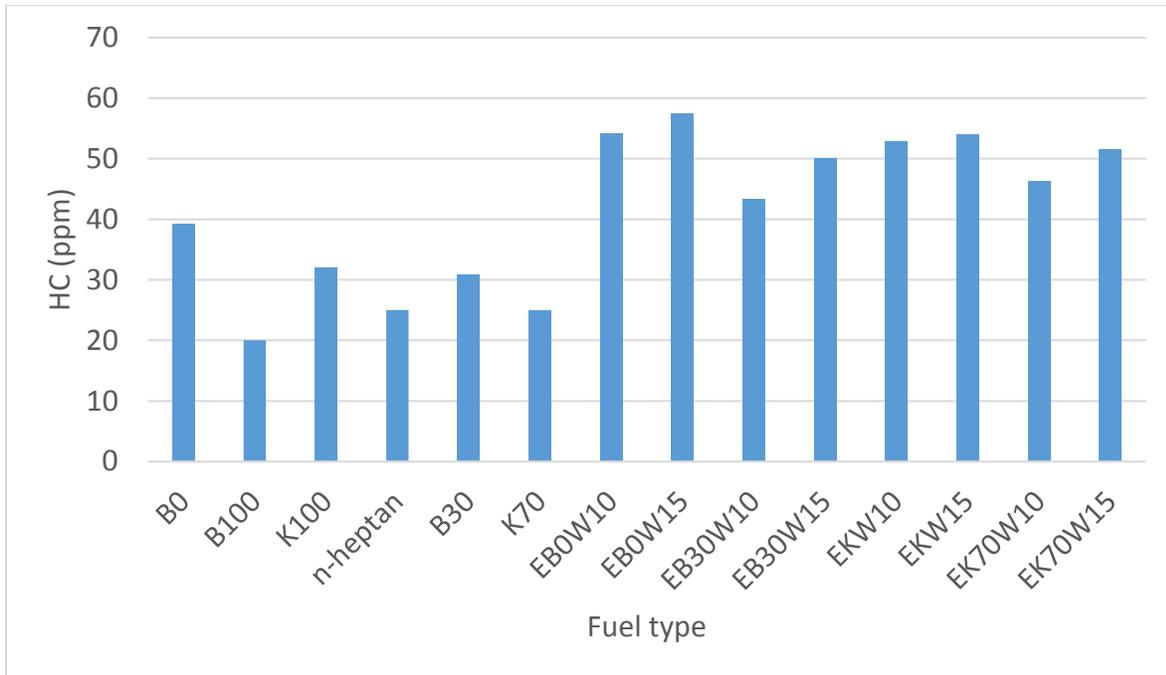


Figure 4.32 HC emission of various fuel at 1500 engine speed

4.7 Emulsion Fuel Cost Analysis

The emulsion fuel consists mainly of diesel, emulsifiers and water. In this study, the emulsion fuels were prepared using a blender (Osterizer type - 700 Watts). For each batch (600ml) of emulsion fuel, the blender was operated for 15 minutes.

4.7.1 Energy Cost Calculations

To calculate the energy used by the blender for preparing a batch, the following formula was used [115]:

$$\text{Total energy cost} = \left(\text{power in } \frac{\text{watts}}{1000} \right) * \text{hours operating} * \text{cost per kWh} \quad (5)$$

Electricity rates and prices in Ontario, Canada are divided into three categories: 6.5¢ per kWh for off-peak load, 9.5¢ per kWh for mid-peak load, and 13.2¢ per kWh for on-peak load [116]. In this calculation, the mid-peak load will be applied. Therefore, the total energy cost for preparing 600ml of emulsion fuel is \$0.0166 CAD.

4.7.2 Analyzing Emulsion Diesel Components

Emulsion diesel with 10% water consumption was calculated to be 315.1883ml/h at low load engine condition and speed of 1000 rpm. For the same engine condition, diesel consumption was 294.66ml/hr. The following calculation analyzes the emulsion diesel component costs:

- Emulsifier content = $0.02 * 315.1883 = 6.3$ ml/hr;
- Water content = $0.1 * 315.1883 = 31.52$ ml/hr;
- Diesel content = $315.1883 - 31.52 - 6.3 = 277.37$ ml/hr;

The amount of diesel in the emulsion diesel is less than the amount consumed by the engine when the diesel was used (277.37 ml/hr < 294.66 ml/hr);

The emulsifiers consist of Span80 and Tween80. Emulsifiers with 8.25 HLB consist of 36.9% of Tween80, and 63.1% of Span 80. Therefore:

- Span 80 content = 6.3 ml * $0.631 = 3.97$ ml;
- Tween 80 content = $6.3 - 3.97 = 2.33$ ml;

4.7.3 Emulsion Diesel Components Cost Calculations:

Span 80 costs \$1681 CAD/ton (\$1.83 CAD/L), Tween 80 costs \$1293.11 CAD/ton (\$1.55 CAD/L) [117], [118]. The density of both Span 80 and Tween 80 are 0.99 kg/L and 1.09 kg/L, respectively. Calculating the cost of the emulsifiers:

- Span 80 cost = 0.00183 (CAD/ml)* 3.97 ml = 0.0073 CAD;
- Tween 80 cost = 0.00155 (CAD/ml)* 2.33 ml = 0.00361 CAD;

Note: for the emulsifiers cost, a bulk amount was considered.

The diesel price at a local gas station \$107.9 ¢/L. The diesel cost used in the emulsion: ($\$1.079$ CAD/L * 0.27737 L) = $\$0.2993$ CAD.

4.7.4 Comparison between Emulsion Diesel and Conventional Diesel Costs

The overall cost of emulsion diesel with 10% water content: $\$0.2993$ CAD + $\$0.0073$ CAD + $\$0.00361$ CAD + $(315.1883$ ml/600 ml) * $\$0.016$ CAD = $\$0.3186$ CAD.

When the engine operated by diesel fuel under 1000 rpm at low load, the diesel consumption was 294.66ml/hr.

- Diesel cost = $0.29466 \text{ L} * \$1.079 \text{ CAD/L} = \0.3179 CAD .

The following table shows diesel and emulsion diesel with 5%, 10%, and 15% water content cost when the light-duty diesel engine tested under operating conditions of low load and 1000 rpm speed.

Table 4.2 Diesel and emulsion diesel with three different water levels cost at low load and 1000 rpm speed.

Fuel type	Fuel consumption (ml/hr)	Surfactants content in emulsion (ml)	Diesel content in emulsion (ml)	Water content in emulsion (ml)	Total cost CAD	Cost CAD/L
B0	294.66	-	-	-	0.317938	1.079
EB0W5	303.412	6.06824	282.1732	15.1706	0.323034	1.0647
EB0W10	315.1883	6.303766	277.3657	31.51883	0.318567	1.01074
EB0W15	333.144	6.66288	276.5095	49.9716	0.318742	0.957

Finally, it can be concluded that diesel and emulsion diesel with three different water levels represent approximately similar cost at the same engine operating conditions.

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

In this study, urea fractionation and recovered urea were applied to improve the canola biodiesel's CFPs. In addition, the biodiesel was fractionated for the first time using crystal, which is a by-product of urea fractionation. Furthermore, diesel, biodiesel and diesel-biodiesel blends were emulsified with different water levels. Thereafter, emulsion diesel-biodiesel blends, with two different quantities of ammonium hydroxide in the emulsion, were produced. An experimental investigation was conducted on the light-duty diesel engine to explore the performance and emissions of different fuel and emulsion fuel series under various operating conditions. Two idling conditions of a heavy-duty diesel engine were also investigated using various fuels. Although the emulsion biodiesel-diesel blend with ammonium hydroxide was prepared, this investigation was the first to date in terms of engine performance and emission. Finally, the following conclusions have been drawn from this study.

Recovered urea with crystal fractionation provided biodiesel with -18°C CP and -24°C PP with 100% production efficiency. Using recovered urea without methanol for fractionation reduced the biodiesel CP from -2.6°C to -9°C , with 87% production efficiency. Fractionated biodiesel using recovered urea with crystal slightly reduced the biodiesel viscosity, while decreasing its density. Increased water and biodiesel content in the emulsion provided higher viscosity and density than the emulsion bases. Emulsion stability was found to be reduced with the increased water and biodiesel content in the emulsion.

The BSFC of all fuels investigated decreased with an increased engine load and speed. The BSFC of biodiesel-diesel blends increased slightly with an increase in biodiesel in the blend. Higher percentages of ethanol and methanol in biodiesel showed higher BSFC than B100, while a higher percentage of DEE additive in the biodiesel provided a very slight reduction in BSFC. Fractionated biodiesel provided a very slight reduction in BSFC compared to B100 at all engine operating conditions. With respect to DEE additive, fractionated biodiesel blends and additives revealed a slight BSFC increase at all engine operating conditions compared to biodiesel blends and additives, but both showed similar trends. The higher content of both the water and biodiesel in the emulsion fuels as well as increase the ammonium hydroxide in emulsion showed higher BSFC than that which was obtained from the emulsion with less water, biodiesel, and ammonium hydroxide at all engine operating conditions.

