An Experimental Study of Combustion Characteristics of Fatty Acid Methyl Ester Biodiesel

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Abstract

The thesis presents an experimental investigation of combustion performance and emissions of waste cooking oil (WCO) based biodiesel. To evaluate the comparative performance of biodiesel and diesel, combustions tests were conducted using Continuous Combustion rig (CCR) and Land Rover VM diesel engine.

Firstly, physical properties of WCO biodiesel and diesel samples were measured in the laboratory. Elemental analysis of WCO biodiesel showed that there are differences between the functional groups in diesel and biodiesel which lead to major differences in the combustion characteristics of the two fuel types. It was found that biodiesel had 10% lower carbon content, almost no sulphur content for biodiesel and up to 12% more oxygen content compared with diesel. This explains the lower caloric value for WCO biodiesel (up to l8 %) compared with diesel. However, higher oxygen content and double bounds in WCO biodiesel increase its susceptibility to oxidation.

The CCR test results showed an increase in combustion gas temperature with the increases in biodiesel blend ratio in diesel. This was due to a faster reaction rate for biodiesel than that of diesel leading to a faster brakeage of the hydrocarbon chain to release more heat. The engine tests were performed to measure the torque and emissions for different engine speeds and loads. In general a decrease in engine torque with up to 9% for biodiesel was observed, which was due to the lower calorific value of biodiesel compared with that of diesel. The brake specific fuel consumption (BSFC) increased as the biodiesel blend ratio in diesel increases due a greater mass of fuel being injected at a given injection pressure, compared with diesel. Using WCO blends ratio up to 75% in diesel showed a reduction in exhaust emission compared with diesel, however, at the cost of increased fuel consumption. A common conclusion can be drawn in favour of the WCO

biodiesel as being a greener alternative to petro-diesel when used in blend with diesel. However, due to large variations in the biomass used for biodiesel production could lead to variations in physical and chemical properties between biodiesel produced from different biomass. Therefore more stringent standards need to be imposed for biodiesel quality in order to diminish the effect of variation in physicochemical properties on engine performance and emissions. The future work in developing standard test procedures for establishing fuel properties and limits/targets would be beneficial in using a large amount of waste cooking oil in the production of biodiesel, thus contributing to reduction in CO_2 and waste minimisation.

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Nomenclature

$(\ )_{st}$	Indices st indicates stoichiometric conditions
$(A/F)_{rel}$	Relative air to fuel ratio
A	Area of the piston, [m^2]
A/F	Air to fuel ratio
af	Molar flow of species A
ASTM	American Society for Testing and Materials
B0	Neat diesel
B100	Neat biodiesel
B25	Blend of 25% biodiesel and 75% diesel
B5	Blend of 5% biodiesel and 95% diesel
B50	Blend of 50% biodiesel and 50% diesel
B75	Blend of 75% biodiesel and 25% diesel
BB100	Bolton biodiesel, 100% biodiesel
BB20	Bolton biodiesel, 20% biodiesel and 80% diesel
BB50	Bolton biodiesel, 50% biodiesel and 50% diesel
bf	Molar flow of species B
BH	Bushnell and Haas
BP	Engine brake power, [kW]
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
C	Carbon
C13-C25	Fractions of diesel
CCR	Continuous combustion rig
cf	Molar flow of species C
cfu	Colony forming unit
CGT	Combustion gas temperature
CI	Compression ignition
CN	Cetane number

SCO	Specific carbon monoxide
SCO_2	Specific carbon dioxide
c_p	Specific heat
C_v	Calorific value of the fuel, [kJ/kg]
C_xH_y	General chemical formula of a hydrocarbon
dE	Change in energy of a system
df	Molar flow of species D
dH_2O	Distilled water
DI	Direct injection
dU	Change in internal energy of a system
E	Total energy of the system
EA	Excess air
EPA	Environmental Protection Agency
FAME	Fatty acid methyl ester
FFA	Free fatty acids
f_i	Molar flow rate of species i
FID	Flame ionization detector
FMEP	Friction mean effective pressure
FP	Friction power
f_r	Rate of fuel consumption
FT-IR	Fourier Transform - Infrared Spectroscopy
GC-MS	Gas Chromatography - Mass Spectrometry
H	Hydrogen
h	Molar specific enthalpy
$h^\circ_i(T)$	Enthalpy of species i at temperature T, relative to the reference state
H_2O	Water
H_2SO_4	Sulphuric acid
SHC	Specific hydrocarbon
HHV	Higher calorific value

IC	Internal combustion
ICE	Internal combustion engine
IMEP	Indicated mean effective pressure
IMS	Industrial methylated spirits
IP	Indicated power
IV	Iodine value
k	Number of cylinders
L	Length of the stroke, [m]
LCV	Lower calorific value
m_a	Mass of air
MEA	Malt extract agar
MEP	Mean effective pressure, [N/m^2]
M_f	Molar mass
m_f	Mass of fuel
MIC	Microbiologically influenced corrosion
N	Engine speed, [rpm]
NO	Nitric oxide
No. 1-D	Grade No. 1 special purpose, light distillate fuel for automotive diesel engine requiring high volatile fuel
No. 2-D	Grade No. 2 general purpose, middle distillate fuel for automotive diesel engine
No. 3-D	Grade No. 3 distillate oil for burners requiring low viscosity fuel
No. 4-D	Grade No. 4 commercial heating oil for burners not equipped with pre-heaters
NO_2	Nitrogen dioxide
SNO	Specific nitrogen oxide
N_T	Total number of moles
O	Oxygen
O_2	Oxygen

O_3	Ozone
p_0	Reference pressure, 1atm
pH	Is a measure of activity of the hydrogen ion
PM	Particulate matter
Q	Rate of heat transfer to the system
RME	Rapeseed methyl ester
rpm	Rotational speed of the engine, rotations per minute
S	Sulphur
SB100	Sheffield biodiesel, 1000% biodiesel
SB20	Sheffield biodiesel, 20% biodiesel and 80% diesel
SB50	Sheffield biodiesel, 50% biodiesel and 50% diesel
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SOx	Sulphur oxides
spp.	Species
SRB	Sulphur reducing bacteria
t	Temperature
T	Torque, [Nm]
T_0	Reference temperature, is 298K
TA	Theoretical air
THC	Total unburnt hydrocarbon
U_1	Internal energy of a system at initial state
U_2	Internal energy of a system at final state
UBHC	Unburned hydrocarbon
ULS	Ultra-low sulphur
VOC	Volatile organic compound
WCO	Waste cooking oil
W_x	Rate at which work is done by the system on its surrounding
y_{CO2}	Mole fraction of carbon dioxide

YEA	Yeast extract agar
y_{H2O}	Mole fraction of water
y_{N2}	Mole fraction of nitrogen
y_{SO2}	Mole fraction of sulphur dioxide
$\Delta h_r(T_1)$	Enthalpy of reaction at temperature T_1
δQ	Infinitesimal of heat supplied to the system by its surroundings
δW	Infinitesimal of work done by the system by its surroundings
λ	Air to fuel ratio
Φ	Equivalent ratio
$\bar{e}$	Energy per unit mass or mass specific energy
$\bar{h}$	Mass specific enthalpy
$\bar{f_i}$	Mass flow rate entering the control volume
$\bar{f_j}$	Mass flow rate leaving the control volume
$\bar{v}$	Mass specific volume

Chapter 1 -Introduction

1.1. Introduction

Last century has seen rapid industrialisation and urbanisation leading to problems of global environmental pollution and energy deficit in many countries. The AA Public Affairs Fuel Price Report showed that the UK has the seventh highest petrol price in Europe and the second highest diesel price [1]. Limited fossil resources, continuously increasing fuel cost and issues related to global warming lead to necessity of finding new substitutes for petroleum diesel. However, the continued development in the past decades of internal combustion (IC) engines makes it difficult for alternative fuels to compete with petroleum fuels.

The transportation sector is one of the main contributors to the formation of ground-level ozone. Emissions also have a negative effect on the environment due to their intrinsic toxicity, which cause the ozone formation mechanism and their direct or indirect influence on the "greenhouse effect". Incomplete combustion in IC engines produces a series of emissions such as unburned hydrocarbons, solid particles, aldehydes, polycyclic aromatic hydrocarbons, carbon monoxide, nitrogen oxides, and sulphur oxides. In some congested urban areas, engine emissions such as CO, NOx, HC and particulates often may exceed the limits regulated by law. In order to meet the European Emission Trading System (EU ETS) operational phases starting from December 2007 and ending in December 2020, the Environment Agency has introduced more stringent restrictions regarding acceptable limits of exhaust emissions and diesel engine characteristics. All these emissions are closely related first to the fuel type, and second to the diesel engines characteristics.

In response to the environmental problems created by pollution and to the issue of fossil fuel depletion alternative solutions have been taken into consideration.

Using biodiesel fuels in place of petroleum derived fuels is essential for reducing the dependence on foreign oil and emissions that harm air quality. The collection of waste cooking oil for biodiesel production supports both the reduction in dependency upon landfill sites as a means of waste disposal and reducing the use of petroleum fuels for energy generation.

Biodiesel has lower pollutant emissions compared with diesel, which makes it a cleaner-burning alternative to petroleum fuel, and can be used neat or in blends with diesel fuels in various proportions, in the classical diesel engines.

Although biodiesel brings a significant number of positive aspects, several negative aspects should be considered, i.e. biodiesel biodegradability, the capacity of an engine to operate on various fuels, engine efficiency and emissions.

Biodiesel has the advantage of being biodegradable. However, biodegradability makes biodiesel more susceptible to microbial contamination than petroleum fuels. Certain types of bacteria and fungi can grow in diesel or biodiesel fuel tanks. These micro-organisms can be either aerobic or anaerobic but typically require at least a small amount of water to be present. The presence of moisture in fuel can be a result of the final washing stage during the manufacturing process or the absorption of moisture and contaminants from condensation during the fuel storage. Biodiesel is more hygroscopic than diesel, thus resulting in biodiesel having a greater capacity for absorbing moisture compared to diesel fuel. Free fatty acids are formed as a consequence of hydrolyses of ester bonds, this result in a decrease in pH value of the hydrocarbon. Microbiological growth is one of the consequences of biodiesel’s biodegradability. With the biotic degradation reactions, the properties of biodiesel also change, leading to an increase in biodiesel’s corrosivity, changes in physical and chemical properties, therefor a poor fuel quality.

Some properties of the oil such as viscosity, melting point, thermal stability, cetane index, are directly related to the chemical composition of the biomass used. Therefore, the chemical properties of oils obtained from different raw materials vary.

Conventional diesel engines are designed for a particular type of fuel. When high blends of biodiesel in diesel are used in internal combustion (IC) engines, the engines show decrease in performance and efficiency due to the differences in physical properties between diesel and biodiesel. There are differences between the emission characteristics for biodiesel and diesel. However, there are some advantages of using biodiesel in IC engines which are:

- Emit less CO and HC compared with diesel fuel;
- Reduced smoke and odours;
- Contains almost no sulphur;
- The high flash point makes the biodiesel safer for storage compared to diesel;
- In neat form biodiesel is biodegradable being safer for handling;
- Higher cetane number compared with diesel fuel;
- Biodiesel can be used in diesel engines for lubrication purpose;
- In low blend can be used in diesel engine without any modification;
- Naturally oxygenated fuel.
- Biodiesel made from waste oils help the environment by recycling the waste.

Some of the disadvantages of using biodiesel are:

- High cloud point resulting in crystallization at higher temperature compared with diesel fuel;
- Higher viscosity than diesel fuel;
- Shorter shelf life compared to diesel and more prone to biodegradation;
- Lower calorific value compared with diesel fuel;
- Relative higher NOx to diesel fuel;
- Biodiesel cannot completely replace fossil fuel.

Biodiesel could contribute to the decrease in the demand for fossil fuel when use in blend with petroleum diesel. Generally, biodiesel has lower energy content compared with diesel. The yearly net energy per hectare of fuel crop required in order to sustain the continue increase in energy demand and the issues of food price rising that this can trigger make biodiesel unfeasible to completely replace petro-diesel.

Numerous experiments have been performed on a diesel engine operating under various conditions using biodiesel derived from soybean, rapeseed, palm and Jatropha oil, but not as much research was done in engine emissions and performance using biodiesel made from waste cooking oil (WCO). Biodiesel produced from waste cooking oil has potential to be used in engines instead of diesel and offering environmental benefits. For example it will reduce domestic waste and it does not compete with food crops.

The aim of the present research is to evaluate the "quality" of biodiesel produced from waste cooking oil. To achieve this a series of experimental investigations of biodiesel biodegradability, combustion characteristic, emissions and its performance in compression ignition (CI) engine are carried out.

The experiment investigations were conducted over a period of three years, in the following stages; firstly, the microbiological contamination of biodiesel was investigated, then the emissions characteristics of biodiesel using a Continuous Combustion Rig (CCR) were evaluated and finally the engine emissions and performance characteristics of VM 2400 diesel engine using various diesel biodiesel blends were obtained. It was not possible to obtain the entire biodiesel from one supplier over the entire experimental period because there were changes in the biodiesel suppliers. Although the fuel suppliers were different, the biodiesel properties were found to be very similar. Therefore there would be little or no significant effect on the engine performance and emissions between the biodiesel from different suppliers.

The physical properties of the biodiesel from the three suppliers are presented in Table 1-1.

Table 1-1 Physical properties of the biodiesel fuels investigated

Physical Properties of	**Bolton Biodiesel**	**Sheffield Biodiesel**	**VEPower Biodiesel**	**Diesel**
Specific gravity	0.886	0.878	0.882	0.834
Kinematic viscosity at 40°C (mm^2/s)	4.48	4.46	4.47	3.5
Lower calorific value (MJ/kg)	33384.256	33399.628	33374.209	41098.325
Sulphur, wt%	<1	<1	<1	0.50
Cloud point °C	-13	-11 to 16	-11 to 16	-9 to 10
Pour point °C	-8	-12	-10	-30
Iodine number	127.07	124.37	122.99	-

The overall quality of neat biodiesel and various proportions of biodiesel-diesel blends are compared with diesel, to evaluate its performance in IC engines and environmental benefits.

1.2. Objectives

The following objectives of investigation were set in order to achieve this aim:

- A review of the literature on fuel biodegradation and biodiesel used as substitute on CI engines;
- Evaluation of microbial contamination for biodiesel and diesel and biodiesel blends in various proportions: diesel 100% - biodiesel 0% (B0), diesel 50% - biodiesel 50% (B50) and diesel 0% - biodiesel 100% (B100);
- Evaluation of characteristic emissions from a laminar premixed flame for diesel 100% - biodiesel 0% (B0), diesel 75% - biodiesel 25% (B25), diesel 50% - biodiesel 50% (B50), diesel 25% - biodiesel 75% (B75) and diesel 0% - biodiesel 100% (B100);
- Evaluation of Land Rover VM 2400 diesel engine performance and emissions using different diesel – biodiesel blends: B0, B25, B50, B75 and B100;

1.3. Thesis Layout

A range of theoretical and experimental techniques was used for achieving the objectives and aim of the research.

The Evaluation of WCO biodiesel was focussed on 3 main issues as shown in Figure 1-1:

- Microbiological contamination test - a comparative study between diesel and biodiesel available at the petrol station.
- Pilot scale combustion test - exhaust emissions from a laminar premixed flame.
- Performance and emission test from diesel engine using biodiesel.

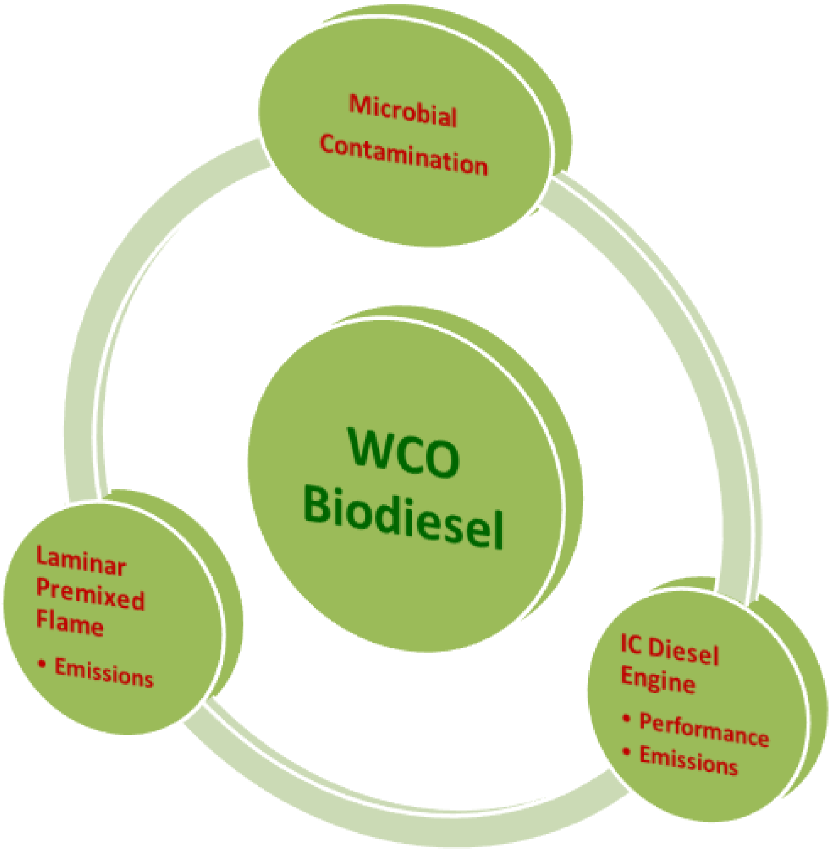

Figure 1-1: An overview of biodiesel main area analysed

Figure 1-2 shows the proposed methodology. The chart presents three main parts of the research, with the central part representing the study divided into three main sections which are the fuels properties, continuous combustion rig (CCR) and compression ignition (CI) engine.

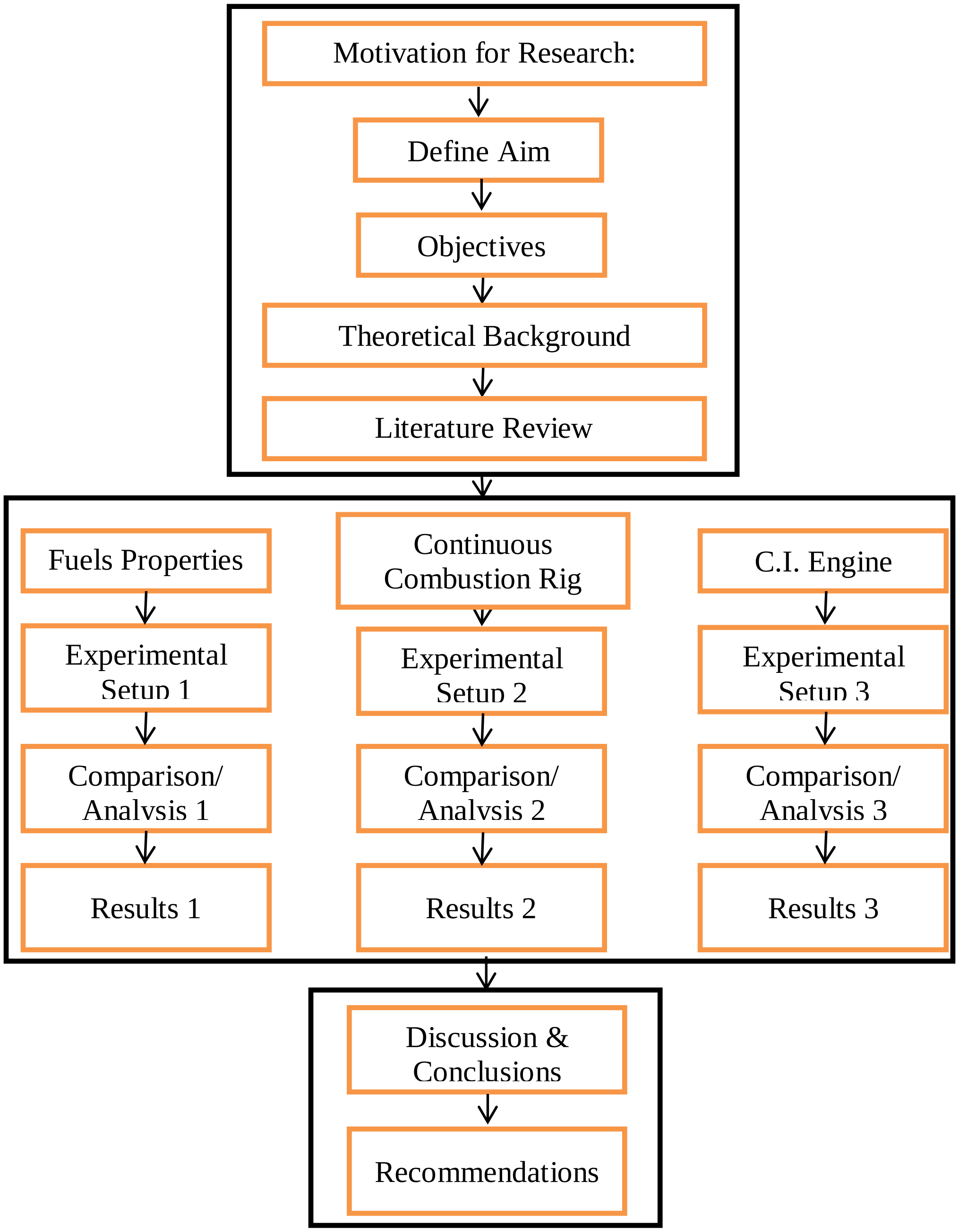

Figure 1-2: Flow chart of research methodology

The main issues related to the use of WCO biodiesel as a substitute for diesel were evaluated. Microbial contamination of the fuel is one of the main factors which lead to biodegradation and changes in physicochemical properties of the fuel, leading to a fuel of a poor quality. The use of low quality fuel in a diesel engine can result in engine operation malfunctions, decrease in performance and increase in emissions.

This thesis comprises of eight chapters. Chapter 1 introduces the world wide problems of energy based on petroleum fuels and its pollutant emissions impact on the environment, and defines the aim and objectives of the research. Chapter 2 provides a theoretical background of the subject in order to comprehend the aspects of fuel biodegradability and its characteristic emissions when used in premixed combustion and unmodified CI engines.

Chapter 3 presents a review of the published scientific literature on fuel biodegradability and performance, efficiency and emissions from CI engines using different types of biodiesel under various engine operating conditions. Chapter 4 presents the physical and chemical properties of diesel, neat WCO biodiesel and various blends of the diesel and WCO biodiesel fuel investigated, and the diesel and biodiesel microbiological degradation. Chapter 5 describes the methodology, experimental setup and results from the experimental evaluation of the exhaust emissions from diesel, WCO biodiesel and various blends of diesel and biodiesel burned in a continuous combustion rig (CCR). Chapter 6 describes the methodology, experimental setup and results from the experimental evaluation of Waste Cooking Oil Biodiesel in a Land Rover Diesel Engine.

Chapter 7 and Chapter 8 present overall discussion and conclusions of the experimental work.

Chapter 9 provides recommendations for further research of the WCO biodiesel as a potential substitute or blend for petroleum petro-diesel.

Chapter 2 -Theoretical Background

2.1.Introduction

In this chapter the physical properties of diesel and biodiesel and their predisposition to microbial contamination are discussed. Notions of combustion fundamentals are also presented along with the performance parameters of an internal combustion engine.

2.2.Fuels

Liquid fuels are generally complex mixtures of long chains of hydrocarbon species. Fuel compositions consist mainly of mass fractions of carbon, hydrogen, sulphur, oxygen, nitrogen, ash and traces of metals. Fuel properties and combustion characteristics of diesel and biodiesel are discussed in detail in the following section.

2.2.1. Diesel

Fractions of diesel (C13 - C14 to C20 - C25) are used to produce diesel and household fuels [2]. Diesel composition contains paraffinic, naphthenic, aromatic and mixed hydrocarbons with distillation limits between 200 and 400 °C. Diesel with higher distillation range contains sulphur, oxygen and nitrogen compounds, and small proportions of metal compounds. In most cases this comes from the process of diesel distillation, from hydro-cracking, or fractions of thermal cracking as it is refined from the extraction of aromatic compounds.

The characteristics of diesel engines require two categories of diesel fuel properties: to ensure the smooth operation and fuel system performance (cold filter plugging point and cloud point, viscosity, water content) and the operating performance of engines (cetane, volatility, sulphur content, etc.).

The cold filter plugging point and cloud point temperatures of diesel affect the proper functionality of diesel engines especially in low temperature environments, whereas paraffin precipitation may cause clogging in a diesel fuel system. Therefore, it is necessary for diesel engines to have a low cloud point and cold filter plugging point temperature.

One of the main diesel properties is the cetane number. There are four different classes of hydrocarbons as cetane decreases in order: paraffin, iso-paraffin, naphthenic, aromatic. Paraffinic hydrocarbons have the disadvantage of a high temperature of crystallization, high cloud point and pour point temperature which involves a specific processing of mixture fractions. Thus, diesel is selected from paraffinic or naphthenic oils, and then fractionated so that they meet the requirements for cloud point temperature.

The American Society for Testing and Materials (ASTM), has classified diesel in four grades:

- Grade No. 1-D is a light distillate fuel usually used in light trucks and busses, and during the winter time grade 1-D is blended with grade 2-D in order to improve the cold flow properties of the fuel.
- Grade No. 2-D is a middle distillate fuel, suitable for high speed engines that operate mostly at high load.
- Grade 3D diesel is the highest quality diesel fuel ultra-low sulphur, suitable for marine engines.
- Grade No. 4-D is a heavy distillate fuel used mainly in medium speed engines. Due to its high viscosity it is required heating in order to improve the spray atomization.

Pollutant emissions from diesel engines are correlated directly with the quality characteristics of the diesel fuel used. The main pollutants from diesel emissions are unburned hydrocarbons, solid particles, aldehydes, polycyclic aromatic hydrocarbons, carbon monoxide, and nitrogen oxides. Experimental research on the incomplete combustion of the fuel mixture, fuel pyrolysis, on intermediary combustion products, and respectively on the diesel engine processes which lead to the formation of substances that form the initial components of smoke particles and coal deposits, showed the complex influence of physical and chemical fuel properties. The main fuel properties that influence the emissions of particulate pollutants are the sulphur content, chemical composition and volatility, cetane number, density and viscosity.

Sulphur content of diesel. Diesel fuel generally contains more sulphur than biodiesel. In diesel fuel formulation, the trend shows continuous reduction in sulphur content in order to reduce the SO_2 emissions and particulate matter. High sulphur content in fuel lead to increase in the amount of insoluble organic fractions, as a result of the oxidation of small quantities (1 to 3%) of sulphur components in the fuel, resulting in forming SO_2, SO_3 and H_2SO_4.

Chemical composition and volatility. Lowering the total aromatic content in diesel would results in reduction in emissions of unburned hydrocarbons and particulate matter, especially at values under 30% aromatic hydrocarbons. The emissions from diesel were found to be influenced by following factors:

- The ambient temperature has a remarkable influence on both fuel consumption and emissions of pollutants;
- Increased levels of polycyclic aromatic hydrocarbons, and particularly the tri-cyclic from diesel fuel, lead to increases of NOx emissions, particulates and smoke;
- Mono-aromatic hydrocarbons have no effect on emissions, therefore the total aromatic content of fuel is not an adequate indicator of a fuel's pollutant emissions;
- Distillation limits influence the emissions. With the increase in initial and final distillation temperature, NOx, HC, CO emissions, smoke and fuel consumption increase.

Cetane (CN). Diesel cetane number is correlated with the level of emissions. With the increase in cetane number a reduction of CO, HC, the volatile particulates fraction, and even the noise could be achieved. High cetane number in the range of 49 to 52 can reduce particulate emissions by up to 0.01 g / km [3].

Diesel fuel density. Volumetric mass density is an important property of the fuel because it controls the amount of fuel that is compressed and burned in the combustion chamber. The higher the fuel density the more fuel is injected in the combustion chamber, which can result in an increase in HC and CO and decrease in NOx and PM [4]

Diesel fuel viscosity. Higher viscosity could worsen spray and atomisation, and therefore increase the CO and soot emissions [5].

Improvement or correction of petroleum product grades can be achieved by adding small amounts of additives, which is less expensive and easier than fuel reformulation. The most commonly used additives in diesel are detergent additives and cetane additives. Detergent additives have shown effectiveness in reducing emissions of unburned hydrocarbons, particulate and the soluble organic fraction of particles. Additives increasing the cetane number produce a particular reduction in emissions of the particulate soluble organic fraction.

2.2.2. Biodiesel

Biodiesel is a renewable fuel that can be produced from raw vegetable oils, used cooking oils, animal fats, algae and lignocelluloses biomass. The production of biodiesel from vegetable oil is not encouraged because it triggers issues related to food shortage. Other types of biomasses, such as lignocelluloses and algae, are also suitable for biodiesel production, but the technological process is still under development and the production cost is high. The waste cooking oil used as biomass for biodiesel production presents the greatest advantage of recycling considerable amount of waste oil from restaurants and households.

Biodiesel is generally defined as the mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. It is obtained through decomposition of triglyceride (which represents the main constituent of vegetable oils and animal fats) into glycerine and fatty acid after a chemical reaction with an alcohol in presence of a catalyst (sodium or potassium peroxide). Transesterification reaction is the most used technological process for biodiesel production. Transesterification improves biodiesel fuel quality by decreasing its viscosity, density, and maintaining the same heating value.

Biodiesel consists of a mixture of naturally formed fatty acids [6; 7]. Some properties of the oil such as viscosity, melting point, thermal stability, cetane index, are directly related to the chemical composition of the biomass used. Therefore, for oils obtained from different raw materials, the chemical properties vary. Compared with diesel, biodiesel has slight increased cetane number, almost no sulphur content, low amount of aromatics, lower volatility and a short distillation temperature interval.

Biodiesel is almost 100% biodegradable and has less carbon dioxide emissions and particulate matter. However, issues of biodiesel biodegradability and the emissions level are in direct correlation with the percentage of diesel added into blend. The increase in diesel blend ratio in biodiesel will result in changes in viscosity, density, and also changes in biodiesel biodegradability and emissions. A reduction of CO_2 between 50% and 80% was observed for engines using waste oil biodiesel compared with petro-diesel [7-11]. The life cycles of CO_2 emissions should be taken into consideration in order to assess the biodiesel effect on greenhouse gases.

Physical and chemical properties of biodiesel, such as viscosity, cloud point, cetane number and biodiesel stability vary with the nature of biomass used. There are differences between diesel and biodiesel properties, as well as between biodiesel produced from different biomass. The differences in physicochemical properties between diesel and biodiesels have a direct effect over the internal combustion engine which was designed for diesel fuel.

Storage stability. Storage stability refers to the capacity of the fuel to maintain its properties during long-term storage. One of the main issues during long term storage are the oxidative attack and the water contamination and microbial growth. These can lead to reactions that take place inside of the fuel, which result in changes in physicochemical properties of the fuel, in this way affecting the fuel stability. Biodiesel is more hygroscopic than diesel fuel. This means that biodiesel stored over a long period of time could absorbs more water compared with petro-diesel. The presence of water or moisture as a result of the fuel tank condensation could lead to issues such as microbial contamination of the fuel, and fuel tank corrosion. The high moisture present in fuel reduces the fuel heat of combustion, which results in start-up problems in engines, emits more smoke and produced less power. The microbial growth could plug the filters and lead to engine operation failure.

2.3.Diesel and Biodiesel Microbiological Degradation

Various types of aerobic and anaerobic bacteria and fungi can grow in diesel fuel tanks. For an organism to grow and multiply inside of a certain environment, at least a small amount of water is necessary to be present. The organisms, generally, develop at the water-fuel interface, however some organisms can be found suspended in the fuel layer. Fuel contamination can lead to fuel filters blockage, increase in the fuel acidity and corrosion of the fuel tank. Limited experimental data were available for microbial inhabiting biodiesel. Due to the nature of biodiesel, biodiesel was expected that to be at higher risk of microbial contamination compared with petro-diesel. In order to control the microbial contamination of the fuel, it is important to eliminate the factors that could favour the microbial development. Eliminating the moisture and avoiding the fuel contact with open air could prevent the microbial contamination, although these two parameters are difficult to be controlled during fuel handling and storage. Fuel additive such as biocide and anti-fungal could enhance the fuel stability to microbial contamination, however these could affect the biodegradability and toxicity of biodiesel.

Due to high content of carbon, oxygen and hydrogen, biodiesel is a good environment for microbes to inhabit. Water is heavier than fuel and presents itself as a "water bottom" in a fuel tank. A small amount of water is enough for microbes to survive, multiply and grow. It is impossible to prevent water from condensation in the varying temperatures. Moisture and water are generally infested with micro-flora and introduce microbes to a rich carbon source.

Water typically enters fuel tanks through vents and seals as humidity in the air. The water condenses or is dissolved into the fuel, or is found as free water collected at the bottom of the fuel tank, and can become acidic leading to the corrosion of the fuel tank. The other major problem associated with water contamination is that it contributes to microbial growth. There are species of yeast, fungi, and bacteria that will develop at the interface between the fuel and any free water that has collected at the bottom of a storage tank. The organisms metabolise the hydrocarbon and the resulted by-product can cause filter plugging. The amount of free water in the sample depends primarily on the quality of the "housekeeping" practices followed by the fuel distributors and consumers. Frequently draining the water from storage tanks, ensuring that vents and seals do not allow rainwater to enter, and not drawing from the bottom of the tank, should prevent large amounts of free water from entering the system.

Contamination or dilution of the lubricating oil of diesel engines using biodiesel represents a major concern for the engine manufactures. Biodiesel consist of low volatility fuel components, compared with petro-diesel. When biodiesel is injected into the engine combustion chamber, the low volatile components left partially burned can deposit on the cylinder head and wall, over a period of time [2].

2.3.1. Microbes that Inhabit Diesel

In the literature available it is shown that the microorganisms that grow in diesel and biodiesel are bacteria and fungi. Bacteria are single –cell organisms which do not have a membrane-bound nucleus, while fungi have a defined nucleus. The nucleus is the organelle which contains most of the cell`s genetic material [12]. Microbes can also be classified by their activity and oxygen requirements: aerobes bacteria, anaerobes bacteria and facultative anaerobes.

a) Aerobic bacteria

Bacteria that require oxygen are called aerobes bacteria. The aerobes bacteria can contaminate the fuel, but they cannot survive in an environment containing less than minimum concentration of oxygen.

Many studies have shown that different species are able to adapt to different conditions. Some of the most common and well known aerobic bacteria have been exhibited in diesel.

Pseudomonas species have been isolated in the contamination of diesel [13]. *Pseudomonas* is a gram-negative bacterium. Bacteria are consider gram-negative because of their characteristic staining properties under the microscope, where they do not stain or are decolourised by alcohol during the gram method of staining [14]. *P. aeruginosa* is one of the most prevalent aerobic bacteria found inhabiting diesel. *P. aeroginosa* has the advantage over many other bacteria that it is capable of adapting its lipopolysaccharide cell wall to cater for inhabiting in diesel [15]. Lipopolysaccharide is a compound in which a lipid molecule is bound to a polysaccharide by a covalent bond. Certain bacteria cell walls contain Lipopolysaccharide. The role of gram-negative lipopolysaccharide strains is to help stabilize the membrane structure of bacteria and to protect it from certain chemicals [14].

P. citronellolis has been isolated metabolising crude oil derivatives, monoterpenes (a form of hydrocarbon). *P. citronellolis* is capable of metabolising acyclic monoterpenes under anaerobic conditions. *Pseudomonas* is capable of metabolising in aerobic or anaerobic conditions by metabolising oxygen or nitrate as a terminal electron acceptor [16]. If *P. citronellolis* can metabolise an acyclic hydrocarbon, there could be possibilities of it metabolising and biodegrading diesel.

Species of *Bacillus* are frequently found in diesel. Bacilli are facultative organisms and are conveniently suited to a diesel tank. Bacillus are highly resistant to many forms of biocide that are introduced to diesel for sterility [13].

One method of biodegradation of diesel is the production of a bio-surfactant. An *Aeromonas spp.* (species name not identified) is capable of producing bio-surfactants that can emulsify hydrocarbons.

Other bacteria exhibited in diesel are Aerobacter, *Brevibacterium, Micrococcus, Rhodococcus* [17] and *Geobacillus spp.* [18].

b) Anaerobic bacteria

Anaerobes bacteria are organisms that do not require oxygen for growth. The anaerobes bacteria are classified in three categories:

- Obligate anaerobes are organisms that are harmed by the presence of oxygen
- Aero-tolerant organisms are organisms that do not use oxygen for growth, but can tolerate its presence
- Facultative anaerobes are organism that can grow without oxygen, but use oxygen if it is present
- Facultative anaerobes have a critical role in the process of contamination. Facultative anaerobes bacteria consume oxygen, and consequently create a suitable environment for anaerobes bacteria growth.

There are two major microorganisms isolated from diesel storage tanks that are capable of metabolising diesel. One of these is Sulphur Reducing Bacteria (SRBs) [13]. SRB is aided by diesel, as it serves as a direct electron donor for sulphate. SRB causes biodegradation of the diesel tank. Sulphides corrode metals and in doing so could be the cause of irreversible corrosion, and weakening the structure of the diesel tank [19]. The SRBs are slow growth bacteria [20]. Examples of SRBs are Desulfovibrio, Desulfococcus [21] and Defulsfobacterium [17].

Denitrifying bacteria are anaerobic bacteria capable of metabolising diesel constituents, such as ethyl benzene. Ferric iron reducing bacteria are metabolisers of constituents of diesel, in particular, toluene. Toluene is an octane enhancer and is introduced to diesel. The genus *Geobacter* has been the only reported anaerobic bacteria to metabolise toluene [19]. There are not many other ferric iron reducing bacteria that have reported in diesel.

The *methanogenic archaea* can inhabit and metabolise hydrocarbons. *Methanogens* convert hydrocarbons into carbon dioxide (CO_2) and many other compounds. *Methanogens* are part of the subclass *Proteobacteria* [19].

c) Fungi

The other major microorganism isolated from storage tanks is *Hermoconis resinae* [13; 17; 22]. *Hermoconis resinae,* also known as *Cladosporum resinae, a* member of the phylum ascomycota [23], was also found inhabiting diesel. *Cladosporum resinae* is a fast growing fungus that can form a bio-film usually at the water/diesel interface. A bio-film in a diesel tank can cause many problems for uptake of diesel by the engine and the increased surface area gained by microorganism for the metabolism of diesel. The major limiting nutrients that *H. resinae* can metabolise are nitrogen and phosphorous, both of which can be found in diesel. *H. resinae* is resistant to hostile environments as it will sporulate during times of stress (i.e. depletion of the water bottom). *H. resinae* is the degrader of diesel and of fuel in general.

Some bioremediation methods exploit some soil fungi to clear diesel pollution. Due to their capability of metabolising hydrocarbons there have been isolations of some fungus in diesel tanks that have also been identified in bioremediation. *Fusarium, Gliocladmium, Mucor, Penicillium, Scopulariopsis* and *Trichoderma* have been identified as major organisms in bioremediation of diesel [24].

Other fungi that have been shown to exhibit growth in diesel also include *Acremonium, Aspergillus, Cephalosporium, and Chaetomium.* Fungi metabolise the carbon from diesel and release carbon dioxide, organic acids, alcohols and esters resulting in alteration of the diesel quality. Fungi are typically found growing in diesel in contrast to bacteria. Whereas bacteria commonly grow in crude oil, fungi appreciate the more refined products. Bacteria exhibit in the water bottom, whereas fungi usually exhibit a wider range of conditions and resources in which it could survive and reproduce [17].

Yeasts are classified in the kingdom Fungi, and are capable of inhabiting diesel [17]. Yeasts are capable of metabolising aromatic compounds and hydrocarbons.

Species of yeast isolated and characterised were *Pichia membranaefaciens*, *Candida rugosa* and *C. tropicalis*. *C. tropicalis* showed the highest biodegradability for phenols [25]. This shows the potential of yeast of inhabiting diesel.

Microbes, like any other organisms cannot survive without water. Only few microbes can grow in fuel itself. Water can get into the fuel storage system through various ways. Condensation is one of the problems that cannot be easily controlled. Generally microbes find their growth at the interface between fuel and water. Bacteria first colonise the interface and the resulting by-product are surfactants and lipopolysaccharides, also known as scinnogens [26]. Membranous scinnogens can act as solid surfactants, enabling bacteria to metabolise the fuel hydrocarbons. Similarly, at the solid-liquid interface the lipopolysaccharides are generally referred as the glycocalix [27].

Certain microbes do not metabolise hydrocarbons. However, those microbes that metabolise hydrocarbons can produce toxic metabolites that other species use as nutrients [28]. These can result in an accelerated fuel bio-deterioration due to the presence of a wide diversity of microbes.

2.4. Bio-fouling of Diesel

Bio-fouling or biological fouling is the degradation of a surface as a result of accumulation of organisms on a wetted surface. The greater the number of carbon atoms in a compound the easier it is for a microbe to metabolise it. The fuel contamination leads to fuel biodegradation and bio-fouling. These have as consequences blockage of pipes, blockage of valves, fouling of injectors, which leads to shorter lifetimes for diesel engines. During storage and transportation, the micro-flora continues to increase because of the moisture in the water bottom of the fuel tank.

2.4.1. Conditions for Bio-fouling of Diesel

To increase the shelf life of diesel, certain stabilisers are added during the refinery process. The additives also increase the diesel cetane number. However, these additives are a source of nutrient for some microbes [13]. Octane enhancers are esters which are added to diesel to inhibit microbial growth and biodegradation. Octane enhancers also lower the emission of volatile organic compounds. However, these additives create a good environment for the growth of microbes in diesel, whereas, biodiesel due to the high carbon content naturally provides a more favourable environment for microbial growth, compare with diesel.

Nutrients factors involved in microbial growth in diesel/biodiesel are:

a) **Carbon** is contained in high amounts in diesel/biodiesel, and combined with other nutrients provide a suitable medium for microbial colonies growth. The carbon in diesel and biodiesel comes in various forms and it can determine the range for a variety of micro-flora.

b) **Temperature.** The conditions for microbes to survive and grow in diesel tanks are favourable. Outside environmental temperatures can be unpredictable and microbes can tolerate between 4°C to 60°C and above [29]. The metabolism of microbes also generates heat which is able to add to the environmental temperatures exhibited within the diesel tank [30]. High temperature inside of the fuel tanks can destabilise diesel as a result of cetane stabilizer denaturation. Cetane stabilisers may act as minor nutrient for micro-flora, the denaturation would add to changes in chemical composition [31].

c) **pH.** Microbes that inhabit fuel have a preference for neutral pHs: conditions between pH 4 and pH 9 will suit a wide range of microbes [32]. The products produced by the microbes generally lower the pH making the water interface more acidic [22].

d) **Oxygen** is normally present in diesel and accumulates during the refuelling stage. The majority of microbes that degrade diesel are aerobic. The presence of oxygen allows the biodegradation of hydrocarbons in the diesel. An increase in aeration does increase a microbe`s hydrocarbon metabolism, however, a concentration of oxygen as low as 0.1 ml 1^{-1} is sufficient [17]. Having a completely anaerobic tank does not ensure sterility. Anaerobic and facultative microbes are able to utilise this environment and are capable of metabolising hydrocarbons within diesel [22].

e) **Water** is essential for microbes to grow. A minimum of 1% water will suffice for growth. The water can be present as a water bottom, with a clear diesel/water interface [17] or as water –in oil-mixture. Droplet size in a water-in-oil mixture would be in the range of 1.0 – 10 µm in diameter and are able to sustain micro-flora in diesel. Quality standards would normally allow a maximum of 0.1% water in diesel.

f) **Mineral and minor nutrients.** Some of the limiting factors in diesel and diesel/water are some of the essential minerals. Iron, iron ions and other ions are limited in diesel and diesel/water, but within a metallic diesel tank ions are present. The biodegradation of the tank increases metal ion concentration in diesel [17].

Water is used as part of the extraction process and ships use water for ballast. Fresh and ocean water contain low concentration of sulphates. Sulphates are an alternative electron acceptor to oxygen and will cater for the anaerobic micro-flora. Sulphur reducing bacteria (SRB) are some of the few bacterial organisms who can metabolise sulphates [17].

Phosphorus and nitrogen are also present in fuel at very low concentration (<1 ppm) [13]. These are nutrients that could serve as limiting factors for restricting growth within a diesel tank. Although this will limit growth, this will not limit the biodegradation of diesel [22].

2.5. Comparison Biodiesel – Diesel

The characteristics and functions of biodiesel are very similar to diesel. There are only two differences between diesel and biodiesel: the hydrocarbon content and the biomass used.

Yielding diesel requires the technique of distillation of crude oil. Crude oil is extracted from beneath Earth`s surface and can be distilled into many fractions, one of which is diesel. This method is quite a contrast to transesterification of rapeseed oil into biodiesel. Distillation of crude oil is where diesel has originated. Differences between the derivatives distilled from ground extracted crude oil and rapeseed transesterified oil is the common characteristic of petrochemical biomarkers; these are found within crude oil and are used to distinguish diesel from other diesel types [33].

Diesel and biodiesel exhibit similarities in their carbon atom content. Diesel has a carbon atom quantity between 15 and 22 rapeseed biodiesel has a carbon atom quantity between 16 and 22. Moreover, soya oil biodiesel has a carbon atom quantity 15 and 22 [22].

Researchers showed a difference in quantity of each fatty acid that is exhibited in diesel and biodiesel. Palmitic acid is found to be 20% of the total amount in diesel [34]. Palmitic acid was exhibited at 3% of the total amount in biodiesel [6].

Diesel is known to contain high amount of sulphur; this makes diesel a pollutant fuel. Biodiesel contains low amount of sulphur, in accordance with the European standard [35]. Both diesel and biodiesel contain sulphur and can influence the niche that a particular microbe might exploit.

The biodiesel's advantage over the diesel consists of the reduction of the harmful emissions without causing any severe engine damage. Some aspects of biodiesel have been found to enhance engine performance. Biodiesel is generally cheaper, renewable and does not emit any carcinogens. The emissions that are produced are less harmful to society [35].

2.6.Fuel Stability

A fuel is considered unstable when it undergoes changes in the physiochemical properties. Previous studies showed that storage conditions such as the temperature, atmosphere and presence of pro-oxidant metals can affect the quality of the fuel stored over a long period of time.

A fuel with high thermal stability refers to the fuel resistance to decomposition at high temperatures. These changes take place where the diesel engine reaches high temperatures. The injection system of the diesel engine could reach temperatures of up to 100°C, whereas for the engine injector tip, the temperature could reach up to 300°C.

Oxidative stability refers to the tendency of fuels to react with oxygen at temperatures near ambient. The presence of air inside of the fuel tank can provide the oxygen necessary for the fuel oxidation reaction to take place. Generally, the rate of reaction doubles with every 10°C increase in temperature [36]. The oxidation reactions are much slower than thermal oxidations, which take place at elevated temperatures. As a result of oxidation, the oxides formed on the aluminium parts often dislodge, producing varnish deposits and sediments.

Storage stability refers to the stability of the fuel while it is kept in long-term storage. Some metals have a catalytic effect on the biodiesel oxidation process. Especially in long term storage, the contact with metals such as copper, and copper containing alloys, lead, tin, and zinc should be avoided. Oxidative reaction is an important issue of storage stability. Storage stability includes not only the presence of oxygen, but also the moisture which could introduce contaminants in the fuel during the period of storage.

The unsaturated oils are more predisposed to the oxidation attack. The oxygen attach to the carbon element present in hydrocarbon molecule forming a hydro-peroxide molecule. The unsaturated biodiesel, containing multiple double bonds in its molecule, is highly susceptible to oxidation. Iodine Value (IV) or the iodine index are generally used to evaluate the content of hydro-peroxide in the fuel. Oils with high IV, such as soybean oil (has IV range from 130 to 135) are highly predisposed to oxidation while animal fats with low IV, such as tallow (has IV range from 30 to 48) are less susceptible. Linoleic and linolenic acids, with two or three bonds, respectively, oxidise fast. The hydro-peroxides could either break apart in short chain aldehydes and acids, or they could form dimmers and polymers. The short chain acids lead to a decrease in the flashpoint, while the polymerisation could results in an increase in viscosity and formation of insoluble sediments and varnish deposits [37]. As a result of fuel polymerisation a high molecular weight of insoluble sediments and gums could formed. The acid formation as a result of polymerisation might cause fuel system corrosion, and the hydro-peroxides are very unstable and have the tendency to react with elastomers. The effect of the polymerisation can range from changes in biodiesel chemical composition to physical properties of biodiesel. These could result in increase in fuel viscosity, and affect the engine efficiency, and therefore the exhaust emissions.

2.7. Combustion

A large quantity of the world`s energy comes from the combustion of fossil fuels, as presented in Figure 2-1 [38]. The downside of fossil fuels is the high amount of pollutant emissions released from combustion. The amount of pollutant emissions are strictly regulated by legislations in most of the developed countries. In order to conform to these norms new greener sources of energy are of interest today, together with the development of new ideas on how to achieve better combustion [39].

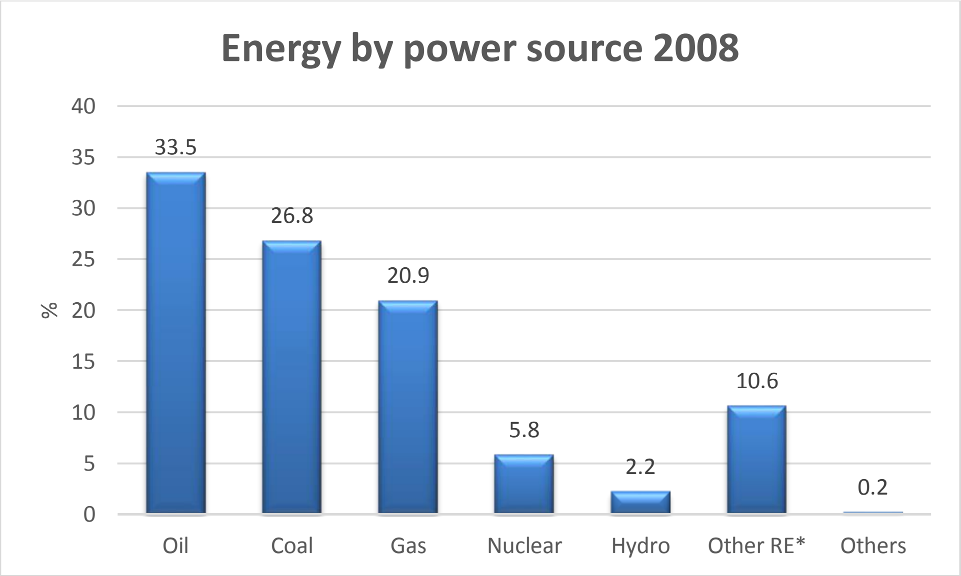

Figure 2-1: Energy by power source 2008 (38)

NOTE: Source: IEA *`=solar, wind, geothermal and biofuels

Combustion is defined as rapid oxidation producing heat, or both heat and light. The slow oxidation is a combustion process, as well, which generate little heat and no light. The slow oxidation occurs close to a catalytic surface at low temperatures, while the combustion process which takes place, for example, in burners and engines, is rapid oxidation which transforms the energy stored in the chemical bonds to heat [39].

A typical engine combustion reaction and the resulted components from the reaction are presented in equation (1).

$$Fuel + Air(N_2 + O_2) \rightarrow CO_2 + CO + H_2O + N_2 + O_2 + (HC) + \\ + O_3 + NO_2 + SO_2 + NOx + PM \tag{1}$$

where fuel can be - diesel = C_nH_m or

- biodiesel = $C_aH_bO_2$.

Carbon dioxide (CO_2) is a colourless, odourless gas that results from petroleum fuel combustion. CO_2 directly affects the human health and contributes to "greenhouse gas effect" [39].

Carbon monoxide (CO) is a result of the incomplete combustion of the fuel. Vehicles powered by diesel release carbon monoxide emissions. Common conditions for the carbon monoxide to form are when the air-fuel ratio in the engine is low, at cold engine start and at high altitudes, where the content of oxygen in the air is low [39].

At the high temperature conditions in the engine, nitrogen and oxygen atoms in the air react to form various nitrogen oxides, known as NO_x. Nitric oxide (NO), like hydrocarbons is the precursor of ozone. Nitrogen dioxides are considered major air pollutant and contribute to the formation of acid rain.

Hydrocarbons (HC) emissions or unburnt hydrocarbon are a result of a partially burnt molecule. Hydrocarbons are major pollutants. Together with nitrogen oxides and in the presence of sunlight contribute to ground-level ozone.

Sulphur oxides (SOx) are colourless gases formed due to the presence of sulphur in fuel. Sulphur oxides are very harmful for human health and environment.

Particulate matter (PM) are tiny solid or liquid particles of soot, dust, smoke, fumes, and aerosols. PM causes human health problems, visibility reduction and contribute to air pollution [39].

The results of the complete combustion process are CO_2, water and heat of combustion or energy. During combustion, the combustible part of fuel is subdivided into a volatile part and a solid residue. The fuel`s volatile components evaporate together with a part of carbon in the form of hydrocarbons, combustible gases, and carbon monoxide released by thermal degradation of the fuel [40] [39].

The fuel is heated above the ignition temperature in the presence of an oxidant. When complete combustion occurs, the combustible elements C, H and S react with oxygen content of air to form CO_2, H_2O and mainly SO_2.

If the oxidant necessary for the reaction to be sustained is not enough, then the exhaust gas is partially cooled below the ignition temperature and the combustion process remains incomplete. As a consequence of the partial combustion, carbon monoxide (CO), unburned carbon (HC) and various hydrocarbons (C_nH_m) are formed [39].

Complete combustion can be achieved only if the right amount of fuel and oxidiser is supplied. Air is commonly used for oxidising the fuel. The air consists of a mixture of 20.9% oxygen and 79.1% nitrogen by volume, or 23.3% oxygen and 76.7% nitrogen by mass. Nitrogen reduces the combustion efficiency by absorbing heat from the combustion of fuel and diluting the flue gases [40]. Thus, every mole of oxygen necessary for the combustion, introduces 3.78 mole of nitrogen.

There are three important factors which need to be achieved for a good combustion:

1) The temperature should be above the ignition temperature of the fuel, for the fuel to ignite and maintain the combustion,
2) Turbulence, swirls or intimate mixing of the fuel and oxidant, and
3) Sufficient time for the combustion to complete.

The results of a hydrocarbon fuel complete combustion are carbon dioxide and water. The water vapours produced after combustion absorbs heat from the flue gas, which would otherwise be available for heat transfer [39].

The stoichiometric relation for complete combustion of a hydrocarbon fuel, C_nH_m becomes:

$$C_nH_m + \left(n + \frac{m}{4}\right)(O_2 + 3.78N_2) \rightarrow nCO_2 + \frac{m}{2}H_2O + 3.78\left(n + \frac{m}{4}\right)N_2 \qquad (2)$$

Thus for every mole of fuel to be burned it is required $4.78(n + m/4)\ mol$ of air and resulting $[4.78(n + m/4) + m/4]\ mol$ combustion products.

The products of combustion are generally expressed in terms of mole fractions since the mole fraction does not vary with the temperature or pressure. The product mole fractions of complete combustion C_nH_m ful are:

$$y_{CO_2} = \frac{n}{4.78(n + m/4) + m/4} \qquad (3)$$

$$y_{H_2O} = \frac{m/2}{4.78(n + m/4) + m/4} \qquad (4)$$

$$y_{N_2} = \frac{3.78(n + m/4)}{4.78(n + m/4) + m/4} \qquad (5)$$

For most common fuels, the only chemical information available is its elemental composition on a mass basis. Consider a fuel that contains 86.9% C, 12.9% H, 0.07% O_2, 0.02 N, 0.09% S and 0.02% ash by weight. The molar composition may be determined by dividing each mass percentage by the atomic weight of the constituent, Table 2-1. For convenience in stoichiometric calculations the composition is normalised with respect to carbon.

Table 2-1: Fuel molar composition

Element	**wt [%]**	**mol/ 100g**	**mom/ mol C**
C	86.9	÷ 12.011 = 7.235	÷ 7.235 = 1
H	12.9	÷ 1.0079 = 12.798	÷ 7.235 = 1.769
O	0.07	÷ 15.999 = 0.00438	÷ 7.235 = 0.001
N	0.02	÷ 14.007 = 0.00143	÷ 7.235 = 0.0002
S	0.09	÷ 32.065 = 0.00281	÷ 7.235 = 0.0004
Ash	0.02		÷ 7.235 = 0.0028 g/mol C

The chemical formula that can be used to describe this particular fuel is:

$$CH_{1.769}N_{0.001}O_{0.0002}S_{0.0004} \tag{6}$$

The molar mass of the fuel is:

$$M_f = 100/7.235\big[g/mol\ C = 13.82[g/mol\ C]\big] \tag{7}$$

The combustion at stoichiometric condition is:

$$\begin{aligned} &CH_{1.769}N_{0.001}O_{0.0002}S_{0.0004} + \alpha(O_2 + 3.78N_2) \\ &\qquad \rightarrow CO_2 + 0.885\ H_2O + 0.0004\ SO_2\ (3.78\ \alpha + 0.0005)N_2 \end{aligned} \tag{8}$$

Where $\alpha = (2 + 0.885 + 0.0008 - 0.0002)/2 = 1.44$

The fuel/air mass ratio for stoichiometric combustion is:

$$\left(m_f/m_a\right)_{st} = \frac{13.82\ [g/mol\ \ C]}{1.44(31.998 + 3.78 \times 28.014)[g/mol\ C]} = 0.696 \tag{9}$$

The total number of moles of gaseous combustion products per mole of C is:

$$N_T = 1 + 0.885 + 0.0004 + 3.78 \times 1.44 + 0.0005 = 7.329 \tag{10}$$

The species mole fractions in the combustion products are:

$$y_{CO_2} = \frac{1}{7.329} = 0.136 = 13.6\ \% \tag{11}$$

$$y_{H_2O} = \frac{0.885}{7.239} = 0.122 = 12.2\ \% \tag{12}$$

$$y_{SO_2} = \frac{0.0004}{7.239} = 0.0000553 = 55.3\ ppm \tag{13}$$

$$y_{N_2} = \frac{3.78 \times 1.44 + 0.0005}{7.239} = 0.752 = 75.2\ \% \tag{14}$$

In real life it is very difficult to achieve stoichiometric combustion, thus in order to allow sufficient oxidant for the fuel it is preferable to operate the combustors with more than stoichiometric amount of air. The fuel/air ratio is used to define the operating conditions of a combustor. The fuel/air ratio required for stoichiometric combustion varies with the fuel composition [39].

The stoichiometric condition is used as reference point for systems operating on different fuels [39]. The equivalent ratio, Φ, is defined as the fuel/air ratio normalised with respect to the stoichiometric fuel/air ratio:

$$\emptyset = \frac{(m_f/m_a)}{(m_f/m_a)_{st}} \tag{15}$$

For	$\Phi < 1$ means fuel-lean combustion,

$\Phi = 1$ stoichiometric combustion, and

$\Phi > 1$ means fuel-rich combustion.

The stoichiometric ratio, λ, is the actual air/fuel ratio normalized with respect to stoichiometric air/fuel ratio:

$$\lambda = \frac{(m_a/m_f)}{(m_a/m_f)_{st}} = \frac{1}{\phi} \tag{16}$$

The percentage excess air, EA, is defined as:

$$EA = (\lambda - 1) \times 100 \tag{17}$$

The percentage theoretical air, TA, is:

$$TA = \lambda \times 100\% \tag{18}$$

The products of combustion vary with the equivalence ratio. The combustion conditions could be expressed in terms of a fuel/air ratio, and also in terms of the amount of excess oxygen in the combustion products.

2.7.1. First Law of Thermodynamics

The first law states that the sum of all energies is constant in an isolated system, with no mass transfer and no energy transfer taking place.

$$dE = \delta Q - \delta W \tag{19}$$

Where E represents the total energy of the system and includes the internal energy, U, the kinetic energy and the potential energy. The kinetic and potential terms can be neglected.

The change in internal energy dU of a system is given by the sum of the heat transferred and the work to the system,

$$dU = \delta Q - \delta W \tag{20}$$

As a general convention, the energy added to the system is taken as positive and the energy taken from the system is taken as negative.

Integrated over a finite change of state from state 1 to state 2, the equation (20) becomes:

$$U_2 - U_1 = Q_{12} - W_{x12} \tag{21}$$

In general practice, the fuel and air enter the combustion zone across certain boundaries, and combustion products are exhausted across other boundaries. Therefore, the expression can be derived for the change in state of a fixed volume in space, called control volume [39].

$$E_2 - (E_1 + \bar{e}\delta m) = Q_{12} + p\bar{v}\delta m - W_{x12} \tag{22}$$

Where $\bar{e}$ denotes the energy per unit mass or mass specific energy of δm,

$\bar{v}$ is the mass specific volume and is equal with 1/ρ,

$p\bar{v}\delta m$ is the work done on the combined system by the environment when the small volume enter the control volume surface,

W_x represents any work other than that associated with that volume displacement.

The over-bars denote mass specific properties.

Rearranging the terms, eq. (22) becomes:

$$E_2 - E_1 = \bar{e}\delta m + p\bar{v}\delta m + Q_{12} + -W_{x12} \tag{23}$$

$$dE = (\bar{e} + p\bar{v})\delta m + dQ - dW_x \tag{24}$$

The time rate of change of the energy in a control volume with a number of entering and exiting mass flows can be express as [39]:

$$\frac{dE}{dt} + \sum_{j,out} \left(\bar{e}_j + p\bar{v}_j\right) \bar{f}_j - \sum_{i,in} (\bar{e}_i + p\bar{v}_i)\, \bar{f}_i = Q - W_x \tag{25}$$

Where $\bar{f}_j$ and $\bar{f}_i$ are the mass flow rates leaving or entering the control volume,

Q is the rate of heat transfer to the system, and

W_x is the rate at which work is done by the system on its surrounding other than that associated with flows across the control volume boundary.

Neglecting the kinetic and potential energy contribution to the total energy, eq. (25) becomes:

$$\frac{dU}{dt} = \sum_{i,in} \bar{f}_i\, \bar{h}_i - \sum_{j,out} \bar{f}_j\, \bar{h}_j + Q - W_x \tag{26}$$

Where the mass specific enthalpy, $\bar{h}$, is defined as:

$$\bar{h} = \bar{u} + p\bar{v} \tag{27}$$

Rewriting the eq. (26) and (27) on a molar basis:

$$\frac{du}{dt} = \sum_{i,in} f_i\, h_i - \sum_{j,out} f_j\, h_j = Q - W_x \tag{28}$$

Where $h = u + pv$ denotes the molar specific enthalpy,

f_i is the molar flow rate of species i.

Consider the forward reaction occurring at steady state and constant pressure and isothermal conditions, as presented in Figure 2-2 [39]:

$$aA + bB \rightarrow cC + dD$$

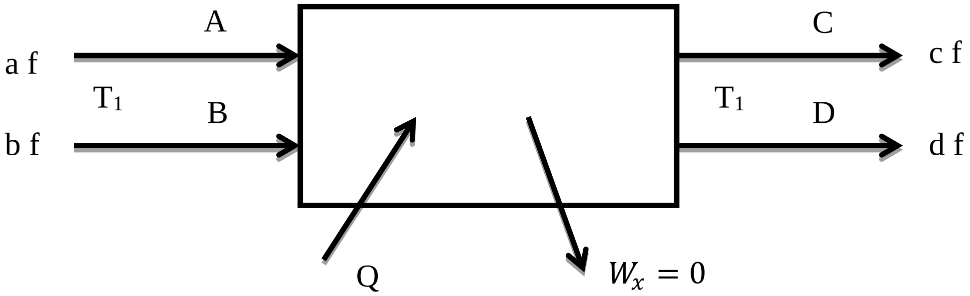

Figure 2-2: Isothermal steady flow reactor

Appling the steady-state form of eq. (28) to the system present in Figure 2-2:

$$cfh_C(T_1) + dfh_D(T_1) - afh_A(T_1) - bfh_B(T_1) = Q \tag{29}$$

Where $W_x = 0$ as no work is done by the combustion gases,

af, bf, cf and df denotes the molar flow of A, B, C and respectively D into the volume control at the temperature T_1.

Dividing eq. (29) by f obtains the heat transfer per mole necessary to maintain the process at a constant temperature, $T = T_1$:

$$ch_C(T_1) + dh_D(T_1) - ah_A(T_1) - bh_B(T_1) = \frac{Q}{f} = \Delta h_r(T_1) \tag{30}$$

Eq. (30) is called the enthalpy of reaction, $\Delta h_r(T_1)$ which is the difference between the molar specific enthalpies of the products and reactants at stoichiometric conditions. In order to define the enthalpy of a species it is necessary to consider a reference state at which the enthalpy it is taken to be zero. Generally, the reference temperature and pressure are taken to be $T_0 = 298K$ and $p_0 = 1atm$ [39].

The enthalpy of the reactants and products at the same temperature, T is called the enthalpy of the formation. By definition, the enthalpies of formation of the elemental reference compounds are zero [39]. The enthalpy of species i at temperature T relative to the reference state is:

$$h_i^{\circ}(T) = h_i(T) - h_i(T_0) + \Delta h_{fi}^{\circ}(T_0) \tag{31}$$

The superscript ° denotes evaluation with respect to the chemical reference state. The sensible enthalpy term may be evaluated as an integral over temperature of the specific heat constant pressure, $c_p = (\partial h/\partial T)_p$ which is:

$$h_i(T) - h_i(T_0) = \int_{T_0}^{T} c_{p,i}(T`)dT` \tag{32}$$

The specific heat, $c_{p,i}$ is dependent of temperature, therefore it can be approximated as a linear function of temperature:

$$c_{p,i} \approx a_i + b_iT \tag{33}$$

The approximation considered in eq. (33) estimates the value of sensible enthalpy for a range of temperature between 300 and 3000 K.

The first law of thermodynamics for a chemically reacting open system becomes:

$$\frac{dU}{dt} + \sum_{j,out} f_j\left[h_j(T) - h_j(T_0) + \Delta h^{\circ}_{f,j}(T_0)\right] - \sum_{i,in} f_i\left[h_i(T) - h_i(T_0) + \Delta h^{\circ}_{f,i}(T_0)\right] = Q - W_x \tag{34}$$

If the chemical composition and thermodynamic properties of the fuel are known, eq. (34) can be used to approximate temperature changes, heat transfer, or work performed in combustion systems [39].

2.7.2. Adiabatic Flame Temperature

Combustion reactions occur very fast – in the order of 1ms - and little heat or work transfer takes place on the time scale of combustion. For this reason the maximum temperature achieved in the combustion process is often near that for adiabatic combustion. This so-called adiabatic flame temperature can be calculated by applying the first law of thermodynamics to an adiabatic combustor [39].

Considering a steady-flow combustor burning fuel with composition CH_m, the combustion stoichiometry for fuel-lean combustion is:

$$CH_m + \frac{\alpha_s}{\emptyset}(O_2 + 3.78N_2) \rightarrow CO_2 + \frac{m}{2}H_2O + \alpha_s\left(\frac{1}{\emptyset} + 1\right)O_2 + \frac{3.78\alpha_s}{\emptyset}N_2 \tag{35}$$

where $\alpha_s = 1 + m/4$.

The first law of thermodynamics becomes:

$$
\begin{aligned}
f\Bigg[&\left[h(T)-h(T_0)+\Delta h_f^{\circ}(T_0)\right]_{CO_2}+\frac{m}{2}\left[h(T)-h(T_0)+\Delta h_f^{\circ}(T_0)\right]_{H_2O}\\
&+\alpha_s\left(\frac{1}{\emptyset}-1\right)\left[h(T)-h(T_0)+\Delta h_f^{\circ}(T_0)\right]_{O_2}\\
&+\frac{3.78}{\emptyset}\alpha_s\left[h(T)-h(T_0)+\Delta h_f^{\circ}(T_0)\right]_{N_2}\\
&-\left[h(T_f)-h(T_0)+\Delta h_f^{\circ}(T_0)\right]_f\\
&-\alpha_s\frac{1}{\emptyset}\left[h(T_a)-h(T_0)+\Delta h_f^{\circ}(T_0)\right]_{O_2}\\
&-\frac{3.78}{\emptyset}\alpha_s\left[h(T_a)-h(T_0)+\Delta h_f^{\circ}(T_0)\right]_{N_2}\Bigg]=Q-W_x=0
\end{aligned}
\qquad (36)
$$

The adiabatic flame temperature, T is calculated based on the sensible enthalpy and enthalpy of formation for each of the species. Using the linear approximation for the temperature dependence of the specific heats, equation (32) and (33):

$$
h_i(T)-h_i(T_0)=a_i(T-T_0)+\frac{b_i}{2}(T^2-T_0^2) \qquad (37)
$$

After separating the terms and substituting equation (37) in equation (36), the problem of determination of adiabatic flame temperature is reduced to solving a quadratic equation [39].

2.8. Compression Ignition Engine

2.8.1. Engine Performance

Engine performance is an indication of how efficient the engine converts the chemical energy contained in the fuel into mechanical work. The parameters evaluating the performance of an engine are the following:

a. Brake Power;
b. Brake Specific Fuel Consumption;
c. Brake Mean Effective Pressure;
d. Fuel-Air Ratio;
e. Exhaust Emissions and Smoke;
f. Brake Thermal Efficiency.

a) Engine Brake Power

The Brake Power is the useful mechanical power supplied by an engine as determined by a friction or absorption dynamometer that is applied to the output shaft or fly-wheel of the engine. The measurement of the engine brake power involves the measurement of the engine torque and speed [39]. The brake power is given by equation (37).

$$BP = \frac{2\pi NT}{60} \tag{38}$$

where T = torque [Nm]
N = rotational speed in revolutions per minute.

The total engine power developed in the cylinder is called the Indicated Power (IP). The difference between BP and IP is that the BP is the power left after some power was consumed by the moving parts of the engine due to the friction [39].

Indicated power is an indication of the combustion efficiency or the heat released in the cylinder, and is given by:

$$IP = \frac{MEP \times L \times A \times N \times k}{60} \tag{39}$$

where, MEP = mean effective pressure, [N/m^2], L = length of the stroke, [m],

A = area of the piston, [m^2],

N = rotational speed of the engine, [rpm] (It is N/2 for four stroke engine),

k = number of cylinders.

The power lost due to the moving parts of the engine is called the friction power, FP.

$$FP=IP-BP \tag{40}$$

$$Mechanical\ efficiency = \frac{BP}{IP} = \frac{BP}{FP+BP} \tag{41}$$

b) Brake Specific Fuel Consumption

Brake Specific Fuel Consumption, BSFC, is defined as the ratio between the rate of the fuels consumed and the brake power developed per hour. BSFC is an indication of engine efficiency.

$$BSFC = \frac{f_r}{BP} \tag{42}$$

where f_r = rate of fuel consumption

BP = engine brake power.

c) Brake Mean Effective Pressure

Mean Effective Pressure, MEP, is the pressure applied on the top of the piston, after the compressed air-fuel mixture ignited. MEP can be evaluated based on the engine brake power, equation (43), or based on the indicated brake power, equation (44) [39].

$$IMEP = \frac{IP \times 60}{L \times A \times N \times k} \tag{43}$$

$$BMEP = \frac{BP \times 60}{L \times A \times N \times k} \tag{44}$$

Similarly, the friction mean effective pressure (FMEP) can be defined as,

$$FMEP = IMEP - BMEP \tag{45}$$

From equation (38) and (39) result that torque is related to mean effective pressure by the relation presented in eq. (46)

$$\frac{2\pi NT}{60} = \frac{BMEP \times A \times L \times N \times k}{60} \tag{46}$$

From equation (46) it is observed that the higher is the BEP the more power the engine produces.

d) Fuel-Air Ratio (F/A)

Fuel-air ratio (F/A) is an important parameter for the diesel engine. The ratio of the fuel and air mixture determines the engine combustion efficiency. A combustion takes place at stoichiometric conditions when the ratio of the fuel to air is equal to one. The fuel-air ratio determines if the combustion is lean or rich, the flame propagation velocity and the heat of the combustion [39]. The relative fuel-air ratio, $(F/A)_{rel}$ is given by equation (47).

$$(F/A)_{rel} = \frac{(F/A)_{act}}{(F/A)_{st}} \tag{48}$$

e) Exhaust Emissions and Smoke

With the increasing concern related to the effect of exhaust emissions and smoke on human health and environment, strict regulations were imposed. Nitrogen oxides, sulphur oxides are under strict regulations. Smoke is an indicator of incomplete combustion.

f) Brake Thermal Efficiency

Brake thermal efficiency, (BTE), of an engine is defined as the ratio of the output energy to that of the chemical energy input contained in the fuel. BTE is an indication of efficiency of the engine to convert the chemical energy from a fuel into mechanical energy [39]. Brake thermal efficiency is given by equation (49).

$$BTE = \frac{m_f}{C_v} \tag{49}$$

where, C_v = the calorific value of the fuel, [kJ/kg]

m_f = the mass of the fuel supplied, [kg/sec]

2.8.2. Basic Measurement

There are a large number of parameters that are used to evaluate the engine performance, such as:

a) The engine speed
b) The engine fuel consumption
c) The air consumption
d) The engine brake power
e) The indicated power and friction power
f) The heat going to cooling water and exhaust
g) The exhaust emissions analysis.

Measuring methods and instrumentation used in order to evaluate the engine performance are described in the following.

a) Measurement of Speed

Speed is one of the main engine parameters used in engine`s performance evaluation. The engine speed can be measured using tachometer devices which count the number of revolutions at the engine shaft in a given time. The variations in engine temperature could affect the accuracy of tachometer measurements. In order to minimise the measurement errors, a magnetic pick-up positioned near the wheel attached to the engine shaft produces a pulse for every revolution, and a pulse counter will accurately measure the speed [41].

b) Fuel Consumption Measurement

Another important engine parameter is the fuel consumption. There are two ways of measuring the fuel consumption: gravimetric or volumetric.

i. **Gravimetric Fuel Flow Measurement -** the fuel consumption of an engine can be measured by determining the mass of fuel used in a given time interval. Gravimetric flow measurements are more accurate compared with the volumetric measurements since the weight of the fuel is directly measured, thus avoiding later correction of the fuel specific gravity. Gravimetric type of systems include the actual weighing of fuel consumed, four orifice flow-meter and coriolis flow meter.

ii. **Volumetric Fuel Flow Measurement –** the fuel consumption can be also measured by recording the time required for consumption of a given volume of fuel. Volumetric type flow meter includes burette method, automatic burette flow-meter and turbine flow-meter.

c) Measurement of Air Consumption

Accurate measurements of fuel and air for determining the engine performance is essential. Accurate air flow rate measurements could be achieved quite difficult due to the air flow pulsation caused by the engine`s cycles, as well as due to the air compressibility. The nozzles, orifices and venturi flow meter lead to variation in pressure gradient for a given set of flow conditions, which produce errors in measurements [39; 42; 43].

d) Measurement of Brake Power

The evaluation of the engine brake power involves the measurement of the engine torque and speed. Dynamometer measures both torque and speed. Dynamometers could be classified in two types: absorption or passive dynamometer and transmission or universal dynamometer.

Absorption dynamometers absorb the power developed by the engine, which then is converted and dissipated as heat. Types of absorption dynamometers are Prony brake, rope brake, hydraulic dynamometer, etc. Eddy Current Dynamometers are a type of absorption dynamometers commonly used for engine torque measurements. Eddy Current Dynamometer consists of a stator with electromagnets and a rotor coupled to the engine`s shaft. The rotation of the rotor produces eddy currents in the stator which then are converted to heat. The load is controlled by regulating the current in the electromagnets [39; 41]. A water cooling system is used in order to keep the dynamometer operational at a constant temperature.

A transmission dynamometers has to have the capability to drive the engine at the speed and torque required by the test conditions. The transmission dynamometer consists of a stand, prime mover and absorption device.

e) Heat going to cooling water and exhaust

The temperature of the water cooling entering and leaving the system, as well as the exhaust gas is measured with the help of the thermocouples.

f) Exhaust emissions analysis and smoke

All the substances emitted into the atmosphere as a result of combustion are termed exhaust emissions, and are regulated by law. For combustion of hydrocarbon fuel at stoichiometric conditions, the resultant exhaust emissions would consist of carbon dioxide (CO_2) and water vapours only. However, combustion at stoichiometric conditions is difficult to be achieved and the exhaust emissions consist of carbon monoxide (CO), unburned hydrocarbons (UBHC), volatile organic compounds (VOC), oxides of nitrogen (NOx) and excess oxygen.

The common instruments used to measure the exhaust as are: Flame Ionization Detector (FID), spectroscopic analyser and gas chromatography.

The working principle of a smoke meter is based on the measurements of the soot density as function of the mass of carbon measured in a given volume of exhaust gas. Other smoke measurements are performed using optical measurements. Fixed volume of exhaust gas is passed through the filter paper and the intensity of the smoke stain is measured.

Chapter 3 -Literature Review

3.1. Introduction

In this chapter published literature on diesel and biodiesel fuels has been reviewed with the aim of knowing the scope of the research that has already been carried out in order avoid repetition and to find justification for the proposed research. Most papers that could be sited were based on investigation of engine performance using biodiesel made from various types of feedstock. The mass fractions of biodiesel composition can vary from one biodiesel to another, depending on the biomass used in the production of biodiesel. These variations in physicochemical properties of biodiesel would influence the performance of an engine and the stability of the fuel under storage conditions. Unlike diesel, biodiesel's physicochemical properties can vary widely, therefore understanding of biodiesel`s predisposition to biodegradability and conformity to a specific standard is important. Hence relevant research papers were reviewed to establish the state-of-the-art knowledge about using various types of biodiesel in engines.

3.2. Characterisation of Microbial Contamination in Fuel

The issues of microbial contamination have been studied extensively and several research articles have been published in the technical literature. Important observations from these papers are summarised in this section.

Bacteria and fungi commonly identified in contaminated diesel fuel and accumulation of water at the bottom of the fuel tank are presented in Table 3-1.

Table 3-1: Bacteria and Fungi commonly isolated from diesel fuel [28]

Bacteria	**Fungi**
Pseudomonas species	Hormoconis resinae
Flavobacterium species	Fusarium species
Sarcina species	Candida species
Desulfovibrio species	Aspergillus species
Desulfotomaculum species	
Hydrogenomonas species	
Clostridium species	

Several microorganisms are able to metabolise mineral oil, depending on environmental conditions and supply of nutrition and oxygen content [44]. Microorganism populations composed of *Pseudomonas aeruginosa, Bacillus* species, and *Micrococcus* were effective in degrading hydrocarbons. Short and medium chains of hydrocarbon present an advanced degradation compared with that of longer chains. Mixed microbial cultures accelerate diesel fuel biodegradability, compared with the pure cultures [45].

Mukherji isolated bacteria cultures from an oil field in the Arabian Sea in order to investigate their growth in diesel oil. He noticed thirty-nine per cent of the fuels were degraded under aerobic conditions [46]. Boobathy investigated anaerobic degradation of diesel in sulphate reducing, nitrate reducing, methanogenic reducing, as well as in mixed reducing environment, proving that various microorganisms participate in degrading diesel fuel. During a period of 310 days 81% of diesel fuel was degraded in mixed reducing atmosphere [47]. Pereira and Mundge in their tests showed that biodiesel made from vegetable oil presented an enhanced biodegradability compared with biodiesel made from used edible oil [48].

T. Schleicher tested rapeseed oil methyl ester (RME) neat and in mixture with diesel in 20% RME and 80% diesel by volume (B20) and 5% RME and 95% diesel by volume (B5). Samples were inoculated with microorganisms found in soil. It was found that a higher diesel fuel ratio in diesel-biodiesel mixture resulted in a higher microbial growth, while fungal growth was more in higher RME contents. All inoculated samples showed a reduction in oxidation stability compared with the blank sample. Optical evaluation of the samples showed the formation of turbidity and sediments in B20 and B5, as a result of microbial growth [30].

Blends of biodiesel and 10% by vol. RME resulted in three time higher microbial growth compared with the neat diesel. Blend samples of diesel up to 40% by vol. RME incubated at 25°C present higher microbial growth, while biodiesel concentration over 40% by vol. in diesel mixture promote fungal growth. At higher temperatures, 44°C, the fungal growth was inhibited, while bacterial growth was enhanced [49].

Biodiesel as well as mixtures of diesel and biodiesel were more environmental friendly, compared with neat mineral oil, more rapidly biodegraded in soil and present lower toxicity to aquatic organisms in case of spillage [50; 51].

The fuel composition also determines the rate of the biodegradation. Fatty acid methyl esters (FAME), n-alkanes as well as iso-alkanes, and simple and alkylated aromatic compounds and naphthenes compounds were observed to have a high biodegradation rate [52]. Smaller alkanes are degraded more slowly than the larger ones, but elthylalkanes are degraded less rapidly than methylalkanes [52].

There are three reactions which can affect the quality of biodiesel: the hydrolytic split, oxidation reaction and electrochemical corrosion. The formation of free fatty acids (FFA) can occur due to the presence of water in biodiesel, through hydrolytic split of fatty acid methyl ester (FAME). This is known to causes corrosion of metals and synthetic materials. Volatile secondary compounds can be created through FAME oxidation. Changes in viscosity, boiling point, foam formation and fouling are results of polymerisation reactions [30]. The presence of water in fuel leads to both, chemical corrosion and microbiologically influenced corrosion (MIC). MIC can increase with the increase in biodiesel usage compared with mineral oil [53; 54]. The condensation formed inside of the fuel tank and the formation of volatile organic compounds in vapour phase above the surface of the fuel tank could generate favourable conditions for biofilm formation [28]. MIC can occur at the fuel or water interface with the surface of the storage tank [55-57]. Any irregularity, and or small damage of storage tank surface can provide a friendly environment for MIC. The development of biofilm inside of the storage tank can result in changes in fuel chemical composition [58]. Unrecognised biofilm and microbial growth formation lead to filter and fuel line blockage, which in turn result in operational failure in engine due to fuel starvation. The biofilm is mostly transparent and it could easily go unrecognised [59].

Microbiological contamination of fuel can have a negative impact on fuel tanks, on the fuel distribution line of the engine, injector, fuel filters, piston rings, and cylinder as well as combustion quality. A result of microbiological growth is fuel polymerisation, increased fuel acidity which leads to accelerated corrosion of e.g. fuel tanks, fuel distribution line, due to sulphur reducing bacteria (SRB).

3.3. Engine Performance with Biodiesel

A review of literature research in diesel and biodiesel is presented in order to highlight the similarities and differences in the performance of the two fuel types. The most frequently used was either direct injection single cylinder engine or 4-cylinder indirect injection engine. The biodiesel fuels used in the reviewed studies were composed of methyl esters produce from different oils mostly soy bean, rapeseed, and waste vegetable oil.

A decrease in CO_2, particulate matter (PM), carbon monoxide (CO) and sulphur oxides (SOx) was observed with the use of biodiesel. However an increase in NOx up to 15.7% was reported for 100% biodiesel (B100) [60; 61]. Biodiesel is a natural oxygenated fuel, with a content of oxygen up to 10% and a higher cetane number compared with diesel fuel. W. Quin and co-workers [62] investigated the effect of O_2 enrichment air on the combustion characteristics of fuel-lean methane/air flames.

Their test results showed that enhanced oxygen improves the combustion efficiency which resulted in reduced fuel consumption, lowered flame temperature and reduced NOx emissions. The reduction in NOx emissions when using O_2 enriched air was justified as being due to the lower flame temperature and reduced N contents in the combustion air.

> "The reduction of NO*x* is caused by the synergistic effect of temperature and N_2 concentration reductions as more O_2 is added" [62].

The differences in combustion gas between biodiesel and petro-diesel were expected due to the differences in the chemical composition. In the published literature it was found that short chained fatty acid methyl esters (FAME) and the saturated compounds could be associated with higher flame temperature, thus higher tendency for thermal NOx formation [63]. NOx emissions from a jet-stirred reactor were measured and the results showed that at 0.5-2.5ms residence time a minimum NOx of 3.5ppm (15% O_2 and 6.5atm) was measured. For residence time under 0.5ms an increase in NOx emissions was observed. This was explained by the increased presence of free radicals in the reactor which could result in higher NOx formation [64].

The Environmental Protection Agency (EPA), in their review showed an increase in NOx emissions as the biodiesel content was increased.

An increase in NOx was also observed by McCormick and Graboski et al. [60; 65]. They tested a single-cylinder research engine at 2000rpm and various loads with three waste oil biodiesel fuels. At low engine load they observed a slight decrease in NOx. However, it was observed an increase in NOx with the increase in engine load. A 70% reduction in HC emissions with neat biodiesel compared with petro-diesel was reported in the EPA`s review [66]. However, few researchers found similar HC emissions for biodiesel and diesel [67-71]. Only a small number of publications reported an increase in HC emissions for biodiesel compared with diesel [72]. EPA considers as a general trend a reduction by almost 50% in CO when biodiesel was used, compared with conventional diesel [66]. Krahl et al. [73] compared biodiesel from rapeseed oil with both low and ultra-low sulphur diesel and obtained approximately 50% reduction in CO emissions for biodiesel compared with diesel. Similar results were obtained by Graboski et al. [74].

Due to the EPA`s regulatory standards the level of primary pollutant emissions such as CO, CO_2 and HC emissions have been reduced, except the level of NOx. NOx refers to nitrogen oxide (NO) and nitrogen dioxide (NO_2) which are one of the main contributors to the formation of ground level ozone. The ground level ozone, one of the main contributors to the greenhouse effect is formed due to the chemical reactions that occur in the presence of sunlight between volatile organic compounds and NO_2. When NOx reacts with water in the air, nitric acid (NO) is formed. As with sulphur oxides (SOx), NO contributes to the formation of acidic rain and can cause health problems for human`s respiratory system. An in-depth understanding of the nitrogen oxides formation is essential since nitrogen oxides are one of the principal contaminants resulted from the combustion process.

3.3.1. Engine Brake Power (BP)

In order to compare the efficiency and emissions from an engine using different fuels, it is necessary that the tests to be carried out under same engine operating conditions. Tsolakis [75] compared ultra-low sulphur (ULS) diesel and rapeseed biodiesel fuels by defining three engine operating conditions in a single-cylinder naturally aspirated direct injection diesel engine by setting engine speed and load. Various tests were performed on direct and indirect diesel engine. The engine test conditions covered 25%, 50%, 75% and 100% load and various engine speed [65; 75-79]. The test results showed that for the same fuel consumption, full load and engine speed conditions, biodiesel presented a reduction by 8% in power output compared with diesel fuel. This decrease in power output was due to the biodiesel’s low heating value. Tests using sunflower oil biodiesel in engine at various speeds and medium and full load, showed a loss in torque and power between 5% and 10% compared with diesel, with the increase in engine speed [80]. When comparing waste-oil biodiesel and diesel fuels at full-load engine conditions, the loss of torque was only between 3% and 5% with biodiesel [81]. Test results from engine with ultra-low sulphur diesel, neat palm oil biodiesel and 20% palm biodiesel blend ratio in diesel, showed a reduction by 3.5% for neat biodiesel and by 1% for the blend [82-84]. Few researchers also have found an increase of brake power and torque for engine with biodiesel. An increase in torque by 6.1% was reported for engine with tall biodiesel B70 (70% biodiesel – 30% diesel) compared with diesel fuel [85-87]. They explained that the increase in torque was due to the higher cetane number of biodiesel, higher density and viscosity and improved combustion compared with that of diesel.

Some authors reported a reduction in brake power and torque when biodiesel with low calorific value was used in diesel engine. It was reported between 3% and 8% reduction in engine torque and power for cotton seed biodiesel compared with diesel [88]. They explained that the decrease in engine efficiency was due to difficulties in the fuel atomisation. Southwest Research Institute reported a reduction in engine brake power for 20% biodiesel blend ratio in diesel and for neat biodiesel, by 2% and 8% respectively, compared with diesel [89]. Tests on a 6-cylinder DDC (Detroit Diesel Corp.) engine with rapeseed oil, soybean oil and cottonseed oil biodiesel were performed at engine speed of 1200 rpm and 2000 rpm. The results showed similar brake power for biodiesel compared with that of diesel [90; 91].

The reduction in brake power and torque for engines with biodiesel was considered to be due to the higher viscosity of biodiesel compared with that of diesel. Tests were performed in a turbocharged engine with biodiesel using different injection pumps. At engine conditions of 1400 rpm and full load, it was observed that the volume of biodiesel injected using two different injection pumps was higher with 1.2% and 3.2% compared with that of diesel [92]. It order for the biodiesel to be injected in the cylinder at the same viscosity with that of diesel, the biodiesel injection temperature was increased. At these engine operating conditions the results showed an increase in the volume of diesel injected as a result of its low density compared with that of biodiesel [86]. The low density of diesel resulted in high flow rate through orifices compared with biodiesel. The biodiesel`s high bulk modulus and high pressure wave propagation due to the biodiesel`s high speed of sound, could result in advanced injection due to the advanced needle lift of the injector nozzle. [90; 93; 94]. This and the biodiesel high viscosity lead to an advanced start of injection [92; 95; 96]. The temperature and the peak pressure inside of the cylinder can be reduced by delaying the start of combustion. These resulted in a reduction in nitric oxides, and also in engine thermal efficiency and brake power [85].

The conclusions derived from the literature survey were that, using biodiesel in diesel engines resulted in a decrease in engine power, and the increase in brake fuel consumption would compensates the lower heating value of biodiesel compared with diesel. However, some researchers reported a slight improvement in engine efficiency due to the lubrication property of biodiesel.