The BTE of all fuels investigated increased when increasing the engine load and speed. The BTE of biodiesel-diesel blends increased slightly when increasing the biodiesel content in the blends; the additives also improved the BTE. The fractionated biodiesel blends and additives showed similar trends to biodiesel blends and additives; however, the BTE value of each fractionated biodiesel series gave a slightly higher BTE compared to normal biodiesel fuel series at all engine operating conditions. All emulsion fuels had improved the engine BTE, and higher amount of biodiesel and water levels in the emulsion resulted in higher BTE. EB40W15 improved the BTE by 3.1% and 15.7% than EB0W15 and B0, respectively, at engine conditions of high load and speed of 2100 rpm. At the same operating conditions, EB40W15 provided higher BTE than EB100W2.5 by 5.32%.

All fuel series contributed to increased NO_x emission with an increase in engine load and increase biodiesel content in blend. B100 provided approximately 11% higher NO_x than B0 at high load, and 2100 rpm engine speed. However, all biodiesel additives showed a slight NO_x emission reduction compared to B100; the highest reduction (9.3%) was obtained from B100M10 at engine operating conditions of medium load and 2100 rpm speed. All fractionated biodiesel fuel series showed a similar NO_x emission trend in the biodiesel fuel series. However, all fractionated biodiesel blends provided higher NO_x emission than biodiesel blends at all engine operating conditions. FB100 at low load and 2100 rpm contributed to higher NO_x by 8.9%. Emulsion biodiesel diesel blends had a significant NO_x emission reduction, the highest of which was obtained with the emulsion that obtained at higher level of water compared to their bases and conventional diesel. B100W2.5 had comparable results of NO_x emission obtained from B0. EB30W10A5 showed higher NO_x emission than EB30W10 by approximately 15.25% at medium engine load and 2100 rpm speed.

The smoke opacity of all fuel series investigated revealed a similar trend with engine speed and load, whereby they increased with an increased engine load. Increase biodiesel content in emulsion resulted in an increase in smoke opacity, while the additive represented lower smoke opacity than B100 at all engine operating conditions. B100's smoke opacity increased by 54.8% when compared to B0 at an engine speed of 2100 rpm at high load. Increased water content in the emulsion has proven to reduce smoke opacity, and EB0W15 showed lower smoke compared to all other fuels at all engine operating conditions. Increasing the ammonium hydroxide in the emulsion

resulted in smoke opacity reduction; the highest quantity of ammonium hydroxide in the emulsion showed a higher reduction.

The CO emission of all fuel series decreased with an increase in engine speed and load; 3000 rpm with high engine load revealed the lowest emission. Biodiesel increase in biodiesel-diesel blends decreased the CO emission at all engine operating conditions. B100, at 2100 rpm engine speed at high load, reduced CO emissions by 22.22% more than B0. Increase DEE in the biodiesel provided a noticeable reduction (about 9% reduction of B100DEE10) when compared to B100 at all engine operating conditions. Alcohol additives contributed to emitting higher CO emission than B100, but the CO emission was still lower than B0. The fractionated biodiesel fuel series revealed similar CO emission trends as the biodiesel fuel series, with the main difference being that the biodiesel fuel series contributed to a very slight CO emission increase at all engine operating conditions than FB100.

Increasing the water content in the emulsion resulted in a significant increase in CO emissions when compared to the emulsion's base fuel. EB100W2.5% showed similar results of CO emission to that obtained from B0 at all engine operating conditions. However, EB100W2.5 provided higher CO emission than B100, and it was 27.4% higher than B100 at high load and a speed of 3000 rpm. EB30W10A5 at engine operating conditions of 2100 rpm and high load showed a CO emission reduction by 9.8% and 27.5% compared to EB30W10A2.5 and EB30W10A0, respectively. The HC emission of all fuel series investigated showed an HC reduction when the engine load, speed and biodiesel content were increased. The B100 provided an average HC emission reduction over B0 by 75% at engine operating conditions of low load and 2100 rpm speed. The fractionated biodiesel fuel series had a similar HC emission trend as that of the biodiesel fuel series, but it was slightly higher for fractionated biodiesel series. Increasing the water content in the emulsion was found to increase the HC emission at all engine operating conditions. EB100W2.5 provided lower HC than B0 by about 66% at engine operating conditions of medium load and 2100 rpm speed. Similarly, the HC emission of emulsion ammonium hydroxide fuel increased slightly when increasing the percentage of ammonium hydroxide in the emulsion.

The biodiesel NO_x emission of the heavy-duty diesel engine had the highest values at both operating conditions investigated, while emulsion diesel with 15% water had the lowest NO_x emission among all fuel investigated. B100 and n-heptane showed lower CO emissions compared to all fuels investigated. A significant CO emission increase was noticed by increasing the water

content in the emulsion, and EKW15 at engine speed of 1200 had higher CO emission. Among all fuels tested via the heavy-duty diesel engine, B100 had lower HC emission. The emulsion fuels had the highest HC emission than all fuel series. EB0W15, at engine speed of 1500 rpm, represented HC emission higher than B0 and K100 by 31.83% and 44.35%, respectively.

The cost analysis of emulsion diesel with three different water content, revealed that the consumption of EB0W10 increased by approximately 6.5% over B0 for the same engine operating conditions. However, the engine consumed less amount of diesel when the engine tested with emulsion diesel. At low load and 1000 rpm engine speed, the engine consumed 5.87% less diesel when the engine was running with EB0W10 than B0. Additionally, the cost of emulsion diesel has approximately shown similar costs compared to B0.

5.2 Recommendations

Although the present study fulfilled the principal objectives of this research, the following work is proposed to refine and progress the study findings:

1. Further investigation into optimization emulsion fuel stability and figuring out emulsifiers with acceptable CFPs to be usable for long term even in coldest climatic regions.
2. With the high production efficiency of fractionated biodiesel obtained from this study, I would like to suggest using clod flow improvers such as Wintron Synergy to improve fractionated biodiesel's CFPs further.
3. The study has indicated that emulsion fuel with high level water tend to have significantly lower NOx emission but higher HC and CO emissions. The effort should include to reduce and control CO and HC emissions by using DOC.
4. A comparison between emulsion fuel and EGR system effects on engine exhaust emission will be useful.

Appendices

Appendix A: Biodiesel diesel blends and biodiesel additives performance and emission tested by light-duty diesel engine.

A.1 Engine performance and emissions of biodiesel diesel blends and biodiesel additives at 1000 rpm

Load	Low load						Medium load						High load					
Fuel	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
B0	240.1	32.9	153	3.2	234	55	227.9	34.7	198	5.0	219	45	224.4	35.2	234	7.9	181	40
B20	244.9	33.0	155	6.4	230	40	230.9	35.0	205	8.4	209	35	230.0	35.2	242	9.7	179	30
B40	249.6	33.2	160	8.3	222	35	235.8	35.1	208	9.4	195	30	235.0	35.2	246	11.2	170	20
B60	256.1	33.1	163	10.8	211	30	241.7	35.1	214	12.0	187	25	241.4	35.1	254	13.1	163	15
B80	265.0	32.9	165	13.2	206	25	247.3	35.2	221	14.7	171	20	247.6	35.2	260	15.3	157	10
B100	272.8	32.8	171	16.4	198	15	253.0	35.3	225	18.9	165	10	253.8	35.2	265	18.5	149	5
B100DEE5	274.7	32.7	168	14.1	163	15	249.0	36.0	222	17.1	151	10	250.6	35.8	253	16.7	128	7
B100DEE10	275.6	32.7	159	13.6	152	17	246.7	36.6	212	15.9	139	15	248.3	36.3	235	14.9	116	9
B100E5	275.1	32.8	169	14.8	200	10	252.0	35.8	218	17.3	176	5	254.1	35.5	241	16.3	161	5
B100E10	277.0	33.3	164	13.0	237	8	252.8	36.5	209	15.3	199	4	255.0	36.2	234	15.1	181	3
B100M5	275.0	33.2	170	14.5	209	10	251.3	36.3	219	16.9	173	8	253.5	36.0	249	16.4	147	5
B100M10	276.9	33.7	165	13.2	226	9	252.0	37.0	208.5	15.6	189	4	254.2	36.7	238	14.8	186	4

A.2 Engine performance and emissions of biodiesel diesel blends and biodiesel additives at 2100 rpm

Load	Low load						Medium load						High load					
Fuel	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
B0	230.9	34.2	150	2.7	191	50	220.9	36.8	179	4.4	169	40	213.1	37.9	202	5.6	153	35
B20	235.0	34.4	154	4.3	187	35	225.5	37.1	183	5.5	165	30	217.3	38.0	207	6.3	149	25
B40	239.7	34.6	157	5.6	177	30	234.1	37.1	186	6.9	157	25	222.2	38.1	211	7.87	145	20
B60	246.7	34.5	161	6.9	163	25	238.9	37.2	193	7.9	149	20	228.1	38.1	217	8.9	138	20
B80	252.1	34.7	164	7.2	154	20	245.1	37.3	197	9.2	137	15	234.1	38.2	225	10.7	129	10
B100	257.6	34.8	166	8.3	143	13	251.0	37.8	205	10.4	125	10	239.3	38.2	231	12.4	123	8
B100DEE5	258.0	35.3	160	8.1	142	13	251.7	37.8	200	9.9	117	8	240.7	38.3	227	11.3	119	5
B100DEE10	256.7	35.3	148	6.8	129	12	251.3	37.9	184	8.1	121	8	240.8	38.5	210	10.1	113	5
B100E5	254.6	35.3	154	7.9	146	8	250.0	37.8	200	9.1	131	5	243.6	38.4	229	11.1	134	3
B100E10	258.4	35.9	147	6.2	157	7	255.9	37.9	187	7.9	152	4	245.0	38.9	215	9.8	148	3
B100M5	258.5	35.4	162	8	147	10	253.8	37.8	202	9	128	8	243.8	38.5	226	11	120	5
B100M10	260.2	35.7	155	6.5	154	8	254.1	38.0	186	8.5	147	5	245.2	39.3	219	9.8	138	4

A.3 Engine performance and emissions of biodiesel diesel blends and biodiesel additives at 3000 rpm

Load	Low load						Medium load						High load					
Fuel	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
B0	225.0	35.1	142	2.1	180	45	216.7	36.8	168	2.9	157	35	202.7	39.0	189	4.1	143	30
B20	229.6	35.2	149	2.98	173	35	220.5	37.0	171	3.78	152	25	206.8	39.1	191	5.2	139	20
B40	236.0	35.2	155	3.89	169	30	225.5	37.0	174	4.51	149	25	211.6	39.1	196	5.9	134	18
B60	242.3	35.3	163	4.56	163	25	231.1	37.1	180	5.24	144	20	216.7	39.2	201	6.4	127	15
B80	247.8	35.3	172	5.63	156	20	236.2	37.2	185	6.5	137	15	221.4	39.3	209	7.89	119	8
B100	254.3	35.6	181	6.9	145	10	241.3	37.2	192	7.9	131	7.5	226.1	39.4	214	8.9	111	5
B100DEE5	255.8	35.6	179	5.3	146	15	243.8	37.3	187	6	126	10	227.0	39.5	206	6.3	105	8
B100DEE10	253.5	35.7	160	4.1	136	17.5	240.1	37.5	166	4.7	127	15	224.6	39.7	181	5.3	102	13
B100E5	256.0	35.8	170	3.2	147	10	246.2	37.2	178	3.9	137	7.5	229.2	39.6	202	4.8	116	3
B100E10	262.6	35.8	158	3	159	7.5	246.2	38.0	164	3.4	146	5	234.6	39.8	188	4.2	129	3
B100M5	259.6	35.7	174	3.9	148	10	245.8	37.6	181	4.1	137	7.5	233.2	39.6	203	5.1	113	5
B100M10	261.3	35.9	169	3.3	155	7	246.9	38.3	179	3.6	141	5	237.9	39.8	198	4.4	131	3

Appendix B: Fractionated biodiesel diesel blends and biodiesel additives performance and emission tested by light-duty diesel engine.

B.1 Engine performance and emissions of fractionated biodiesel diesel blends and fractionated biodiesel additives at 1000 rpm

Load	Low load						Medium load						High load					
	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
B0	238.5	33.1	153	3.2	234	55	227.0	35.2	198	5.0	219	45	220.8	36.3	234	6.9	181	40
FB20	243.2	33.2	161	5.0	225	50	230.0	35.5	208	6.1	205	40	225.3	36.6	250	7.3	175	35
FB40	247.8	33.3	169	6.4	216	40	234.7	35.6	219	7.2	189	35	226.3	36.7	265	8.4	161	25
FB60	254.1	33.3	176	8.4	207	35	240.6	35.5	227	9.5	177	30	232.7	36.6	272	10.1	151	20
FB80	262.9	33.5	184	10.2	199	30	246.1	35.6	239	11.5	161	25	237.8	36.8	283	12.3	146	20
FB100	270.6	33.6	197	12.8	188	25	251.7	35.8	247	13.9	154	20	239.7	36.9	295	15.1	139	10
FB100DE5	270.4	33.5	181	12.0	191	26	247.8	36.5	239	13.3	157	20	240.8	37.6	289	14.4	144	15
FB100DEE10	268.3	33.6	172	11.1	195	30	245.6	37.0	219	12.1	165	25	237.6	38.2	261	13.2	151	16
FB100E5	272.8	33.7	186	12.1	193	15	250.8	36.2	233	13.6	168	10	243.8	37.3	281	14.8	157	4
FB100E10	274.7	33.9	170	11.2	201	18	251.5	36.9	221	11.9	181	13	244.5	38.0	264	13.0	169	5
FB10M5	272.7	33.8	191	12.2	189	20	250.0	36.8	236	13.7	161	15	243.0	37.9	283	14.6	153	5
FB10M10	274.6	34.2	173	11.0	195	18	250.7	37.4	225	11.8	179	16	243.7	38.5	262	12.9	164	7

B.2 Engine performance and emissions of fractionated biodiesel diesel blends and fractionated biodiesel additives at 2100 rpm

Load	Low load						Medium load						High load					
	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
B0	230.4	34.2	150	2.7	191	50	220.6	36.9	179	4.4	169	40	212.9	38.9	202	5.6	153	35
FB20	234.5	34.4	158	3.6	185	40	225.1	37.1	189	4.9	160	35	217.0	38.9	211	6.2	148	30
FB40	239.2	34.5	170	4.5	172	30	233.7	37.3	197	5.6	148	30	222.0	38.9	218	7.1	139	25
FB60	245.1	34.4	179	4.9	158	25	239.5	37.5	207	6	139	22.5	227.9	39.0	227	7.8	131	20
FB80	250.5	34.6	187	5.2	148	20	245.7	37.6	218	6.2	126	20	233.9	39.1	236	8.6	122	15
FB100	255.9	34.8	195	5.3	137	15	249.6	37.8	225	7.4	117	12.5	239.0	39.2	246	9.2	112	10
FB100DE5	253.7	35.2	189	5.1	143	15	249.2	37.9	218	7.1	128	12.5	240.4	39.2	234	8.4	121	10
FB100DEE10	252.1	35.4	171	4.7	146	12.5	247.9	38.0	203	6.5	131	12.5	238.6	39.4	218	7.5	127	10
FB100E5	256.9	34.9	182	4.9	150	12.5	251.5	37.9	219	7.3	134	10	243.3	39.3	238	8.2	126	7
FB100E10	256.7	35.8	167	4.6	158	12	252.4	38.0	211	6.2	149	7.5	243.6	39.7	226	7.6	141	5
FB10M5	256.8	35.4	182	5	146	14	252.4	37.9	220	7	129	10	243.4	39.4	239	8.3	123	7.5
FB10M10	258.5	35.9	165	4.5	160	12.5	252.7	38.1	206	6.4	143	7.5	243.9	40.0	228	7.5	135	6

B.3 Engine performance and emissions of fractionated biodiesel diesel blends and fractionated biodiesel additives at 3000 rpm

Load	Low load						Medium load						High load					
	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
B0	224.7	35.1	142	2.1	180	40	216.5	36.8	168	2.9	157	35	202.6	39.0	189	3.7	143	30
FB20	229.3	35.2	151	2.5	169	35	220.3	36.8	176	3.4	149	30	206.6	39.3	198	4.1	136	25
FB40	235.6	35.3	162	2.9	164	30	225.3	37.0	189	3.9	146	25	211.5	39.3	205	4.7	131	20
FB60	241.9	35.4	172	3.4	157	25	230.8	37.2	197	4.3	140	20	216.6	39.4	214	5.2	122	15
FB80	247.4	35.5	183	3.8	143	20	235.9	37.3	205	4.8	131	15	221.2	39.5	222	5.9	113	10
FB100	253.9	35.6	198	4.6	129	10	241.0	37.3	216	5.6	121	8	226.0	39.5	231	6.5	104	6
FB100DE5	252.3	35.6	185	3.9	132	15	241.5	37.3	205	4.8	126	12	225.8	39.7	226	5.9	111	11
FB100DEE10	251.1	35.7	175	3.6	141	18	238.8	37.5	196	5.1	136	16	223.4	39.8	219	6.1	119	14
FB100E5	258.5	35.7	177	3.8	142	10	245.9	37.5	206	4.6	136	8	233.0	39.8	221	5.2	116	5
FB100E10	262.1	35.9	159	3.4	151	8	245.9	37.8	191	4.0	140	5	234.4	39.9	211	5.0	121	3
FB10M5	259.1	35.6	180	3.7	139	10	245.5	37.7	211	4.9	135	8	236.0	39.8	224	5.7	118	6
FB10M10	260.9	36.0	167	3.3	150	9	246.6	38.0	196	4.2	143	7	237.7	40.0	215	5.3	126	3

Appendix C: diesel, biodiesel, Biodiesel diesel blends and their emulsion performance and emission tested by light-duty diesel engine.