3.3.2. Brake Specific Fuel Consumption (BSFC)

Brake specific fuel consumption (BSFC) is a measure of engine efficiency. At fixed engine operating conditions, BSFC is the ratio between the amount of fuel consumed and the power generated by the engine. An increase of 14% in fuel consumption for engine with biodiesel would be expected due to the lower calorific value of biodiesel compared with diesel [97]. Biodiesel contains up to 10% oxygen in its composition, compared with diesel. This lead to reduction in biodiesel calorific value. Various tests were performed on engine with neat soybean oil biodiesel and various biodiesel blend ratio in diesel (20%, 35% and 65%) in order to assess the effect of oxygen content on brake specific fuel consumption [97]. The experimental results showed a correlation between brake specific fuel consumption and the oxygen content in the fuel. The oxygen content in the fuel resulted in the increase in BSFC, rather than when the oxygen enriched air was used [98]. BSFC was observed to increase with the decrease in biodiesel calorific value. Some studies showed that brake fuel consumption in case of neat soybean biodiesel increased from 13% to 18% compared with diesel fuel, while blends of 20% soybean biodiesel (B20) showed an increase in BSFC in the range of 3% to 9% [89]. Similar results were obtained from diesel engine with palm oil biodiesel. An increase by 16.7% in BSFC was obtained for diesel engine with neat palm oil biodiesel, and by 3.3% for 20% palm oil biodiesel blend ratio in diesel compared with ultra-low sulphur diesel [82].

An increase by 2.5% in BSFC was observed for diesel engine with 20% soybean biodiesel blend ratio in diesel, and an increase by 14% in BSFC for neat soybean biodiesel compared with diesel [99; 100]. These variability in the experimental results could be due to the differences in the engine type used and the engine operating conditions. The BSFC from 1.9 l diesel engine with rapeseed biodiesel was investigated at various engine operating conditions [78]. The test results showed a correlation between the loss in calorific value and the increase in BSFC. Similar results were obtained from a single cylinder research engine with rapeseed biodiesel [75]. The influence of physico-chemical properties of biodiesel on bake specific fuel consumption was also investigated. Oxidised and non-oxidised soybean biodiesel were tested in a 4.5 litres engine [101]. The results showed an increase by 15.1% in BSFC for neat oxidised biodiesel, and by 13.8% for the case of non-oxidised biodiesel. Most of the authors explained the increase in brake specific fuel consumption to be a consequence of the loss in biodiesel calorific value. Few authors explained the increase in BSFC to be caused by the higher density of biodiesel compared with that of diesel [65]. A few other studies found small increase or similar brake specific fuel consumption for engine with neat cottonseed biodiesel and waste olive oil biodiesel compared with diesel fuel [87; 102].

In summary, as a general trend, the brake specific fuel consumption was observed to increase with the increase in biodiesel blend ratio in diesel and with the decrease in biodiesel calorific value.

3.3.3. Brake Thermal Efficiency (BTE)

Thermal efficiency is the measure of efficiency of fuel combustion, expressed as the ratio between power output and the energy introduced in the system. Where the energy introduced into the system is the product of the injected fuel's mass flow rate and the lower heating value. The inverse of thermal efficiency is referred to as brake specific energy consumption, which is another parameter to be considered when different fuels are compared. In their research many authors would have observed no significant change in thermal efficiency when using biodiesel. Various types of biodiesel were tested in diesel engine and the results showed that the thermal efficiency was similar for biodiesel diesel [78; 97; 99; 101; 103]. Hamasaki et al. [72] tested biodiesel with different acid values in a single cylinder engine, at various engine load and constant speed, and found similar thermal efficiency in all cases.

Puhan et al. [65] compared ester from mahua ethyl ester oil to normal diesel and found that the brake thermal efficiency of mahua ethyl ester was comparable with diesel. It was observed 26.36% for diesel whereas 26.42% for mahua ethyl ester. Kaplan et al. [80] reported an increase in brake thermal efficiency due to the improved combustion and reduction in friction between the moving parts of the engine when biodiesel used. Lin et al. [82] tested neat palm oil biodiesel and in 20% blend ratio in diesel in an indirect injection diesel engine, and reported a decrease in efficiency by 2.3%.

Labeckas and Slavinskas [68] tested blends of 5%, 10%, 20%, 36% and 100% rapeseed oil biodiesel in a 4.75 litres engine under different steady modes. The results obtained showed a maximum thermal efficiency for 5% to 10% blends. Murillo et al. [104] tested diesel and different blends of used cooking oil biodiesel in a marine 3-cylinder naturally aspired engine. To the contrary, his results for blends of 10%, 30% and 50% biodiesel showed lower efficiency compared with highest efficiency obtained from neat biodiesel.

Most of the authors found no significant change in thermal efficiency for biodiesel compared with diesel fuel. The increase in fuel consumption for biodiesel was due to the biodiesel lower calorific value compared with that of diesel, hence the engine efficiency with biodiesel was observe to be similar to that of diesel.

3.4. Pollutant Emissions from Biodiesel

Pollutant emissions are harmful to human health and environment. Any gases released into the atmosphere in high concentrations, such as those from vehicles, or as a result of fossil fuel combustion are strictly regulated by law. Pollutant emission could be classified in two categories: primarily pollutants and secondary pollutants. Primarily pollutants such as unburnt hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NOx), and particulate matter (PM) could react in the atmosphere and form secondary pollutants. These affect the air quality and lead to formation of ground-level ozone, smoke, ozone depletion and climate change. Therefore, restrictions on pollutant emissions became more stringent.

3.4.1. Total Hydrocarbon Emissions (THC)

Many authors observed a decrease in THC emissions for engines with biodiesel compared with diesel [101; 105-109]. The Environmental Protection Agency review showed a 70% reduction of THC with pure biodiesel with respect to conventional diesel [66]. However, a few studies reported no significant differences [67- 70] or increase [72] in THC emissions from engine with biodiesel compared with that from diesel. Some authors reported reduction in unburnt hydrocarbon emission for engine with high biodiesel blend ratio in diesel, while for engine with low biodiesel blend, an increase in unburnt hydrocarbon emission was observed [110]. These results were explained to be either due to the small content of biodiesel blend ratio in diesel, or due to very low unburnt hydrocarbon emissions, which were lower than the detection range of the gas analyser [67-70]. Most of the studies reported a reduction by up to

70% in unburnt hydrocarbon when biodiesel was used compared with that of diesel [73; 111; 112].

The influence of biodiesel content together with other parameters such as the presence of oxidative catalytic convertor, the injection pressure and the quality of the diesel used as a baseline has been also analysed. Charlet et al. [113], and Lapuerta et al. [77; 114] tested biodiesel from rapeseed oil in a direct injection engine, and respectively cardoon and sunflower biodiesel in an indirect injection engine. They reported similar reduction in THC emissions from engine at various operating conditions. Few researchers reported a reduction in THC emissions only at low engine operating conditions, for engine with sunflower oil biodiesel [115]. Munack et al. [116] and Aakko et al. [67] tested biodiesel fuels from rapeseed, soybean and used cooking oil on a diesel engine on the ECE R49 test cycle. The results showed a reduction in THC emissions when biodiesel fuels were used, but this decrease was higher when the engine was not equipped with a catalytic converter. Leung et al. [117] observed an increase in THC emissions with the increase in injection pressure for both diesel and biodiesel fuels. The EPA review [66] reported reductions by 70% in THC emissions for neat biodiesel compared with conventional diesel fuel, and up to 50% compared with high cetane and low-density petro-diesel. Other studies reported reductions between 30% and 40% in THC emissions for engine with rapeseed, soybean and palm oil biodiesel compared with diesel [118]. A reduction by 20% in THC emissions was observed for engine with biodiesel compared with high cetane and ultra-low sulphur diesel [118]. Test performed in a turbocharged and direct injection engines with waste cooking oil and soybean oil biodiesel showed a reduction by 50% in THC emissions compared with diesel [95; 99]. Some studies reported a correlation between THC emissions and the biodiesel saturation and the carbon chain length in biodiesel. The test results showed greater reduction in THC emissions with the increase in biodiesel saturation and with the increase in carbon chain length in biodiesel [103; 119]. Graboski et al. [103] carried out engine tests with methyl and ethyl pure esters and conventional biodiesel fuels, in order to observe the effect of the alcohol type on the engine emissions. Their results showed that the alcohol used in the biodiesel production does not have any significant effect on engine emissions with biodiesel. Few researchers investigated the effect of biodiesel oxidation on the engine emission. They compared non-oxidized biodiesel with oxidised biodiesel with a peroxide values ten times higher than the original one. The results showed a reduction in THC emissions for the engine with oxidised biodiesel. These results were explained by the increased cetane number and the presence of peroxide in the biodiesel [96].

Several reasons have been found for the decrease in THC emissions. The oxygen content found in the molecule of biodiesel leads to complete and clean combustion [89; 107]. Unburnt hydrocarbon emissions decreased with the increase in oxygen content in the combustion air or in the molecule of fuel [98]. The cetane number was observed to affect greatly the engine emissions. Researchers reported combustion delay for fuels with high cetane number [107; 120; 121]. These resulting in reduction in unburnt hydrocarbon emissions [96; 122]. Advanced injection was also reported for engines with biodiesel, due to the physical properties of biodiesel. The advanced injection was observed to contribute to the increase in nitric oxides emissions and lower the unburnt hydrocarbon emissions [123].

3.4.2. Carbon Monoxide Emissions (CO)

Many authors observed a decrease in CO emissions compared with diesel, when biodiesel was used in diesel engines [66; 89; 107; 120; 121]. Few studies showed no significant differences in carbon monoxide emissions between diesel and biodiesel [69; 72]. Krahl et al. [73] compared biodiesel from rapeseed oil with both low and ultra-low sulphur diesel fuels and obtained a reduction by 50% in CO emissions for biodiesel. Similar results were obtained from a turbocharged engine with various blends of biodiesel and diesel fuel [74; 112]. Krahl et al. [35] reviewed some studies and reported 15% reduction for biodiesel compared with petro-diesel.

Several researchers investigated the effect of engine load, biodiesel blend ratio in diesel and the effect of an oxidative catalyst on carbon monoxide formation. Most authors pointed out the effect of engine load on the carbon monoxide emissions. Some researchers observed a reduction in CO emissions with the increase in engine load, while others found a greater reduction in CO emissions from engine at low load [93]. The Environmental Protection Agency, in their review reported a reduction by 45% in CO emissions compared with conventional diesel, and by 35% when high cetane number, low density diesel was used as baseline [66].

Few researchers investigated the effect of oxidative convertor on engine emissions. They observed an increase in CO emissions for the engine equipped with convertor, while for the engine without the convertor, the CO emissions were reduced [67; 116].

The influence of biodiesel type on engine emissions was study. The EPA found grater reduction in CO emissions from animal fat biodiesel compared with vegetable oil biodiesel [66]. A grater reduction in CO emissions were observed for rapeseed oil biodiesel compared with soybean oil biodiesel. These results lead to the conclusion that the CO emissions decreased with the increase in biodiesel saturation. Similarly, reduction in CO emissions were observed from engine with waste cooking oil biodiesel compared with soybean oil biodiesel [95; 99]. Other researchers assessed the effect of carbon chain length on engine emissions. They tested diesel engine with lauric (C12:0), palmitic (C16:0) and oleic (C18:1) methyl ester biodiesel [119]. They observed a reduction in CO emissions with the increase in carbon chain length in biodiesel. The effect of biodiesel oxidation on engine emissions was studied. Three waste cooking oil biodiesel with different acid value where tested in a diesel engine in order to assess the effect of fuel acid value on engine emissions [72]. The results showed increase in CO emissions with the increase in biodiesel acid value, as a result of high hydro-peroxide concentration in biodiesel [72; 96].

Several reasons have been proposed to explain the reduction of CO when biodiesel is used in diesel engines. Due to the fact that biodiesel is a natural oxygenated fuel, the additional oxygen in the biodiesel content enhanced the fuel combustion, thus reducing CO emissions [89; 107; 124].

Most of researchers reported reduction in CO emissions from engine with oxygenated fuel or when oxygen enriched air was used [98]. The decrease in CO emissions was also justified by the higher cetane number of biodiesel [107; 120; 121; 124]. The higher the cetane number, the lower is the probability of fuel-rich zone formations. Some authors explained the reduction in CO emissions from engine with biodiesel to be due to the advanced injection and combustion [123].

3.4.3. Nitric Oxides Emissions (NOx)

Most authors in their work reported a slight increase in NOx emissions when using biodiesel fuel in diesel engine. However, some authors observed NOx increase only at certain engine operating conditions, while others found similar NOx emissions between diesel and biodiesel. Few studies reported even a decrease in NOx emissions for biodiesel compared with diesel fuel.

Tests performed in a 6-cylinder diesel engine under different loads with 10%, 20%, 30% and 40% soybean biodiesel blends showed up to 15% increase in NOx from engine with 40% biodiesel blend ratio in diesel [125]. A Cummins engine was tested under steady operating conditions with diesel and neat biodiesel and the results showed increase by 16% in NOx emissions for biodiesel compared with that from diesel [126]. Few other papers reported, also increase in NOx from engines with biodiesel [35; 74].

Some authors investigated the dependence of NOx on the engine type and the engine operating conditions. Three engines were tested at transient operating conditions, with blend of 1800ppm diesel sulphur content and 10% sunflower biodiesel blends [69]. They reported both increase and decrease in NOx emissions, which were attributed to the differences in engine technology.

Tests on a single cylinder research engine at 2000rpm and various loads with three waste oil biodiesel showed slight decrease in NOx emissions at low loads, while at high engine load the NOx increased [72].

ECE R49 test cycle and urban transient cycle tests were performed for comparative reasons [105]. The tests results showed an increase by 9.5% in nitric oxide emissions for ECE R49 test cycle, and 6.5% reduction in NOx for transient urban cycle.

Other researchers pointed out that the increase in NOx emissions from test performed in an engine bench are higher than those measured from vehicles [95]. This was due to the fact that the engine load set on the test bench are usually higher than those in the vehicles.

Tests were performed on four different heavy duty engines turbocharged, naturally aspirated, direct and indirect injection. NOx emissions from these engines with neat biodiesels, diesel and 20% biodiesel blend ratio in diesel were measured and the test results showed no significant difference in NOx emissions [127]. Other authors measured NOx emissions from nine vehicles with 35% soybean biodiesel blend ratio in diesel and they reported no significant difference in NOx due to the engine type [128].

Only a few studies reported a decrease in NOx emissions for diesel engine with biodiesel compared with diesel [102; 114]. Tests performed in diesel engine with ethyl and methyl ester biodiesel showed a reduction by 10% in NOx emission compared with diesel fuel [112]. Similar reduction by 5 to 10% in NOx emissions was obtained from Caterpillar engine at transient cycle with neat soybean biodiesel [2].

The Environmental Protection Agency in their review reported an increase in NOx emissions with the increase in biodiesel blend ratio in diesel [66]. Most of the authors explained that the increase in NOx emissions was caused by the advanced injection which was triggered by the biodiesel physical properties. The biodiesel high viscosity, density, compressibility and sound velocity resulted in higher injection pressure compared with diesel fuel [129]. The increase in NOx emissions at high engine load was attributed to the shift in start of combustion. Biodiesel has lower compressibility compared with diesel. This resulting in faster propagation of biodiesel towards the injectors and earlier needle opening [70; 92; 101; 118; 119; 129]. However, few authors found injection delay for engine with biodiesel compared with ultra-low sulphur diesel [130].

The influence of biodiesel type on NOx emissions was also investigated. Some authors found correlations between the increase in NOx emissions and the decrease in carbon chain length and unsaturation esters in biodiesel [103]. Several other studies also reported NOx increase with the increase in iodine number [103; 131]. The EPA concluded in their report that NOx emissions vary direct proportional with the biodiesel un-saturation [66; 95]. Some authors explained the increase in NOx emissions as a results of the adiabatic flame temperature and the different intermediate combustion products [119]. The adiabatic flame temperature was observed slightly higher for biodiesel [77; 132; 133]. Cheng et al. [134] tried to maintain both the start of combustion and the rate of premixed combustion unchanged. He tested three primary reference fuel blends in an effort to match precisely the ignition delay and premixed burn fraction of the reference fuel to that of B100. Each primary reference fuel blend was a mixture of *n*-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane, in the appropriate quantities to achieve a desired cetane number. The test results showed an increased in NOx for biodiesel due to the reduced soot radiative heat transfer, which resulted in high flame temperature.

Other authors explain the NOx increase due to the increased cetane number of biodiesel, which leads to an advanced combustion by shortening the ignition delay [101]. The oxygen content in biodiesel, resulted in more oxygen available in the engine combustion chamber which could promote NO formation [106; 135]. Iida et al. [135] and Song et al. [136] found that both the oxygen content in fuel and the oxygen enriched air contributed to the increase in NOx emissions. The oxygen enriched air was observed to result in higher NOx formation compared with the oxygenated fuel [77]. The high cetane number of biodiesel could lead to advance combustion. This could lead to reduction in pressure and temperature in the combustion chamber, resulting in a reduction in NO emissions [106].

Few authors found that biodiesel chemical composition influenced NOx formation. They observed that a relation between the content of saturated esters in biodiesel and NOx formation. A reduction in nitric oxides was observed with the increase in ester saturation content in biodiesel [137].

Some authors concluded that the increase in NOx formation for diesel engine with biodiesel was due to the advance injection. The fuel spray characteristics was another hypotheses considered to justify the increase in NOx. The fuel physical properties such as viscosity, surface tension and boiling temperature can influence the droplet size and spray distribution, droplet evaporation, droplet moment of inertia and heat dissipation. These could influence the start of combustion, the fuel-air mixture and diffusion, and consequently the NO formation [74].

3.4.4. Particulate Matter Emissions (PM)

Most authors observed a noticeable decrease in PM emissions with the increase in biodiesel content [74; 77; 101; 105; 128; 129]. Reductions by 20% to 40% in PM emissions was observed from heavy-duty engines with biodiesel [35]. Many researchers reported greater reduction in PM emissions from diesel engine with biodiesel [72; 77; 138; 120]. Researchers reported reductions by 70% in PM emissions from engine with neat biodiesel and by 45% from engine with 20% biodiesel blend ratio in diesel [31; 45]. Engine tests were performed with soybean oil biodiesel and waste cooking oil biodiesel and the authors reported a reduction by 65% in PM emissions [99; 139]. Few studies reported even higher reductions, between 75% and 91%, in PM emissions from engine with biodiesel compared with those from diesel [140; 141].

Few researchers reported similar PM emissions from diesel and biodiesel [70] or even found increase in PM emissions compared with diesel fuel [112; 116; 120].

Correlations between the biodiesel blend, the engine load and particulate matter emissions were observed. Test results showed reduction in PM emissions with the increase in biodiesel blend ratio in diesel at both transient and steady state engine operating conditions [79]. Many studies reported greater reduction in PM emissions from engine at high load [72; 117; 137; 142; 143]. The authors explained these reduction in PM emissions to be due to the oxygen content in biodiesel which lead to complete combustion. Small reductions in PM emissions were observed from engine with biodiesel compared with high cetane ultra-low sulphur diesel [66; 144].

Several explanations for the reduction in particulate matter were found in the literature. A reason for the decrease of PM emissions was considered to be the oxygen content in the biodiesel molecule, which enabled complete combustion in fuel-rich regions inside of the combustion chamber, due to the diffusion flame [74; 77; 106; 128; 137; 145; 146], and promotes the oxidation of the already formed soot. When engines with oxygenated fuel were tested, a greater reduction in PM emissions was obtained compared with the case of oxygen enriched air [106]. The lower stoichiometric need of air in the case of biodiesel combustion, reduces the probability of fuel-rich regions in the non-uniform fuel/air mixture [77]. The decrease in aromatic content obtained by Schmidt and Van Gerpen by blending diesel fuel with octadecane (C18H38) provided a significant reduction in PM emissions, which was even more significant when soybean-oil biodiesel was added in the blend [106].

The effect of biodiesel type on PM emissions was also investigated. Some authors reported a reduction in PM emissions with the increase in biodiesel saturation [66]. Others authors reported a reduction in PM emissions with the decrease in carbon chain length in biodiesel and due to the low oxygen content [119]. Few authors reported no difference in PM emissions due to the difference in biodiesel feedstock. Similar reductions in PM emissions were obtained from engine with soybean oil biodiesel and waste cooking oil biodiesel compared with those from diesel [95; 99]. A general agreement found in the published literature, was that the reduction in PM emissions was due to the oxygen content in the fuel [103; 147].

3.5. Justification of Objectives

From the literature review of a majority of research papers published regarding engine performance using biodiesel and the specific emissions characteristics, the following general conclusions were drawn:

- Engine brake power was found lower for biodiesel with up to 8% compared with diesel for most of the biodiesels over a wide operating conditions;
- The majority of authors found an increase in brake specific fuel consumption when biodiesel was used, while just few papers stated a not significant change compared with diesel;
- The majority of the publications show similar brake thermal efficiency for diesel and biodiesel;
- A significant decrease in THC emissions were found in most of research papers;
- CO emissions from biodiesel were found to be lower compared with diesel, when engine was under high load operating conditions. Also it was stated that the biodiesel nature has an influence on CO emissions. Some authors found a decrease in CO by advancing the injection and combustion;
- NOx emissions were found by the large majority of authors to be higher for biodiesel compared to diesel;
- PM from biodiesel is lower compared with diesel;
- The experiments presented in literature were performed on single cylinder engines, two strokes and four strokes engines.

In the literature reviewed it has been observed that the investigations of biodiesel are spread over biodiesel made from various exotic biomasses. Biodiesel made from waste cooking oil and other waste oils is increasingly being made and promoted because it reduces waste and offers environmentally friendly utilisation of waste oil. However, information on the basic properties and performance data of such biodiesel is scarce. This research aims to provide an overview of biodiesel made from waste cooking oil focussing on three main aspects of biodiesel: microbiological contamination, diesel engine performance using waste cooking oil biodiesel and emissions characteristics from WCO biodiesel. The effect on engine performance using biodiesel made from waste cooking oil is also experimentally investigated in a dynamometer, using a 4 stoke Land Rover diesel engine.

3.6. Methodology

A range of theoretical and experimental techniques were used for achieving the objectives and aim of the research. A combination of microbiological tests, pilot scale combustion tests and performance test in diesel engine were performed.

- **Measuring of Fuel properties & microbial contamination**

The biodiesel analysed was obtained from the market from three UK providers. First, waste cooking oil biodiesel was obtained from two different sources for comparison of microbial contamination and biodegradation test. The fuel samples to be tested were prepared as 20, 50 and 100% biodiesel blends with diesel and were duplicated.

The biodiesel obtained from the third source was used for combustion investigations tests. The samples prepared to be tested on a CCR and a DI engine were 25, 50, 75 and 100% biodiesel and diesel blends.

The fuel properties were measured for neat diesel and biodiesel and the physical and chemical properties for the various diesel-biodiesel blends were deduced analytically. FT-IR analyses of each fuel sample were run in order to assess the diesel-biodiesel blend. Neat diesel and biodiesel samples were analysed for their functional groups by GC-MS in order to provide a more specific characterisation of the fuel composition tested.

- **Combustion characteristics**

Combustion in the Continuous Combustion Rig (CCR) of various diesel-biodiesel blends were investigated to provide an insight on the characteristic products from the combustion of biodiesel at various equivalence ratios, focusing the attention on NO formation.

- **Engine performance**

Biodiesel blends were also tested in an unmodified direct injection diesel engine over a wide range of set of operational conditions. The engine performance was analysed in terms of engine brake power, brake specific fuel consumption, brake thermal efficiency and carbon monoxide, unburned hydrocarbon, nitrogen oxides and carbon dioxide emissions.

Finally various performance data obtained from these tests was analysed to establish correlations between different parameters.

Chapter 4 - Measuring Fuel Properties and Microbial Contamination

4.1. Fuel Properties Measurements

The fuel properties have a significant effect on the performance and emission characteristics of an engine. The physical properties of the biodiesel, diesel and blends of diesel with biodiesel used in the experiments, such as density, viscosity and calorific value were determined. Fuel elemental analyses, diesel and biodiesel spectrum were determined by Fourier Transform – Infrared Spectroscopy (FT-IR) and Gas Chromatography – Mass Spectrometry (GC-MS).

The experiments to measure fuel calorific value, fuel density, fuel viscosity, CHNOS elemental analysis and FT-IR spectra of fuel were performed. The experimental procedure for each test is explained and the results are presented in this chapter.

4.2. Biodiesel Samples Preparation

Blended samples of WCO biodiesel with diesel were made by intense mixing of both with the help of a stirrer at ambient temperature. All the blends were prepared and stored overnight before being tested. The fuel blends were prepared on volume basis. The nomenclature of the blends is given as follow:

B0 – Neat diesel
B25 – Blend of 25% biodiesel and 75% diesel
B50 – Blend of 50% biodiesel and 50% diesel
B75 – Blend of 75% biodiesel and 25% diesel
B100 – Neat biodiesel

4.3. Biodiesel Calorific Value

The higher calorific value i.e. gross or total heat value of a fuel, whether solid or liquid, is the quantity of heat produced by complete combustion of a given mass of a fuel, usually expressed in joules per kilogram. A bomb calorimeter is used to determine the higher calorific value of the fuel.

4.3.1. Apparatus

The calorific value of net biodiesel and diesel was determined using a Parr 6200 Bomb calorimeter. The schematic view and the working principle of the calorimeter are presented in Figure 4-1.

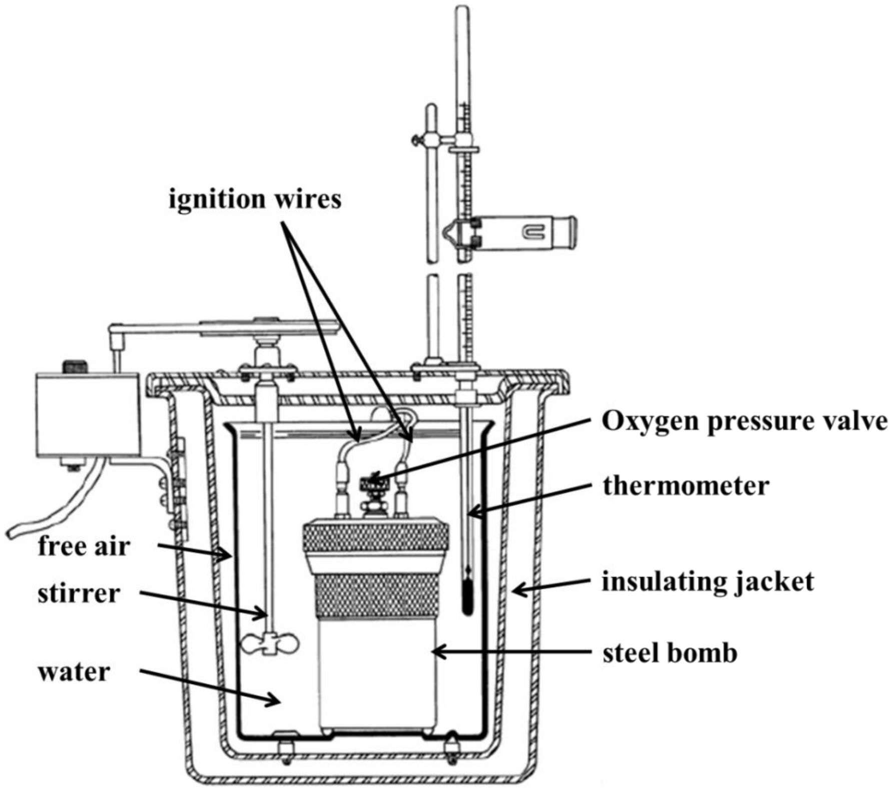

Figure 4-1: Bomb calorimeter principle

The bomb calorimeter is made from high pressure stainless steel coated with an acid resistant metal. The threaded cover can be screwed on to the main body of the bomb. The cover has two terminals for electrical connections to the mains. A screwed steel wire form one connection and the other wire passes through an insulated plug protected against the high temperature inside the bomb. A silica crucible is kept in position by two projecting ends on two wires. A fuse wire of known mass is joined to the two wires keeping it in contact with the fuel. The whole calorimeter is kept submerged in a water jacket that surrounds the calorimeter. A motor driven stirrer constantly agitates the water keep its temperature uniform. The speed of the stirrer is kept within the range 150-200rpm.

4.3.2. Procedure

1. A measured amount of fuel is placed into the crucible.
2. The cover of the bomb is tightened to hold the body in a stand.
3. Oxygen is allowed to enter the bomb very slowly as to ensure that the sample does not spill in the crucible until the pressure is 20bar and then the oxygen cylinder`s valve is closed.
4. The sealed bomb is then immersed in a bucket filled with known quantity of water (2 litres).
5. The fuel is ignited and the heat released by fuel burning the fuel is transmitted to water and thus its temperature rises.
6. A thermometer with a reading resolution up to 1/100th of a degree measure the temperature rise of water bath.
7. The higher calorific value of the fuel is calculated from the temperature increase.

4.3.3. Methodology

A small sample of fuel is accurately weighed and burned in an atmosphere of oxygen within the bomb immersed in stirred water bath. The energy released by the fuel sample through combustion results in a rise in water bath temperature. The total energy liberated is known as the increase of temperature and the thermal capacity of the bomb, water and water bath container. Calculations are simplified by taking thermal capacity of the bomb and water container as mass of water, which is termed as water equivalent of calorimeter. The higher heating value is measured by the Parr 6200 instrument. Conforming to ASTM D240, the lower calorific value (LCV) for liquid fuels can be calculated when knowing the percentage of hydrogen in the fuel using the following correlation:

$$LCV = 1.8HCV - H$$

Where LCV is lower calorific value, HHV is higher calorific value, and H represents the percentage hydrogen content in the fuel.

4.4. Density Measurement

Density of neat biodiesel and diesel was calculated from separate mass and volume measurements.

4.4.1. Apparatus

In order to measure the density of the samples, three 100ml graduated cylinders and a scale with a reading resolution of 0.01 grams were used.

4.4.2. Procedure

A 100ml clean, dry graduated cylinder was weighted. The distilled water, diesel and biodiesel fuel were kept at 20°C room temperature. The cylinder was filled with

100ml distilled water and was weighed on a scale and the weight was recorded. A second and third dry graduated cylinder was filled with 100ml diesel fuel, weighed on the scale and the weight was recoded. After each sample was weighing, its density was calculated.

4.4.3. Methodology

Density is a measure of the “compactness” of matter within a substance and is defined by the equation:

$$\rho = m/V$$

Where ρ is the density, m is the mass of the liquid weighted and V is the volume of the liquid measured.

The standard metric units in use for mass and volume respectively are kilograms and cubic centimetres. Thus, density has the unit kilograms/cubic centimetres (kg/cm^3).

4.5. Viscosity Measurement (EN ISO 3104)

The viscosity is an important physical property of the fuel since it determines the optimum storage, operating and handling conditions. For measuring the fuel viscosity a capillary viscometer was employed. The kinematic viscosity of the fuel is determined by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity can be measured by multiplying the kinematic viscosity by the density of the liquid. The range of the kinematic viscosities covered by this method is 0.2 to 300000mm^2/s, at all temperatures. The ASTM standard specification of this procedure is D445.

4.5.1. Apparatus

Figure 4-2 represents the capillary viscometer used to measure the viscosity of the biodiesel and diesel.

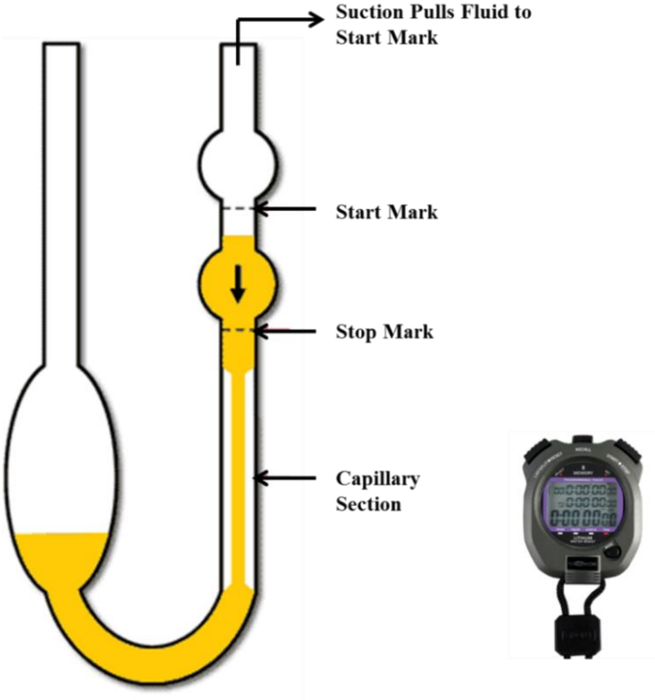

Figure 4-2: Schematic representation of the capillary viscometer apparatus

The apparatus is composed of a calibrated viscometer of the glass capillary tube, capable of being used to determine kinematic viscosity within the limit of precision, viscometer holders, temperature controlled bath, calibrated liquid glass thermometer of range 0-100°C and a stopwatch capable of taking reading with a resolution of 0.1s.

4.5.2. Methodology

A fixed volume of fuel is allowed to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature, and the time is measured. The kinematic viscosity is the product of measured flow time and the calibration constant of the viscometer.

4.6. CHNOS Elemental Analysis

Carbon, hydrogen, nitrogen, oxygen and sulphur (CHNOS) elemental analysis of neat biodiesel and diesel were performed to determine the carbon, hydrogen, nitrogen, oxygen and sulphur content in the fuel.

4.6.1. Methodology

- Determination of Total Oxygen in Liquid, Chemical & Hydrocarbon Products was performed following MT/ELE/21 standard. The oxygen analysis was performed using EA Instruments 1110 oxygen analyser.
- Determination of Carbon, Hydrogen and Nitrogen using a Thermoflash 2000 analyser was performed using MT/ELE/13 standard.
- Determination of Sulphur by combustion with UV fluorescence using Antek 9000 analyser was performed following MT/MCR/12 standard.

MT/ELE/01 standard was used for determination of metals by ICP-OES.

4.7. Biodiesel by Fourier Transform-Infrared Spectroscopy

Neat diesel, biodiesel and various blends of diesel and biodiesel were analysed by FT-IR in order to observe useful differences between the samples.

4.7.1. Apparatus

Fourier transform - infrared spectra of the fuel samples were collected on a Varian 800 Scimitar Series FT-IR spectrometer. The schematic representation of the FT-IR is presented in Figure 4-3.

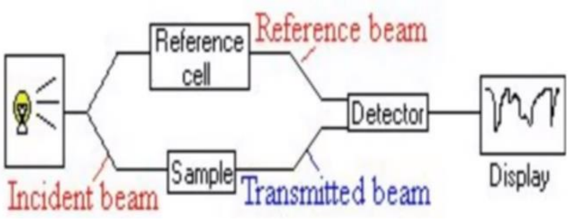

Figure 4-3: Schematic representation of FT-IR

Figure 4-4: NaCl sample plate

4.7.2. Methodology

The instrument was setup to scan between 400 and 4500cm^{-1}. The sample holder is scanned in order to collect the background information which later will be reduced from the sample scan. After the sample was prepared, the sample holder is fixed into the FT-IR analyser and scanned.

Samples of neat biodiesel B100, B25, B50, B25 and neat diesel, B0 were analysed by FT-IR. Using a sterile pipette, a drop of the liquid sample was placed on the face of a highly polished salt plate (NaCl), and then the second plate was placed on top of the first plate, so as to spread the liquid into a thin layer between the plates and clamp the plate together, Figure 4-4. The sandwich plates were then mounted onto the sample holder. After each sample was analysed, the salt plate used was washed with acetone in order to remove any residue from the previous sample.

4.8. Biodiesel Composition by GC-MS

Samples of neat biodiesel and diesel were analysed in order to identify the compounds in samples using gas chromatography–mass spectrometry (GC-MS). GC-MS identification is based on retention time and mass spectrum.

4.8.1. Apparatus

The fuel samples were tested using Varian 450GC – Varian 240-MS.

4.8.2. Methodology

Samples of diesel and biodiesel were prepared for GC-MS analyses. Using a sterile syringe with an attached filter, 10 microliters of neat biodiesel and respectively diesel fuel samples taken respectively were poured in a sterile vial bottle and mixed with 1ml of pure hexane. Using a sterile pipette, 2ml of the prepared solution were placed into a vial bottle and placed into the GC-MS automated sampler. One 2ml vial bottle was also prepared with pure hexane for reference.

The following method was followed for sample analysis:

- Column 500°T
- Acquisition
    - Low mass 40 m/z
    - High mass 1000 m/z
    - Start at 5 min.
    - End at 30 min.
- Ionisation source: electron ionization (EI)
- Injection temperature 250°C
- Split ratio 50
- Oven Column

    - 50°C to 280°C
    - rate 10°C/min
    - hold 5min
    - total time 30min
- Injection volume 1μL.

4.9. Diesel and Biodiesel Microbiological Degradation

4.9.1. Introduction

Biodiesel degradation is enforced under the presence of microorganisms that find good growth conditions in the barrier between water and fuel. Microorganism population composed of strains of *Pseudomonas* and *Micrococcus* proved to be especially effective in degrading hydrocarbons. The differences exhibited in microbial growth, when two different types of biodiesels and diesel fuel were tested could prove that the chemical composition within the biodiesel and diesel samples were an important factor for the specificity of microbial growth. The chemical composition can be anything subtle, such as grade of diesel used, like low or normal sulphur or volume of medium used. Another factor taken into consideration is the inoculums added to the biodiesel bottles. The effect of microbial growth could affect the engine performance and in the long term lead to harmful effects on diesel engine operability.

The biodiesel samples were obtained from two suppliers, Bolton and Sheffield, who also supplied the petrol stations with biodiesel in various blends. The experiments aimed to assess the “end user” biodiesel under microbial contamination compared with diesel. All biodiesel samples were previously treated with additive to improve the cold flow properties and stability to microbiological contamination. The additives used in preventing the microbial contaminations act primarily by inhibiting the quorum sensing of bacteria. Quorum sensing is a system of stimulus and response which coordinates gene expressions according to the density of their population.

4.9.2. Experimental Programme

Experiments were conducted to investigate the effect of unknown consortia of microorganisms, which were previously collected from diesel tank sludge and soil, upon biodiesel. A water bottom was created by using Bushnell and Haas [BH] medium, and the rest of the space was filled with diesel, biodiesel, or a blend of diesel and biodiesel in different proportions.

The experiment was observed over a ten week incubation period to assess levels of spoilage. The main aim of the investigation was to observe microbial growth, and report effects of microbial growth over physical properties of fuel.

4.9.3. Methodology

Biodiesel made from waste oil, provided from two different sources within of UK, Bio UK Fuels (Sheffield) Ltd and Bolton Alternative Fuels Coop were investigated. Each BH medium was contaminated with a mixture of diesel tank sludge and soil (10ml per 200ml). Different blends of biodiesel and diesel (standard mineral diesel), and contaminated BH medium, in total volumes 1L sterile Duran bottles, were produced as follows:

- Diesel – BH: 800 ml : 200 ml
- Bolton Biodiesel – BH: 800 ml : 200 ml
- Diesel – Bolton Biodiesel – BH: 400 ml : 400 ml : 200 ml
- Diesel – Bolton Biodiesel – BH: 640 ml : 160 ml : 200 ml
- Sheffield Biodiesel – BH: 800 ml : 200 ml
- Diesel – Sheffield Biodiesel – BH: 400 ml : 400 ml : 200 ml
- Diesel – Sheffield Biodiesel – BH: 640 ml : 160 ml : 200 ml

Samples, each conducted in duplicates, were incubated in a 22ºC incubator for 10 weeks.

Before the samples were inoculated, with a selected tank sludge and soil, the microbial population was enumerated on Yeast Extract Agar (YEA) and Malt Extract Agar (MEA) plates. Using serial dilutions, colony forming unit (cfu) were calculated for inoculation into biodiesel bottles. The calculated cfu that was inoculated into biodiesel was 7.66×10^{6} cfu ml^{-1} of sludge/soil mixture, which resulted in a total inoculators of 1.4×10^{8} cfu per sample.
During a six weeks period of incubation, visual observations of the changes in the biodiesel bottles were noted at an interval of fourteen days. Changes were noted in biodiesel and water bottom colour, and the presence of microbial growth for each sample.

10ml of liquid from water at the bottom of each bottle were taken at fourteen days, twenty-eight days, and fourteen-two days, fifty-six days, seventy-days after inoculation. The samples were gently swirled prior to sampling ensuring a good mix of micro-flora (even if none were visible). 10ml samples were taken from the water bottom using a sterile 10ml graduated pipette, stored in sterile universal tubes, and were used for inoculating agar plates and for pH measuring.

After extraction, using a sterile pipette, 100µl consortia of micro-organisms were spread on each YEA and MEA plates. Using serial dilutions, 10^{0}, 10^{-2}, 10^{-4}, colony forming unit (cfu) were calculated for each inoculated biodiesel sample. Counts of cfu were conducted after incubation at fourteen days, twenty-eight days, and forty-two days.

The techniques for bacterial identification started with gram staining. Colonies of distinguished morphologies were sub-cultured onto fresh YEA plates, for identification. Colonies from plates exhibiting bacterial growth were Gram stained, and then further analysed to genus level [148]**.** The bacterial identification was performed using the API 20NE V7.0 kit (bioMerieux) according to manufactures instructions, for the identification of Gram-negative rods, combining eight conventional tests, twelve assimilation tests and a database.

The API 20 NE strip consists of API AUX Medium, and micro-tubes containing dehydrated substrates. Colonies of identical morphology extracted from the Petri plate are necessary for API 20NE test. Bacterial identification was performed following the manufacturer`s instructions. The reactions are read according to the Reading Table and the identification was obtained by using the APIWEB software.

Supplementary tests for 42ºC incubation were suggested by APIWEB software. A colony from each plate was spread onto fresh YEA plates, for twenty-four hours incubation at 42ºC. The results were interpreted according with the specification suggested by APIWEB results.

Measuring of the pH was done in line with extractions that were taken every fourteen days. pH was measured using an electronic pH meter which was calibrated towards the acidic pHs. The electrode was kept sterile using Industrial Methylated Spirits (IMS) and rinsed with distilled water (dH_2O) to prevent dehydration to the electrode. The pH was measured at 25ºC.

4.10. Results

The results of experimental measurements of physical properties, CHNOS elemental analysis and microbial contamination of diesel and biodiesel fuel are presented. The measured physical properties of diesel and biodiesel are listed in Table 4-1.

Table 4-1: Physical properties of diesel and biodiesel

	Diesel (B0)	**Bolton Biodiesel (B100)**	**Sheffield Biodiesel (B100)**	**VEPower Biodiesel (B100)**
Specific gravity [g/cc]	0.834	0.852	0.862	0.882
Viscosity at 40°C [mm^2/s]	3.5	4.45	4.43	4.47
Lower calorific value [MJ/kg]	41098.325	332992.56	333996.28	33374.209

Properties of diesel and biodiesel blend were calculated by using the formula:

$p_{blend} = xp_d + (1-x)p_b$, where p is property, x fraction of diesel.

Elemental analyses of neat biodiesel and diesel samples were performed and the results are presented in Table 4-2. The elemental analyses was perform for VEPower biodiesel. The data were useful for the estimation of residence time of NOx emissions measured from a laminar premixed flame.

Table 4-2: Biodiesel and Diesel elemental analyses from ITS Testing Laboratory

Analysis	**Units**	**VEPower Biodiesel**	**Diesel**
Carbon content	%wt/wt	76.0	86.9
Hydrogen content	%wt/wt	11.9	12.9
Nitrogen content	%wt/wt	0.02	0.02
Oxygen content	%wt/wt	11.7	0.07
Sulphur content	mg/kg	5.2	900
Concentration of Silver	mg/kg	<1	<1
Concentration of Aluminium	mg/kg	<1	<1
Concentration of Boron	mg/kg	<1	<1
Concentration of Barium	mg/kg	<1	<1
Concentration of Calcium	mg/kg	3	<1
Concentration of Chromium	mg/kg	<1	<1
Concentration of Copper	mg/kg	<1	<1
Concentration of Iron	mg/kg	<1	<1
Concentration of Potassium	mg/kg	62	<7
Concentration of Magnesium	mg/kg	<1	<1
Concentration of Manganese	mg/kg	<1	<1
Concentration of Sodium	mg/kg	<8	<8
Concentration of Nickel	mg/kg	<1.5	<1.5
Concentration of Phosphorous	mg/kg	<1.5	<1.5
Concentration of Lead	mg/kg	<1.5	<1.5
Concentration of Sulphur	mg/kg	<30	651
Concentration of Silicon	mg/kg	<1	<1
Concentration of Tin	mg/kg	<1	<1
Concentration of Titanium	mg/kg	<1	<1
Concentration of Vanadium	mg/kg	<1	<1
Concentration of Zinc	mg/kg	1	<1

4.10.1. Biodiesel by Fourier Transform-Infrared Spectroscopy Results

Fourier Transform-Infrared (FT-IR) is a method of infrared spectroscopy. Infrared radiation is passed through a sample, where some of it is absorbed by the sample and some passes through. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. An infrared spectrum can be divided into two regions for examination. The region from 4000 to 1500 cm^{-1} provides information about the functional group and the region from 1500 to 600cm^{-1}, also called the fingerprint region, provides a unique pattern for each organic compound.

Samples of diesel (B0) and blends of diesel and biodiesel (B25, B50, B75 and B100) were prepared and analysed by FT-IR. Figure 4-5 shows FT-IR spectrum of diesel and biodiesel samples in the region from 3800 to 2800 cm^{-1}.