C.1 Engine performance and emissions of different fuels and their emulsions at 1000 rpm [102]

Load		Low load						Medium load						High load					
Fuel	Water (%)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
B0	0	240.3	33.5	152	3.8	216	45	230.0	35.0	195	5.1	201	40	226.1	35.6	238	6.3	170	33
	5	242.0	35.0	137	3.4	361	46	231.7	36.5	162	4.6	273	43	227.8	37.2	219	5.7	273	36
	10	243.7	36.7	118	3.2	443	48	233.4	38.3	136	4.3	329	42	229.5	38.9	198	5.4	329	36
	15	245.4	38.5	111	3.1	557	48	235.1	40.2	128	4.0	437	42	231.2	40.9	172	5.2	437	36
B10	0	241.3	33.7	154	4.51	203	35	231.0	35.2	198	6.0	191	29	227.1	35.8	241	7.3	164	33
	5	243.1	35.2	138	4.01	346	37	232.8	36.7	175	5.3	279	31	228.9	37.4	229	6.1	267	34
	10	244.9	36.9	117	3.92	413	37	234.6	38.5	160	5.2	351	32	230.7	39.2	210	5.8	329	35
	15	246.7	38.8	98	3.67	519	37	236.3	40.5	140	5.0	462	32	232.5	41.2	193	5.3	453	35
B20	0	242.1	33.9	157	5.76	198	30	231.8	35.4	206	7.1	187	25	227.9	36.0	251	9.9	163	27
	5	243.9	35.4	139	4.91	316	31	233.6	37.0	178	6.7	268	25	229.7	37.6	230	7.7	259	27
	10	245.7	37.2	119	4.62	391	32	235.4	38.8	159	6.3	343	25	231.5	39.5	203	6.9	322	29
	15	247.5	39.1	105	4.49	512	32	237.2	40.8	139	6.0	444	25	233.3	41.5	194	6.4	446	29
B30	0	242.8	34.1	160	6.85	182	26	232.5	35.6	206	8.3	185	20	228.6	36.3	254	10.4	159	25
	5	244.6	35.7	138	6.23	308	26	234.3	37.3	186	7.5	251	21	230.4	37.9	233	9.0	249	26
	10	240.3	33.5	152	3.8	216	45	230.0	35.0	195	5.1	201	40	232.2	39.8	203	8.2	319	27
	15	242.0	35.0	137	3.4	361	46	231.7	36.5	162	4.6	273	43	233.9	41.9	192	7.5	411	27
B40	0	243.7	36.7	118	3.2	443	48	233.4	38.3	136	4.3	329	42	229.7	36.5	255	11.4	157	18
	5	245.4	38.5	111	3.1	557	48	235.1	40.2	128	4.0	437	42	231.5	38.2	232	9.9	217	21
	10	241.3	33.7	154	4.51	203	35	231.0	35.2	198	6.0	191	29	233.3	40.1	207	8.9	299	21
	15	243.1	35.2	138	4.01	346	37	232.8	36.7	175	5.3	279	31	235.1	42.2	188	8.0	379	21
B100	0	259.5	34.4	175	16.4	165	15	241.0	37.1	225	18.9	165	13	245.7	36.4	265	18.5	149	12
	2.5	261.1	35.1	159	15.9	210	17	244.5	37.5	208	18.4	199	15	247.4	37.1	248	17.2	172	13.2

C.2 Engine performance and emissions of different fuels and their emulsions at 2100 rpm [102]

Load		Low load						Medium load						High load					
Fuel	Water (%)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
B0	0	230.9	34.8	150	2.2	191	41	227.9	35.3	181	3.4	161	33	222.1	36.2	222	4.5	159	28
	5	232.6	36.4	132	2.0	326	42	229.6	36.9	159	3.1	286	35	223.8	37.8	209	4.1	257	31
	10	234.3	38.1	116	1.9	383	43	231.3	38.6	139	2.9	332	34	225.5	39.6	196	3.9	292	33
	15	236.0	40.1	99	1.8	475	43	233.0	40.6	122	2.7	449	34	227.2	41.6	160	3.6	409	32
B10	0	231.9	35.0	151	2.8	185	30	228.9	35.5	184	4.0	161	22	223.1	36.4	228	5.2	141	19
	5	233.7	36.6	134	2.6	297	30	230.7	37.1	163	3.6	227	23	224.9	38.0	209	4.6	206	19
	10	235.5	38.4	110	2.4	343	31	232.5	38.9	154	3.3	292	25	226.7	39.9	178	4.0	270	21
	15	237.3	40.3	103	2.3	436	33	234.3	40.9	129	3.0	397	25	228.5	41.9	165	3.0	378	20
B20	0	232.7	35.3	159	3.4	181	25	229.7	35.7	186	4.7	158	21	223.9	36.6	231	5.6	139	19
	5	234.5	36.9	129	2.9	292	26	231.5	37.3	168	4.2	243	22	225.7	38.3	204	5.0	243	19
	10	236.3	38.7	119	2.7	339	26	233.3	39.2	150	3.9	276	22	227.5	40.2	181	4.3	279	20
	15	238.1	40.7	107	2.4	437	27	235.1	41.2	140	3.5	379	22	229.3	42.3	165	3.6	374	20
B30	0	233.4	35.5	162	3.9	173	21	230.4	36.0	188	5.1	151	18	224.6	36.9	237	5.9	135	16
	5	235.2	37.2	134	3.4	284	22	232.2	37.6	171	4.6	251	18	226.4	38.6	205	5.4	240	16
	10	237.0	39.0	125	3.1	333	23	234.0	39.5	150	4.0	287	19	228.2	40.5	179	5.0	280	16
	15	238.7	41.1	107	2.9	417	23	235.7	41.6	139	3.8	353	19	229.9	42.6	163	4.4	334	16
B40	0	234.5	35.7	163	4.7	172	15	231.5	36.2	190	5.8	149	12	225.7	37.1	238	6.8	133	10
	5	236.3	37.4	148	4.1	246	15	233.3	37.9	171	5.3	228	13	227.5	38.8	215	6.0	213	11
	10	238.1	39.3	128	3.8	327	15	235.1	39.8	150	4.7	259	13	229.3	40.8	190	5.6	249	12
	15	239.9	41.4	108	3.5	411	17	235.9	41.9	138	4.3	352	14	231.1	43.0	179	5.1	316	12
B100	0	239.1	37.4	174	8.3	143	15	242.3	36.9	205	10.4	125	10	224.0	39.9	256	8	123	12
	2.5	240.5	38.1	161	7.9	199	16	244.6	37.5	185	10	168	12	229.3	40.0	236	9	157	13.2

C.3 Engine performance and emissions of different fuels and their emulsions at 3000 rpm [102]

Load		Low load						Medium load						High load					
Fuel	Water (%)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
B0	0	235.0	34.2	142	1.9	183	39	228.7	35.2	169	2.3	157	30	224.1	35.9	179	3.0	148	24
	5	236.7	35.8	121	1.6	262	41	230.4	36.7	133	2.0	221	30	225.8	37.5	144	2.6	208	26
	10	238.4	37.5	105	1.5	305	43	232.1	38.5	118	1.9	281	31	227.5	39.3	135	2.4	229	26
	15	240.1	39.4	93	1.4	407	43	233.8	40.5	118	1.9	341	31	229.2	41.3	141	2.2	296	26
B10	0	236.0	34.4	146	1.8	179	21	229.7	35.4	178	2.3	152	17	225.1	36.1	188	3.1	136	15
	5	237.8	36.0	119	1.4	245	22	231.5	37.0	139	2.1	203	17	226.9	37.7	155	2.7	188	16
	10	239.6	37.7	107	1.4	297	22	233.3	38.7	125	2.0	239	18	228.7	39.5	136	2.5	217	17
	15	241.4	39.7	91	1.2	375	23	235.0	40.7	113	1.6	307	18	230.5	41.5	125	2.3	276	17
B20	0	236.8	34.6	151	2.0	176	21	230.5	35.6	181	3.9	147	18	225.9	36.3	185	4.7	131	15
	5	238.6	36.2	121	1.7	237	22	232.3	37.2	157	3.2	200	20	227.7	38.0	169	4.1	182	18
	10	240.4	38.0	107	1.5	292	22	234.1	39.0	134	2.8	235	20	229.5	39.8	142	3.4	212	18
	15	242.2	40.0	90	1.3	356	22	235.9	41.1	114	2.3	279	21	231.3	41.9	129	2.9	241	18
B30	0	237.5	34.9	152	2.4	172	18	231.2	35.8	182	4.1	143	12	226.6	36.6	187	5.0	128	14
	5	239.3	36.5	129	2.4	236	19	233.0	37.5	160	4.0	187	15	228.4	38.3	167	4.4	177	15
	10	241.0	38.3	117	2.1	273	17	234.7	39.4	139	3.3	218	16	230.2	40.2	148	3.6	206	16
	15	242.8	40.4	110	1.9	322	18	236.5	41.5	122	4.9	254	17	231.9	42.3	131	3.1	232	16
B40	0	238.6	35.1	152	3.2	172	12	232.3	36.0	184	4.5	142	11	227.7	36.8	194	5.8	129	8
	5	240.4	36.8	129	3.1	236	12	234.1	37.7	161	4.2	182	12	229.5	38.5	171	5.0	175	9
	10	242.2	38.6	117	2.8	273	13	235.9	39.6	140	4.0	216	12	231.3	40.4	152	4.2	204	10
	15	245.0	40.4	110	2.6	322	13	237.7	41.4	126	4.3	239	12	234.1	42.2	139	3.7	227	13
B100	0	244.4	36.6	181	6.9	145	9	233.0	38.3	192	7.3	131	10	225.9	39.6	214	8.9	111	5
	2.5	246.0	37.3	157	6.5	196	10	235.1	39.0	171	6.8	174	11	228.0	40.2	198	8.2	158	8

Appendix D: Emulsion biodiesel diesel blends with 10% water content and (2.5% and 5%) ammonium hydroxides performance and emission tested by light-duty diesel engine.

D.1 Engine performance and emissions of emulsion fuels with ammonium hydroxide at 1000 rpm

Load		Low load						Medium load						High load					
Fuel	AH (%)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
EB0W10	0	252.2	35.4	118	3.2	443	47.9	232.2	38.5	136	4.3	329	42.01	236.9	37.7	198	5.42	329	35.9
	5	252.5	35.9	126	2.7	427	48	234.2	38.7	159	4.2	328	42.5	239.3	37.8	218	5.24	308	35
	10	253.0	36.3	131	2.3	412	50	234.7	39.1	165	3.9	299	45	240.0	38.3	229	5	289	36.7
EB10W10	0	253.9	35.6	117	3.92	413	37	235.3	38.4	160	5.17	351	31.5	239.9	37.7	210	5.84	329	34.7
	5	254.0	36.0	127	3.12	399	37.5	235.5	38.9	162	4.81	325	32.5	240.5	38.1	220	5.7	284	27
	10	254.3	36.5	132	2.94	380	40	235.9	39.3	170	4.5	306	34	241.2	38.5	231	5.3	279	28.5
EB20W10	0	256.2	35.7	119	4.62	391	31.8	236.5	38.6	159	6.31	343	24.6	241.4	37.8	203	6.91	322	28.5
	5	256.5	36.1	130	4.3	371	32.5	236.8	39.1	167	5.8	319	25	241.8	38.3	238	6.37	294	26
	10	257.1	36.5	135	3.9	360	35	237.4	39.5	174	5.51	302	28	243.0	38.6	243	6.12	270	28
EB30E10	0	257.5	35.9	112	5.86	382	26.8	238.5	38.7	160	6.97	337	21.4	243.8	37.9	203	8.22	319	26.7
	5	257.3	36.4	135	4.9	367	27.5	239.0	39.2	170	6.3	315	22.5	243.6	38.4	238	7.89	289	22.5
	10	257.9	36.7	141	4.7	349	30	241.6	39.2	179	5.7	294	26	244.9	38.7	247	7.13	263	25

D.2 Engine performance and emissions of emulsion fuels with ammonium hydroxide at 2100 rpm

Load		Low load						Medium load						High load					
Fuel	AH (%)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
EB0W10	0	243.1	36.7	116	1.9	383	43	232.8	38.4	139	2.9	332	34	219.3	40.7	196	3.9	292	33
	5	250.5	36.1	128	1.7	357	45	235.7	38.4	153	2.8	300	35	220.3	41.1	214	3.6	251	35
	10	251.7	36.5	132	1.6	341	48	236.1	38.9	164	2.4	284	38	221.1	41.5	220	3.5	229	38
EB10W10	0	243.5	37.1	110	2.4	343	31	234.5	38.5	154	3.3	292	25	223.0	40.5	178	4.0	270	21
	5	251.9	36.3	133	2.3	327	38	236.3	38.7	167	3.4	279	33	225.4	40.6	217	3.8	239	28
	10	253.8	36.6	141	2.0	318	40	237.2	39.1	173	3.2	270	35	226.8	40.9	229	3.6	217	29
EB20W10	0	241.1	37.9	119	2.7	339	26	236.3	38.7	150	3.9	276	22	223.5	40.9	181	4.3	279	20
	5	243.6	38.0	134	2.5	305	33	237.7	38.9	168	3.5	259	28	226.8	40.8	223	4.0	233	20
	10	244.8	38.3	144	2.2	291	36	238.9	39.3	175	3.3	241	30	228.5	41.1	235	3.8	205	22
EB30E10	0	244.7	37.8	125	3.1	333	23	237.4	38.9	150	4.0	287	19	223.9	41.3	179	5.0	280	16
	5	245.0	38.2	138	2.9	289	29	239.1	39.1	168	4.0	246	20	228.1	41.0	228	4.8	225	20
	10	246.8	38.4	147	2.6	282	32	240.3	39.4	177	3.8	232	23	229.4	41.3	239	4.2	203	23

D.3 Engine performance and emissions of emulsion fuels with ammonium hydroxide at 3000 rpm

Load		Low load						Medium load						High load					
Fuel	AH (%)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)	BSFC (g/kWh)	BTE (%)	NOx (ppm)	Smoke (%)	CO (ppm)	HC (ppm)
EB0W10	0	236.5	37.8	105	1.5	305	42.5	230.1	38.8	118	1.9	281	31.4	221.0	40.4	135	2.4	229	26
	5	242.2	37.4	124	1.3	279	42.5	232.0	39.0	130	1.7	259	32.5	223.9	40.4	142	2.2	209	27.5
	10	247.0	37.2	132	1.2	262	45	236.0	38.9	136	1.5	250	35	225.2	40.8	149	2.0	196	29
EB10W10	0	238.1	37.9	107	1.4	297	22.3	231.3	39.1	125	2.0	239	17.6	222.7	40.6	136	2.5	217	16.5
	5	243.9	37.5	129	1.3	271	37.5	233.3	39.2	134	1.8	222	27.5	225.8	40.5	143	2.3	195	22.5
	10	248.5	37.3	135	1.2	259	40	237.9	39.0	141	1.6	210	30	229.1	40.5	152	2.1	187	25
EB20W10	0	239.4	38.2	107	1.5	292	22.3	233.1	39.2	134	2.8	235	20.4	224.2	40.8	142	3.4	212	18
	5	245.4	37.7	129	1.3	253	37.5	235.4	39.3	138	2.4	219	22.5	226.5	40.9	149	2.9	189	19
	10	251.8	37.2	138	1.1	241	40	240.8	39.0	147	2.1	203	25	231.7	40.5	156	2.7	177	20
EB30E10	0	241.0	38.3	117	2.1	273	17.3	232.7	39.7	139	3.3	218	16	225.9	40.9	148	3.6	206	15.5
	5	247.1	37.9	131	1.8	244	32.5	237.3	39.4	145	2.9	206	22.5	230.4	40.6	154	3.2	181	17.5
	10	253.6	37.4	139	1.5	229	35	243.6	38.9	153	2.6	197	22.5	234.9	40.3	161	3.0	169	19

Appendix E: Heavy-duty diesel engine emission form various fuels and emulsion fuels

E.1 Heavy-duty diesel engine average emission fueled with various fuel at two idling conditions

Engine speed	1200 (rpm)			1500 (rpm)		
Fuel type	NOx (ppm)	CO (ppm)	HC (ppm)	NOx (ppm)	CO (ppm)	HC (ppm)
B0	198	304.7	42	203.4	263.2	39
B100	223	214.2	25	220.7	132.8	20
K100	235	271.2	43	210.5	286.8	32
n-heptan	232	176.5	27	218.0	119.6	25
B30	211	289.3	36	210.6	206.8	31
K70	237	259.3	37	215.5	242.4	25
EB0W10	174	570.8	56	148.4	431.2	54
EB0W15	165	604.7	59	136.1	450.2	58
EB30W10	179	488.7	43	160.2	409	43
EB30W15	172	514.3	50	147.3	426.8	50
EKW10	188	579.2	53	144.6	465.8	53
EKW15	175	598.8	57	136.9	493.4	54
EK70W10	200	501.7	46	167.1	440.6	46
EK70W15	190	512.7	53	147.8	462.6	52

Appendix F: Measuring equipment used



Figure F.1 Weighing scale

Figure F.2 Viscometer

Figure F.3 Calorimeter

Figure F.4 Dynamometer

Figure F.5 Master-sizer 2000



Figure F.6 multi-gas analyzer.

Figure F.7 CO analyzer

Figure F.8 Smoke opacity meter

Figure F.9 Graduated cylinder.

Figure F.10 Thermometer

References

- [1] “Oil.” [Online]. Available: <https://www.iea.org/about/faqs/oil/>. [Accessed: 17-Apr-2017].
- [2] “Short-Term Energy Outlook - U.S. Energy Information Administration (EIA).” [Online]. Available: https://www.eia.gov/outlooks/steo/report/global_oil.cfm. [Accessed: 17-Apr-2017].
- [3] “Basic Statistics,” *Canadian Association of Petroleum Producers*. [Online]. Available: <http://www.capp.ca/publications-and-statistics/statistics/basic-statistics>. [Accessed: 20-Apr-2017].
- [4] S. C. Government of Canada, “Sales of fuel used for road motor vehicles, by province and territory (Alberta, British Columbia, Yukon, Northwest Territories, Nunavut),” 14-Nov-2016. [Online]. Available: <http://www.statcan.gc.ca/tables-tableaux/sum-som/101/cst01/trade37c-eng.htm>. [Accessed: 20-Apr-2017].
- [5] A. Faiz, C. S. Weaver, and M. P. Walsh, *Air pollution from motor vehicles: standards and technologies for controlling emissions*. World Bank Publications, 1996.
- [6] N. Nordin, “Introduction to combustion in diesel engines,” *PowerPoint PDF File. Scania*, 2005.
- [7] W. Zhang, Z. Chen, W. Li, G. Shu, B. Xu, and Y. Shen, “Influence of EGR and oxygen-enriched air on diesel engine NO–Smoke emission and combustion characteristic,” *Applied Energy*, vol. 107, pp. 304–314, Jul. 2013.
- [8] N. R. Council and others, *Open access and the public domain in digital data and information for science: proceedings of an international symposium*. National Academies Press, 2004.
- [9] National Research Council (U.S.), National Research Council (U.S.), and National Research Council (U.S.), Eds., *Cost, effectiveness, and deployment of fuel economy technologies for light-duty vehicles*. Washington, D.C: National Academies Press, 2015.
- [10] S. P. R. Yadav, C. G. Saravanan, and M. Kannan, “Influence of injection timing on DI diesel engine characteristics fueled with waste transformer oil,” *Alexandria Engineering Journal*, vol. 54, no. 4, pp. 881–888, Dec. 2015.