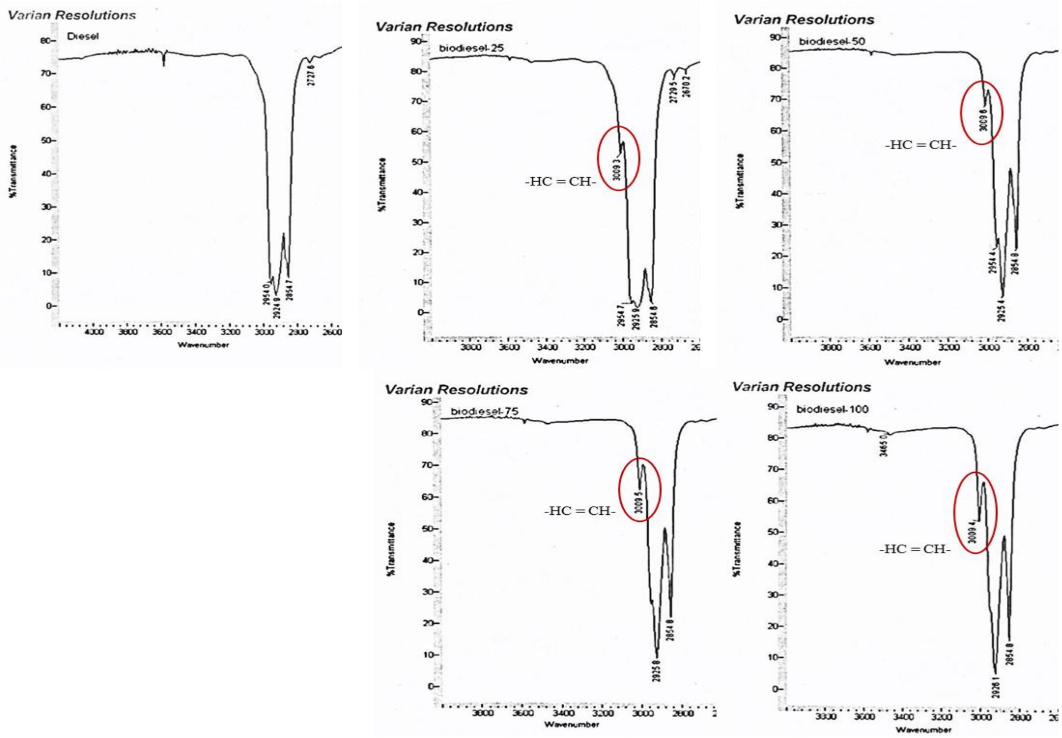

Figure 4-5: FT-IR spectrum of B0, B25, B50, B75 and B100 in the region from 3800 to 2800 cm^{-1}

The band presence in the region of 3009.4 cm^{-1} was observed only in the biodiesel samples. It is observed that with the increase in biodiesel blend in diesel, bands arise at 3009.4 cm^{-1}. This represents –HC=CH–stretching and the increase in intensity represents the increase in unsaturation of biodiesel samples (149).

Figure 4-6 show a comparison between diesel an biodiesel samples in the region 1740 cm^{-1}. The presence of band at 1740 cm^{-1} indicates the presence of carbonyl group (C=O) (149). It is observed that the carbonyl band evolution is proportional to an increase of biodiesel blend in diesel. The double bound denotes unsaturation.

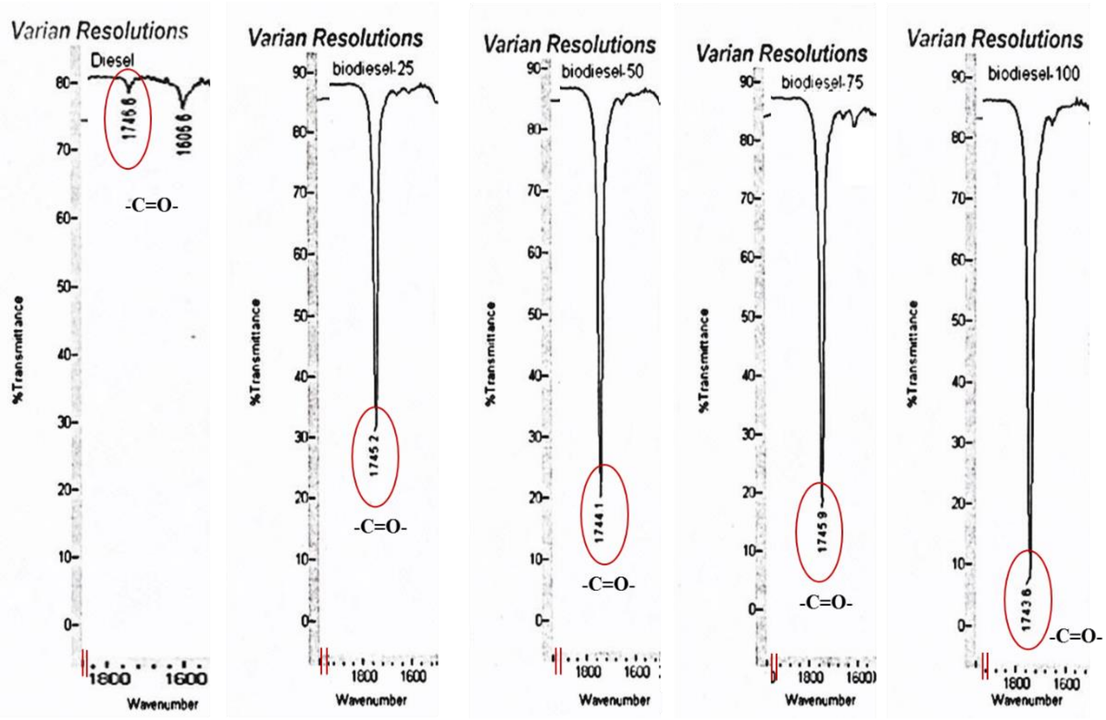

Figure 4-6: FT-IR spectrum of B0, B25, B50, B75 and B100 in the region from 1800 to 1600 cm^{-1}

Figure 4-7 shows a comparison between spectrum of diesel and biodiesel in the region from 1600 to 600 cm^{-1}. The band in the region of 1462 cm^{-1} represents the C=C functional group. These unsaturated compounds may not have significant effect on cold flow properties of biodiesel and therefore additives or improvers should be added to biodiesel for better performance.

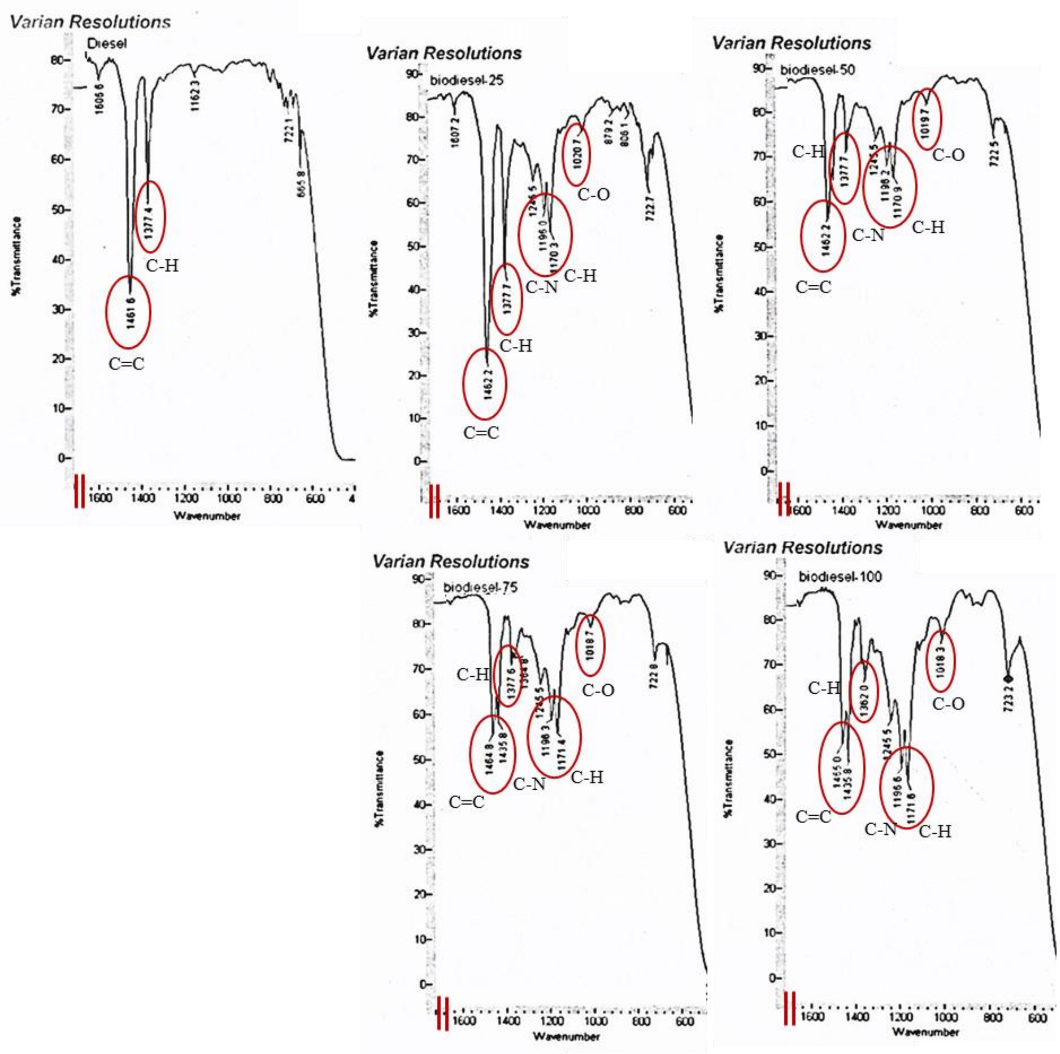

Figure 4-7: FT-IR spectrum of B0, B25, B50, B75 and B100 in the region from 1600 to 600 cm^{-1}

The band in the region of 1196 cm^{-1} represents the C-N cyanide group detected with stretch mode of vibration, which may indicate the presence of undesirable contaminant at the point of purifying biodiesel.

FT-RI spectrum of biodiesel shows a band in the region 1170 cm^{-1} and 1019 cm^{-1}, corresponding to C-H and C-O single bonded functional group. Single bonds represent saturated compounds in the fuel. A high content of saturated compounds in a fuel can lead to pour cold flow properties during cold weather operations. However, the presence of double bounds (C=C, C=O) which are most abundant enhance the cold flow properties of the fuel, but may increase the biodiesel susceptibility to oxidation.

4.10.2. Biodiesel Composition by GC-MS Results

Tables 4-3 and 4-4 present the mass fraction compounds identified in diesel and respectively biodiesel fuel.

Table 4-3: Results of NIST Libraries for Diesel Spectrum

Compound	**Formulae**	**Mol. Wt.**	**Probability**
Cyclodecasiloxane, eicosamethyl-	$C_{20}H_{60}O_{10}Si_{10}$	740	77.54
9-Desoxo-9-x-acetoxy-3-desoxy-7.8.12-tri-O-acetylingol-3-one	$C_{28}H_{38}O_{10}$	534	65.58
3,9.beta.;14-15-Diepoxypregn-16-en-20-one, 3,11.beta.,18-triace	$C_{27}H_{34}O_9$	502	60.97
Penylalanine, 4-amino-N-t-butyloxycarbonyl-, t-butyl ester	$C_{18}H_{28}N_2O_4$	336	74.16
N-Ethyl-4-propyl-4-octanamine	$C_{13}H_{29}N$	199	68.80
Naphthalene, 1,2,3,4-tetrahydro-	$C_{10}H_{12}$	132	75.57

Table 4-4: Results of NIST Libraries for WCO Biodiesel Spectrum

Compound	**Formulae**	**Mol. Wt.**	**Probability**
Hexacosanoic acid, methyl ester	C27H54O2	410	80.93
Methyl 22-methyl-tetracosanoate	C26H52O2	396	68.39
Tetracosanoate acid, methyl ester	C25H50O2	382	88.28
Tricosanoic acid, methyl ester	C24H48O2	368	74.65
9-Desoxo-9-x-acetoxy-3-desoxy-7.8.12-tri-O-acetylingol-3-one	C28H38O10	534	68.75
Methyl 20-methyl-heneicosanoate	C23H46O2	354	78.99
Eicosanoic acid, methyl ester	C21H42O2	326	82.29
Methyl 9.cis.,11.trans.t.13.trans.-octadecatrienoate	C19H32O2	292	69.53
Cyclodecasiloxane, eicosamethyl-	C20H60O10Si10	740	73.75
Methyl 14-methylhexadecanoate	C18H36O2	284	64.47
Pentadecanoic acid, 14-methyl-, methyl ester		270	82.97
Cyclodecasiloxane, eicosamethyl-	C20H60O10Si10	740	87.68
Methyl 13-methyltetradecanoate	C16H32O2	256	81.02
Cyclononasiloxane, octadecamethyl-	C18H54O9Si9	666	96.93
Tridecanoic acid, 12-methyl-,methyl ester	C15H30O2	242	75.95
Cyclooctasiloxane, hexadecamethyl-	C16H48O8Si8	592	93.07
Nonanedioic acid, dimethyl ester	C11H20O4	216	86.74
Cycloheptasiloxane, tetradecamethyl-	C14H42O7Si7	518	98.10
Nonanoic acid, 9-oxo-, methyl ester	C10H18O3	186	69.87

The analysis of the samples performed on FT-RI, GC-MS and CHNSO elemental analysis confirm the presence of oxygen in biodiesel molecule and C=C double bounds. Biodiesel is more oxidised compared with diesel which leads to a lower heating value for biodiesel.

4.10.3. Diesel and Biodiesel Microbiological Degradation Results

Samples of diesel (B0), biodiesel (B100) and blends ratio of 20% and 50% biodiesel in diesel were prepared in duplicates. The samples were inoculated with a consortia of microorganisms collected from a diesel tank sludge and soil and then incubated for a period of seventy days. In order to assess any microbial activity, every fortnight a series of measurement was taken: (a) visual observations of the samples were noted, (b) bacteria and fungi colony forming unit were counted and (c) the sample`s pH were measured. At the end of the incubation period of seventy days, the gram negative bacteria were identified and the dry mass of biodiesel was measured.

Before incubation every sample was bright colour and translucent. After fourteen days from inoculation, diesel samples (B0) and Sheffield biodiesel (SB20) exhibited a change in fuel colour and water bottom presented opaque. At the bottom of the samples and at the fuel/water interface sand size particles were observed. The change in the fuel opacity and the presence of particles represent a visible sign of microbial activity. Bolton biodiesel (BB) samples presented a weak and slow microorganism growth compared with diesel samples. The water bottom of BB samples was still clear after fourteen days from incubation.

After twenty-eight days from inoculation there were observed differences in microorganism growth for each sample. With the exception of BB100 samples, all others diesel and biodiesel samples became opaque, the fuel as well as the water bottom. The colour of the diesel samples became dark yellow. BB100 samples were more translucent than SB100 samples. The microbial growth in the water bottom of all BB samples has a sandy aspect, but the water bottom was still translucent. One of the two SB20 samples presented a microbial growth in the biodiesel. All SB samples present microbial growth bigger in size than that of BB samples. This means that the microbial activity in SB samples is higher compared with that of BB samples. A higher microbial growth can be associated with a higher microbial activity and rate of fuel metabolization. These lead to changes in the chemical composition of the fuel, which can affect the physical properties of the fuel. BB20 samples showed formation of a bio-film which consisted of free-floating microorganisms at the water/fuel interface and adhering to the bottle surface.

After forty-two days from inoculation, the microbial growth from SB20 sample stabilized at the water/biodiesel interface. The water bottom was opaque for all the samples, with the exception of BB100 which appeared translucent with less microbial growth compared with those from BB50 and B20 samples.

After fifty-six days from inoculation, samples SB20 and SB50 exhibited a bio-film formation.

After seventy days from inoculation, the water bottom of all SB samples became more translucent but displayed fine suspended particles in the water bottom layer. It was also observed that for the samples with a high biodiesel ratio in diesel, the presence of microbial growing was lower in comparison with high diesel contents. This is due to the fact that during the biodiesel manufacturing process, microbial inhibitors additives were added to the biodiesel, making biodiesel more resistant to microbial contamination compared with diesel.

In the following the pH variation for diesel and biodiesel samples during a period of seventy days incubation are presented.

Figures 4-8 and 4-9 show the variation of pH measured in the twenty-eighth day, forty-second day, fifty-sixth day and seventy day from inoculation. The pH level presented an increase during the period of fifty-six days incubation, and then a drop in pH level was observed in the seventy day. During incubation period, the pH levels vary from pH 7.0, which is the Bushnell and Haas medium pH in initial week to pH 6.72 (SB20) and 7.11 (BB50) in week ten.

Figure 4-8 shows the variation of pH for diesel (B0) and Bolton biodiesel samples which are indicated as (BB). Bolton biodiesel blends were indicated as BB20 (20% biodiesel-80% diesel), BB50 (50% biodiesel-50% diesel) and BB100 (neat biodiesel). It was observed that the sample BB100 has the lowest pH between all the samples during the incubation period of seventy days, followed by the sample BB20.

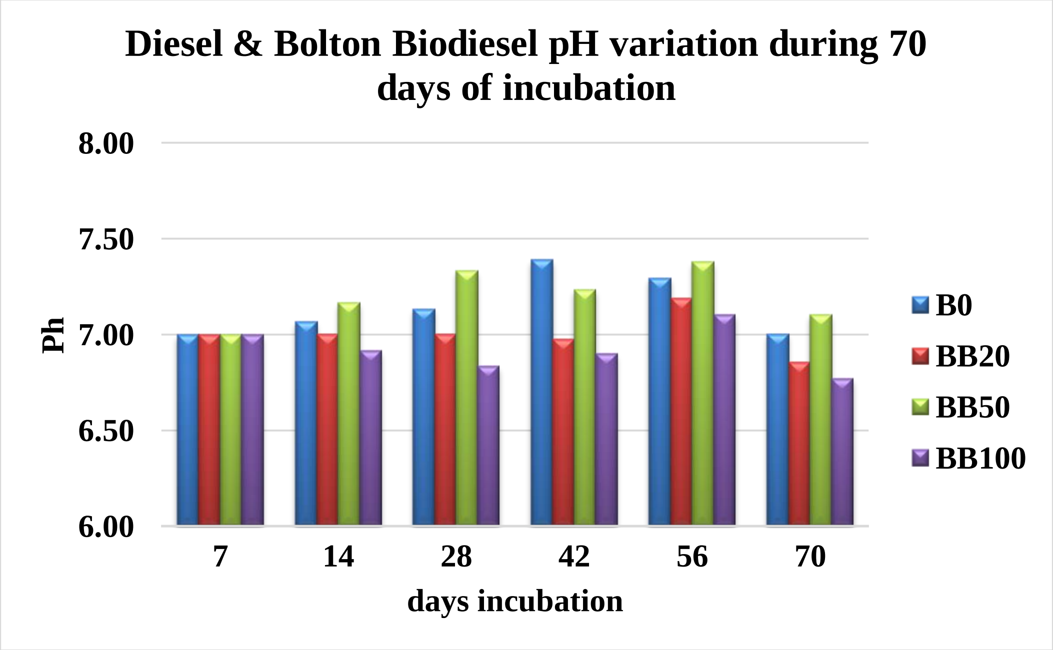

Figure 4-8: Cluster column graph shows the variation in pH over the weeks of incubations of the Bolton biodiesel samples. The pHs were measured in the sterile universal battles that were taken every fourteen days.

Figure 4-9 shows the pH variation for diesel (B0) and Sheffield biodiesel (SB) during seventy days incubation period. The Sheffield biodiesel samples were indicated as SB20 (20% biodiesel-80% diesel), SB50 (50% biodiesel-50% diesel) and SB100 (neat biodiesel). It was observed that with the decrease in biodiesel blend in diesel, the pH decreases.

The results showed a decrease in pH after seventy days from incubation for all biodiesel samples, except diesel fuel pH which showed similar value compared with the initial week.

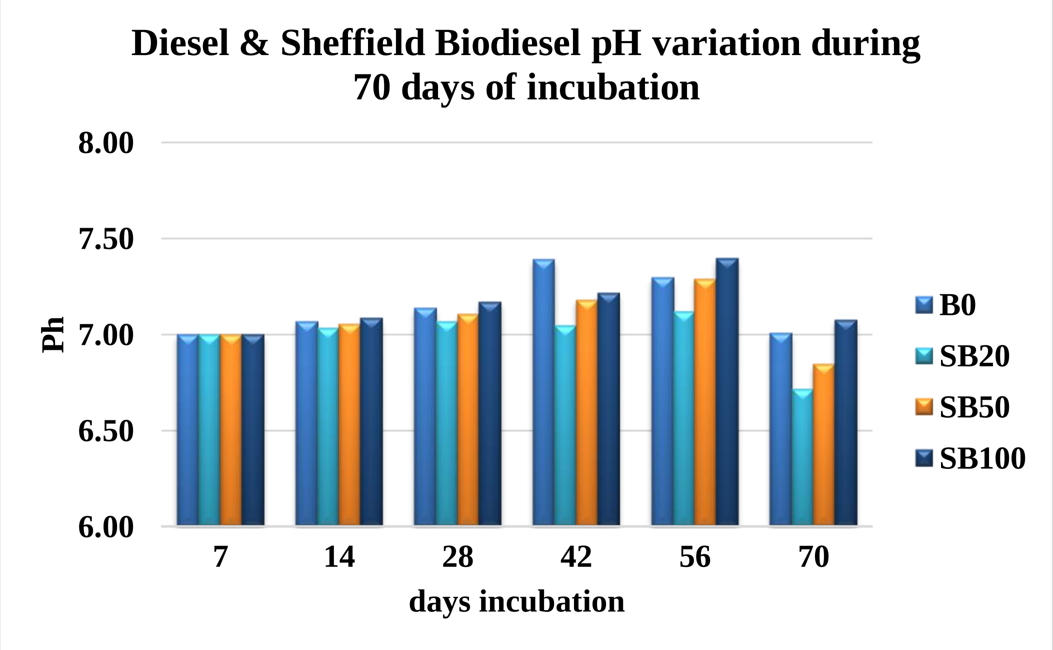

Figure 4-9: Cluster column graph shows the variation in pH over the weeks of incubations of the Bolton biodiesel samples. The pHs were measured in the sterile universal battles that were taken every fourteen days.

Counts of colony forming units (cfu) were conducted after incubation for fourteen, twenty-eight, forty-two, fifty-six and seventy weeks, and are presented in Figures 4-10 – 4-13. Consortia of microorganisms from inoculated biodiesel samples were spread on YEA and MEA from serial dilution of 10^0, 10^{-2} and 10^{-4}.

Figures 4-10 and 4-11 show the colony forming units (cfu) of bacteria growth on diesel, Bolton biodiesel and Sheffield biodiesel. Results show lower bacteria cfu for Bolton biodiesel compared with Sheffield biodiesel.

Figure 4-10 shows the results for bacteria cfu for Bolton biodiesel. It was observed that during of 70 days of incubation diesel (B0) sample showed a constant increase in bacteria cfu. After forty-two days of incubation sample B20 showed the higher bacteria cfu between all samples, while B50 followed by B100 showed lower bacteria cfu compared with B0.

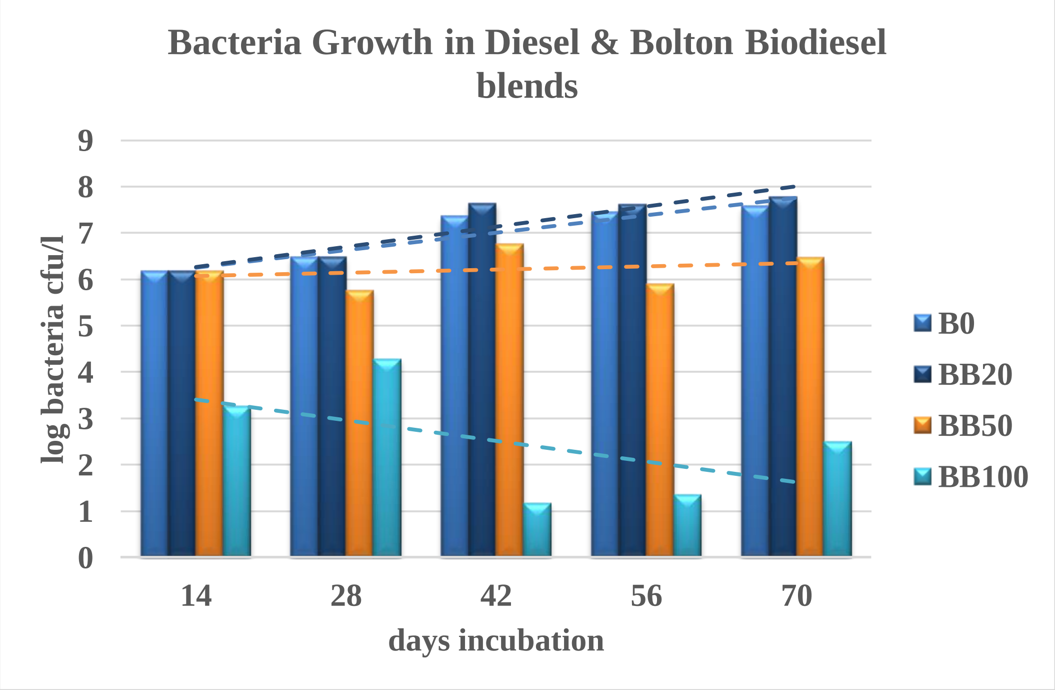

Figure 4-10: Log of colony forming unit of bacteria per litre of diesel and Bolton biodiesel sample

Figure 4-11 shows the results for bacteria cfu for Sheffield biodiesel. Results show an increase in bacteria cfu during seventy days of incubation. The results of bacteria cfu from Bolton biodiesel and Sheffield biodiesel show a consistency in the dependency between the biodiesel blend and bacteria cfus. With the increase in Sheffield biodiesel blend in diesel it was observed a decrease in bacteria cfu. After fifty-six days from incubation SB50 was the only sample showing the higher bacteria growth.

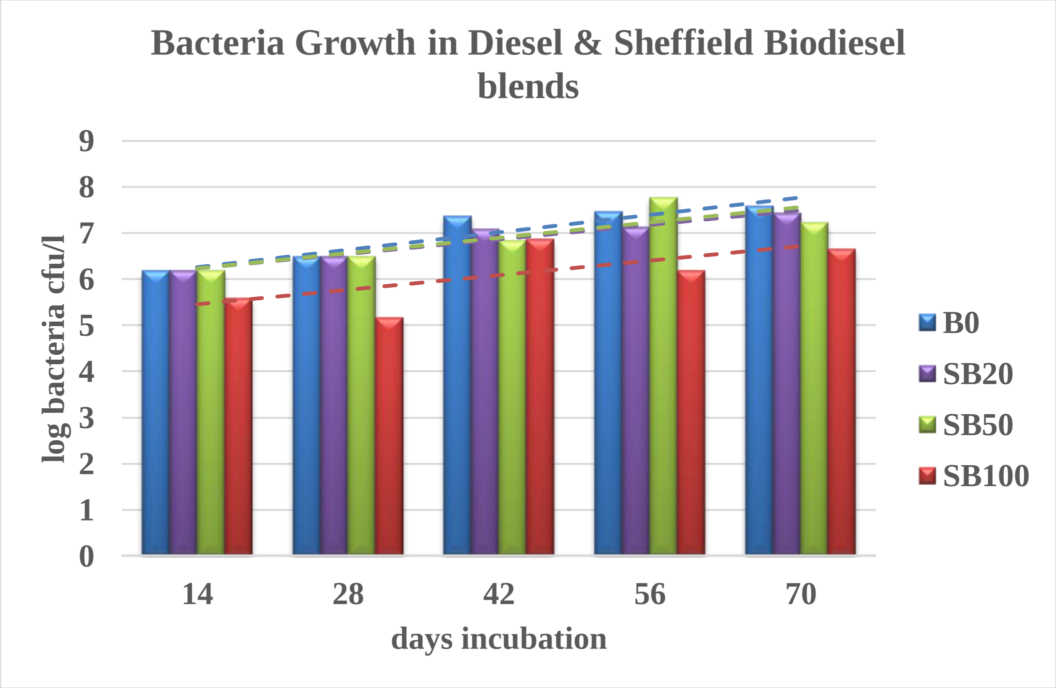

Figure 4-11: Log of colony forming unit of bacteria per litre of diesel and Sheffield biodiesel sample

Figures 4-12 and 4-13 show the colony forming units of fungi growth on diesel, Bolton biodiesel and Sheffield biodiesel.

The results presented in Figure 4-12 show that Bolton biodiesel exhibited the lower fungi growth between all the samples. During seventy days of incubation it was observed a decrease in fungi cfu for most of the samples. After twenty-eight days no fungi cfu was detectable in BB100 sample.

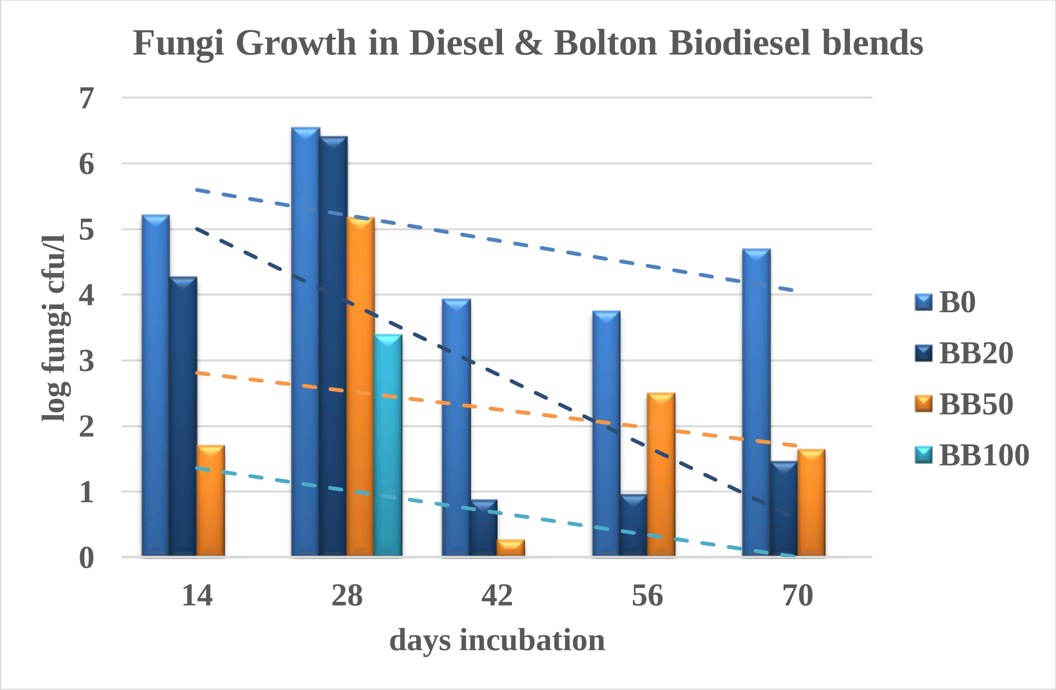

Figure 4-12: Log of colony forming unit of fungi per litre of diesel and Bolton biodiesel sample

Figure 4-13 show the results of fungi cfu from Sheffield biodiesel. The lower fungi cfu was detected in SB100 sample. At fourteen days from incubation all SB samples shows similar fungi cfu, excepting SB100. As a general trend it was observed a slower decrease in fungi cfu during seventy days from incubation compared with Bolton biodiesel was observed.

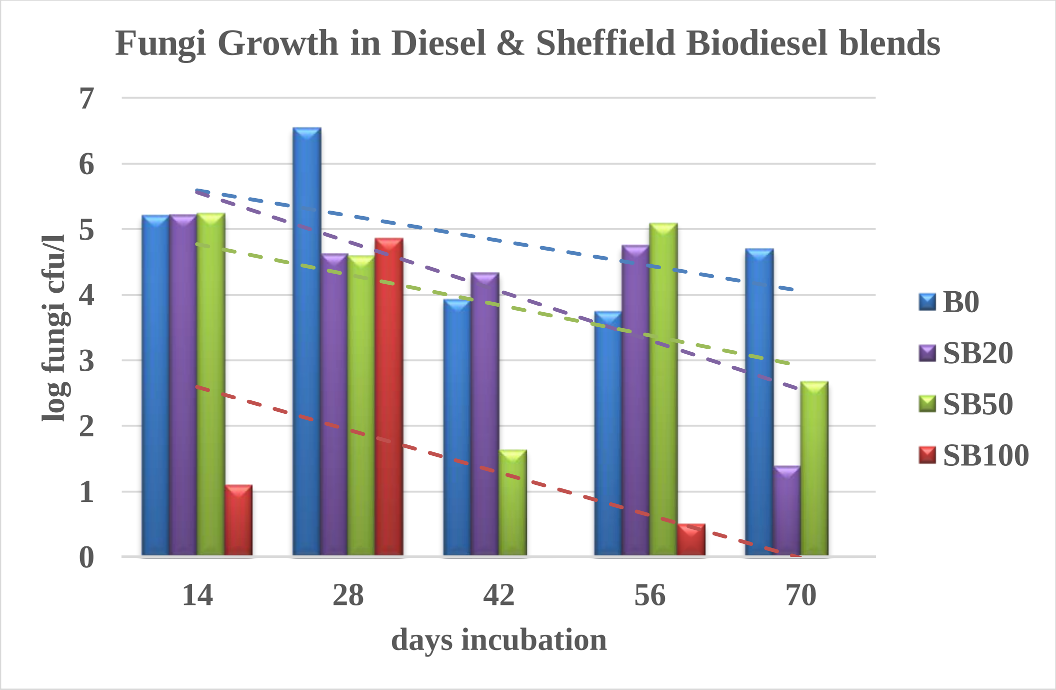

Figure 4-13: Log of colony forming unit of fungi per litre of diesel and Sheffield biodiesel sample

Figure 4-14 presents the result of dry biomass, measure in gram per litre, after seventy day from incubation. Sample SB50 show the highest dry biomass between all the samples followed by SB20 and BB100. Sample B0 measured one of the lowest dry biomass. The dry biomass is one of the indicators of fuel biodegradation. The results showed that Bolton biodiesel was more prone to bacteria contamination compared with diesel.

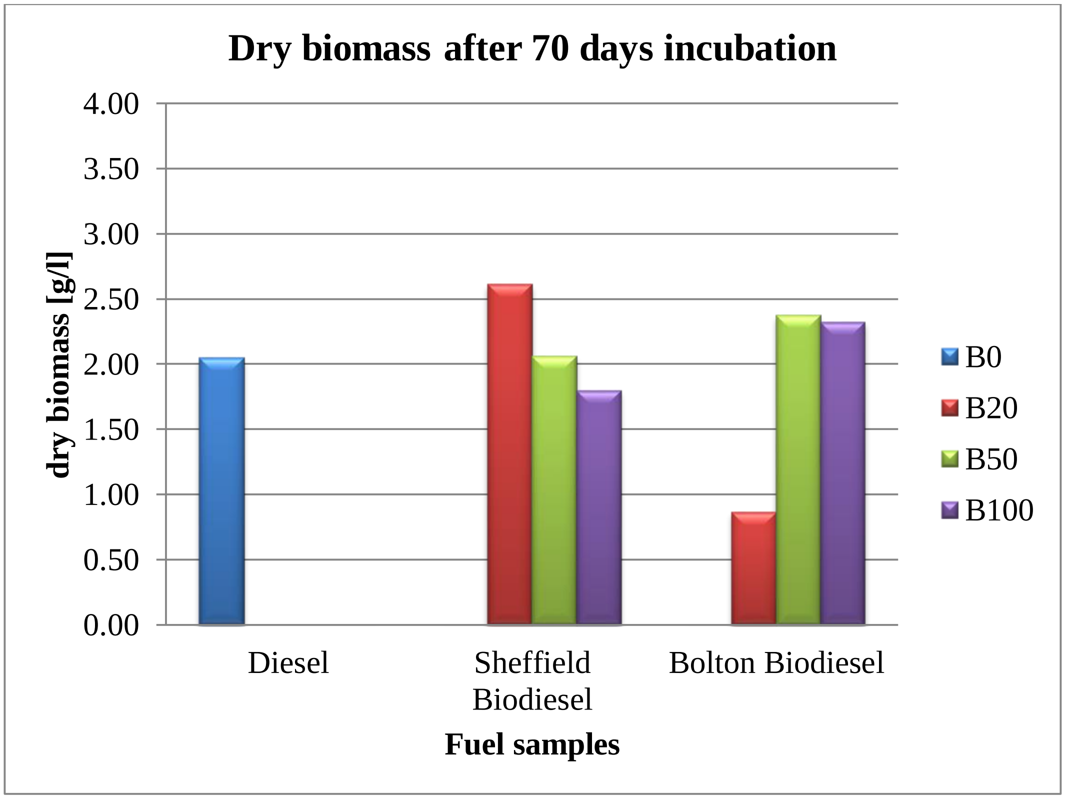

Figure 4-14: dry biomass measured after 70 days from incubation; where B0 represents diesel, B20, B50 and B100 represent 20%, 50% and 100% biodiesel (SB and BB respectively) blend ratio in diesel

Particularly interesting were the sample Bolton B100, which had the lower cfu average 2.46x10^3 ml^{-1}. The higher cfu exhibited was counted for the samples from Sheffield.

Table 4-5 shows the gram stain results obtained from spread plates taken after fifty-eight days of extractions.

Table 4-5 - Gram stain results in week six of extractions

Code	**Gram**	**Size**	**Shape**
B0	-	1µm	Rod
B0	-	1µm	Rod
BB20	-	1µm	Rod
BB20	-	1µm	Rod
BB50	-	1µm	Rod
BB50	-	1µm	Rod
BB100	-	1µm	Rod
BB100	+	1µm	Coccus
SB20	+	1µm	Coccus
SB20	+	1µm	Coccus
SB20	+	1µm	Coccus
SB20	-	1µm	Rod
SB20	-	1µm	Rod
SB50	+	1µm	Coccus
SB50	+	1µm	Coccus
SB50	-	1µm	Rod
SB50	-	1µm	Rod
SB100	-	1µm	Rod

Note: Microscope magnification= 1000x

It was observed two different shapes of bacteria, rod and Coccus shape, all having approximately 1µm size. The majority of bacteria that were gram stained were being measured as gram negative rods and were identified using API 20NE V7.0 kit (bioMerieux) and the results are presented in Table 4-6.

Table 4-6 shows identification of microorganisms grow on inoculated petri dish from the extraction in the fifty-sixth day.

Table 4-6 - Microorganisms that were identified on each petri dish

Samples		**Description**	**Bacteria Identification**
Diesel	**B0**	Fungi - white; red transparent Yeast - white; transparent	P. aeruginosa[1]
Bolton	**B100**	Yeast-yellow	Chaetomium[2] Pseudomonas aeruginosa[3]
	B50	Yeast - white; yellow transparent	Chaetomium[4]
	B20	Fungi - white/red Yeast - white	Burkholderia pseudomallei[5]/P. aeruginosa[5] P. aeruginosa[6]
Sheffield	**B100**	Yeast - white and yellow transparent	P. luteola
	B50	Yeast - white; transparent	Pseudomonas stutzeri[7] Ralstonia pickettii[8] P. aeruginosa/P. alcaligenes
	B20	Fungi Yeast	P. aeruginosa[9] P. putida/Comamonas testosteroni/P. alcaligenes

Note: 1. ID% – 99.9% P. aeruginosa; 2. Additional test; 3. ID% – 99.9% P. aeruginosa; 4. Additional test; 5. Additional test; 6. ID% – 99.9% P. aeruginosa; 7. Additional test; 8. ID% - 95.1% Ralstonia pickettii; 9. ID% - 89.2% P. aeruginosa;

Identifying the fungi would confirm the predominant microorganisms that are capable of inhabiting biodiesel. Microscopy and fungal literature was used to identify the fungi. Particularly interesting growth was shown in the plates from Bolton B20 and Bolton B100. The growths on the plates were streaked onto YEA and MEA plates and incubated for a week. Growth exhibited from the Bolton B20 and B100 showed a definitive structure, and the closed genus was Chaetomium. The structure of Chaetomium was further clarified by test confirmation, using milk agar with cetyl trimethylammonium bromide.

4.11. Conclusions

Biodiesel and diesel samples were prepared and the main physical properties of the fuel were measured. The difference in the physical properties between the WCO biodiesel from the three suppliers was small. Therefore, the emissions and engine performance for the other WCO`s biodiesel are expected to be similar with the results from WEPower biodiesel that was investigated.

The test results from the elemental analyses of the fuel have shown up to 12% oxygen in biodiesel compared with diesel. The sulphur concentration in biodiesel was twenty-two time less compared with the sulphur concentration of diesel, which makes biodiesel friendly to human health and environment. The test results show that biodiesel caloric value was lower compared with diesel due to the high content of oxygen and lower carbon to hydrogen ratio compared with diesel.

The FT-IR spectra from diesel and biodiesel has shown peaks that do not overlap. TF-IR analysis is a useful method to identify possible functional groups present in diesel and biodiesel. The functional groups can provide information on the stability of biodiesel fuel. The absorption corresponding to C-O stretches reveals that the molecule contains ester functional group. The carbonyl absorption peak shows a direct proportional evolution with the increase in biodiesel blend in diesel.

Samples of biodiesel from two suppliers were assessed for microbial contamination and the results were compared with diesel. The test results have shown that once the biodiesel was treated with additives, the growth of bacteria and fungi was significantly reduced compared with the bacteria and fungi exhibited by diesel. Between biodiesel samples, Bolton biodiesel shown lower microbial growth compared with Sheffield biodiesel. These differences could be caused by the development of certain fungi, such as Chaetomium which can inhibit bacteria development. The genus Chaetomium fungi are considered to be a rich source of novel and bioactive secondary metabolites which is antibiotic and exhibit enzyme inhibitory [150].

Chapter 5 -Evaluation of Biodiesel Combustion in a Continuous Combustion Rig (CCR)

5.1. Introduction

In order to study the exhaust emissions from various diesel and biodiesel blends it was important to eliminate all the physical aspects that influence the combustion. Unlike in the diesel engine, by using CCR the combustion conditions could be controlled, consequently the physical phenomena that affect combustion could be reduced; thus enabling just the chemical aspect of combustion to be analysed. Therefore the purpose of the burner was to produce a laminar premixed flame, and to control the air flow rate, fuel flow rate and pressure. These variables allowed tests on diesel and biodiesel fuels under various test conditions. Since NO variations were dependent upon the operational condition, a minimum concentration of NO could be achieved. Hence operational conditions could be optimised according to the fuel type. Results provide theoretical basis for emission control of NOx and improve operation parameters when using biodiesel instead of diesel fuel.

5.2. Experimental Method and Instrumentation

5.2.1. Experimental Setup

The laboratory combustion rig used in this research was composed of a horizontal cylinder (12) and an evaporating chamber (7) separated by a porous disc (9), two fuel tanks (2), temperature reader (6 &11), gas analyser (13) and system acquisition (14). The combustion rig was made of stainless steel in order to protect against any catalytic reaction.

A schematic diagram of the experimental system is shown in Figure 5-1.

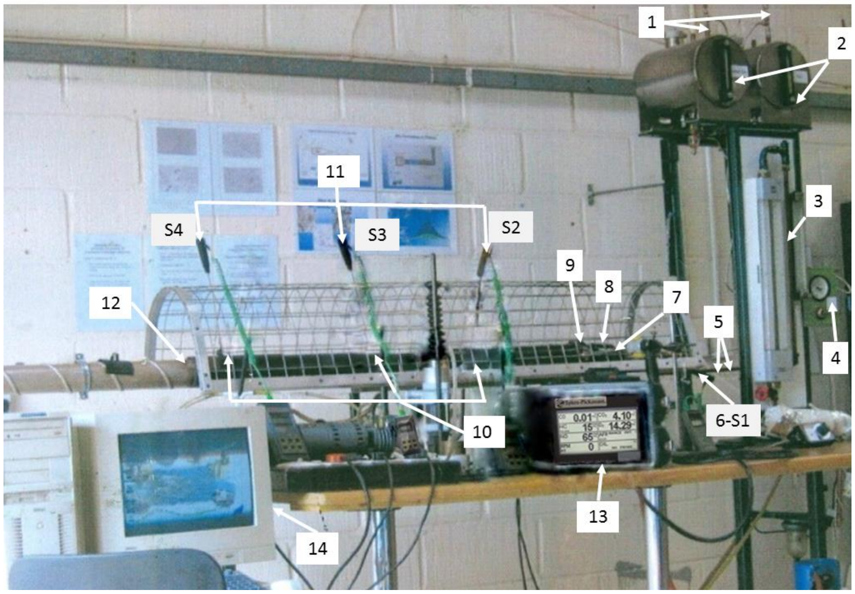

Figure 5-1: Continuous combustion rig (CCR)

1- Air line system for fuel pressure; 2- Fuel tanks; 3- Air flow meter; 4- Pressure gage; 5- Fuel line & air line; 6- Evaporating chamber thermocouple port S1; 7- Evaporating chamber; 8- Ignition port; 9- Sintered disc; 10- Temperature and exhaust gas sampling ports; 11- Thermocouples port S2, S3 and S4; 12- Burner; 13- Gas analyser; 14- Data acquisition system.