- [11] A. K. Agarwal, D. K. Srivastava, A. Dhar, R. K. Maurya, P. C. Shukla, and A. P. Singh, "Effect of fuel injection timing and pressure on combustion, emissions and performance characteristics of a single cylinder diesel engine," *Fuel*, vol. 111, pp. 374–383, Sep. 2013.
- [12] L. Wei, C. Yao, G. Han, and W. Pan, "Effects of methanol to diesel ratio and diesel injection timing on combustion, performance and emissions of a methanol port premixed diesel engine," *Energy*, vol. 95, pp. 223–232, Jan. 2016.
- [13] S. Tangöz, S. O. Akansu, N. Kahraman, and Y. Malkoç, "Effects of compression ratio on performance and emissions of a modified diesel engine fueled by HCNG," *International Journal of Hydrogen Energy*, vol. 40, no. 44, pp. 15374–15380, Nov. 2015.
- [14] A. Fayyazbakhsh and V. Pirouzfard, "Investigating the influence of additives-fuel on diesel engine performance and emissions: Analytical modeling and experimental validation," *Fuel*, vol. 171, pp. 167–177, May 2016.
- [15] Y. İçingür and D. Altıparmak, "Effect of fuel cetane number and injection pressure on a DI Diesel engine performance and emissions," *Energy conversion and management*, vol. 44, no. 3, pp. 389–397, 2003.
- [16] M. M. Roy, J. Calder, W. Wang, A. Mangad, and F. C. M. Diniz, "Cold start idle emissions from a modern Tier-4 turbo-charged diesel engine fueled with diesel-biodiesel, diesel-biodiesel-ethanol, and diesel-biodiesel-diethyl ether blends," *Applied Energy*, vol. 180, pp. 52–65, Oct. 2016.
- [17] M. M. Roy, J. Calder, W. Wang, A. Mangad, and F. C. M. Diniz, "Emission analysis of a modern Tier 4 DI diesel engine fueled by biodiesel-diesel blends with a cold flow improver (Wintron Synergy) at multiple idling conditions," *Applied Energy*, vol. 179, pp. 45–54, Oct. 2016.
- [18] D. Russo, M. Dassisti, V. Lawlor, and A. G. Olabi, "State of the art of biofuels from pure plant oil," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 6, pp. 4056–4070, Aug. 2012.
- [19] J. R. Mielenz, "Ethanol production from biomass: technology and commercialization status," *Current opinion in microbiology*, vol. 4, no. 3, pp. 324–329, 2001.
- [20] S. Chattopadhyay and R. Sen, "Fuel properties, engine performance and environmental benefits of biodiesel produced by a green process," *Applied Energy*, vol. 105, pp. 319–326, May 2013.

- [21] “Use of Biodiesel - Energy Explained, Your Guide To Understanding Energy - Energy Information Administration.” [Online]. Available: https://www.eia.gov/energyexplained/index.cfm?page=biofuel_biodiesel_use. [Accessed: 28-Apr-2017].
- [22] D. Dessureault and J. Zimmerman, “Canada Biofuel Annual 2016,” USDA Foreign Agricultural Service, Attawa, Canada, public distribution CA16038, Aug. 2016.
- [23] Transit Cooperative Research Program, Transportation Research Board, and National Academies of Sciences, Engineering, and Medicine, *Use of Biodiesel in a Transit Fleet*. Washington, D.C.: Transportation Research Board, 2007.
- [24] L. Sun, M. Li, C. Ma, P. Li, and J. Li, “Preparation and Evaluation of Lubricity Additives for Low-Sulfur Diesel Fuel,” *Energy & Fuels*, vol. 30, no. 7, pp. 5672–5676, Jul. 2016.
- [25] M. M. Roy, W. Wang, and J. Bujold, “Biodiesel production and comparison of emissions of a DI diesel engine fueled by biodiesel–diesel and canola oil–diesel blends at high idling operations,” *Applied Energy*, vol. 106, pp. 198–208, Jun. 2013.
- [26] F. Sundus, M. A. Fazal, and H. H. Masjuki, “Tribology with biodiesel: A study on enhancing biodiesel stability and its fuel properties,” *Renewable and Sustainable Energy Reviews*, vol. 70, pp. 399–412, Apr. 2017.
- [27] M. M. K. Bhuiya, M. G. Rasul, M. M. K. Khan, N. Ashwath, A. K. Azad, and M. A. Hazrat, “Prospects of 2nd generation biodiesel as a sustainable fuel – Part 2: Properties, performance and emission characteristics,” *Renewable and Sustainable Energy Reviews*, vol. 55, pp. 1129–1146, Mar. 2016.
- [28] J. Žaglinskis, K. Lukács, and á. Bereczky, “Comparison of properties of a compression ignition engine operating on diesel–biodiesel blend with methanol additive,” *Fuel*, vol. 170, pp. 245–253, Apr. 2016.
- [29] ASTM International, “ASTM D2500-16b Standard Test Method for Cloud Point of Petroleum Products and Liquid Fuels,” ASTM International, 2016.
- [30] ASTM International, “ASTM D7346-15 Standard Test Method for No Flow Point and Pour Point of Petroleum Products and Liquid Fuels,” ASTM International, 2015.
- [31] Jeremy Moorhouse and Michael Wolinetz, “Biofuels in Canada: Tracking progress in tackling greenhouse gas emissions from transportation fuels (Clean Energy Canada, 2016),” Mar. 2016.

- [32] M. Mofijur *et al.*, “Properties and use of *Moringa oleifera* biodiesel and diesel fuel blends in a multi-cylinder diesel engine,” *Energy Conversion and Management*, vol. 82, pp. 169–176, Jun. 2014.
- [33] G. Liu, “Development of low-temperature properties on biodiesel fuel: a review: Low-temperature properties of biodiesel fuel,” *International Journal of Energy Research*, vol. 39, no. 10, pp. 1295–1310, Aug. 2015.
- [34] M.-H. Yuan, Y.-H. Chen, J.-H. Chen, and Y.-M. Luo, “Dependence of cold filter plugging point on saturated fatty acid profile of biodiesel blends derived from different feedstocks,” *Fuel*, vol. 195, pp. 59–68, May 2017.
- [35] S. H. Hamdan, W. W. F. Chong, J.-H. Ng, M. J. Ghazali, and R. J. K. Wood, “Influence of fatty acid methyl ester composition on tribological properties of vegetable oils and duck fat derived biodiesel,” *Tribology International*, Dec. 2016.
- [36] H. M. Mahmudul, F. Y. Hagos, R. Mamat, A. A. Adam, W. F. W. Ishak, and R. Alenezi, “Production, characterization and performance of biodiesel as an alternative fuel in diesel engines – A review,” *Renewable and Sustainable Energy Reviews*, vol. 72, pp. 497–509, May 2017.
- [37] M. Todaka, “Reduction of the Cloud Point of Biodiesel by Combination of Various Factors,” *International Journal of Chemical Engineering and Applications*, vol. 5, no. 6, pp. 479–482, Dec. 2014.
- [38] M. Serrano, R. Oliveros, M. Sánchez, A. Moraschini, M. Martínez, and J. Aracil, “Influence of blending vegetable oil methyl esters on biodiesel fuel properties: Oxidative stability and cold flow properties,” *Energy*, vol. 65, pp. 109–115, Feb. 2014.
- [39] A. Sarin, R. Arora, N. P. Singh, R. Sarin, R. K. Malhotra, and S. Sarin, “Blends of Biodiesels Synthesized from Non-edible and Edible Oils: Effects on the Cold Filter Plugging Point,” *Energy & Fuels*, vol. 24, no. 3, pp. 1996–2001, Mar. 2010.
- [40] P. Verma, M. P. Sharma, and G. Dwivedi, “Evaluation and enhancement of cold flow properties of palm oil and its biodiesel,” *Energy Reports*, vol. 2, pp. 8–13, Nov. 2016.
- [41] M. S. Graboski and R. L. McCormick, “Combustion of fat and vegetable oil derived fuels in diesel engines,” *Progress in energy and combustion science*, vol. 24, no. 2, pp. 125–164, 1998.