Four type-K thermocouples connected to a digital display reader were situated along the combustor. The first thermocouple embedded in the evaporating chamber was used to measure the temperature of the premixed fuel-air. The other three thermocouples measure the combustion gas temperature along the combustion tube at the sampling ports S_2=0.425m, S_3=0.84m and S_4=1.121m.

The evaporating chamber has the dimensions of 65mm internal diameter and 80mm length. The following combustion zone was separated from the evaporating chamber by the porous stainless steel sintered disc mesh size of 250 and diameter 65mm. Fuel and air enters the evaporating chamber which was preheated externally. Therefore the fuel vaporised when it entered the chamber and mixed with air. The fuel-air mixture passed through a sintering disc and produced a laminar premixed flame in the combustion tube.

A sampling device was placed at the 0.425m away from the sintered disc for collecting samples of the exhaust gas in the combustion tube. For analysing the combustion gases Sykes Pickavant SP9550 gas analyser was used. In order to facilitate the gas sampling and allow flue gas to cool down before reaching the analyser sensors, 10mm internal diameter stainless steel tube was designed and attached to the original probe of the gas analyser.

The experiments were carried out using different blend ratios of diesel and biodiesel from VEPower supplier. The fuel blends investigated were neat diesel (B0), 25% biodiesel: 75% diesel (B25), 50% biodiesel: 50% diesel (B50), 75% biodiesel: 25% diesel (B75) and neat biodiesel (B100). Biodiesel was obtained from waste cooking oil. CHSO elemental analysis of diesel and neat biodiesel samples were performed and the results are shown in Table 5-1.

Table 5-1: Fuel specifications from lab analyses for 100kg diesel
Note: a) and b) test results from ITS Testing Service (UK) Ltd c) – estimative values of biodiesel blends from a) and b)

Element	**Standard (UKAS)**	**B0$^{a)}$** **% by wt**	**B25$^{c)}$** **% by wt**	**B50$^{c)}$** **% by wt**	**B75$^{c)}$** **% by wt**		**B100$^{b)}$** **% by wt**
Carbon	MT/ELE/13	86.9	84.18	81.45	78.73		76
Hydrogen		12.9	12.65	12.4	12.15		11.9
Nitrogen		0.02	0.02	0.02	0.02		0.02
Oxygen	MT/ELE/21	0.07	2.978	5.89	8.79		11.7
Sulphur	MT/MCR/12	0.09	0.068	0.045	0.023		0.00052
$H_2$0		0.02	0.11	0.2	0.29		0.38

The amount of air necessary for complete combustion depended on the main fuel constituent compounds: carbon, hydrogen, oxygen and sulphur. The air used as combustion oxidant consisted of 23.20% oxygen and 75.47% nitrogen by weight with traces of other elements.

The oxygen contributes to the oxidation of the elements constituent of diesel fuel such as C, H, S, N and O. The volume of exhaust gas from diesel fuel was calculated at stoichiometric conditions. Assuming that the combustion was complete, the resulting gas would consist of CO_2, H_2O, SO_2, N_2 and O_2. The total combustion gas for diesel was calculated at normal temperature and pressure, (NTP), and stoichiometric conditions.

5.2.2. Methodology

The fuel was fed into the evaporating chamber from a stainless steel tank pressurised by compressed air. The air and fuel flow rate were controlled by calibrated rota-meters. The air was allowed to mix with the fuel in the evaporating chamber. The mixture was heated up and forced out through a stainless steel sintered disc and the flame was produced outside the disc. In order for the system to stabilise and sustain combustion, the combustion rig was allowed to run for about one hour before any samples were taken. The stability of the system was established by checking the temperature along the tube. The temperature of the combustion gas was measured with four type K thermocouples of 2mm in diameter. Before each test, the thermocouples were inspected for cracks to assure minimal catalytic reaction at the surface of the thermocouple. For each set of tests, in order to decrease the errors that could occur during measurements, various temperature and combustion gas readings were recorded. The final value of the temperature and combustion gas represents an average of various measurements. After a set of measurements was finalised, and a new set of parameters were fixed (e.g. the air flow rate was increased), the system was allowed time between 15-20 minutes to stabilise before taking any reading.

The temperature and the combustion gas were measured at the distance of 0.425m from the sintered disc. Samples of combustion gas were extracted through a stainless steel probe and passed into the gas analyser. The gas analyser measures the excess O_2, CO, CO_2, HC, and NO. SP9550 data-log software, allowed the data collected from the gas analyser to be to be recorded in an electronic format.

In order to analyse NO variation with the residence time, samples of combustion gas were taken at fixed interval distance from the sintered disc. The excess O_2, NO, CO,

CO_2 and HC were the measured parameters, at fixed fuel and air flow rate, and constant pressure.

5.2.3. Adiabatic Flame Temperature Calculations

The adiabatic flame temperature was calculated applying the first law of thermodynamics to an adiabatic combustor burning B0, B25, B50, B75 and B100. Equation (50) presents the fuel-lean combustion of diesel fuel for stoichiometric conditions.

$$CH_m + \alpha_s (O_2 + 3.78N_2) \rightarrow CO_2 + m/2\ H_2O + \alpha_s\ O_2 + 3.78\alpha_s N_2 \qquad (50)$$

Where $\alpha_s = 1 + m/4$. The equation for stoichiometric fuel-lean combustion of biodiesel fuel is shown in (51).

$$CH_mO_n + \beta_s (O_2 + 3.78N_2) \rightarrow CO_2 + m/2\ H_2O + \beta_s\ O_2 + 3.78\beta_s N_2 \qquad (51)$$

Where $\alpha_s = 1 + m/4$. Applying the first law of thermodynamics;

$$\Sigma_{j,prod}\ f_j\,[h_j (T) - h_j (T_0) + \Delta h°_{f,j} (T_0)] - \Sigma_{j,in}\ f_j\,[h_j (T) - h_j (T_0) + \Delta h°_{f,j} (T_0)] = Q - W_x = 0 \qquad (52)$$

Where T_0 is the reference temperature, $T_0 = 298K$ and the pressure $p_0 = 1atm$.

The adiabatic flame temperature can be obtained using enthalpy and enthalpy of formation data for each of the species.
The linear approximation for the temperature dependence of the specific heats is $c_{pi} = a_i + b_iT$, therefore,

$$[h_i(T) - h_i(T_0)] = a_i (T-T_0) + b_i/2\,(T^2-T^2_0) \qquad (53)$$

The calorific value of B0 and B100 was obtained experimentally. Based on B0 and B100 values, the higher heating value for B25, B50 and B75 was computed using formula given by equation (54)

$$HHV_{Bxx} = HHV_{B0}D_x + HHV_{B100}B_x \tag{54}$$

Where HHV_{Bxx} is the higher heating value of the blends, HHV_{B0} and HHV_{B100} is higher heating value of diesel, respectively biodiesel, and D_x and B_x represents percentage of diesel respectively biodiesel in blend.

5.3. Results and Discussion

The results of combustion of various blends of biodiesel at different fuel/air equivalence ratio are presented in the following section. The measurements were made to obtain the combustion gas temperature and the characteristics of the exhaust emissions.

5.3.1. Adiabatic Flame Temperature

Table 5-2 shows the main properties of diesel and biodiesel fuel used in the combustion experiment. The fitted molecular formula for each blend and neat fuel was deduced from the elemental analyses of diesel and biodiesel supplied by VEPower ltd.

Table 5-2: Main physicochemical properties of the fuel

Note: c) – estimative values of biodiesel blends from a) and b).

Properties	**Units**	**B0$^{a)}$**	**B25$^{c)}$**	**B50$^{c)}$**	**B75$^{c)}$**	**B100$^{b)}$**
Fitted molecular formula	-	$C_{13}H_{23}$	$C_{19}H_{34}O_2$	$C_{16}H_{29}O_2$	$C_{31}H_{57}O_2$	$C_{17}H_{41}O_2$
High heating value	MJ/kg	41.098	39.167	37.236	35.305	33.374
Density at 20°C	g/m^3	0.834	0.846	0.858	0.87	0.882
Kinematic viscosity	mm^2/s	3.5	3.74	3.985	4.228	4.47

Figure 5-2 shows the variation of adiabatic flame temperature with the increase in biodiesel blend ratio in diesel. The adiabatic flame temperature decreases from 2426K for B0 to 2003K for B100. This was mainly due to the low calorific value of biodiesel compared to diesel.

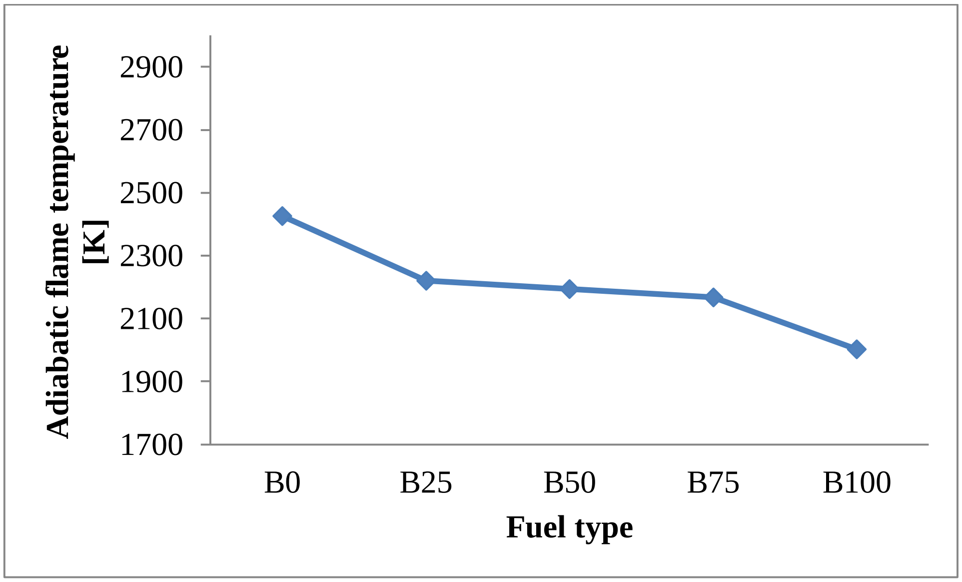

Figure 5-2: Variation of adiabatic flame temperature with biodiesel blend ratio in diesel

5.3.2. Variation of Combustion Gas Temperature with Biodiesel Blends and Fuel/Air Equivalence Ratio

Figure 5-3 presents the variation of combustion gas temperature for various biodiesel blends at fuel/air equivalence ratio of 0.29, 0.16, 0.14 and 0.11. The figure shows a slow increase in combustion gas temperature with the decrease in fuel/air equivalence ratio. Also, it was observed that the blend ratio diesel/biodiesel influences the combustion gas temperature. The increase in biodiesel blend ratio in diesel result in an increase in the combustion gas temperature

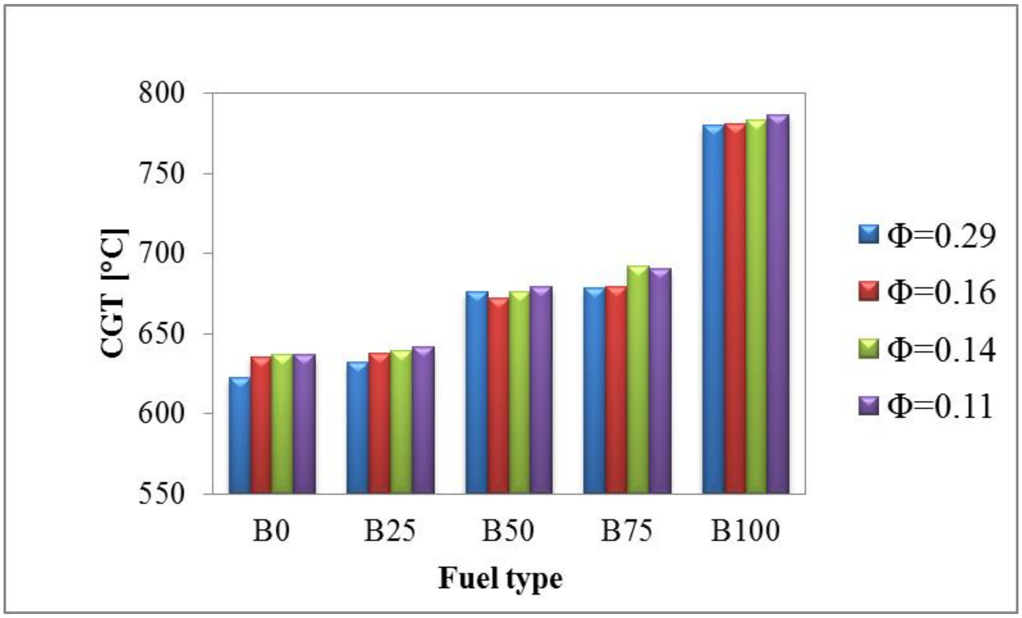

Figure 5-3: Variation of combustion gas temperature from various biodiesel blends at fuel/air equivalence ratio of 0.29, 0.16, 0.14 and 0.11

Figure 5-4 presents the percentage change of combustion gas temperature from base line (B0) at different fuel/air equivalence ratio. For fuel/air equivalence ratio varying from 0.11 to 0.29 it was observed an increases between 12 to 20% in CGT for biodiesel blends compared with diesel. For fuel/air equivalence ratio varying from 0.11 to 0.29 increases between 12 and 20% in CGT for biodiesel blends compared with diesel was observed.

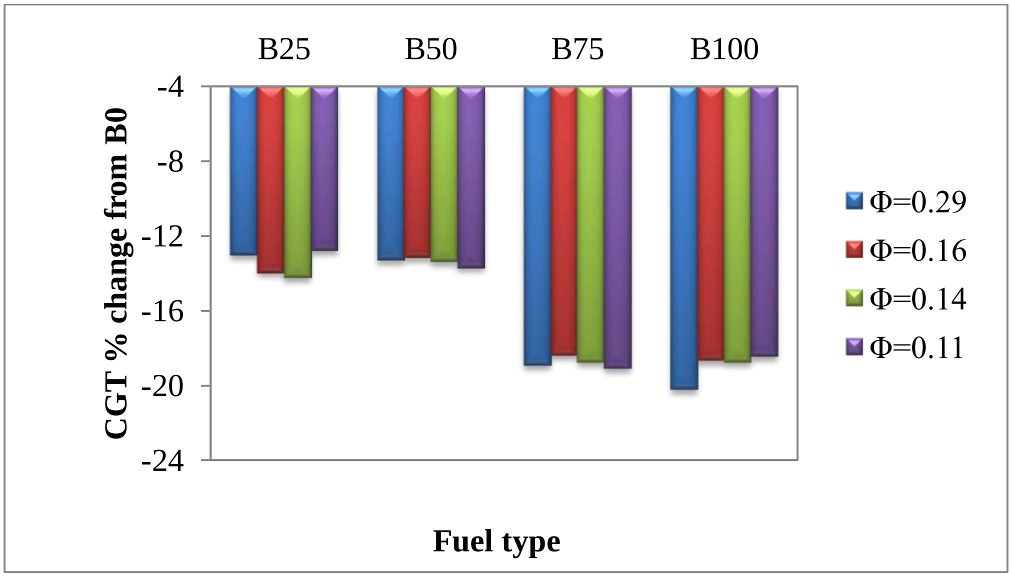

Figure 5-4: % change in CGT from B0 for various fuel/air equivalence ratio and diesel and biodiesel blend

5.3.3. Variation of Specific Nitrogen Oxide with Biodiesel Blends and Fuel/Air Equivalence Ratio

Figure 5-5 shows the variation of specific nitrogen oxide (SNO) from various biodiesel blends at different fuel/air equivalence ratio.

For fuel/air equivalence ratio decreasing from 0.29 to 0.11 it was observed an increase in SNO. It was observed that with the increase in biodiesel blend ration in diesel, SNO increased. This was due to a higher combustion gas temperature compared with that from diesel.

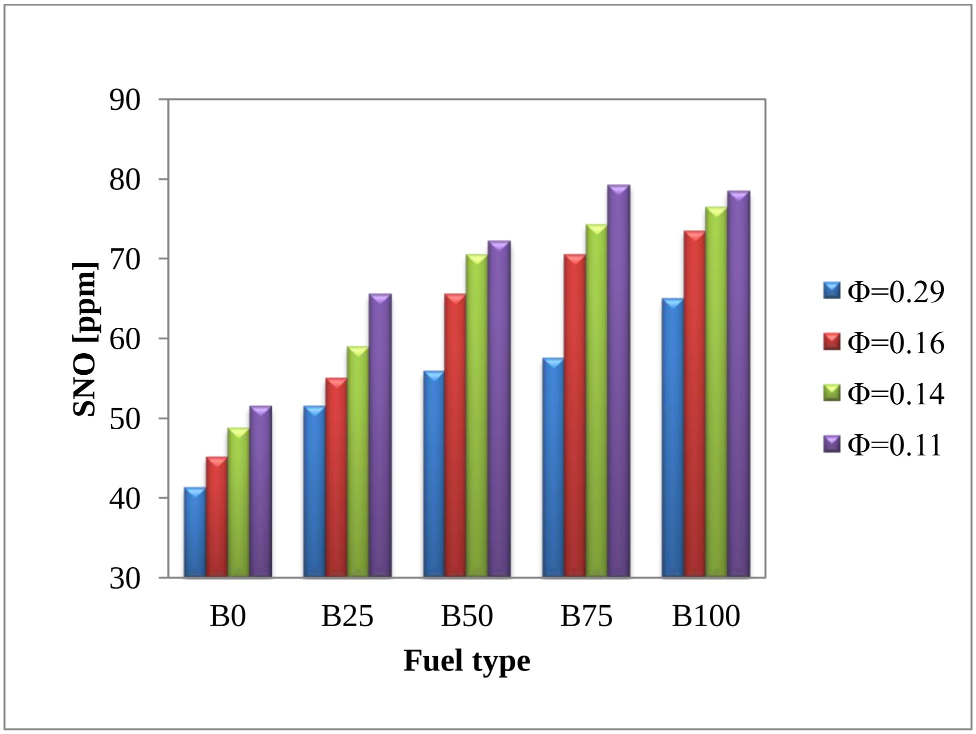

Figure 5-5: Variation of SNO from various biodiesel blends at fuel/air equivalence ratio of 0.29, 0.16, 0.14 and 0.11

Figure 5-6 shows the percentage change in SNO from base line for biodiesel blends at various fuel/air equivalence ratios. The results showed an increase in SNO between 20 to 60% from base line. The lower increase in SNO was recorded for B25 for fuel/air equivalence ratio of 0.14, whereas for B50 and B75 the lower SNO was at the combustion condition of fuel/air equivalence ratio of 0.29. B100 shown the lower SNO at fuel/air equivalence ratio of 0.11.

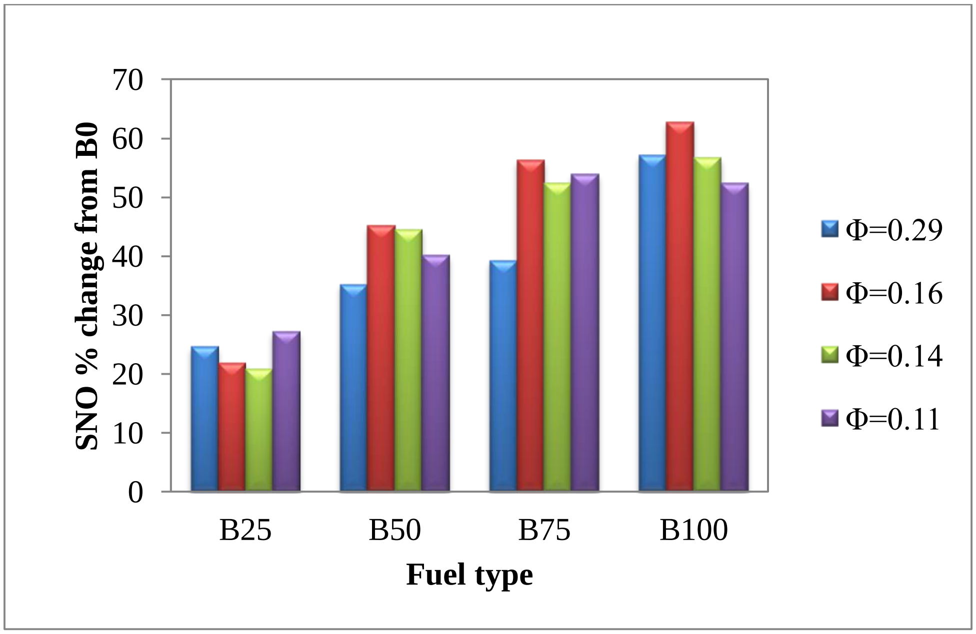

Figure 5-6: % change in SNO from B0 for various fuel/air equivalence ratio and diesel and biodiesel blend

5.3.4. Variation of Specific Carbon Dioxide with Biodiesel Blends and Fuel/Air Equivalence Ratio

Figure 5-7 presents the variation of specific carbon dioxide from biodiesel blends at various equivalence ratios. The results show an increase in SCO_2 with the decrease in fuel/air equivalence ratio. The increase in biodiesel blend in diesel resulted in an increse in SCO_2 compared with diesel. This meant that the addition of biodiesl into diesel would result in an increse in combustion efficency.

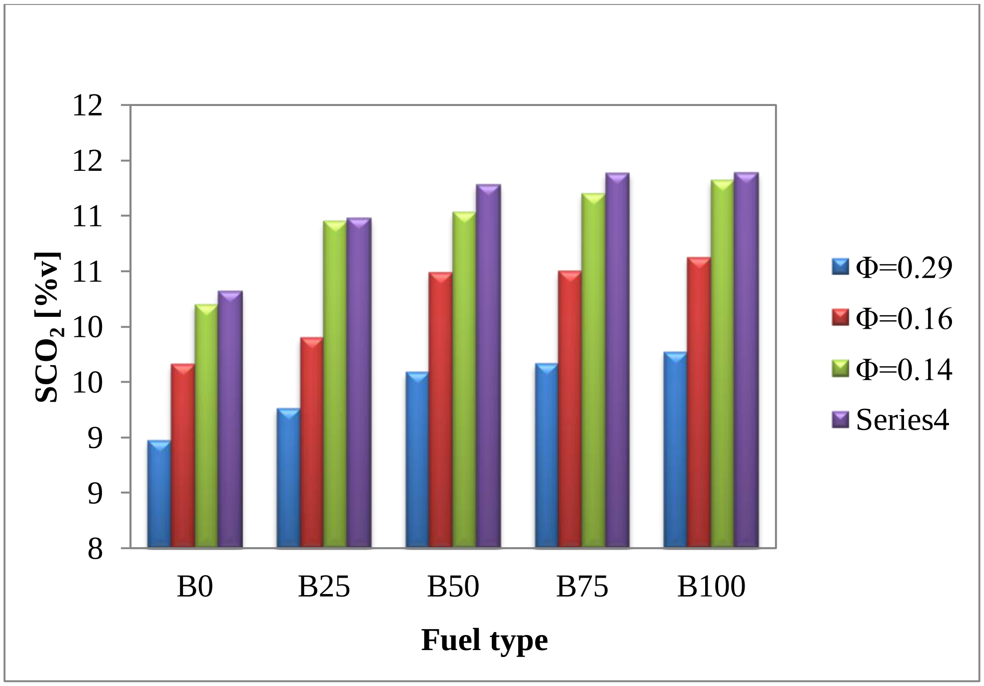

Figure 5-7: Variation of SCO_2 from various biodiesel blends at fuel/air equivalence ratio of 0.29, 0.16, 0.14 and 0.11

Figure 5-8 shows the percentage change in SCO_2 emissions from biodiesel blends at different fuel/air equivalence ratios. For fuel/air equivalence ratio varying between 0.29 to 0.11, the SCO_2 shown an increse from the base line between 2 to 11%. B25 and B100 show the higher SCO_2 emissions, therefore a better combustion at the fuel/air equivalence ratio of 0.14. For B50 and B75 the higher SCO_2 was recoded at the fuel/air equivalence ratio of 0.11.

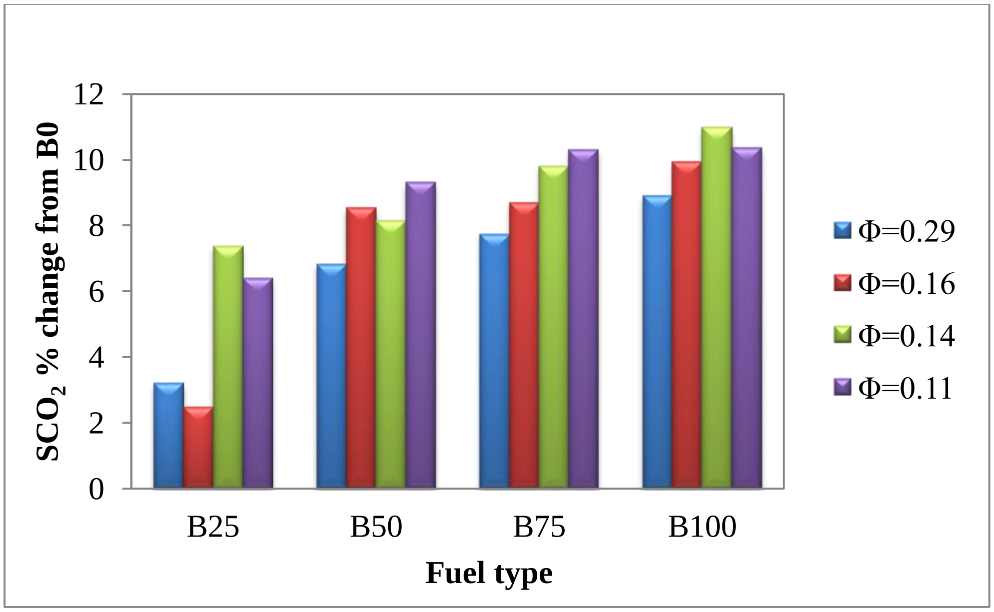

Figure 5-8: % change in SCO_2 from B0 for various fuel/air equivalence ratio and diesel and biodiesel blend

5.3.5. Variation of Specific Carbon Monoxide with Biodiesel Blends and Fuel/Air Equivalence Ratio

Figure 5-9 presents the variation of specific carbon monoxide from different biodiesel blends at various fuel/air equivalence ratios. The results shown that for fuel/air equivalence ratios varying from 0.29 to 0.11, the SCO emissions decreases. It was also, observed that by increasing the biodiesel blend ratio in diesel, the SCO emissions decreased compared with diesel.

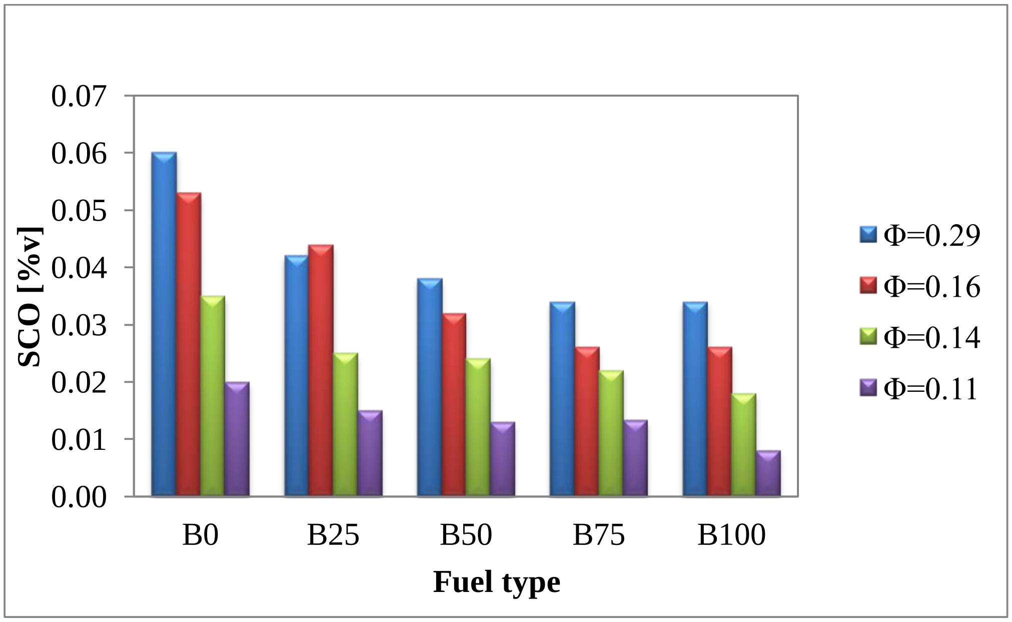

Figure 5-9: Variation of SCO from various biodiesel blends at fuel/air equivalence ratio of 0.29, 0.16, 0.14 and 0.11

Figure 5-10 presents the percentage change in SCO emissions from various diesel and biodiesel blends at different fuel/air equivalence ratio. For combustion at fuel/air equivalence ratio varying between 0.29 and 0.11, a reduction from baseline between 15 to 60% in SCO was observed. B25 shows a decrease in SCO of 30% from baseline when combustion conditions are at fuel/air equivalence ratio of 0.29. B50 and B75 show the higher decrease in SCO at fuel/air equivalence ratio of 0.16, whereas for B100 shows the higher reduction in SCO at fuel/air equivalence ratio of 0.11.

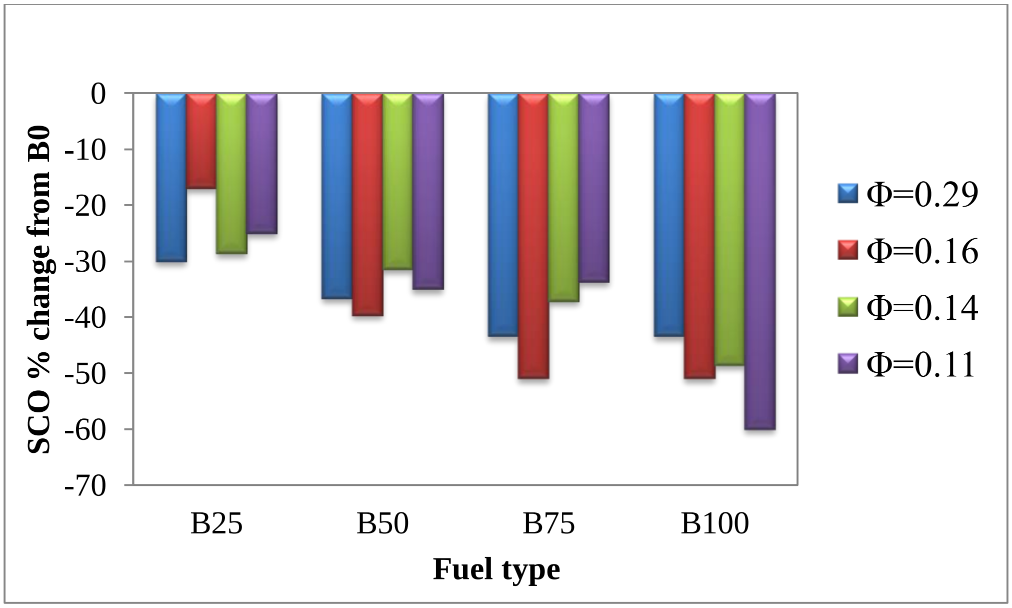

Figure 5-10: % change in SCO from B0 for various fuel/air equivalence ratio and diesel and biodiesel blend

5.3.6. Variation of Specific Hydrocarbon with Biodiesel Blends and Fuel/Air Equivalence Ratio

Figure 5-11 presents the variation of unburned specific hydrocarbon emissions from various diesel and biodiesel blends at various fuel/air equivalence ratios. The results show a decrease in SHC emissions with the increase in biodiesel blend ratio in diesel.

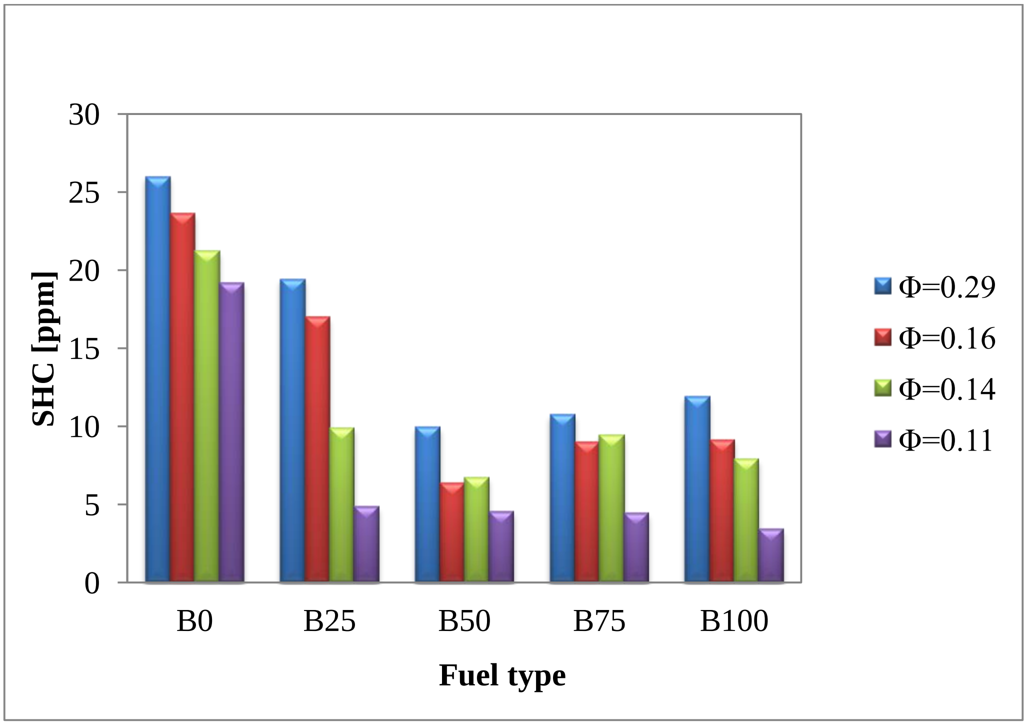

Figure 5-11: Variation of SHC emissions from various biodiesel blends at fuel/air equivalence ratio of 0.29, 0.16, 0.14 and 0.11

Figure 5-12 shows the percentage change in SHC emissions from base line for various blends of diesel and biodiesel at different fuel/air equivalence ratios. The results show that with the decrease in fuel/air equivalence ratio form 0.29 to 0.11, the SHC emissions decrease between 25 to 80% from base line. The higher decrease in SHC emissions resulted at fuel/air equivalence ratio of 0.11 for all biodiesel blends.

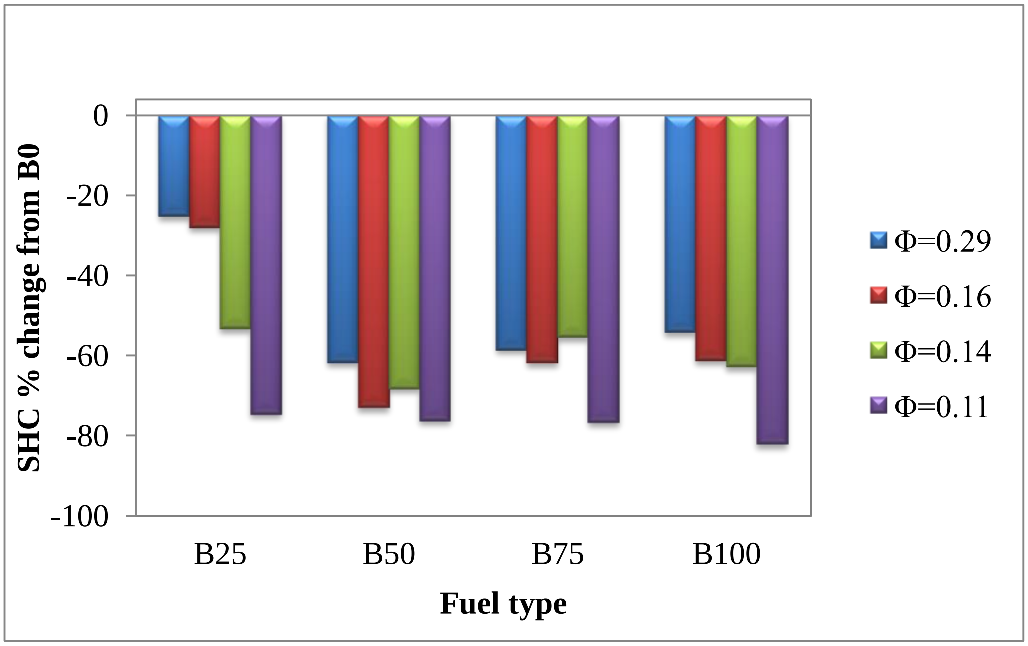

Figure 5-12: % change in HC from B0 for various fuel/air equivalence ratio and diesel and biodiesel blend

The relationship between diesel/biodiesel ratio in the blend and the adiabatic temperature and the formation of pollutant emissions were obtained. The adiabatic flame temperature decreased from B0- 2426K to B100- 2003K, as the biodiesel blend in diesel was increased. This was due to the fact that the calorific value of neat biodiesel was 19% lower compared with diesel fuel. Tests were performed at various fuel/air equivalence ratios for each fuel. The results showed that the combustion gas temperature for neat biodiesel and biodiesel blends was higher than that of diesel combustion gas. The increase in the CG temperature for biodiesel blends with higher concentration of biodiesel in diesel blend can be due to the oxygen content in the biodiesel molecule, resulting in a more intense combustion compared with diesel. The blend ratio of biodiesel in diesel influenced the formation of pollutant emissions. An increased in NO and CO_2 with the increase in biodiesel blend ratio in diesel It was observed. The increase in CO_2 emissions when using biodiesel was a result of better combustion compared with diesel fuel, due to the fact that the molecule of biodiesel contains up to 12% oxygen. The effect of diesel-biodiesel blend on formation of HC emissions became more obvious when the combustion become leaner. The test results showed that HC emissions decreased with the increase in biodiesel ratio in diesel for all biodiesel blends compared with diesel. The oxygen content in biodiesel molecules leads to a more intense and complete combustion, resulting in lower HC emissions compared with diesel fuel. The optimum combustion conditions were found at fuel/air equivalence ratio of 0.11. At this fuel/air equivalence ratio it was obtained the highest decrease in HC and CO with the lower increase in NO for most biodiesel blends was obtained.

5.3.7. Variation of Combustion Gas from Diesel and Biodiesel with Residence Time

Figure 5-13 presents the SNO variation with residence time at equivalence ratio of 0.06. The results show higher SNO emissions from WCO biodiesel (B100) compared with diesel (B0). A sharp decrease in SNO emissions from diesel, decreasing from 90 to 68ppm for the residence times between 0.03 – 0.1s, then NO stabilises to 62ppm between 0.1 and 0.4s was observed. Compared with diesel, SNO emissions of WCO biodiesel (B100) show a constant decrease from 120ppm to 98ppm for residence time between 0.04 and 0.5s.

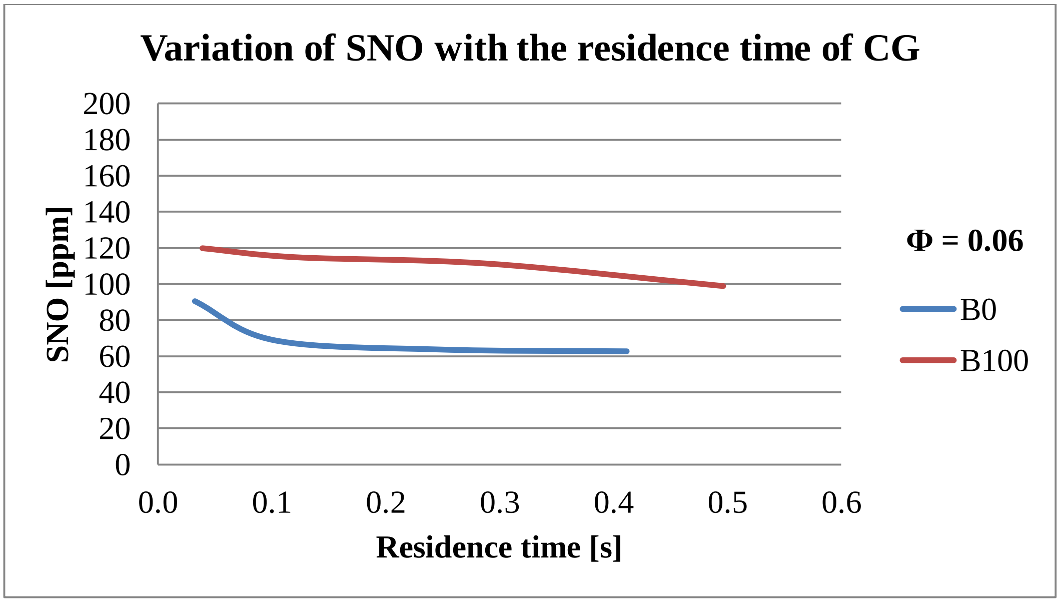

Figure 5-13: Specific nitric oxide emissions variation with equivalence ratio of 0.06 for diesel and biodiesel

Figures 5-14 and 5-15 present the variation of exhaust emissions from B0, B25, B50, B75 and B100 at equivalence ratio of 0.01 and residence time of 0.22s. Figure 5-14 show the variation of specific carbon monoxide (SCO) from diesel, biodiesel and various blends of diesel and biodiesel. Results show that for all biodiesel blends, SCO emissions are lower compared with diesel fuel. It was observed that with the increase in biodiesel blend in diesel, the SCO emissions decreased.

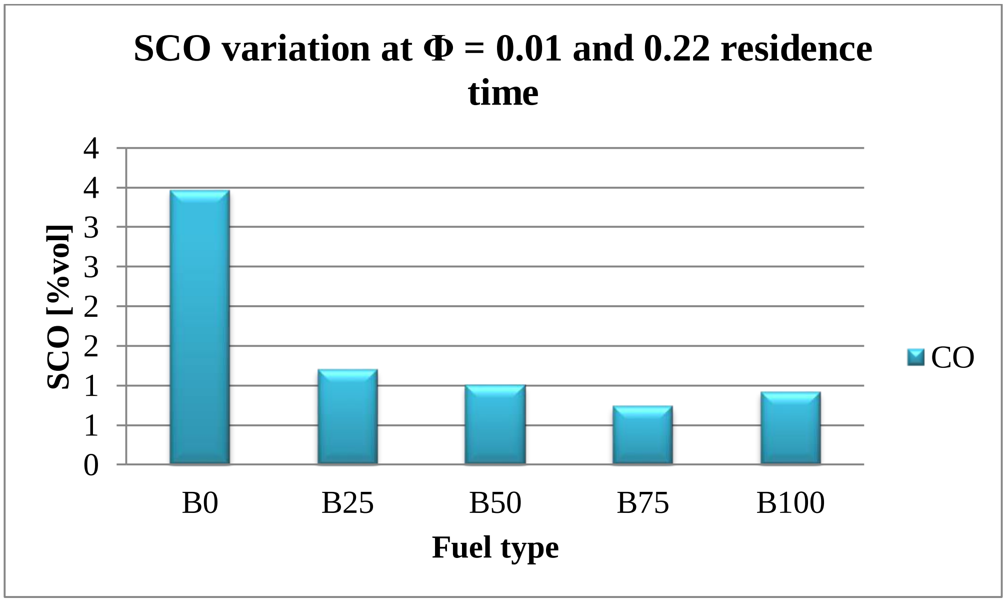

Figure 5-14: Evaluation of specific carbon monoxide emissions variations from diesel and biodiesel burned in CCR at equivalence ratio 0.01 and residence time of 0.22s

Figure 5-15 shows the variation of specific carbon dioxide (SCO_2) from diesel and biodiesel blends. It was observed that with the addition of biodiesel in diesel, CO_2 emissions increased. A high CO_2 emission means a better combustion. Thus, the addition of biodiesel to diesel blend in diesel will improve the combustion.

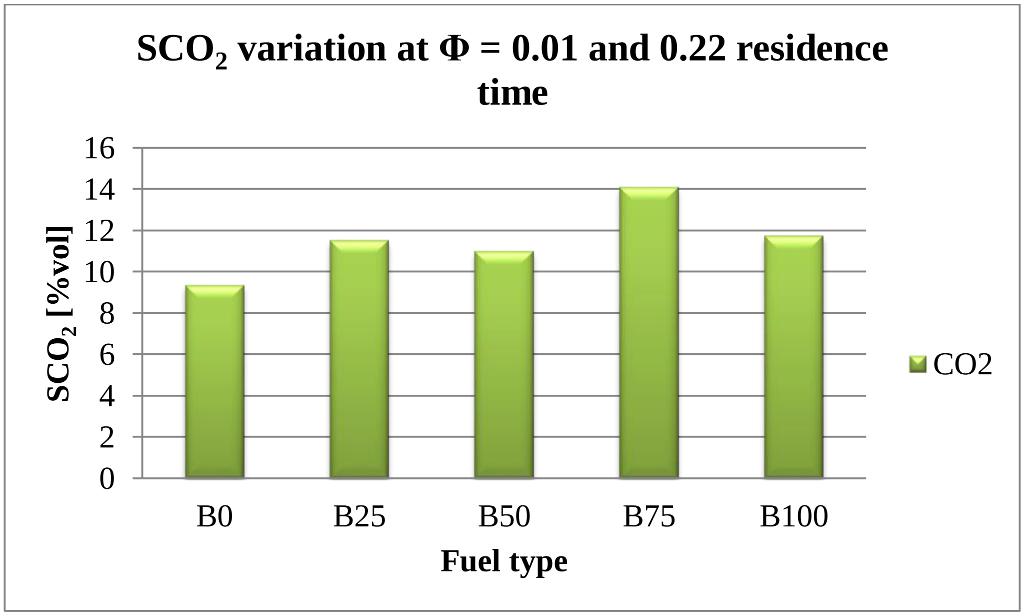

Figure 5-15: Evaluation of specific carbon dioxide emissions variations from diesel and biodiesel burned in CCR at equivalence ratio 0.01 and residence time of 0.22s

The results presented in Figures 5-16 and 5-17 show the relation between unburned specific hydrocarbon (SHC) and the temperature of the combustion gas. The lower the unburned HC emissions, the higher was the temperature of the combustion gas and the more efficient the combustion.

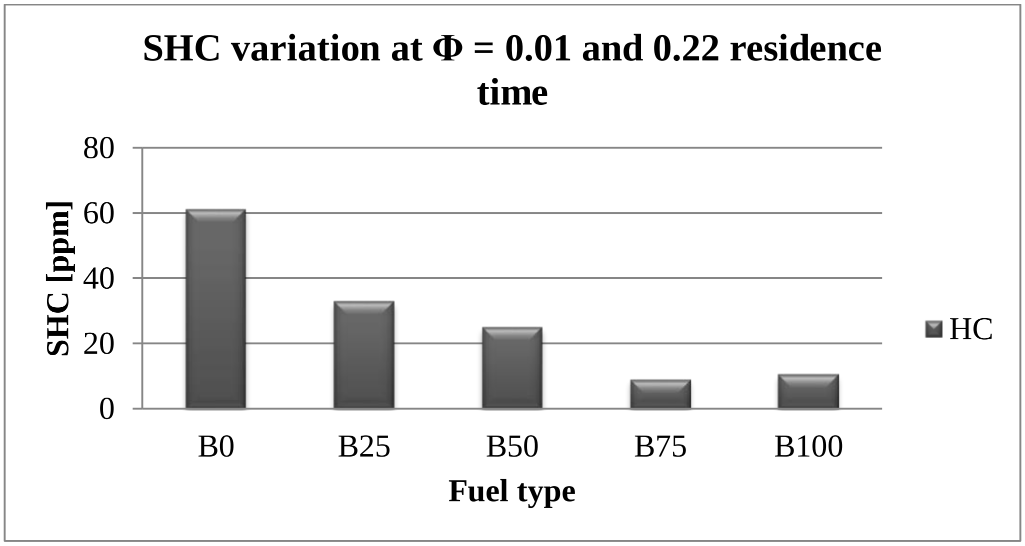

Figure 5-16: Evaluation of unburned specific hydrocarbon emissions variations from diesel and biodiesel burned in CCR at equivalence ratio 0.01 and residence time of 0.22s

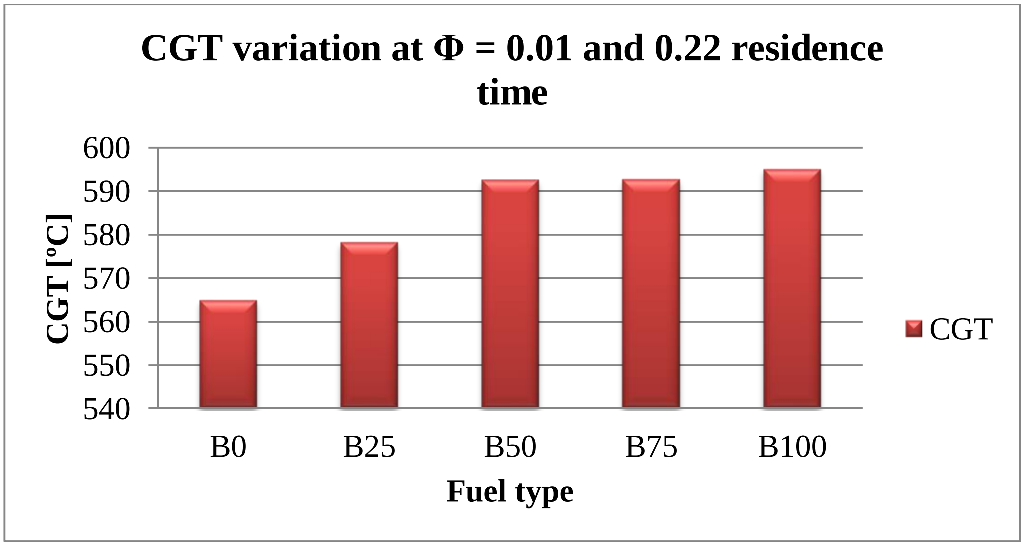

Figure 5-17: Evaluation of combustion gas temperature from diesel and biodiesel burned in CCR at equivalence ratio 0.01 and residence time of 0.22s

The test results show a direct relation between the biodiesel blend and the SHC emissions and CGT. High decrease in SHC emission with the increase in biodiesel blend in diesel, it was observed, this leading to a cleaner combustion of the fuel compared with the combustion of a neat diesel.

Figure 5-18 shows the variation of nitric oxide from diesel and biodiesel at fixed combustion conditions. The results show an increase in SNO emissions compared with diesel. The biodiesel blend radio in diesel seems to have a significant influence on SNO formation.

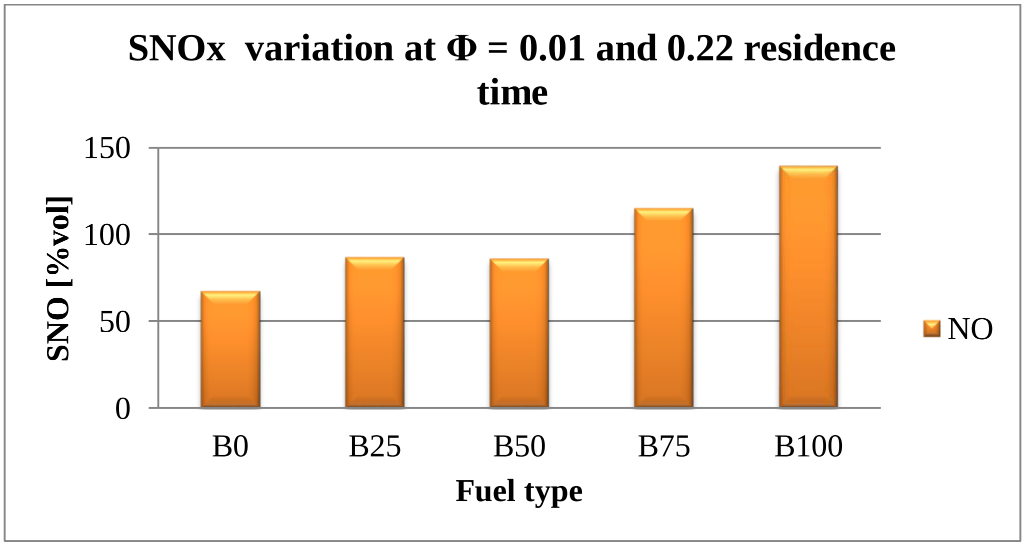

Figure 5-18: Evaluation of nitric oxide emissions from diesel and biodiesel burned in CCR at equivalence ratio 0.01 and residence time of 0.22s

5.4. Conclusions

In order to assess the influence of biodiesel blend on combustion emissions, a range of tests were conducted on various blends of diesel and biodiesel. The results have shown that with an increase in ratio of biodiesel in the blend, combustion gas temperature increases. The high temperature of the combustion gas leads to higher

SNO formation compared with diesel. The thermal and prompt are the main mechanisms for the nitrogen oxides formation [151]. The prompt NO formation can be due to the high presence of CH in the reaction zone. The FT-IR results have shown that biodiesel contained higher CH bonds in its molecule compared with diesel. C-N elemental group was also observed in the biodiesel molecule, whereas C-N groups were not identified in diesel spectrum. The oxygen content in biodiesel molecule and the content of unsaturated compounds lead to more heat release during the combustion process. This results in a more intense combustion compared with diesel, leading to high combustion gas temperatures. The combustion reaction rate for biodiesel was higher compared with diesel, leading to a faster brakeage of the hydrocarbon chain which release more heat.

The increase in biodiesel blend ratio in diesel shows a decrease in SHC and SCO emissions compared with diesel. This was attributed to the complete combustion of biodiesel. The completeness of the combustion was also observed in the increase in CO_2 with the increase in biodiesel ratio in diesel.

Chapter 6 - Evaluation of Biodiesel in a Land Rover Diesel Engine

6.1. Introduction

In this chapter details of experimental methodology, engine instrumentations and the results of the experiments conducted on a direct injection diesel engine are presented. The engine was fuelled with neat Waste Cooking Oil (WCO) biodiesel and WCO biodiesel-diesel blends. The results are compared with that of baseline diesel. These test results would be useful for engines fuelled with WCO biodiesel working under similar operating conditions, and for imminent research work in development of biodiesel.

6.2. Experimental Method and Instrumentation

A thorough investigation has been performed in order to understand the engine performance with neat biodiesel and various blends of WCO biodiesel-diesel under various engine operating conditions. The engine used for this study was a turbocharged four stroke, direct injection (DI) Land Rover VM Motori engine.

Neat WCO biodiesel and WCO biodiesel-diesel blends were tested in a Land Rover VM 2400 diesel engine under steady state conditions. A turbocharged engine is more sensitive to fuel quality. The VM 2400 water cooled diesel engine with the specifications given in Table 6-1 was connected to a dynamometer and used as testing platform.

Table 6-1: Engine Specifications

Manufacturer	VM Motori, Iri-Finmeccanica group
Engine type	4 cylinders, direct injection, water cooled, compression ignition engine
Bore/Stroke	92 mm/90 mm
Approximate engine capacity	2393 cm^3
Compression ratio	21:1
Compression pressure	235.3 to 255 N/cm^2
System pressure at 2000 rpm	44 to 49 N/cm^2
Oil pressure at 2000 rpm	4.1 to 45 N/cm^2
Idle speed	800 to 830 rpm
Injector open pressure	155 bar
Injector nozzle diameter	0.87 mm
Firing order	1, 3, 4, 2,
Dynamometer controlling type	Electromagnetic brake

A schematic and illustrative layout of the engine test rig are presented in Figures 6-2 – 6-5.

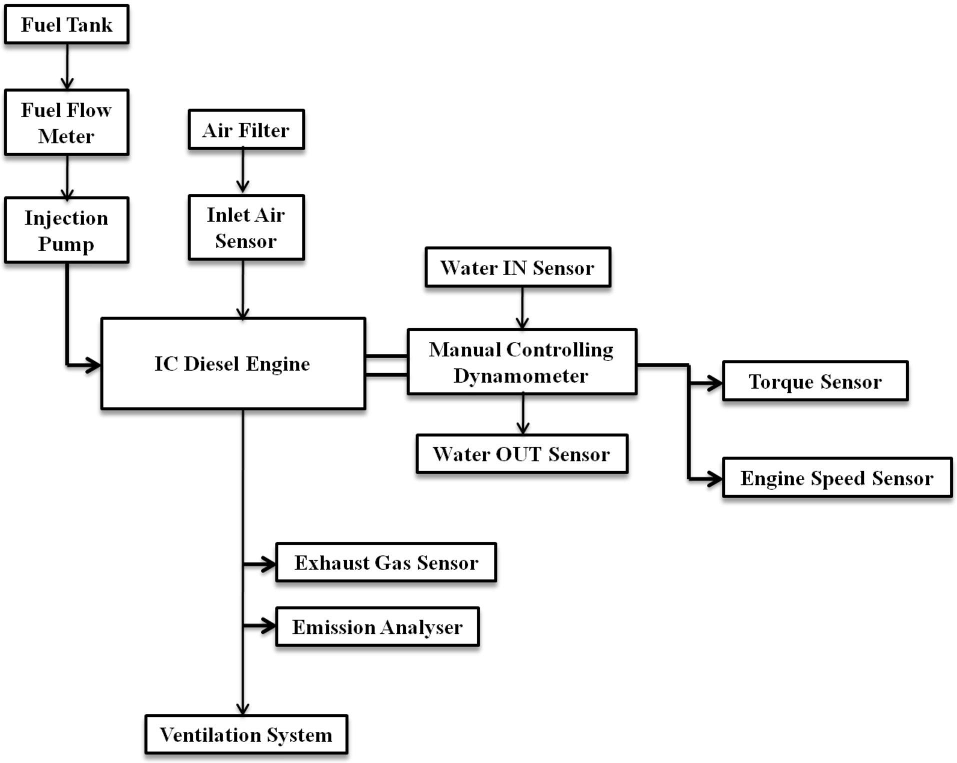

Figure 6-1: Schematic diagram of experimental test rig

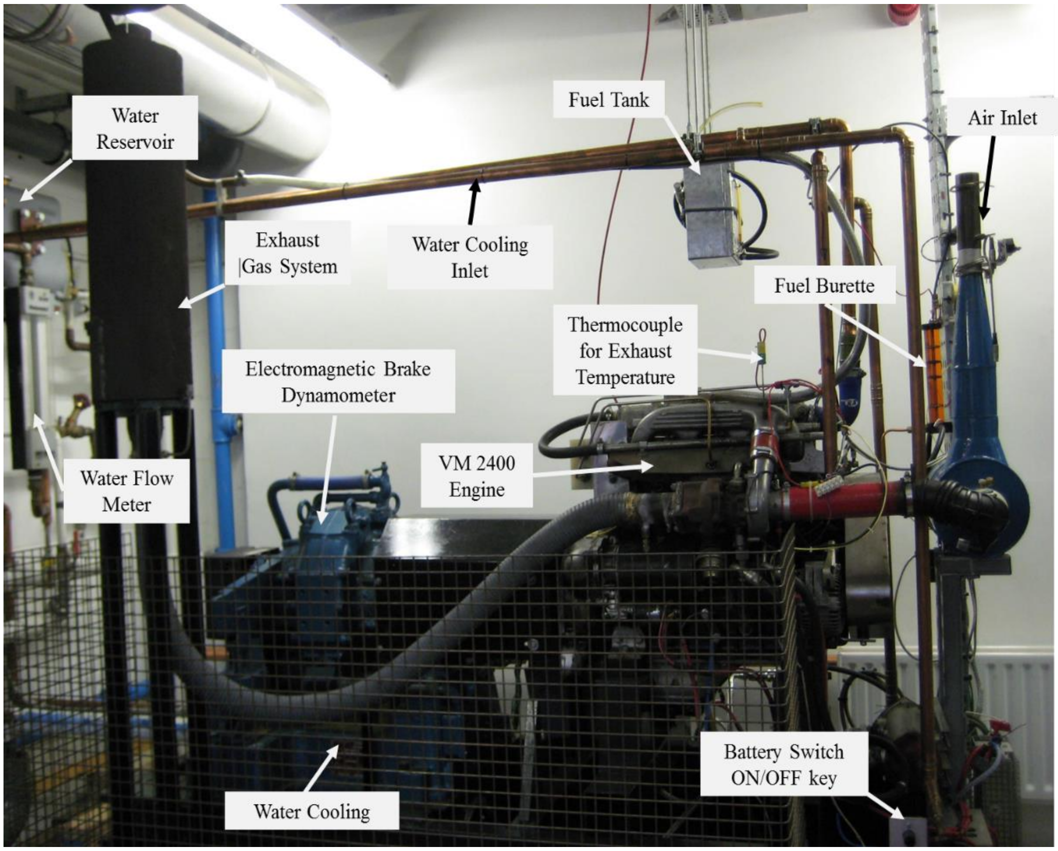

Figure 6-2: Diesel engine test rig

Figure 6-3: SP9550 exhaust gas analyser

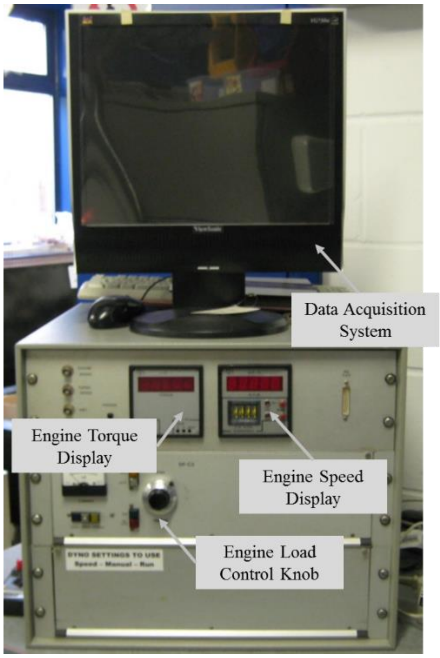

Figure 6-4:Load bank

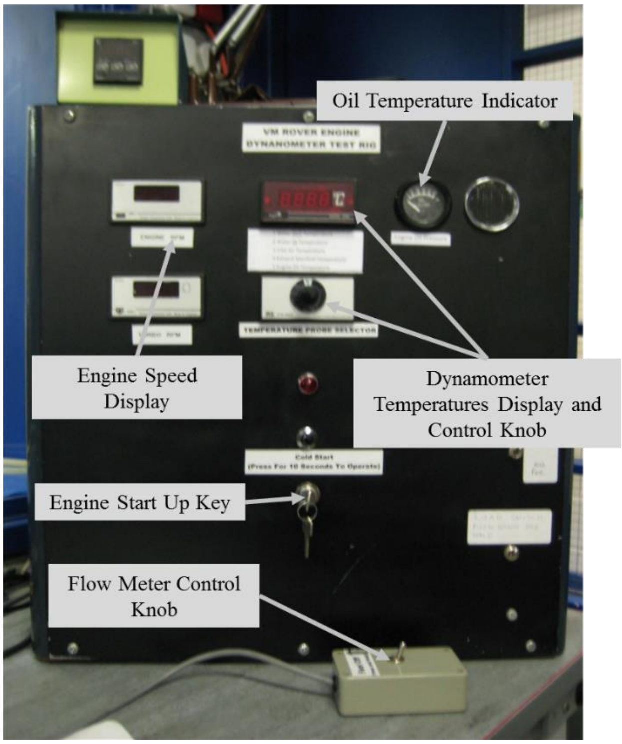

Figure 6-5: Dynamometer control panel

The test rig was instrumented to measure and control the engines basic parameters such as engine torque, speed, load, volumetric fuel flow rate and exhaust emissions. Several thermocouples installed at strategic points in the engine were used to measure the temperature of water coolant and the exhaust manifold. The coolant was achieved by electrically driven pumps, with the temperatures controlled by water fed heat exchangers. The thermocouples used were type K from Omega Engineering Inc. The temperatures were shown on a multi-point electronic temperature display unit. The thermocouples were accurate within ±2.2 °C.

A graduated sight glass made by Plint & Partners Ltd., mounted on the test rig was used to measure the volumetric fuel flow rate. External conditions for each test have been recorded in every aspect. The test rig installation is shown in Figures 6-2 – 6-5. A 5 litre detachable aluminium fuel tank was attached to the engines rig in order to facilitate easy evacuation of the remaining fuel after each test. Before taking any records for a new fuel, the engine was run for 1 hour under various conditions. The engine was water-cooled, and the water circulated through the engine was controlled to maintain a constant outlet water temperature.

The engine was run first with diesel in order to generate baseline data. Blend ratio of 75/25 (B25), 50/50 (B50), 25/75 (B75) and 0/100 (B100) were tested to analyse the impact of biodiesel concentration on engine performance and emissions. Torque, brake specific fuel consumption (BSFC), brake power (BP), brake thermal efficiency (BTE) and exhaust emissions were observed.

Neat diesel was also tested before and after using WCO biodiesel blends as a baseline. The series of tests were conducted using each fuel with the engine working at the conditions presented in Table 6-2.

Table 6-2: Engine conditions

Engine Speed [rpm]																			
2000					**2500**					**3000**					**3500**				
Engine load [%]																			
15	25	50	75	100	15	25	50	75	100	15	25	50	75	100	15	25	50	75	100

The engine speed was fixed at 2000, 2500, 3000 and 3500rpm. For each fixed speed the engine was tested under 15, 25, 50, 75 and respectively 100% load respectively. After each set up of engine conditions the engine was run and allowed to stabilize for approximately 25 minutes before any measurements were taken. In order to minimize the errors, each engine parameter was measured seven times and the data for each operating condition was averaged.

Neat diesel and blends of diesel and biodiesel with the properties presented in Table 6-3 were tested under various engine cycles.

Table 6-3: Fuel properties

Fuel type	**Density [g/cm^3]**	**Kinematic viscosity [mm^2/s]**	**Lower calorific value [kJ/kg]**
B0	0.834	3.5	41098.33
B25	0.846	3.74	39167.3
B50	0.858	3.99	37236.27
B75	0.87	4.23	35305.24
B100	0.882	4.47	33374.21

Table 6-4: Resolution of measurements

Measurements	**Accuracy**
NO	±1 ppm
CO	±0.01 %
CO_2	±0.1 %
HC	±1 ppm
O_2	±0.01 %
Speed	±2 rpm
Torque	±0.1 Nm
Time	±5 %
Sample flow rate 5 l/min.	
Computed results	**Resolution**
Fuel volumetric rate	±1%
Power	±1%
Brake specific fuel consumption	±1.5%
Efficiency	±1.5%

In each test, volumetric fuel consumption, engine speed, torque and exhaust emissions, such as nitrogen oxides (NO), carbon monoxide (CO), total unburned hydrocarbon (HC), carbon dioxide (CO_2) and excess oxygen (O_2) in the exhaust gas were measured.

6.3. Results

6.3.1. Effect of WCO Biodiesel-Diesel Blending on Engine Torque

The torque percentage differences from baseline for a range of biodiesel and diesel blends are shown in Figures 6-6 – 6-9. Torque measurements were recorded at 2000, 2500, 3000 and 3500 rpm and the engine load was varied from 15% to 100% load. The results showed a reduction in engine torque with the increase in biodiesel blend ratio in diesel. As the engine load increased, a decrease in torque was observed for all biodiesel blend ratios.

Figure 6-6 shows the variation of torque with load and biodiesel blend for engine set at 2000 rpm. The test results showed up to 9% decrease in torque for neat biodiesel (B100) compared to base line.

Figure 6-7, as the engine speed was increased to 2500 rpm, the torque difference between biodiesel blends and baseline decreases substantially. The results showed a reduction in torque for B100 of up to 4% compared to baseline.

Figures 6-8 – 6-9, at 3000 and 3500 rpm and at low and medium load, biodiesel blends showed similar variation in the torque values. The test results showed a decrease in torque of up to 5.5% and 4% respectively, from the baseline. Maximum decrease in torque for WCO biodiesel compared with diesel fuel was 9% and was observed at 2000 rpm. This was attributed to the lower calorific value of biodiesel compared with that of diesel.

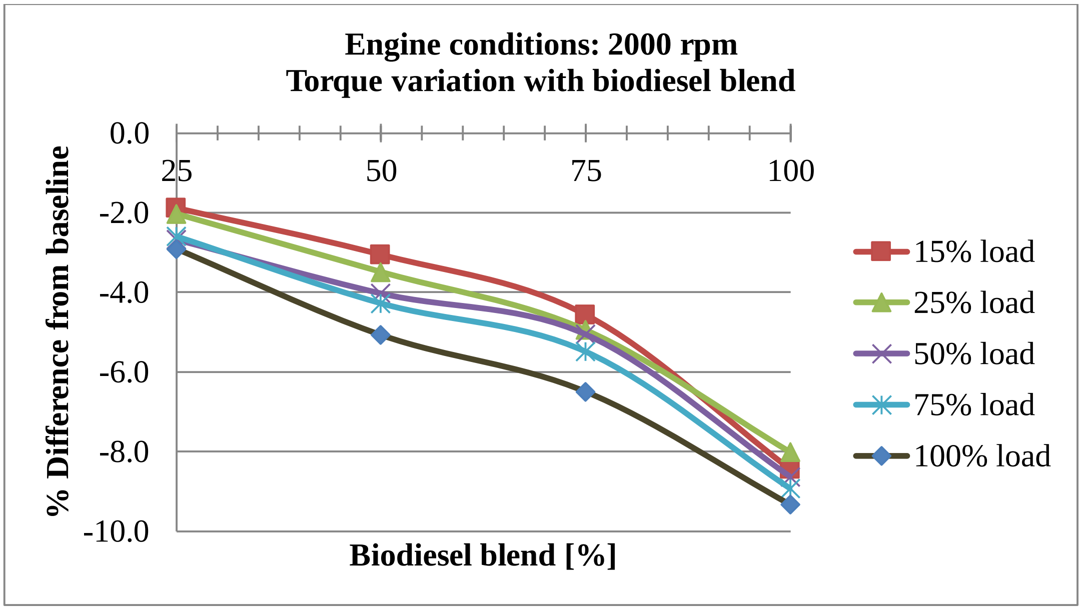

Figure 6-6: Variation of torque with WCO biodiesel-blend at 2000 rpm and various load conditions

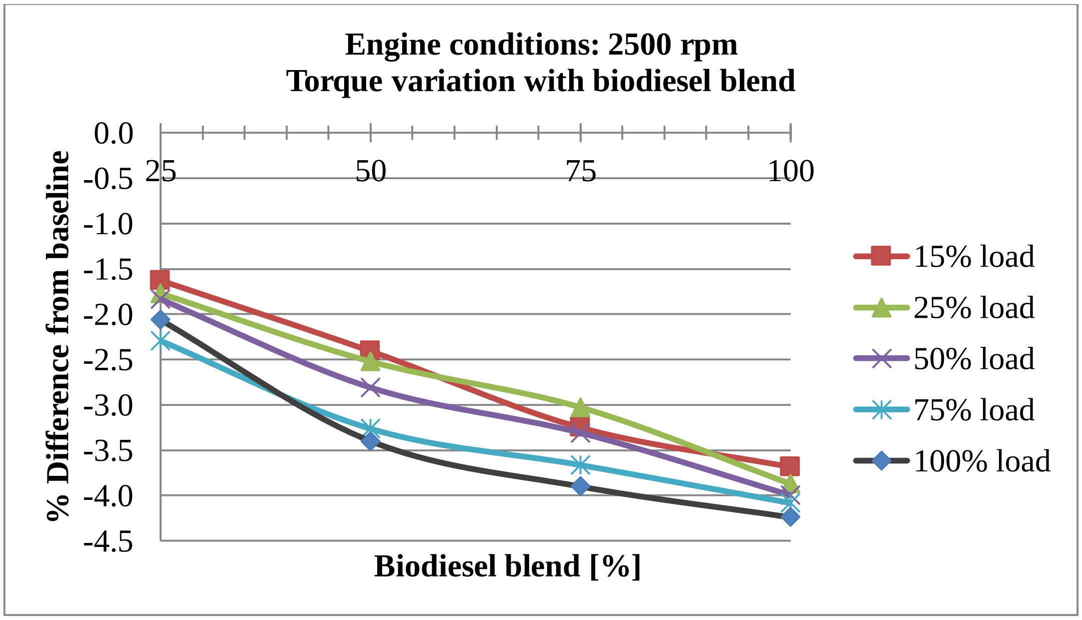

Figure 6-7: Variation of torque with WCO biodiesel-blend at 2500 rpm and various load conditions

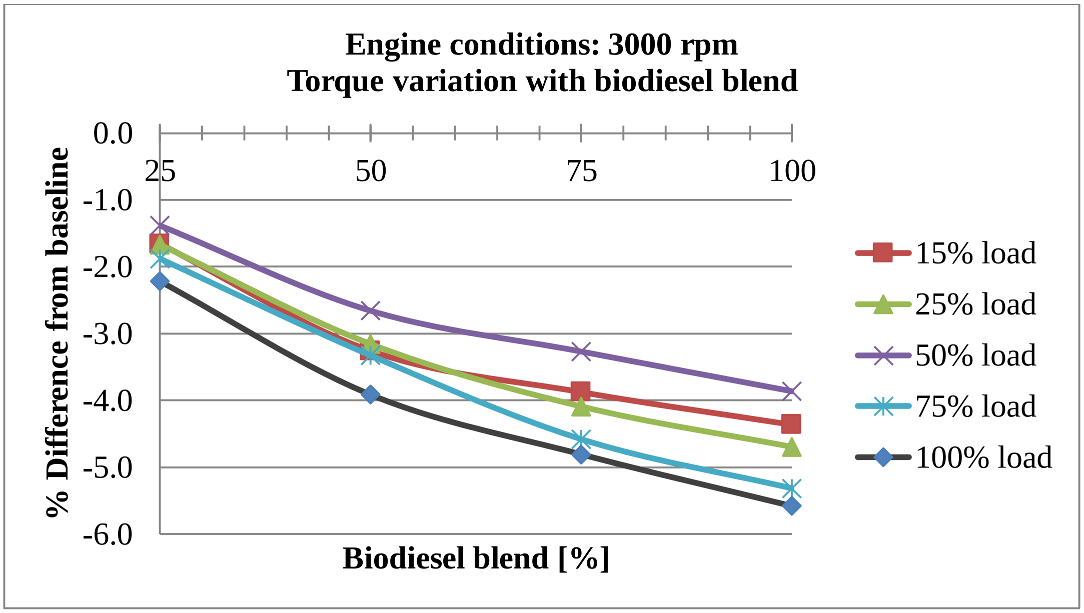

Figure 6-8: Variation of torque with WCO biodiesel-blend at 3000 rpm and various load conditions

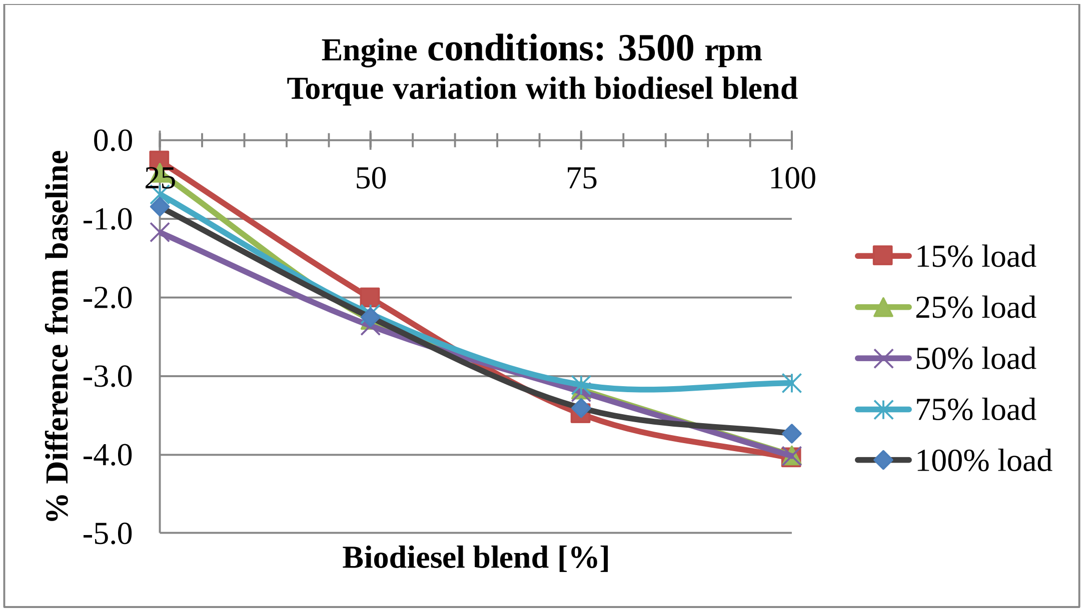

Figure 6-9: Variation of torque with WCO biodiesel-blend at 3500 rpm and various load conditions

6.3.2. Effect of Diesel and WCO Biodiesel Blend on Engine Brake Specific Fuel Consumption (BSFC)

The brake specific fuel consumption is defined as the fuel flow rate per unit power output. It is a measure of the efficiency of the engine in using the fuel supplied to produce work. It is desirable to obtain a lower value of BSFC, meaning that the engine uses less fuel to produce the same amount of work. This is one of the most important parameters to compare when testing various fuels.

$$BSFC = m_f/BP \text{ [kg/kW h]}$$

Where m_f is the mass flow rate of fuel and BP is engine brake power. The fuel flow rate is determined by using a graduated sight glass and a chronometer watch.

$$m_f = v_f \times \rho_f \times 3600/t \text{ [kg/h]}$$

Where v_f is volume of fuel measure, which was 50 cc, ρ_f is fuel density and t is the time measured until 50 cc of fuel is consumed, measured in seconds. The BP was calculated using the formula:

$$BP = 2\pi NT/\ (60\times1000) \text{ [kW]}$$

Where N is engine speed, measured in rpm and T is the engine torque, measured in Nm. In order to determine accurately the BSFC accurately, seven measurements of the mass fuel flow rate were recorded.

The effect of WCO biodiesel-diesel blend on BSFC for fixed engine conditions is presented in Figures 6-10 – 6-13. The BSFC was observed to decrease with the increase in engine load. As expected, the test results showed higher fuel consumption when biodiesel blend ratio was increased compared with the baseline.

Neat WCO biodiesel has high density and viscosity, but lower heating value when compared with diesel (Table 6-3). The higher density of WCO biodiesel caused greater mass of fuel injection at a given injection pressure. These result in an increase in BSFC with the increase of WCO biodiesel blend ratio in diesel fuel. For most biodiesel blends, an increase in BSFC with respect to decreasing engine load was observed.

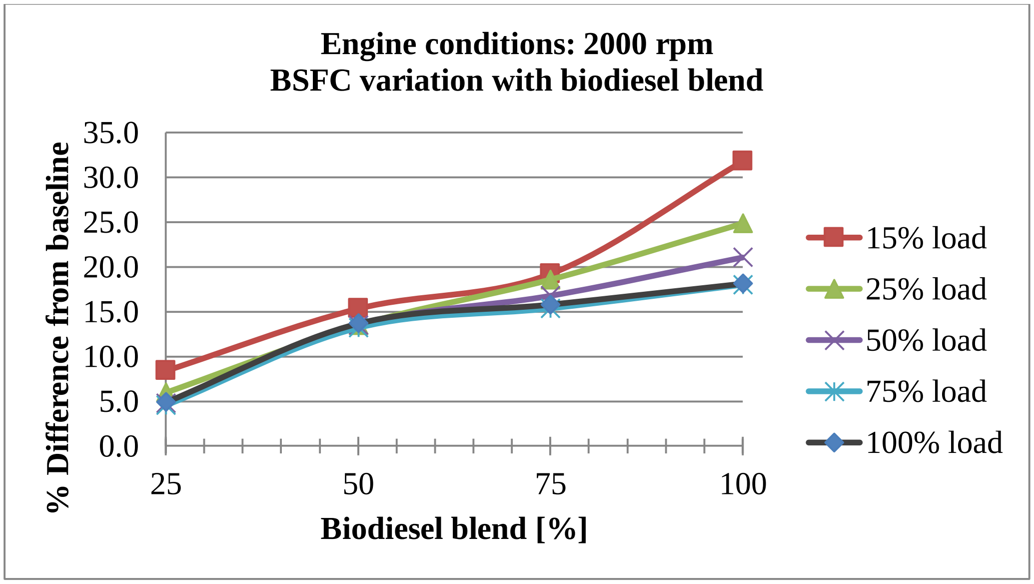

Figure 6-10: Variation of BSFC with WCO biodiesel-blend at 2000 rpm and various load conditions

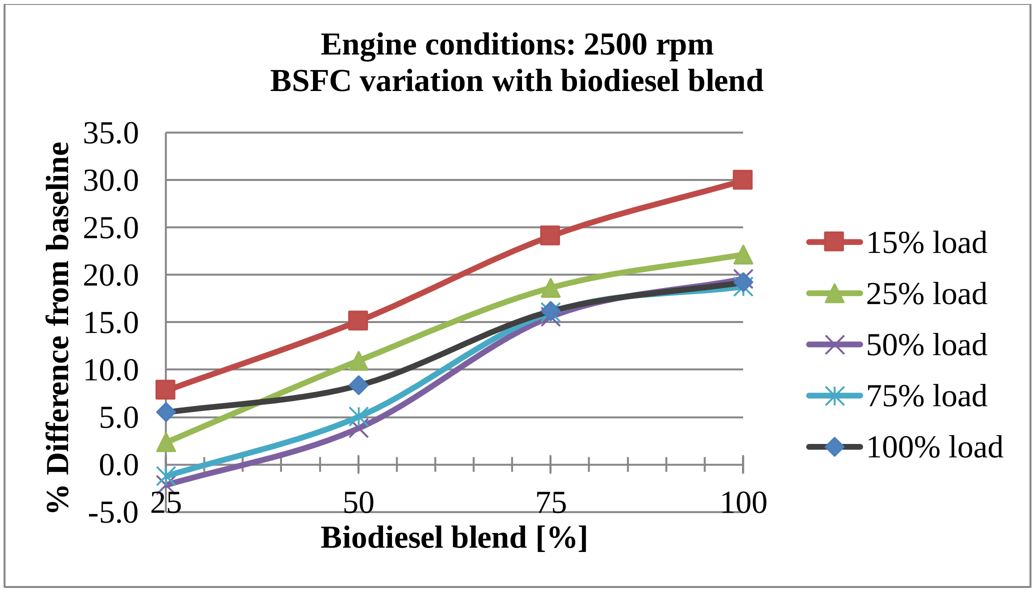

Figure 6-11: Variation of BSFC with WCO biodiesel-blend at 2500 rpm and various load conditions

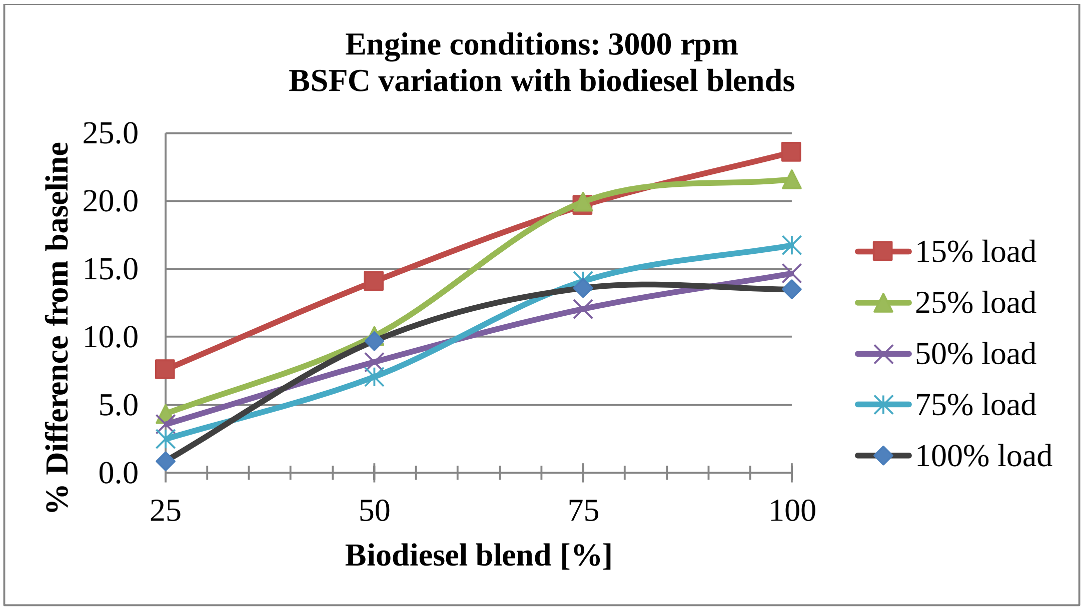

Figure 6-12: Variation of BSFC with WCO biodiesel-blend at 3000 rpm and various load conditions

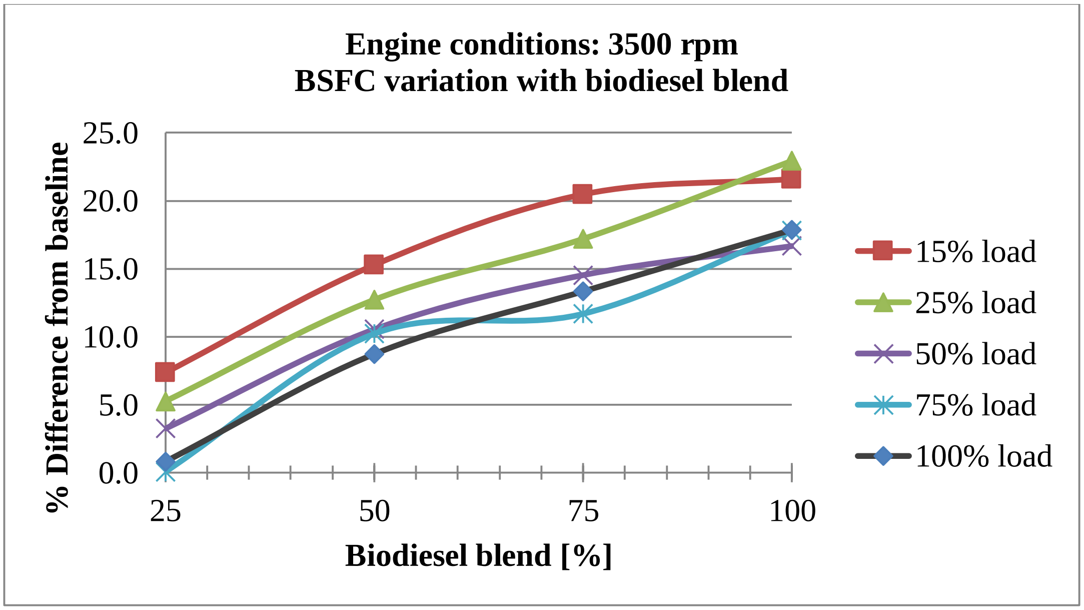

Figure 6-13: Variation of BSFC with WCO biodiesel-blend at 3500 rpm and various load conditions

6.3.3. Effect of Diesel and WCO Biodiesel Blend on Engine Brake Thermal Efficiency (BTE)

Brake thermal efficiency (BTE) is the ratio of the thermal power available in the fuel to the power the engine delivers to the crankshaft. This depends greatly on the manner in which energy is converted since the efficiency is normalised with the heating value of the fuel. The heating value of red diesel and WCO biodiesel blends are presented in Table 6-3. Considering these values the BTE was determined using the formula:

$$BTE=BP/\ (v_f \times Q_{HV})\ [\%]$$

Where BP is the rate of energy output, engine brake power, v_f is the volume of fuel consumed per hour, and Q_{HV} is the fuel heating value of the fuel. Figures 6-14 – 6-17 show the variation of brake thermal efficiency with biodiesel blend for various speed and engine load conditions.

At 2000 rpm, reduction in BTE was observed for all biodiesel blends at low engine load conditions. For high biodiesel blend ratios i.e. B75 to B100, BTE increased for 50 to 100% engine load. B75 and B100 showed 4% increase in BTE compared with the baseline (Figure 6-14).

As shown in Figure 6-15, at 15% and 25% engine load conditions, BTE was close to that of the baseline. At engine load of 50, 75 and 100% all biodiesel blends showed an increase in BTE when compared with the baseline. The high increase in BTE (up to 10%) was observed for B100 at 100% engine load.

In Figures 6-16 – 6-17, variation in BTE at 3000 and 3500 rpm for various blend ratios is shown. B25, B50 and B75 showed a decrease in BTE for low engine load. B50 showed a reduction in BTE of 5% and 3% compared with the baseline at 3000 rpm and 3500 rpm respectively. B75 and B100 showed an increase in BTE at a high engine load.