- [42] Q. Liu, S. Singh, and A. Green, “High-Oleic and High-Stearic Cottonseed Oils: Nutritionally Improved Cooking Oils Developed Using Gene Silencing,” *Journal of the American College of Nutrition*, vol. 21, no. sup3, p. 205S–211S, Jun. 2002.
- [43] T. Buhr *et al.*, “Ribozyme termination of RNA transcripts down-regulate seed fatty acid genes in transgenic soybean,” *The Plant Journal*, vol. 30, no. 2, pp. 155–163, 2002.
- [44] G. Graef *et al.*, “A high-oleic-acid and low-palmitic-acid soybean: agronomic performance and evaluation as a feedstock for biodiesel,” *Plant Biotechnology Journal*, vol. 7, no. 5, pp. 411–421, Jun. 2009.
- [45] M. E. González Gómez, R. Howard-Hildige, J. J. Leahy, and B. Rice, “Winterisation of waste cooking oil methyl ester to improve cold temperature fuel properties,” *Fuel*, vol. 81, no. 1, pp. 33–39, Jan. 2002.
- [46] S. Nainwal, N. Sharma, A. S. Sharma, S. Jain, and S. Jain, “Cold flow properties improvement of *Jatropha curcas* biodiesel and waste cooking oil biodiesel using winterization and blending,” *Energy*, vol. 89, pp. 702–707, Sep. 2015.
- [47] Á. Pérez, A. Casas, C. M. Fernández, M. J. Ramos, and L. Rodríguez, “Winterization of peanut biodiesel to improve the cold flow properties,” *Bioresource Technology*, vol. 101, no. 19, pp. 7375–7381, Oct. 2010.
- [48] R. O. Dunn, *Improving the cold flow properties of biodiesel by fractionation*. INTECH Open Access Publisher, 2011.
- [49] O’Brien and Richard D, *Fats and oils: formulating and processing for applications*. CRC press, 2008.
- [50] G. Knothe, “Improving biodiesel fuel properties by modifying fatty ester composition,” *Energy & Environmental Science*, vol. 2, no. 7, p. 759, 2009.
- [51] R. O. Dunn, M. W. Shockley, and M. O. Bagby, “Improving the low-temperature properties of alternative diesel fuels: Vegetable oil-derived methyl esters,” *J Am Oil Chem Soc*, vol. 73, no. 12, pp. 1719–1728, Dec. 1996.
- [52] R. D. Lanjekar and D. Deshmukh, “A review of the effect of the composition of biodiesel on NO_x emission, oxidative stability and cold flow properties,” *Renewable and Sustainable Energy Reviews*, vol. 54, pp. 1401–1411, Feb. 2016.
- [53] D. Mei, Y. Luo, W. Tan, and Y. Yuan, “Crystallization behavior of fatty acid methyl esters and biodiesel based on differential scanning calorimetry and thermodynamic

- model,” *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 38, no. 15, pp. 2312–2318, Aug. 2016.
- [54] R. Ghanei, “Improving cold-flow properties of biodiesel through blending with nonedible castor oil methyl ester,” *Environ. Prog. Sustainable Energy*, vol. 34, no. 3, pp. 897–902, May 2015.
- [55] W. Zhao *et al.*, “Improving the cold flow properties of high-proportional waste cooking oil biodiesel blends with mixed cold flow improvers,” *RSC Adv.*, vol. 6, no. 16, pp. 13365–13370, 2016.
- [56] Z. Guo, S. Wang, and X. Wang, “Stability mechanism investigation of emulsion fuels from biomass pyrolysis oil and diesel,” *Energy*, vol. 66, pp. 250–255, Mar. 2014.
- [57] S. S. Reham, H. H. Masjuki, M. A. Kalam, I. Shancita, I. M. Rizwanul Fattah, and A. M. Ruhul, “Study on stability, fuel properties, engine combustion, performance and emission characteristics of biofuel emulsion,” *Renewable and Sustainable Energy Reviews*, vol. 52, pp. 1566–1579, Dec. 2015.
- [58] V. Castel, A. C. Rubiolo, and C. R. Carrara, “Droplet size distribution, rheological behavior and stability of corn oil emulsions stabilized by a novel hydrocolloid (Brea gum) compared with gum arabic,” *Food Hydrocolloids*, vol. 63, pp. 170–177, Feb. 2017.
- [59] A. NEEDS, “time-saving guide to emulsifier selection,” 1976.
- [60] Y. Li, Z. Zhang, B. Ge, X. Men, and Q. Xue, “A versatile and efficient approach to separate both surfactant-stabilized water-in-oil and oil-in-water emulsions,” *Separation and Purification Technology*, vol. 176, pp. 1–7, Apr. 2017.
- [61] T. S. H. Leong, M. Zhou, N. Kukan, M. Ashokkumar, and G. J. O. Martin, “Preparation of water-in-oil-in-water emulsions by low frequency ultrasound using skim milk and sunflower oil,” *Food Hydrocolloids*, vol. 63, pp. 685–695, Feb. 2017.
- [62] C.-Y. Lin and L.-W. Chen, “Comparison of fuel properties and emission characteristics of two- and three-phase emulsions prepared by ultrasonically vibrating and mechanically homogenizing emulsification methods,” *Fuel*, vol. 87, no. 10–11, pp. 2154–2161, Aug. 2008.
- [63] M. R. Seifi, S. R. Hassan-Beygi, B. Ghobadian, U. Desideri, and M. Antonelli, “Experimental investigation of a diesel engine power, torque and noise emission using water–diesel emulsions,” *Fuel*, vol. 166, pp. 392–399, Feb. 2016.

- [64] Shehnaz *et al.*, “Polyaniline-based electrocatalysts through emulsion polymerization: Electrochemical and electrocatalytic performances,” *Journal of Energy Chemistry*, vol. 26, no. 1, pp. 182–192, Jan. 2017.
- [65] F. Y. Hagos, O. M. Ali, R. Mamat, and A. A. Abdullah, “Effect of emulsification and blending on the oxygenation and substitution of diesel fuel for compression ignition engine,” *Renewable and Sustainable Energy Reviews*, vol. 75, pp. 1281–1294, Aug. 2017.
- [66] M. M. Roy, W. Wang, and M. Alawi, “Performance and emissions of a diesel engine fueled by biodiesel–diesel, biodiesel–diesel-additive and kerosene–biodiesel blends,” *Energy Conversion and Management*, vol. 84, pp. 164–173, Aug. 2014.
- [67] G. J. Suppes *et al.*, “Multifunctional Diesel Fuel Additives from Triglycerides,” *Energy & Fuels*, vol. 15, no. 1, pp. 151–157, Jan. 2001.
- [68] S. Imtenan, H. H. Masjuki, M. Varman, I. M. Rizwanul Fattah, H. Sajjad, and M. I. Arbab, “Effect of n-butanol and diethyl ether as oxygenated additives on combustion–emission–performance characteristics of a multiple cylinder diesel engine fuelled with diesel–jatropha biodiesel blend,” *Energy Conversion and Management*, vol. 94, pp. 84–94, Apr. 2015.
- [69] P. Mihaela, R. Josef, N. Monica, and Z. Rudolf, “Perspectives of safflower oil as biodiesel source for South Eastern Europe (comparative study: Safflower, soybean and rapeseed),” *Fuel*, vol. 111, pp. 114–119, Sep. 2013.
- [70] J. E *et al.*, “Effect of different technologies on combustion and emissions of the diesel engine fueled with biodiesel: A review,” *Renewable and Sustainable Energy Reviews*, vol. 80, pp. 620–647, Dec. 2017.
- [71] K. Sivaramakrishnan and P. Ravikumar, “Determination of higher heating value of biodiesels,” *International Journal of Engineering Science and Technology*, vol. 3, no. 11, pp. 7981–7987, 2011.
- [72] M. S. M. Zaharin, N. R. Abdullah, G. Najafi, H. Sharudin, and T. Yusaf, “Effects of physicochemical properties of biodiesel fuel blends with alcohol on diesel engine performance and exhaust emissions: A review,” *Renewable and Sustainable Energy Reviews*, vol. 79, pp. 475–493, 2017.
- [73] M. Krishnamoorthi and R. Malayalamurthi, “Experimental investigation on performance, emission behavior and exergy analysis of a variable compression ratio engine fueled with

- diesel - aegle marmelos oil - diethyl ether blends,” *Energy*, vol. 128, pp. 312–328, Jun. 2017.
- [74] E. Hürdoğan, C. Ozalp, O. Kara, and M. Ozcanli, “Experimental investigation on performance and emission characteristics of waste tire pyrolysis oil–diesel blends in a diesel engine,” *International Journal of Hydrogen Energy*, Jan. 2017.
- [75] H. E. Saleh, “Effect of exhaust gas recirculation on diesel engine nitrogen oxide reduction operating with jojoba methyl ester,” *Renewable Energy*, vol. 34, no. 10, pp. 2178–2186, Oct. 2009.
- [76] H. G. How, H. H. Masjuki, M. A. Kalam, and Y. H. Teoh, “Engine Performance, Emission and Combustion Characteristics of a Common-rail Diesel Engine Fuelled with Bioethanol as a Fuel Additive in Coconut Oil Biodiesel Blends,” *Energy Procedia*, vol. 61, pp. 1655–1659, 2014.
- [77] H. Aydin and H. Bayindir, “Performance and emission analysis of cottonseed oil methyl ester in a diesel engine,” *Renewable Energy*, vol. 35, no. 3, pp. 588–592, Mar. 2010.
- [78] A. M. Ithnin, M. A. Ahmad, M. A. A. Bakar, S. Rajoo, and W. J. Yahya, “Combustion performance and emission analysis of diesel engine fuelled with water-in-diesel emulsion fuel made from low-grade diesel fuel,” *Energy Conversion and Management*, vol. 90, pp. 375–382, Jan. 2015.
- [79] D. H. Qi, H. Chen, R. D. Matthews, and Y. Z. Bian, “Combustion and emission characteristics of ethanol–biodiesel–water micro-emulsions used in a direct injection compression ignition engine,” *Fuel*, vol. 89, no. 5, pp. 958–964, May 2010.
- [80] D. Ogunkoya, S. Li, O. J. Rojas, and T. Fang, “Performance, combustion, and emissions in a diesel engine operated with fuel-in-water emulsions based on lignin,” *Applied Energy*, vol. 154, pp. 851–861, Sep. 2015.
- [81] P. Baskar and A. Senthil Kumar, “Experimental investigation on performance characteristics of a diesel engine using diesel-water emulsion with oxygen enriched air,” *Alexandria Engineering Journal*, vol. 56, no. 1, pp. 137–146, Mar. 2017.
- [82] H. C. Ong, A. S. Silitonga, H. H. Masjuki, T. M. I. Mahlia, W. T. Chong, and M. H. Boosroh, “Production and comparative fuel properties of biodiesel from non-edible oils: *Jatropha curcas*, *Sterculia foetida* and *Ceiba pentandra*,” *Energy Conversion and Management*, vol. 73, pp. 245–255, Sep. 2013.