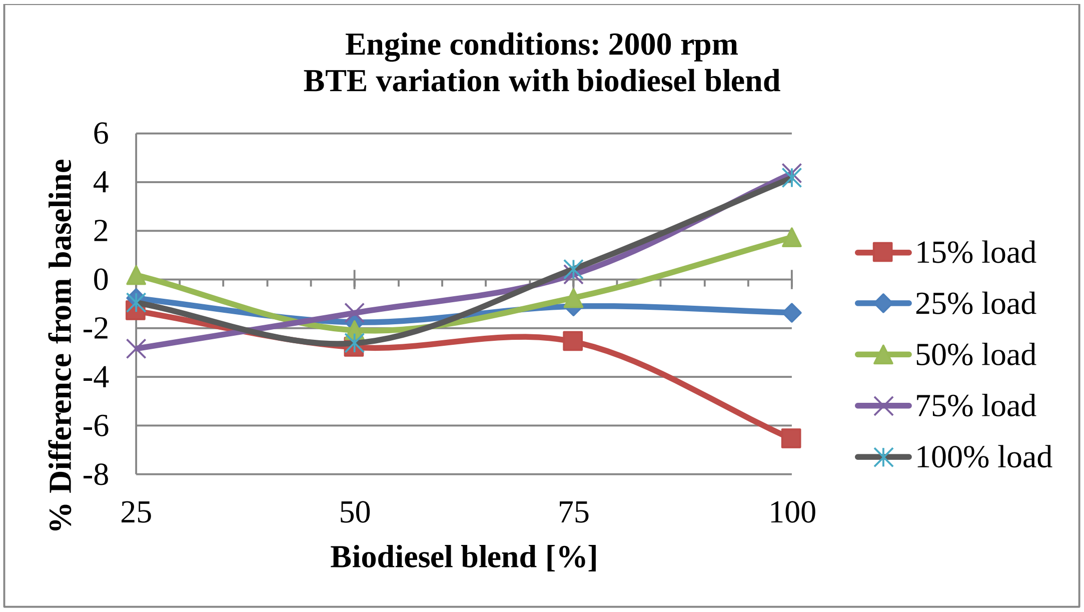

Figure 6-14: Variation of BTE with WCO biodiesel-blend at 2000 rpm and various load conditions

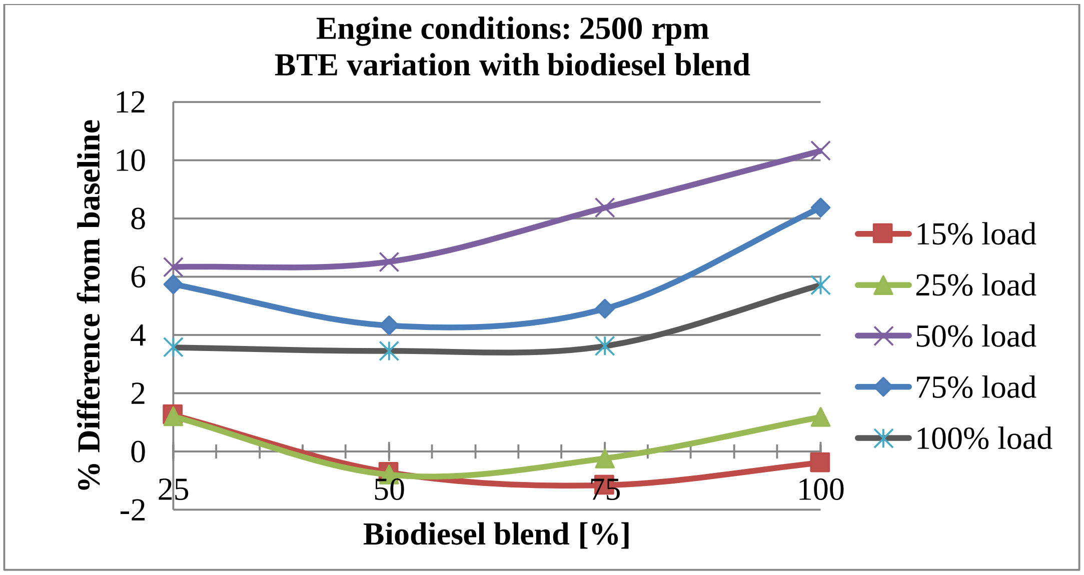

Figure 6-15: Variation of BTE with WCO biodiesel-blend at 2500 rpm and various load conditions

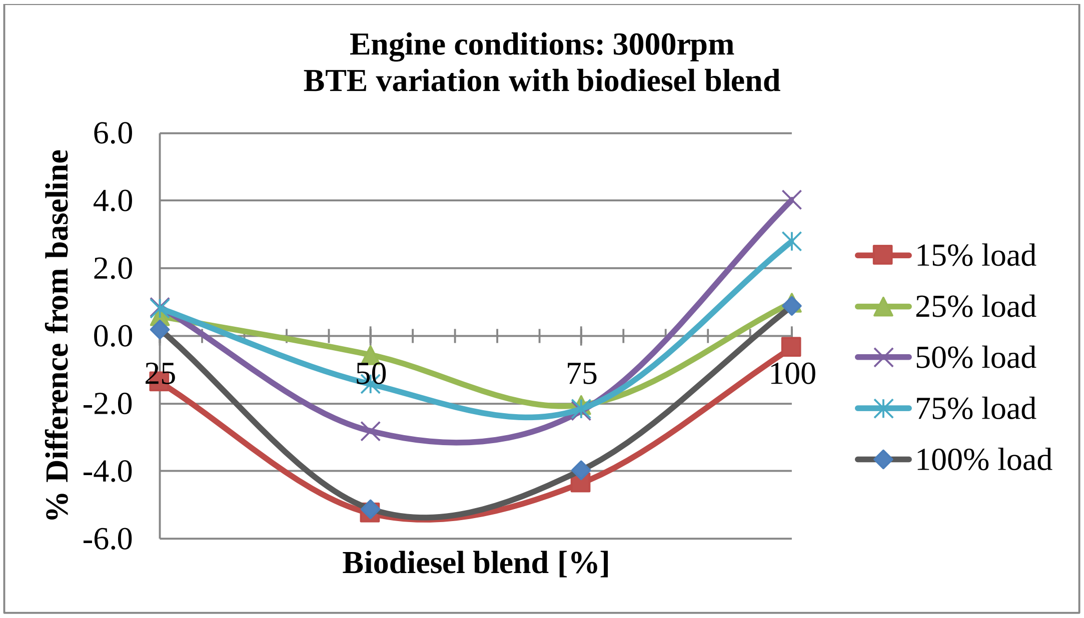

Figure 6-16: Variation of BTE with WCO biodiesel-blend at 3000 rpm and various load conditions

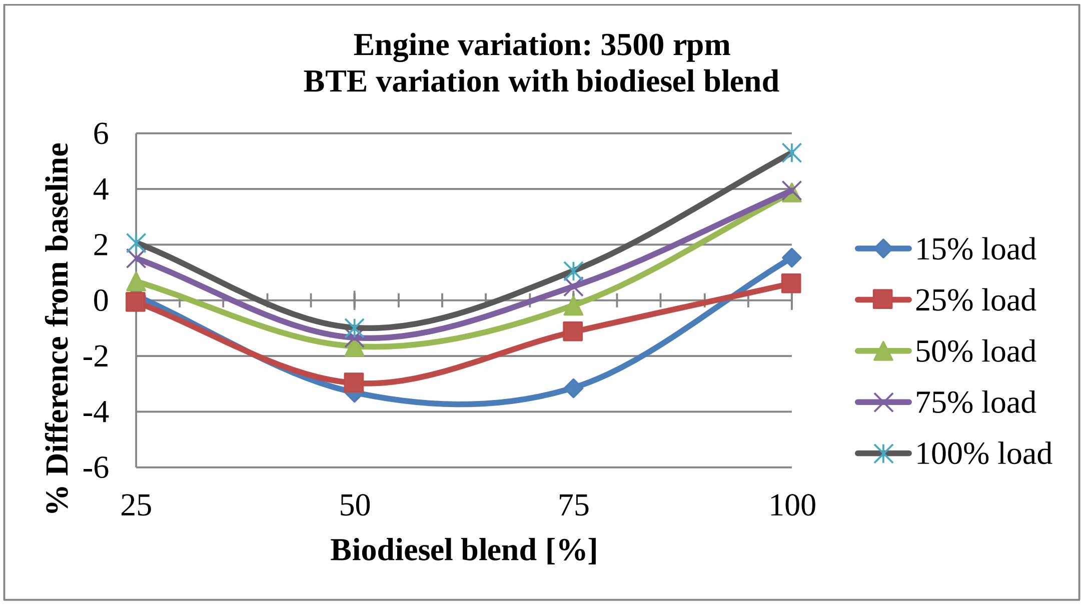

Figure 6-17: Variation of BTE with WCO biodiesel-blend at 3500 rpm and various load conditions

The test results showed an increase in brake thermal efficiency for engine tested under 75% and 100% engine load for most biodiesel blends. At 2500 rpm and 50, 75 and 100% engine load, an increased in BTE for all biodiesel blends was observed. The highest increase in BTE for biodiesel was observed at engine speed 2500 rpm, with an increase of up to 10% from baseline. At a low load and high engine speed the BTE of biodiesel was close to that of diesel. The lowest BTE among all biodiesel blends was recorded for B50.

6.3.4. Effect of Diesel and WCO Biodiesel Blend on Exhaust Emissions

a) Variation of brake specific carbon monoxide (BSCO) Emissions with Load Percentage

Figures 6-18 – 6-21 show the variation of BSCO emissions with respect to variable engine load. It is clear that as the ratio of biodiesel increased in the blend, BSCO decreased compared with diesel. B100 showed the lowest value of BSCO between all biodiesel blends samples. At 2000 rpm, a reduction about 60% in BSCO for biodiesel compared with the baseline was observed, as showed in Figure 6-18.

At 2500 and 3000 rpm, B100 showed the lowest BSCO emission. Figures 6-19 and 6-20 show reduction up to 90% in BSCO for engine set at 2500 rpm and up to 70% for engine set at 3000 rpm.

At 3500 rpm, a reduction in BSCO emissions of up to 75% for neat biodiesel was observed, as shown in Figure 6-21.

The results showed a reduction in BSCO emissions for most biodiesel blends with the increase in engine load. When the engine tests were performed with biodiesel blends the results showed high reductions in BSCO compared with diesel. This was due to a more intense combustion of biodiesel, resulting in a complete combustion compared with diesel. All fuel samples showed similar behaviour, as the load increases BSCO emissions decreased. High biodiesel blend ratio, B75 and B100, showed a higher reduction in BSCO emissions compared with lower biodiesel blends.

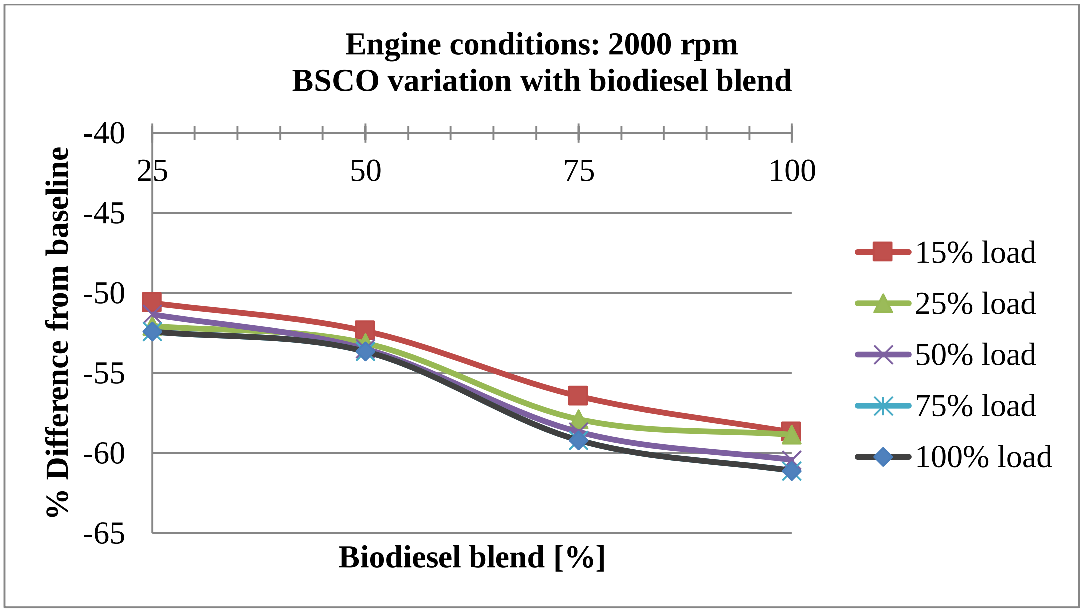

Figure 6-18: Variation of BSCO with WCO biodiesel-blend at 2000 rpm and various load conditions

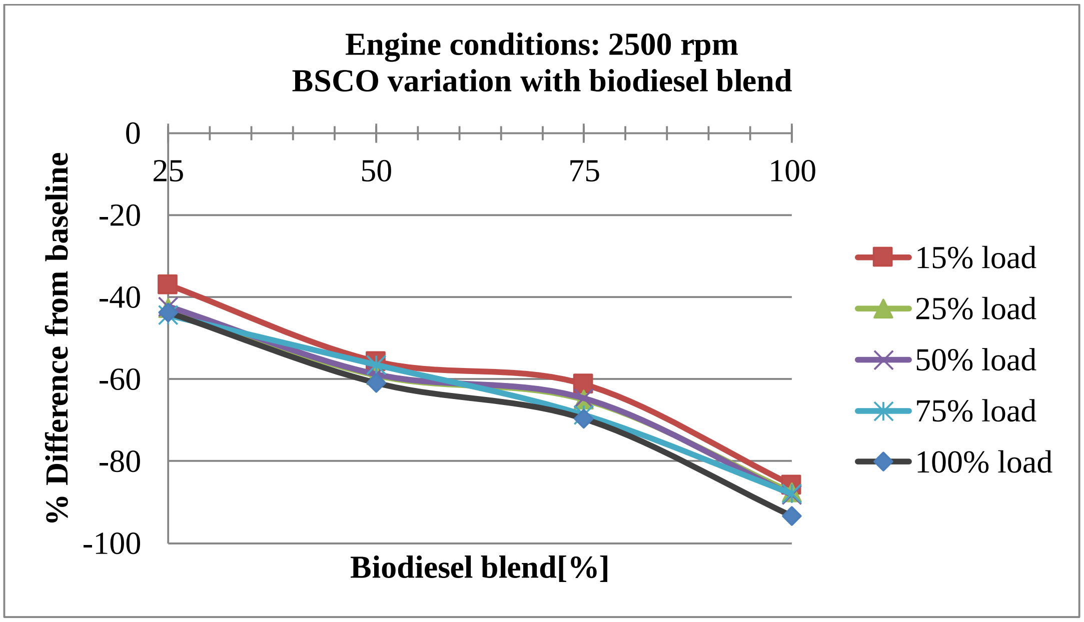

Figure 6-19: Variation of BSCO with WCO biodiesel-blend at 2500 rpm and various load conditions

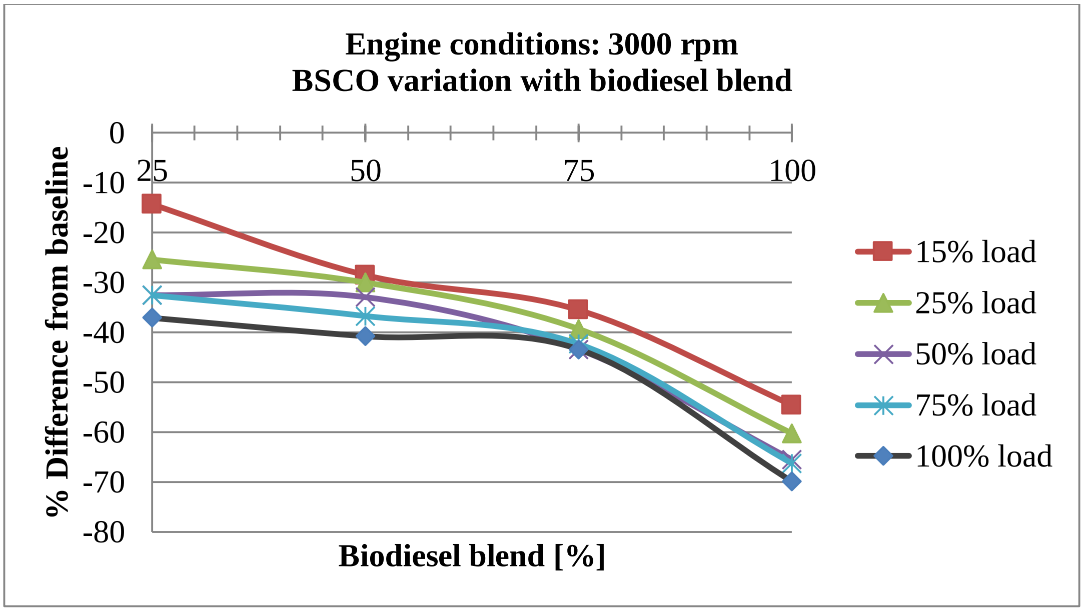

Figure 6-20: Variation of BSCO with WCO biodiesel-blend at 3000 rpm and various load conditions

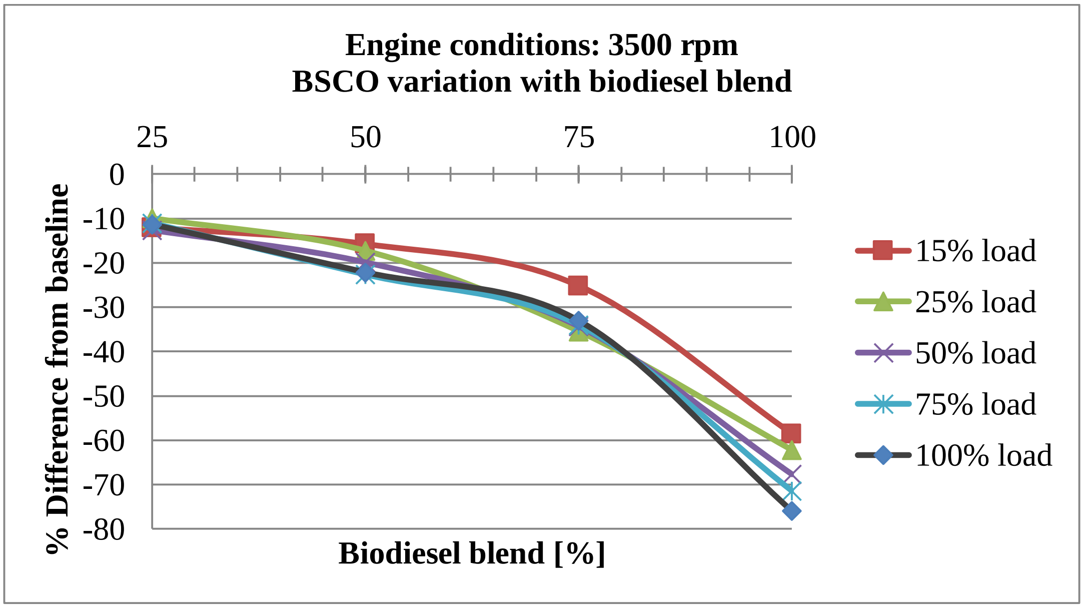

Figure 6-21: Variation of BSCO with WCO biodiesel-blend at 3500 rpm and various load conditions

b) Variation of brake specific un-burnt hydrocarbons (BSHC) Emissions with Load Percentage

Variation of BSHC with the engine load is shown in Figures 6-22 – 6-25. It was observed that BSHC emissions decreased with an increase of engine speed for all biodiesel blends, compared with the baseline.

At 2000 rpm, B50 and B75 showed the highest reduction in BSHC emissions, of up to 27% for engine load of 100% and 15% respectively, compared with the baseline. As the engine speed increases from 2500 to 3000 rpm, B25 and B75 showed a reduction in BSHC emissions of up to 45% compared with the baseline.

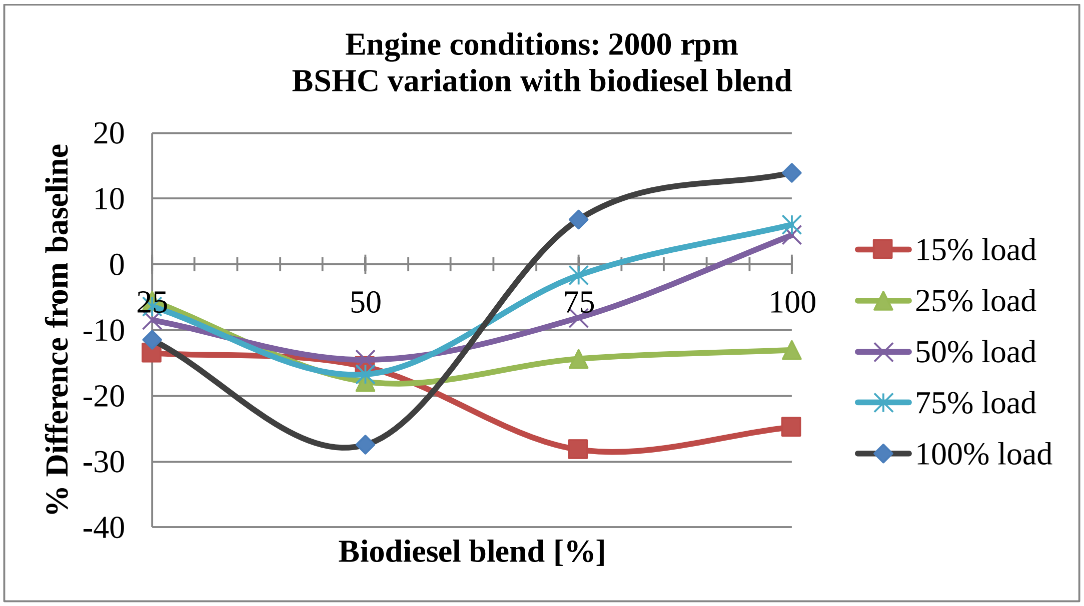

Figure 6-22: Variation of unburned BSHC with WCO biodiesel-blend at 2000 rpm and various load conditions

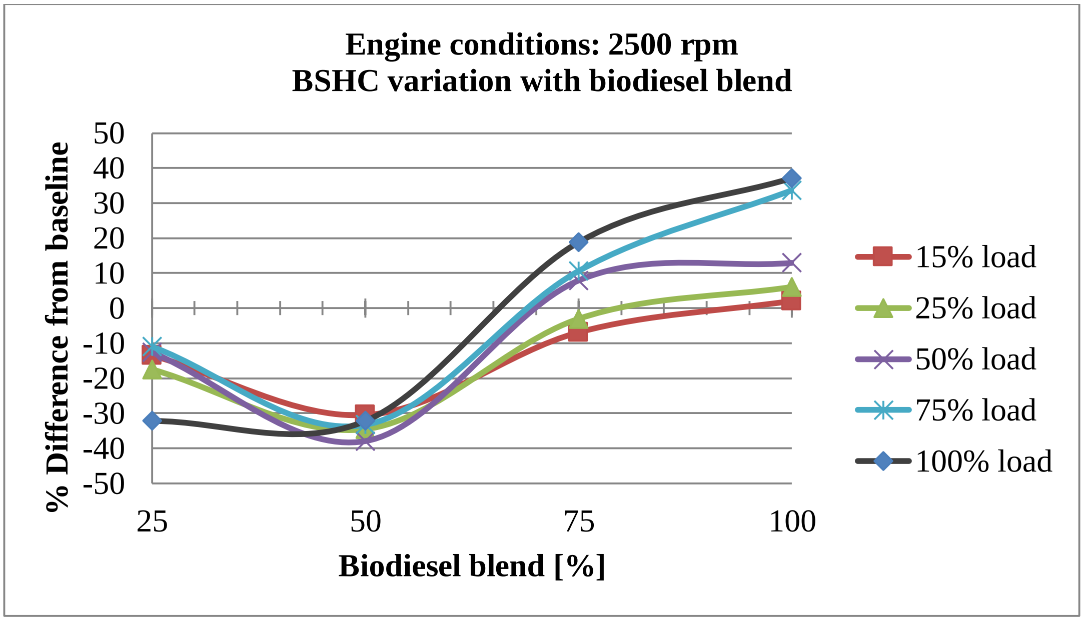

Figure 6-23: Variation of unburned BSHC with WCO biodiesel-blend at 2500 rpm and various load conditions

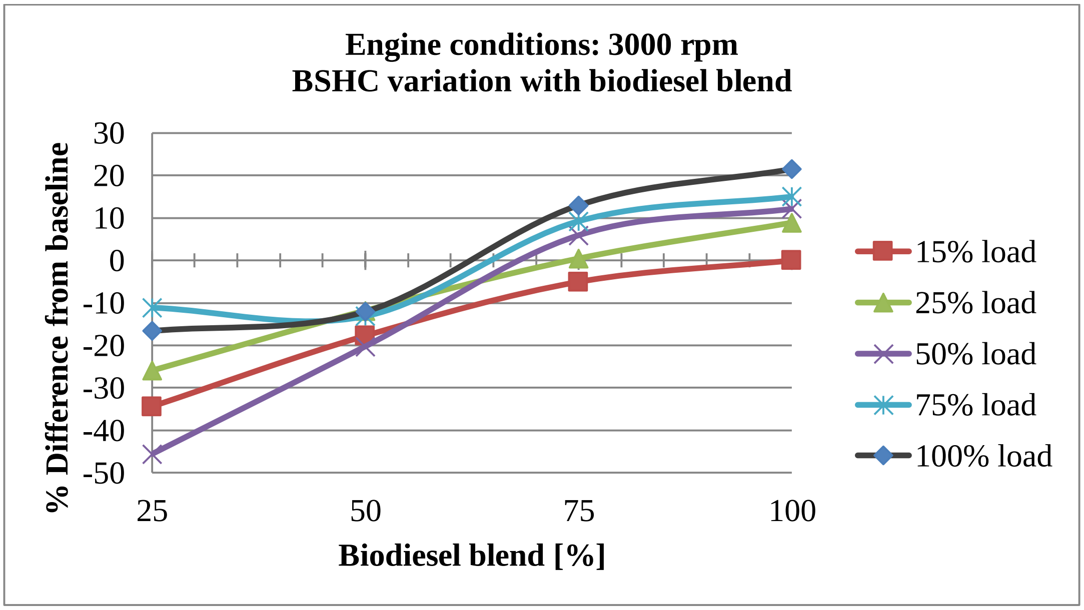

Figure 6-24: Variation of unburned BSHC with WCO biodiesel-blend at 3000 rpm and various load conditions

As shown in Figure 6-25, at 3500 rpm, BSHC emissions decrease with the increase in engine load for blend ratios of B25 and B50. With the increase in biodiesel blend and engine load up to 100% it was observed an increase in BSHC emissions compared with the baseline. At 100% engine load, B50 showed a decrease of up to 30% in BSHC, while B100 showed the highest increase in BSHC emissions of up to 55% from baseline.

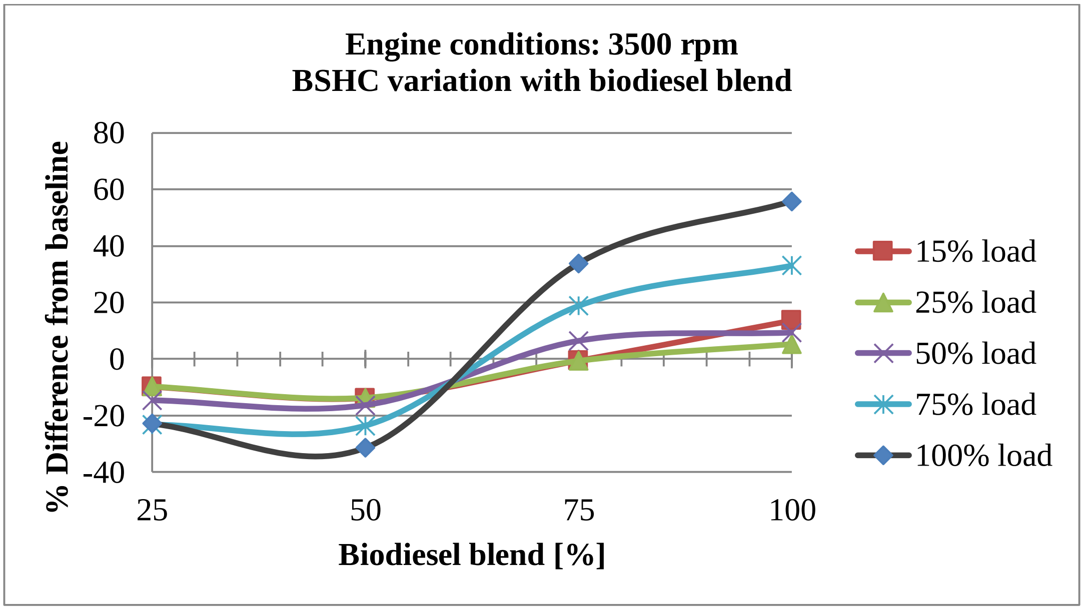

Figure 6-25: Variation of unburned BSHC with WCO biodiesel-blend at 3500 rpm and various load conditions

Test results showed a reduction in BSHC emissions for biodiesel blend ratio under 75% in diesel. With an increase in biodiesel blend ratio in diesel of up to 100%, the BSHC emissions increased. This can be due to the effect of biodiesel viscosity, which has an effect on starting combustion. The effect of viscosity was more accentuated at high biodiesel blends. High viscosity of the neat biodiesel could result in a poor spray atomization due to the larger spray droplets. The larger the size of the droplets, the longer it takes for the droplet to oxidize, compared with the fine spray droplets which have a higher surface area, and therefore the faster is the oxidation process.

c) Variation of $BSCO_2$ Emissions with Load Percentage

Figures 6-26 – 6-29 show the variation of $BSCO_2$ with engine load for various biodiesel blends. An increase in $BSCO_2$ emissions for all biodiesel blends compared with the baseline can be observed.

At 2000 rpm, the results showed an increase in $BSCO_2$ emissions with increase in biodiesel blend ratio of up to 75%, (B75). Neat biodiesel showed lower $BSCO_2$ compared with B75. With an increase in engine load, $BSCO_2$ emissions showed an increase for all biodiesel blends. The trend is similar for 2500 to 3500 rpm as shown in Figures 6-27 – 6-29.

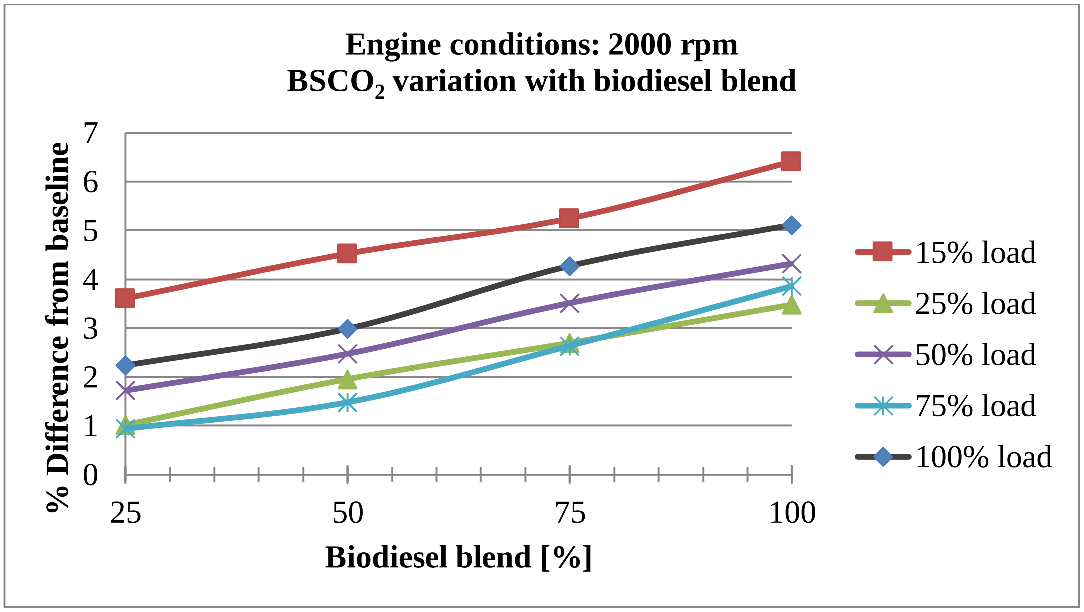

Figure 6-26: Variation of $BSCO_2$ with WCO biodiesel-blend at 2000 rpm and various load conditions

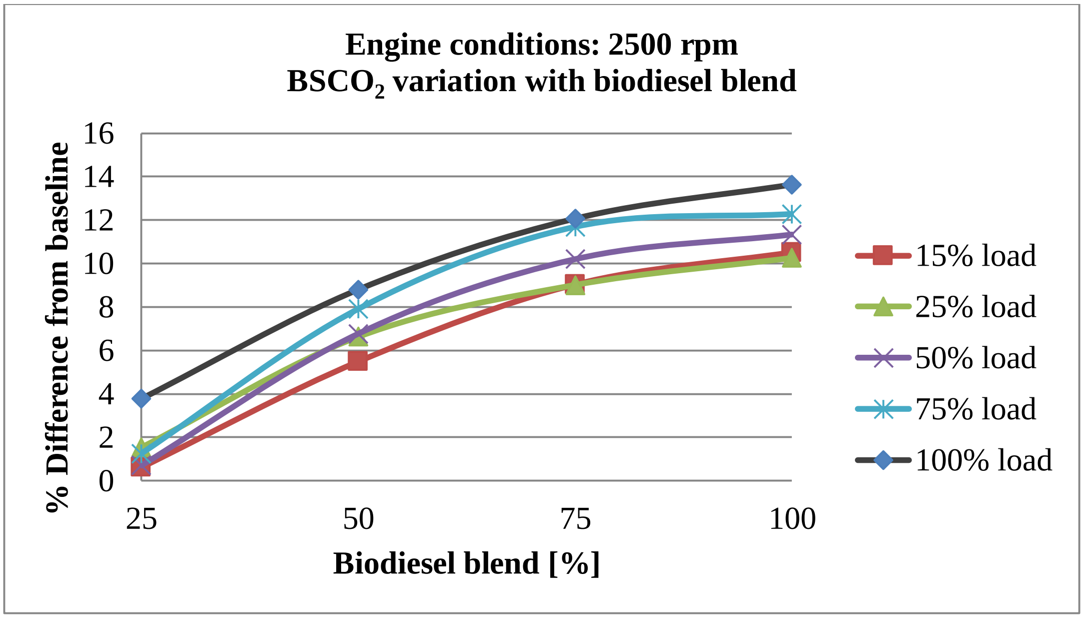

Figure 6-27: Variation of $BSCO_2$ with WCO biodiesel-blend at 2500 rpm and various load conditions

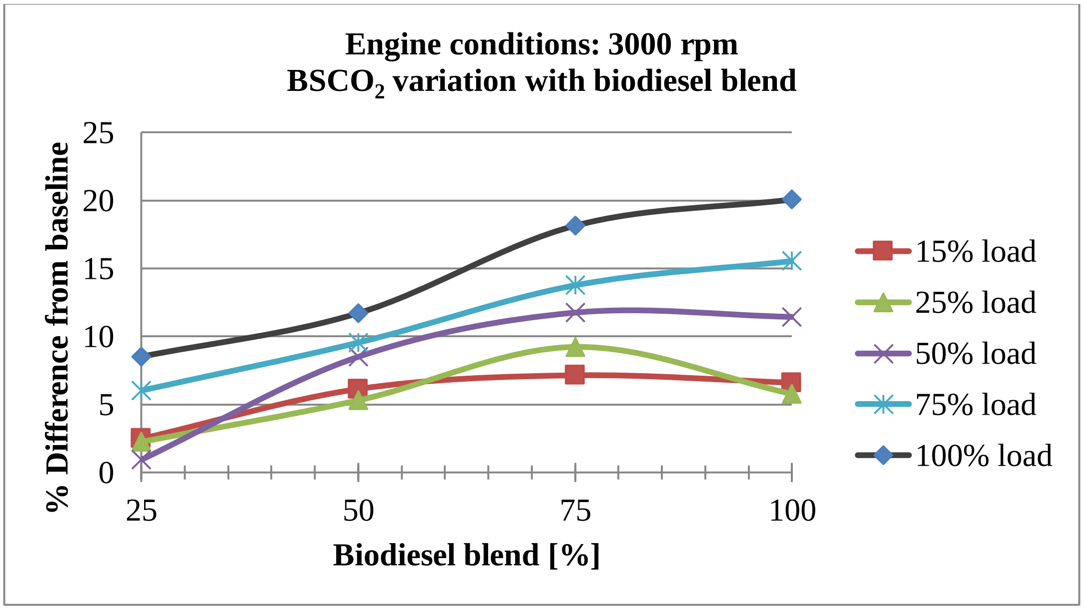

Figure 6-28: Variation of $BSCO_2$ with WCO biodiesel-blend at 3000 rpm and various load conditions

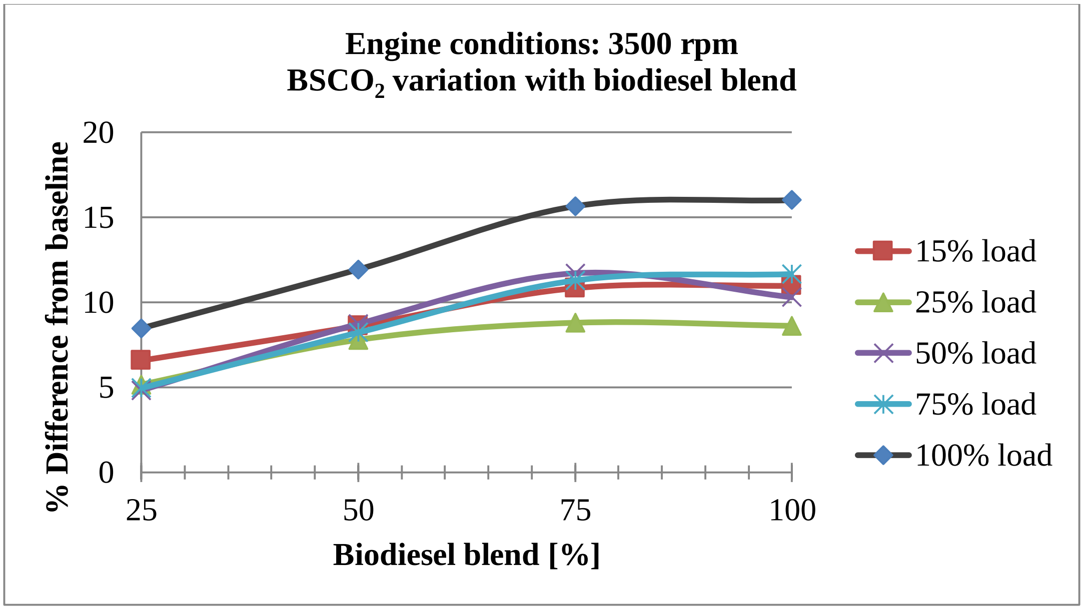

Figure 6-29: Variation of CO_2 with WCO biodiesel-blend at 3500 rpm and various load conditions

Test results showed an increase in BSCO_2 with increase in biodiesel blend, compared with baseline. High CO_2 emissions is a result of an enhanced combustion. When biodiesel blend ratio was increased, the CO and HC emissions decreased and resulted in a cleaner combustion compared with diesel fuel.

d) Variation of brake specific Nitrogen oxide (BSNOx) Emissions with Load Percentage

Figures 6-30 – 6-33 show the variation in BSNOx emissions with the engine load percentage for different WCO biodiesel blends. It can be seen that at all engine operating conditions and for all biodiesel blends BSNOx emissions increase. Most biodiesel blends showed an increase in BSNOx emissions with the increase in engine load.

At 2000rpm, the test results showed an increase of 8%, 28%, 35% and 53% compared with the baseline in BSNOx for B25, B50, B75 and B100 respectively.

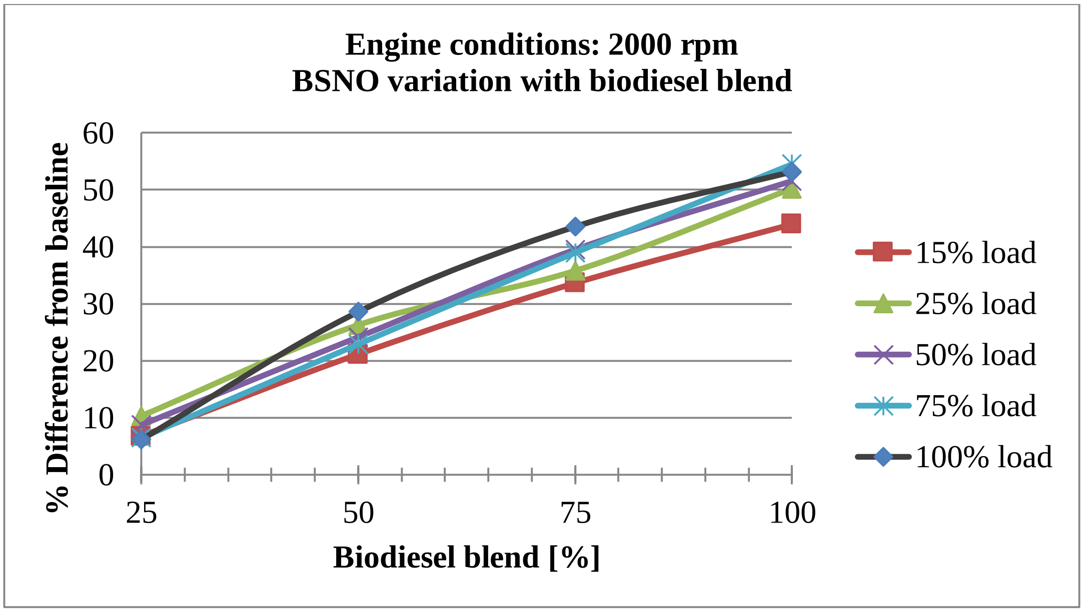

Figure 6-30: Variation of BSNOx with WCO biodiesel-blend at 2000 rpm and various load conditions

Figure 6-31 shows that at 2500rpm, the increase in BSNOx emissions for B25, B50, B75 and B100 was 9%, 18%, 25% and 31% respectively compared with the baseline.

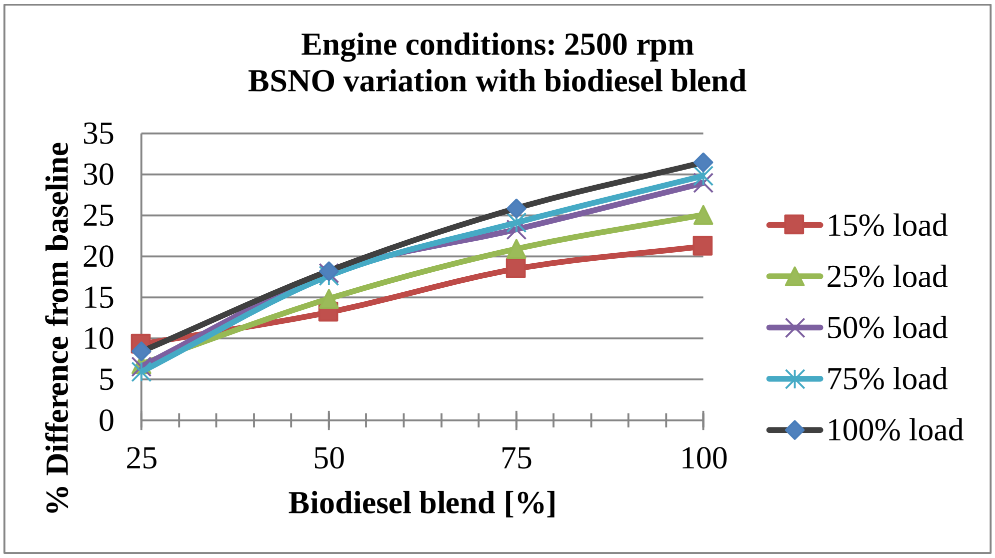

Figure 6-31: Variation of BSNOx with WCO biodiesel-blend at 2500 rpm and various load conditions

At 3000 rpm, B25, B50, B75 and B100 show an increase in the BSNOx emissions of up to 11%, 27%, 41%, and 50% respectively compared with the baseline as shown in Figure 6-32.

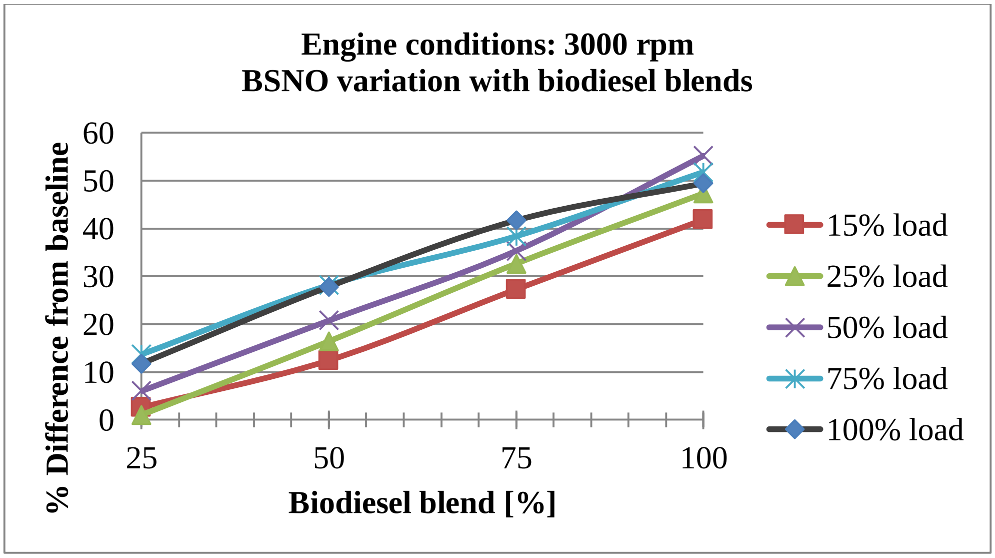

Figure 6-32: Variation of BSNOx with WCO biodiesel-blend at 3000 rpm and various load conditions

Similar trend can be seen at 3500 rpm for all blend ratios in Figure 6-33. Increase in the BSNOx emissions up to 20%, 31%, 41%, and 45% were observed for B25, B50, B75 and B100 respectively.