- [83] A. E. Atabani, A. S. Silitonga, I. A. Badruddin, T. M. I. Mahlia, H. H. Masjuki, and S. Mekhilef, "A comprehensive review on biodiesel as an alternative energy resource and its characteristics," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 4, pp. 2070–2093, May 2012.
- [84] A. S. Silitonga, H. H. Masjuki, T. M. I. Mahlia, H. C. Ong, W. T. Chong, and M. H. Boosroh, "Overview properties of biodiesel diesel blends from edible and non-edible feedstock," *Renewable and Sustainable Energy Reviews*, vol. 22, pp. 346–360, Jun. 2013.
- [85] M. S. Graboski, R. L. McCormick, T. L. Alleman, and A. M. Herring, "The effect of biodiesel composition on engine emissions from a DDC series 60 diesel engine," *National Renewable Energy Laboratory (Report No: NREL/SR-510-31461)*, 2003.
- [86] M. Lapuerta, O. Armas, and J. Rodriguezfernandez, "Effect of biodiesel fuels on diesel engine emissions," *Progress in Energy and Combustion Science*, vol. 34, no. 2, pp. 198–223, Apr. 2008.
- [87] Y. H. Tan, M. O. Abdullah, C. Nolasco-Hipolito, N. S. A. Zauzi, and G. W. Abdullah, "Engine performance and emissions characteristics of a diesel engine fueled with diesel-biodiesel-bioethanol emulsions," *Energy Conversion and Management*, vol. 132, pp. 54–64, Jan. 2017.
- [88] K.-B. Nguyen, T. Dan, and I. Asano, "Effect of double injection on combustion, performance and emissions of Jatropha water emulsion fueled direct-injection diesel engine," *Energy*, vol. 80, pp. 746–755, Feb. 2015.
- [89] R. Senthil, K. Arunan, R. Silambarasan, and others, "Experimental Investigation of a Diesel Engine fueled with emulsified biodiesel," *International Journal of ChemTech Research*, vol. 8, no. 1, pp. 190–195, 2015.
- [90] E. D. Scarpete, "Diesel-Water Emulsion, An Alternative Fuel To Reduce Diesel Engine Emissions. A Review," *Machines, Technologies, Materials*, vol. 7, pp. 13–16, 2013.
- [91] A. K. Hasannuddin *et al.*, "Performance, emissions and lubricant oil analysis of diesel engine running on emulsion fuel," *Energy Conversion and Management*, vol. 117, pp. 548–557, Jun. 2016.
- [92] A. Munack, "Books: Biodiesel – A comprehensive handbook. Martin Mittelbach, Claudia Remschmidt (Ed.)," *Biotechnology Journal*, vol. 1, no. 1, pp. 102–102, Jan. 2006.

- [93] S. P. Singh and D. Singh, “Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review,” *Renewable and Sustainable Energy Reviews*, vol. 14, no. 1, pp. 200–216, Jan. 2010.
- [94] S. D. Romano and P. A. Sorichetti, *Dielectric Spectroscopy in Biodiesel Production and Characterization*. London: Springer London, 2011.
- [95] “Tween® 80 | Sigma-Aldrich.” [Online]. Available: <http://www.sigmaaldrich.com/catalog/substance/tween8012345900565611?lang=en®ion=CA>. [Accessed: 06-Jun-2017].
- [96] “Product Name Span® 80 | Sigma-Aldrich.” [Online]. Available: <http://www.sigmaaldrich.com/catalog/search?term=Span%C2%AE+80&interface=Product%20Name&N=0+&mode=mode%20matchpartialmax&lang=en®ion=CA&focus=productN=0%20220003048%20219853286%20219853082>. [Accessed: 06-Jun-2017].
- [97] H. Firoozmand and D. Rousseau, “Microbial cells as colloidal particles: Pickering oil-in-water emulsions stabilized by bacteria and yeast,” *Food Research International*, vol. 81, pp. 66–73, Mar. 2016.
- [98] S. Geacai, I. Nita, O. Iulian, and E. Geacai, “Refractive indices for biodiesel mixtures,” *UPB Sci. Bull. Series B*, vol. 74, no. 4, pp. 149–160, 2012.
- [99] P.-D. Duh, W. J. Yen, and G.-C. Yen, “Oxidative stability of polyunsaturated fatty acids and soybean oil in an aqueous solution with emulsifiers,” *Journal of the American Oil Chemists’ Society*, vol. 76, no. 2, p. 201, 1999.
- [100] S. K. Hoekman, A. Broch, C. Robbins, E. Cenicerros, and M. Natarajan, “Review of biodiesel composition, properties, and specifications,” *Renewable and Sustainable Energy Reviews*, vol. 16, no. 1, pp. 143–169, Jan. 2012.
- [101] “World Temperatures — Weather Around The World.” [Online]. Available: <https://www.timeanddate.com/weather/>. [Accessed: 19-Jun-2017].
- [102] O. A. Elsanusi, M. M. Roy, and M. S. Sidhu, “Experimental Investigation on a Diesel Engine Fueled by Diesel-Biodiesel Blends and their Emulsions at Various Engine Operating Conditions,” *Applied Energy*, vol. 203, pp. 582–593, Oct. 2017.
- [103] J. Chen and P. Zhang, “Preparation and characterization of nano-sized phase change emulsions as thermal energy storage and transport media,” *Applied Energy*, vol. 190, pp. 868–879, Mar. 2017.

- [104] H. Venu and V. Madhavan, "Influence of diethyl ether (DEE) addition in ethanol-biodiesel-diesel (EBD) and methanol-biodiesel-diesel (MBD) blends in a diesel engine," *Fuel*, vol. 189, pp. 377–390, Feb. 2017.
- [105] E. Torres-Jimenez, M. S. Jerman, A. Gregorc, I. Lisec, M. P. Dorado, and B. Kegl, "Physical and chemical properties of ethanol–diesel fuel blends," *Fuel*, vol. 90, no. 2, pp. 795–802, Feb. 2011.
- [106] W. F. Fassinou, A. Sako, A. Fofana, K. B. Koua, and S. Toure, "Fatty acids composition as a means to estimate the high heating value (HHV) of vegetable oils and biodiesel fuels," *Energy*, vol. 35, no. 12, pp. 4949–4954, Dec. 2010.
- [107] A. Ibrahim, "Investigating the effect of using diethyl ether as a fuel additive on diesel engine performance and combustion," *Applied Thermal Engineering*, vol. 107, pp. 853–862, Aug. 2016.
- [108] C.-Y. Lin and K.-H. Wang, "Diesel engine performance and emission characteristics using three-phase emulsions as fuel," *Fuel*, vol. 83, no. 4–5, pp. 537–545, Mar. 2004.
- [109] E. Buyukkaya, "Effects of biodiesel on a DI diesel engine performance, emission and combustion characteristics," *Fuel*, vol. 89, no. 10, pp. 3099–3105, Oct. 2010.
- [110] X. J. Man, C. S. Cheung, Z. Ning, L. Wei, and Z. H. Huang, "Influence of engine load and speed on regulated and unregulated emissions of a diesel engine fueled with diesel fuel blended with waste cooking oil biodiesel," *Fuel*, vol. 180, pp. 41–49, Sep. 2016.
- [111] L. Xing-cai, Y. Jian-guang, Z. Wu-gao, and H. Zhen, "Effect of cetane number improver on heat release rate and emissions of high speed diesel engine fueled with ethanol–diesel blend fuel," *Fuel*, vol. 83, no. 14–15, pp. 2013–2020, Oct. 2004.
- [112] R. D. Lanjekar and D. Deshmukh, "A review of the effect of the composition of biodiesel on NO_x emission, oxidative stability and cold flow properties," *Renewable and Sustainable Energy Reviews*, vol. 54, pp. 1401–1411, Feb. 2016.
- [113] J. B. Heywood, *Internal combustion engine fundamentals*. New York: McGraw-Hill, 1988.
- [114] İbrahim Aslan Reçitoğlu, K. Altınışık, and A. Keskin, "The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems," *Clean Technologies and Environmental Policy*, vol. 17, no. 1, pp. 15–27, Jan. 2015.

- [115] T. Kubo, H. Sachs, and S. Nadel, “Opportunities for new appliance and equipment efficiency standards: Energy and economic savings beyond current standards programs,” 2001.
- [116] “Electricity rates | Ontario Energy Board.” [Online]. Available: <https://www.oeb.ca/rates-and-your-bill/electricity-rates>. [Accessed: 02-Jul-2017].
- [117] “[Hot Item] Sorbitan Monooleate Span 80,” *Made-in-China.com*. [Online]. Available: </showroom/michaelcn/product-detailKMfEjCJoXIWp/China-Sorbitan-Monooleate-Span-80.html>. [Accessed: 06-Jul-2017].
- [118] “[Hot Item] Supply High Quality 9005-65-6 Tween 80 with Competitive Price,” *Made-in-China.com*. [Online]. Available: <http://ditaichem.en.made-in-china.com/product/wSVEIFXCxZkO/China-Supply-High-Quality-9005-65-6-Tween-80-with-Competitive-Price.html>. [Accessed: 06-Jul-2017].