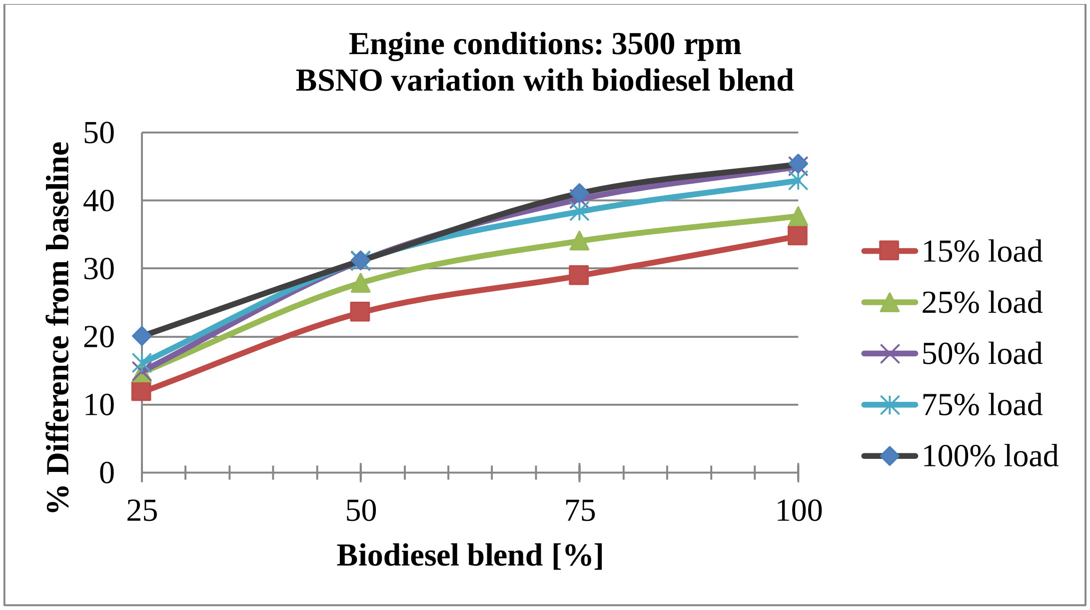

Figure 6-33: Variation of BSNOx with WCO biodiesel-blend at 3500 rpm and various load conditions

The test results showed higher BSNOx emissions for biodiesel compared with diesel. The biodiesel blend ratio and engine load were observed to have a direct effect on NOx increase. It is believed that the presence of oxygen content in biodiesel leads to an increase combustion temperature resulting in an increase in NOx formation. Also the chemical composition of biodiesel can influence the NOx formation [152].

e) Effect of Diesel and WCO Biodiesel Blend on Exhaust Gas Temperature (EGT)

Exhaust gases of an internal combustion engine contain significant enthalpy and may contain unburned combustion products (hydrocarbons). When the air-fuel ratio is high, the amount of incomplete combustion products is likely to be low and when the air/fuel ratio is low, there is an insufficient amount of oxygen to complete combustion. The exhaust gas temperature is related to the determination of system efficiency.

The exhaust gas temperatures for WCO biodiesel-diesel blends are shown in Figure 6-34 – 6-37. The test results showed an increase in EGT for biodiesel blends compared with diesel. At 2000 rpm, B75 shown an increase of 2.5% in EGT, whereas for B100 it was observed an increase of up to 2%, at full engine load.

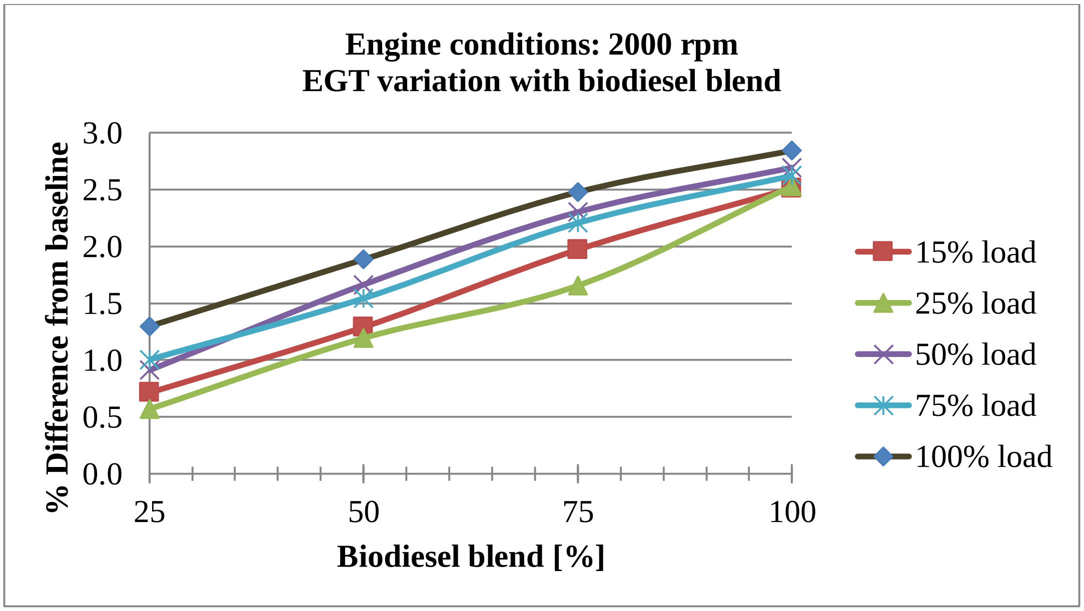

Figure 6-34: Variation of EGT with WCO biodiesel-blend at 2000 rpm and various load conditions

At 2500 rpm, B75, Figure 6-35 shows an increase of up to 3.8% increase in EGT at full engine load and up to 2.4% at low engine load. The EGT increase for B100 was of up to 2.53% for full engine load and up to 1% for a low engine load.

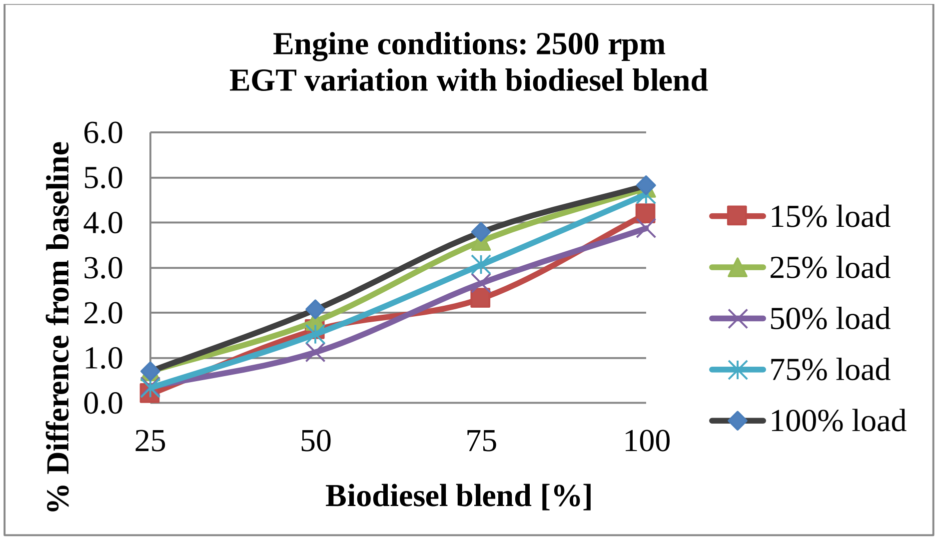

Figure 6-35: Variation of EGT with WCO biodiesel-blend at 2500 rpm and various load conditions

Figure 6-36 shows at 3000 rpm, B75 shows an increase of up to 2.11% in EGT at full engine load and up to 1.5% at low engine load. The EGT increase for B100 was of up to 1.7% for full engine load and up to 0.5% for low engine load.

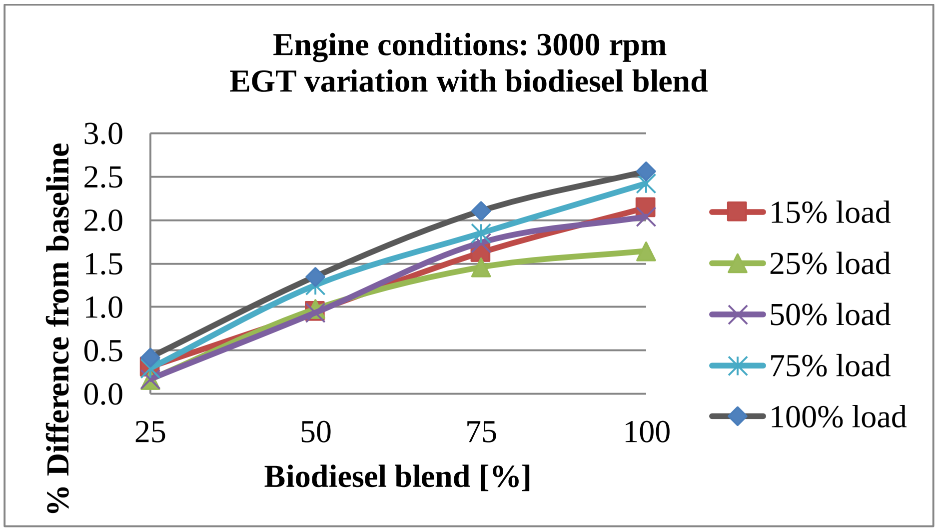

Figure 6-36: Variation of EGT with WCO biodiesel-blend at 3000 rpm and various load conditions

Figure 6-37 shows EGT variation at 3500 rpm. An increase of up to 1.6% in EGT at full engine load and up to 1.5% at low engine load can be seen for B75. The EGT increase for B100 was of up to 1.1% for full engine load and up to 0.4% for low engine load.

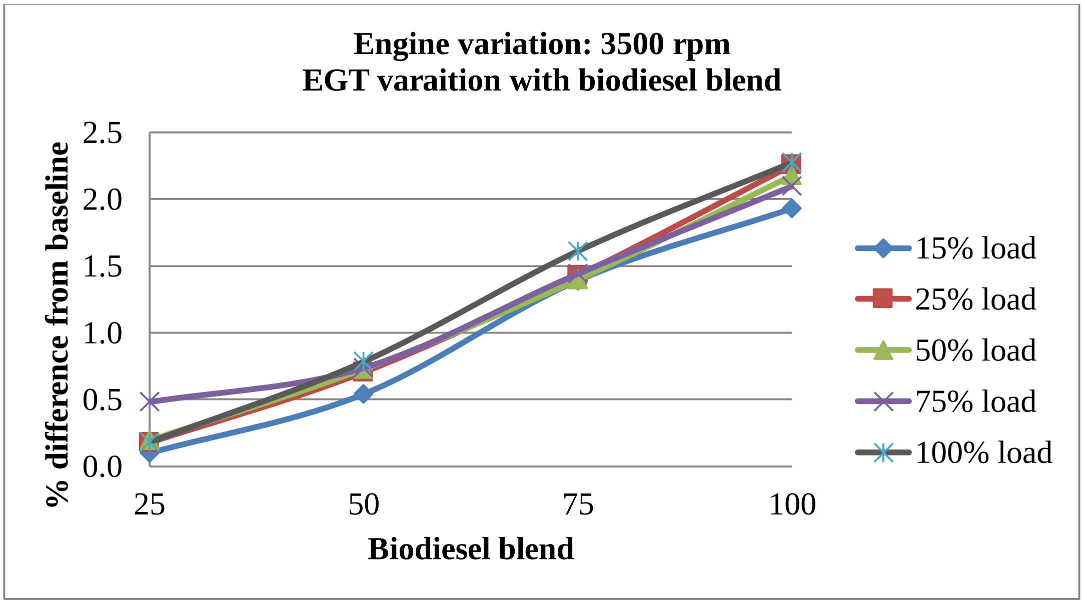

Figure 6-37: Variation of EGT with WCO biodiesel-blend at 3500 rpm and various load conditions

Test results showed an increase in EGT with the increase in biodiesel blend ratio of up to 75%, (B75). At blend ratio higher than 75% the results shows a decrease in EGT. This was due to the decrease in torque for neat biodiesel, which lead to reduction in the engine power. Therefore it is clear that EGT for B100 is lower compared with that for B75. The difference in exhaust gas temperature between biodiesel blends and diesel is low.

6.1. Conclusions

A series of tests were performed in order to assess the performance and emissions of a VM Motori engine using a range of WCO biodiesel blends with diesel. The engine tests were conducted at 2000, 2500, 3000 and 3500 rpm. At each speed, various measurements were taken at 15%, 25%, 50%, 75% and 100% engine load.

The experimental results showed a decrease in engine torque with up to 9% when WCO biodiesel was used. WCO biodiesel has a lower calorific value compared with diesel. This results in a decrease in engine torque, and respectively on engine power.

The brake specific fuel consumption increases with an increase in biodiesel blend ratio in diesel. The higher density of WCO biodiesel results in a greater mass of fuel being injected at a given injection pressure. This together with the lower energy content of biodiesel causes an increase in BSFC compared with diesel.

The thermal efficiency of the engine using WCO biodiesel, at 2000 rpm and 15% and 25% engine load conditions, was observed to decrease up to 3% from the baseline as the biodiesel blend ratio in diesel was increased. At 50%, 75% and 100% engine load, B75 and B100 shown an increase with up to 4% in BTE. The highest increase in BTE for biodiesel was observed at engine set at 2500 rpm, with an increase of up to 9% from baseline. At low load and high engine speed the engine BTE using biodiesel seems to be similar to that of diesel. The engine BTE using WCO biodiesel was seen to increase with the increase in load and engine speed.

The exhaust emissions from engine using WCO biodiesel blends and diesel were measured. The BSHC, BSCO, $BSCO_2$ and BSNOx emissions were obtained and compared with the baseline, (B0). The test results shown a reduction in BSHC and CO emissions for all biodiesel blends compared with the baseline. The lower BSHC was observed at B75. As the biodiesel blend ratio in diesel was increased farther, the decrease in BSHC was reduced compared with B75. This can be caused by the high biodiesel viscosity compared with that of diesel. The viscosity can alter the fuel spray atomization leading to an incomplete combustion. The $BSCO_2$ emissions were higher for the engine using WCO biodiesel compared with diesel. This was expected since an improvement in combustion was achieved with the addition of biodiesel in diesel. The test results showed an increase in EGT for all biodiesel blends. The EGT was observed to increase with the increase in biodiesel blend ratio in diesel, up to B75. A further increase in biodiesel blend ratio up to B100 shown a reduction in EGT compared with that of B75. This is due to the fact that for high biodiesel blend the torque had shown a decrease. The higher increase in EGT for WCO biodiesel was observed at 2500rpm, with up to 3.5% increase from baseline. Higher BSNOx were observed for all biodiesel blends compared with the baseline due to the higher exhaust gas temperature and the higher (up to 12%) oxygen content in biodiesel.

The content of oxygen in biodiesel and the high cetane number of biodiesel is believed to lead to high combustion temperature which results in increased NOx formation compared to diesel.

Chapter 7 -Discussion

The use of waste cooking oil biodiesel was investigated as a possible alternative to petroleum petro-diesel. Waste oils are available worldwide and a greener way to recycle them is for them to be used as biomass in biodiesel production. In present research three main aspects were considered for investigation in order to assess the suitability of biodiesel as a replacement for petro-diesel. Firstly, samples of net diesel, biodiesel, and blends of 25%, 50 and 75% biodiesel and diesel were prepared and the fuel properties and susceptibility of microbial contamination of the biodiesel samples were measured and analysed related to diesel. Secondly, diesel and biodiesel samples were tested in a CCR and the exhaust emissions were recorded and analysed, focussing more on NO formation. And lastly diesel and biodiesel samples were tested in a Land Rover VM Motori diesel engine and the efficiency and exhaust emissions were measured and analysed.

7.1. Fuel Property Measurements

Physicochemical properties of diesel and biodiesel were measured and analysed to compare the performance of the two fuel types in an internal combustion engine. In conformity with previous research it was found that biodiesel is an oxidised fuel, containing 11% oxygen in its composition. This is consistent with the results obtained by FT-RI, GC-MS and bomb calorimeter. The FT-IR spectra from diesel and biodiesel have shown the peaks that do not overlap. FT-IR spectrum of biodiesel has also shown the presence of –HC=CH–stretching, of which increase in intensity represents an increase in unsaturation of biodiesel samples. Also, the presence of double bounds (C=C, C=O) which was found more abundant may enhance the cold flow properties of the fuel, but could increase the biodiesel susceptibility to oxidation.

Results show that with the increase in oxygen content in fuel, the calorific value of the fuel decreases. The test results from the elemental analyses of the fuel showed up to 12% oxygen in biodiesel compared with 0.07% in diesel. Carbon content for biodiesel was 76% compared with 86.9% for diesel. The sulphur concentration was 5.2 mg/kg in biodiesel whereas in diesel the sulphur concentration was 900mg/kg. The lower sulphur concentration makes biodiesel less harmful to human health and environment. These differences in physicochemical properties between biodiesel and diesel lead to differences in combustion and exhaust emissions between diesel and biodiesel. Several types of microbes are able to use hydrocarbon as source of energy. The degradation of hydrocarbons depends on the metabolism of the microorganism and the environmental conditions. Biodiesel contains nutrients and oxygen which can create favourable conditions for the microorganisms to survive and grow by metabolising the biodiesel. The degradation rate of the fuel increases with the growth rate of the microorganism.

This is one of the very few investigations that aimed to look at the growth of microorganism in biodiesel, the microbial community formed and the effect on physical properties of the diesel.

Diesel samples B0, SB50, SB20, BB50 and BB20 had grater microbial growth than SB100, BB100. All Bolton biodiesel bottles presented bubbles at the water bottom interface. Bio-film growth in week four was observed in BB100. Whereas sample SB20 was the only sample who presents a suspended growth in the biodiesel layer. By week six, SB20 and SB20 present a bio-film at the bottom interface with water.

For Bolton biodiesel, a change in pH over ten weeks incubation was observed as the water bottom became more acidic.

One interesting observation that was noticed was that the biodiesel samples became more opaque during the incubation period. The only exceptions for this were BB100 for which the samples were translucent. The change in fuel opacity could be a result of microbial activity. The microorganisms metabolised the hydrocarbon fuel and as a result of this process by-products were formed. These particles could be suspended which might have affected the fuel opacity, or could be found either floating at the fuel-water interface or settled at the bottom.

Over seventy days of inoculation, it was observed that for all samples the microbial growth rose ten to thirty times more than that of the original value. BB20, BB50 sample presents a high bacteria cfu/ml. An interesting observation was for Sheffield biodiesel, SB100 samples which presented a high microbial growth compared with SB20. Microbial population varied depending on fuel composition.

Chaetomium fungal genus was identified in the bottle BB100. *Chaetomium* is predominantly found in diesel tank biodegradation. Biodiesel does not go through the same stages of refinery as diesel does, but still has to undergo transport, packing and any other affiliated processes. During these procedures potential contamination could occur. Chaetomium is particularly noted for degrading organic substances such as cellulose and crude oil [17].

Each pigmented and/or fluorescent colony was sub cultured onto milk agar with a cetyl trimethylammonium bromide and streaked so as to obtain single colonies. Colonies which were 2-4 mm in diameter, show typical pigment production and possess a "halo of clearing" around the colony where the casein had been hydrolysed, these were confirmed *Pseudomonas aeruginosa*. The API 20NE test confirmed the presence of *Pseudomonas aeruginosa* in isolates Diesel B0, BB20, BB100, SB20 and SB50.

P. fluorescens was identified in the samples BB20 and was a common Gram-negative, rod-shaped bacterium [153]. It had an extremely versatile metabolism, which could be found in the soil and in water. It was an obligate aerobe but certain strains are capable of using nitrate instead of oxygen as a final electron acceptor during cellular respiration.

Optimal temperature for growth of *P. fluorescens* is 25-30 degree Celsius. It tested positive for the oxidative test. Some *P. fluorescens* strains presented bio-control properties, protecting roots of some plant species against parasitic fungi [154]. The presence of *P. fluorescens* in biodiesel samples, could explain the reduced fungi presence in Bolton biodiesel samples, compared with Sheffield biodiesel.

Sample SB20 presented *Pseudomonas putida*, which was a gram-negative, rod-shaped, saprotrophic soil bacterium [155]. It demonstrated very diverse metabolism, including the ability to degrade organic solvents such as toluene [156]. This ability had been put to use in bioremediation, or the use of microorganisms to biodegrade oil. Use of *P. putida* is preferable to some other *Pseudomonas* species capable of such degradation as it is a safe strain of bacteria, unlike *P. aeruginosa* for example, which is an opportunistic human pathogen.

For SB50 the preliminary identification suggested the presence of *Comamonas testosteroni* or *P. alcaligenes* (API 65.2% confidence). However, it might be potentially be *P. stu*tzeri (API 26.7% confidence). A further test for growth at 42ºC was performed. This isolate did not grow at 42ºC, therefore the test result eliminates the *P. stutzeri*, and casts doubt over *Comamonas testosteroni*, resulting in a tentative identification in *P. alcaligenes*. *Pseudomonas alcaligenes* is a gram-negative aerobic bacterium used as soil inoculants for bioremediation purposes, as it could degrade polycyclic aromatic hydrocarbons [157].

For BB20 API test suggested *P. fluorescens* 86.4% confidence. However, growth was found at 42ºC which was unusual for *P. fluorescens* and suggested that it might be *Burkholderia pseudomallei* (API 8.6% confidence) or *P. aeruginosa* (API 2.6% confidence).

This highlighted limitations of API for the identification of environmental isolates as it is based on biochemical testes, which could be variable for isolates and the database is limited for environmental bacterial isolates.

Pseudomonas had the ability to metabolize a variety of diverse nutrients. Combined with the ability to form bio-films, they could thus survive in a variety of unexpected places. A simple carbon source, such as soap residue or cap liner-adhesives could be a suitable place for the *Pseudomonas* to thrive.

Microbiological growth was one of the consequences of the biodegradability of biodiesel. The described ways of degradation as described were enforced under the presence of microorganisms which found good growth conditions in the barrier between water and fuel. Microorganism population composed of strains of *Pseudomonas* and *Micrococcus* proved to be especially effective in degrading hydrocarbons.

The chemical composition within the fuel samples were an important factor for the specificity of microbial growth. The chemical composition could be anything subtle, such as grade of diesel used, e.g. low or normal sulphur volume or volume of medium used. Another factor taken into consideration is the inoculums added to the biodiesel samples. Samples of biodiesel from two suppliers were assessed for microbial contamination and the results showed that once the biodiesel was treated with additives, the growth of bacteria and fungi was significantly reduced compared with the bacteria and fungi exhibited by diesel. The specificity of fungi developed in the fuel affected the microbial growth. The presence of Chaetomium and Pseudomonas fluorescens identified in Bolton biodiesel inhibited the bacteria development, due to their bio-control properties. During 70 days of incubation, it was observed a variation of pH value for most fuel samples including diesel fuel. The pH value can be altered by the microbial activity. As a result of the fuel being metabolized, some bacteria could produce acid as by-product which leads to a decrease in the fuel pH. The results of Sheffield biodiesel showed that the biodiesel blend ratio in diesel influenced the pH value. It was observed a decrease in the pH with the decrease in biodiesel blend ratio. On the other hand, the pH measured from Bolton biodiesel samples, showed the lower value for BB100, followed by BB20. B50 showed the highest pH value between Bolton biodiesel samples. Compared with biodiesel samples, diesel showed less variation in the pH during the incubation period. At the end of the incubation period, the fuel samples had been filtered and the dry mass resulted was measured. The results shown higher dry mass for biodiesel samples compared with diesel fuel. Sheffield biodiesel showed the highest dry mass for SB20, followed by SB50 and SB100. The test results from Bolton biodiesel showed an increase in dry biomass with the increase in biodiesel blend ratio in diesel. Bolton biodiesel shown lower dry biomass compared with diesel and Sheffield biodiesel.

Although the test results shown higher bacteria and fungi cfu growth for diesel, compared with Sheffield and Bolton biodiesel, the dry biomass was lower. This could be due to the fact that fungi increased in size rather than number, resulting in higher biomass and lower pH for biodiesel compared with diesel. In case of biodiesel contamination, this could lead to a greater risk for engine fuel filter to get blocked. Before being placed on the market, the biodiesel has been treated with additive inhibitors against bio-fouling. The test results shown a reduction in bacteria and fungi cfu for biodiesel, compared with diesel. Bolton biodiesel shown the lowest cfu between all fuel samples. Chaetomium and Pseudomonas fluorescens were identified in Bolton samples, which is believed to act as bacteria inhibitor and have bio-control properties. However, the dry mass for biodiesel was observed to be higher compared with that from diesel.

7.2.Evaluation of Biodiesel Combustion in Continuous Combustion Rig (CCR)

In order to study the exhaust emissions from various diesel and biodiesel blends it is important to eliminate all the physical aspects that influence the combustion. Therefore combustion tests were conducted in CCR which allowed full control of the combustion conditions in order to observe only the chemical aspect of combustion. The physical phenomena that affect combustion were reduced. The combustion in CCR produced a laminar premixed flame and the emissions from the combustion of samples of diesel and biodiesel blend were observed. The influence of fuel/air equivalence ratio and biodiesel blend ratio on pollutant emission from B25, B50, B75 and B100 were investigated experimentally. The adiabatic flame temperature and combustion gas temperature decreased with the increase in biodiesel blend ratio in diesel. The fuel/air equivalence ratio and diesel-biodiesel blend ratio in fuel influenced the formation of pollutant emissions. The test results showed an increase in SNO at biodiesel blend over 50% in diesel. At fuel/air equivalence ratio of 0.16, B75 had the higher increase in SNOx between all fuels, up to 72% higher compared with B0. The lower HC emissions were recorded for B50 with up to 6.4% reduction compared with diesel. The data from CCR suggested that using neat WCO biodiesel or as a blend in diesel fuel could improve the combustion and have a significant benefit for the environment and human health by reducing the pollutant emissions. At different excess oxygen measured in the combustion gas, B25, B75, B50 and B100 shown an increase in SNOx emissions compared with diesel fuel. Combustion gas temperature showed a drop as biodiesel blend ratio in diesel was increased. SHC emissions from B50 were significantly lower compared to those from diesel fuel. Overall, experimental results have shown that the oxygen concentration and the gas flow residence time are important parameter that affects SNO formation. At longer residence time and low oxygen concentration a reduction in NO was observed.

With the increase in biodiesel blend ratio in diesel, the combustion gas temperature increases, resulting in higher SNOx formation compared with diesel. The prompt NO formation can be due to the abundance of HC=CH in the reaction zone. The FT-IR results have shown that biodiesel contain higher CH bonds in its molecule compared with diesel. C-N elemental group was also observed in the biodiesel molecule, whereas C-N groups were not identified in diesel spectrum. The oxygen content in biodiesel molecule and the content of unsaturated compounds lead to more heat release during the combustion process. This results in a more intense combustion compared with diesel, leading to high combustion gas temperature. The combustion reaction rate for biodiesel is higher compared with diesel, leading to a faster brakeage of the hydrocarbon chain which release more heat.

7.3. Evaluation of Biodiesel in a Land Rover Diesel Engine

Diesel, biodiesel and various blends of diesel and biodiesel were tested in a Land Rover VM Motori diesel engine. The results showed that blends of diesel and biodiesel could be considered for use in diesel engine. The density and viscosity of the three WCO biodiesel procured from different sources within the UK were measured and the result showed higher density and viscosity for WCO biodiesel compared with that for diesel. This was in agreement with observation of other researchers [66; 158; 159]. It was also observed that there is a correlation between density and viscosity of biodiesel [158]. The differences in biodiesel physicochemical properties were reflected on the engine efficiency and performance.

Engine Efficiency

The experimental results showed the best engine efficiency for engine speed of 2500 rpm. At 50, 75 and 100% engine load, all biodiesel blends had an increase in BTE. B75 and B100 shown an increase in BTE with up to 10% compared with diesel. B50 blend had the lowest BTE among all biodiesel blends tested. It was observed a reduction of up to 6% in BTE for B50blend compared with diesel. B25 blend shown similar BTE with diesel fuel with ± 2% at 15% and 25% engine load respectively. However, at the medium and high load it was observed an increase in BTE between 3.5% and 6.5% compared with diesel. Similar results were obtained by Murillo et al. [104] who tested diesel and different blends of used cooking oil biodiesel in a marine 3-cylinder naturally aspired engine. His results for blends of 10%, 30% and 50% biodiesel showed lower efficiency compared to highest efficiency obtained for neat biodiesel. An increase in brake thermal efficiency was observed by Ramadhas who tested rubber seed oil blends in a compression ignition engine for performance and emissions [160]. Kaplan et al. (80), also found an increase in brake thermal efficiency.

The results for BTE for neat WCO biodiesel at medium to high load were in agreement to observation using various biodiesel types reported in literature. This can be justified by improved combustion for biodiesel due to higher oxygen content compared to diesel.

The lower calorific value together with the higher density of WCO biodiesel compared with diesel resulted in an increase in brake specific fuel consumption. With the increase in biodiesel blend ratio in diesel, brake specific fuel consumption increases. An increase in BSFC with the increase in biodiesel blend ratio in diesel, was stated by the majority of the researchers [66; 97; 160; 161] Rahmen, Lakshmi.

The test results show a decrease in engine torque and consequently in the engine brake power. This reduction in power output is due to the biodiesel's low heating value. Many authors also found that the loss of power is lower than expected. Kaplan et al. [80] tested the performance of a diesel engine using sunflower-oil biodiesel and diesel fuels at full and partial loads and at various engine speeds. He observed a decrease in torque and power between 5% and 10% with the increase in engine speed. Merve et. Al [81] compared the waste-oil biodiesel and diesel fuels at full-load engine conditions. He observed a slight decrease in torque between 3% and 5% with biodiesel. A similar result was obtained by Lin et al. [82] when he tested ultra-low sulphur diesel, pure palm-oil biodiesel and a 20% palm biodiesel blend, the loss of power at full load was only 3.5% with pure biodiesel and 1% with the blend.

Exhaust Emissions

The engine test results have shown a decrease in BSCO emissions with the reduction in biodiesel blends ratio in diesel and with the increase in engine load. It was observed a reduction between 5 and 70% in BSCO emissions for biodiesel blends compared with diesel. This is due to a more intense combustion of biodiesel, resulting in a complete combustion compared with diesel. EPA [66] considers as a general trend a reduction of almost 50% of CO when biodiesel is used, compared to conventional diesel fuel. Krahl et al. [73] compared biodiesel from rapeseed oil with both low and ultra-low sulphur diesel and obtained approximately a 50% decrease of CO when biodiesel was used. Similar results obtained Graboski, Rao, [74; 161; 160].

It was observed an increase in CO_2 emissions for all biodiesel blends, compared with diesel. This is due to the combustion improvement when biodiesel is used as additive in diesel. The high oxygen content in biodiesel lead to a more intense combustion, which resulted in a higher rate of NOx formation compared with diesel. The increase in BSNOx was observed to be related to the biodiesel blend ratio in diesel. With the increase in biodiesel blend ratio in diesel, BSNOx emissions showed an increasing trend, compared with diesel. At high engine load it was observed an increase in BSNOx with up to 50% for B100. An increase in NOx with up to 15% was observed by Schumacher et al. [125], who tested a 6-cylinder diesel engine under different loads with 10%, 20%, 30% and 40% soybean biodiesel blends. Graboski [74] tested the engine with neat biodiesel under steady conditions and he observed a 16% increase with respect to diesel fuel NOx emissions.

The test results shown a reduction in BSHC emissions for biodiesel blend ratio less than 75% in diesel. At low medium engine speed it was observed a reduction of 32 and 37 % respectively in BSHC emissions compared with diesel. It was observed a decrease in BSHC emissions with the decrease in engine load. This could be due to the fact that when the load increases, more fuel is injected in the combustion chamber. As the biodiesel has a higher viscosity compared with diesel, these will lead to an incomplete combustion, resulting in high BSHC emissions.

Many authors also observed a decrease in total hydrocarbon (THC) emissions when tested biodiesel compared to diesel [101; 105-109]. Also, there are few studies in the literature which stated no significant differences [67-69; 70] or increases [72] in THC emissions when biodiesel was tested comparing with diesel. Nwafor [111] tested a single-cylinder indirect injection engine with diesel and several blends of rapeseed biodiesel. He observed up to 60% lower THC emissions from pure biodiesel compared with those from petro-diesel. Peterson and Reece [112] and Krahl et al. [73], both testing biodiesel from rapeseed oil, found higher than 50% THC reductions with their biodiesel.

With the increase in biodiesel blend ratio in diesel of up to 100%, the BSHC emissions increased. The increase in fuel viscosity could affect the efficiency of the combustion. Biodiesel has a higher viscosity compared with diesel. The effect of high viscosity of biodiesel on the diesel engine could result in a poor spray atomization, due to the larger droplet size. The larger the droplets are the more time it takes for the droplet to evaporate. Therefore, at high biodiesel blends, where the viscosity is high, this could result in an increase in BSHC emissions compared with diesel. For neat WCO biodiesel or higher biodiesel blend ratio in diesel, over B75, changes in diesel engine parameters, such as fuel injectors, injection pressure and start of combustion could be considered in order to reduce the NOx and HC emissions. Due to the laboratory technical limitations, further investigation on diesel engine combustion characteristics could not be performed.

Chapter 8 -Conclusions

Based on the previous discussions, the following concluding remarks from the three main aspects of biodiesel investigated have been drawn:

- ***Fuel Physicochemical Properties***
    - Physical properties of WCO biodiesel obtained from three different suppliers were measured and the results showed little differences between the samples of biodiesel.
    - WCO showed higher viscosity and specific gravity compared with diesel.
    - Elemental analysis of biodiesel showed almost 10% lower carbon content, almost no sulphur content for biodiesel and up to 12% more oxygen content compared with diesel.
    - The test results showed up to 18% lower caloric value for WCO biodiesel compared with diesel, due to the high content of oxygen and lower carbon to hydrogen ratio compared with diesel.
    - The FT-IR diesel and biodiesel spectrum showed peaks that do not overlap. The differences between the functional groups found in diesel and biodiesel resulted in differences between diesel and biodiesel combustion and emissions. The abundance in double bounds in WCO biodiesel may enhance its cold flow properties, but also the susceptibility to oxidation.
    - Samples of biodiesel from two suppliers were assessed for microbial contamination and the results showed that once the biodiesel was treated with additives, the growth of bacteria and fungi was significantly reduced compared with the bacteria and fungi exhibited by diesel. The specificity of fungi developed in the fuel affected the microbial growth. The presence of Chaetomium and Pseudomonas fluorescens identified in Bolton biodiesel inhibited the bacteria development, due to their bio-control properties.

- ***Continuous Combustion Test***
    - The CCR test results showed that with the increase in biodiesel blend ratio in diesel, the combustion gas temperature increases, resulting in higher SNOx formation compared with diesel. The elemental groups such as HC=CH and C-N which were identified in biodiesel spectrum together with the oxygen content in biodiesel molecule and the content of unsaturated compounds lead to more heat release during the combustion process compared with diesel. These resulted in a more intense combustion compared with diesel. The combustion reaction rate for biodiesel was higher than that of diesel leading to a faster brakeage of the hydrocarbon chain which released more heat.
    - The SHC and SCO emissions from WCO biodiesel were reduced with the increase in biodiesel blend ratio in diesel, due to the complete combustion of biodiesel. The completeness of the combustion was also observed in the increase of CO_2 with the increase in biodiesel ratio in diesel.
- ***Engine Emissions and Performance Test***
    - The tests results performed on VM Motori engine shown a decrease in engine torque with up to 9% when WCO biodiesel was used, which is due to the lower calorific value of biodiesel compared with that of diesel.
    - The BSFC increased with the increase in biodiesel blend ratio in diesel, due to the higher density of biodiesel, which resulted in a greater mass of fuel being injected at a given injection pressure, compared with diesel.
    - At 2000 rpm and 15 and 25% engine load, BTE of the engine using B25, B50 and B75 was lower with up to 3% compared with the baseline. At 50, 75 and 100% engine load, B75 and B100 showed an increase with up to 4% in BTE. The highest increase in BTE for biodiesel was observed at engine set at 2500 rpm, with an increase of up to 9% from baseline. At low load and high engine speed the engine BTE using biodiesel appeared similar to that of diesel. The engine BTE using WCO biodiesel increased with the increase in load and engine speed.

- The exhaust emissions test results from engine using WCO biodiesel showed a reduction in BSHC for biodiesel blend ratio under 75%, and an increase for higher blend ratio in diesel.
- BSCO emissions for all biodiesel blends compared well with diesel.
- BSHC emissions decreased for biodiesel blend ratio under 75% in diesel. As the biodiesel blend ratio in diesel was increased farther up to 100%, BSHC showed an increase, which was more accentuated at high engine load.
- The $BSCO_2$ emissions were higher for biodiesel due to the completeness of combustion achieved with the addition of biodiesel in diesel.
- The EGT was observed to increase with the increase in biodiesel blend ratio in diesel, up to B75. A further increase in biodiesel blend ratio up to B100 showed a reduction in EGT compared with that of B75. This was due to the fact that for high biodiesel blend the torque showed a decrease. The higher increase in EGT for WCO biodiesel was observed at 2500 rpm, with up to 3.5% increase from baseline.
- As an effect of the higher EGT and the content of up to 12% of oxygen in biodiesel, BSNOx increased compared with diesel.

Based on the results of the experimental work carried out during this research on WCO biodiesel available in the market and already treated with additives to enhance the stability to microbial contamination showed a better resistance to microbial growth, compared with petro-diesel. Using WCO blends ratio up to 75% in diesel showed a reduction in exhaust emission compared with diesel, at the cost of an increase in fuel consumption. A common conclusion can be drawn in favour of the WCO biodiesel as being a greener alternative to petro-diesel when used in blend with diesel.

Chapter 9 -Future work

In present work waste cooking oil biodiesel was tested on a Land Rover VM Motori diesel engine. The differences in physical and chemical properties of diesel and biodiesel led to major differences in performance and emissions when tests were performed on an unmodified diesel engine. The test results show a decrease in pollutant emissions when biodiesel blend with diesel was used. The high biodiesel viscosity is believed to alter the combustion at high biodiesel blend ratio.

For an efficient use of biodiesel, two issues should be considered in the future research work: engine adaptation to the new fuel as well as the improvement of the biodiesel quality and lowering the biodiesel viscosity, the development of fuel additives in order to decrease both NOx and PM, and cetane improvers.

Biodiesel is an oxidised fuel since it contains up to 12% oxygen in its composition compared with petroleum diesel which contains 0.07%. More research also needs to be undertaken on biodiesel production. The use of oxidation inhibitors and removal of oxygen content could decrease the combustion temperature and consequently NOx formation. Hydro-treating and hydrogenation process could improve biodiesel quality.

The variation in the biomass used for biodiesel production could lead to variations in physical and chemical properties not only between diesel and biodiesel but also between biodiesel produced from different biomasses. Therefore more stringent standards need to be imposed for biodiesel quality in order to diminish the effect of variation in physicochemical properties on engine performance and emissions. The future work in developing standard test procedures for establishing fuel properties and limits/targets would be beneficial in using a large amount of waste cooking oil in the production of biodiesel, thus contributing to reduction in CO_2 and waste minimisation.

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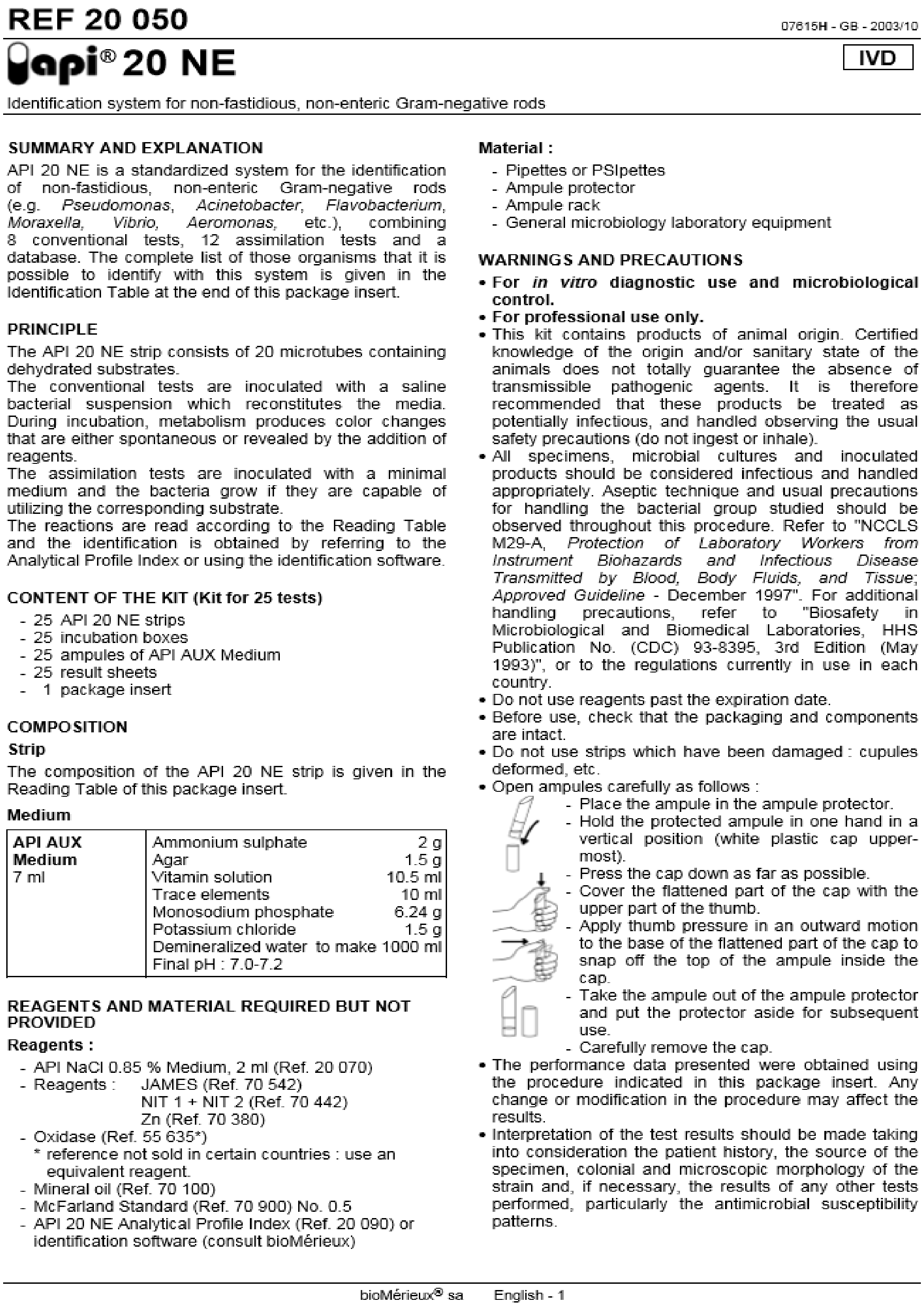
Appendix A – API 20NE V7.0 Bacteria Identification Procedure (bioMerieux)



REF 20 050

07615H - GB - 2003/10

api® 20 NE

IVD

Identification system for non-fastidious, non-enteric Gram-negative rods

SUMMARY AND EXPLANATION

API 20 NE is a standardized system for the identification of non-fastidious, non-enteric Gram-negative rods (e.g. *Pseudomonas*, *Acinetobacter*, *Flavobacterium*, *Moraxella*, *Vibrio*, *Aeromonas*, etc.), combining 8 conventional tests, 12 assimilation tests and a database. The complete list of those organisms that it is possible to identify with this system is given in the Identification Table at the end of this package insert.

PRINCIPLE

The API 20 NE strip consists of 20 microtubes containing dehydrated substrates.

The conventional tests are inoculated with a saline bacterial suspension which reconstitutes the media. During incubation, metabolism produces color changes that are either spontaneous or revealed by the addition of reagents.

The assimilation tests are inoculated with a minimal medium and the bacteria grow if they are capable of utilizing the corresponding substrate.

The reactions are read according to the Reading Table and the identification is obtained by referring to the Analytical Profile Index or using the identification software.

CONTENT OF THE KIT (Kit for 25 tests)

- 25 API 20 NE strips
- 25 incubation boxes
- 25 ampules of API AUX Medium
- 25 result sheets
- 1 package insert

COMPOSITION

Strip

The composition of the API 20 NE strip is given in the Reading Table of this package insert.

Medium

API AUX Medium 7 ml	Ammonium sulphate	2 g
	Agar	1.5 g
	Vitamin solution	10.5 ml
	Trace elements	10 ml
	Monosodium phosphate	6.24 g
	Potassium chloride	1.5 g
	Demineralized water to make	1000 ml
	Final pH : 7.0-7.2	

REAGENTS AND MATERIAL REQUIRED BUT NOT PROVIDED

Reagents :

- API NaCl 0.85 % Medium, 2 ml (Ref. 20 070)
- Reagents : JAMES (Ref. 70 542)
  NIT 1 + NIT 2 (Ref. 70 442)
  Zn (Ref. 70 380)
- Oxidase (Ref. 55 635*)
  * reference not sold in certain countries : use an equivalent reagent.
- Mineral oil (Ref. 70 100)
- McFarland Standard (Ref. 70 900) No. 0.5
- API 20 NE Analytical Profile Index (Ref. 20 090) or identification software (consult bioMérieux)

Material :

- Pipettes or PSIpettes
- Ampule protector
- Ampule rack
- General microbiology laboratory equipment

WARNINGS AND PRECAUTIONS

- **For *in vitro* diagnostic use and microbiological control.**
- **For professional use only.**
- This kit contains products of animal origin. Certified knowledge of the origin and/or sanitary state of the animals does not totally guarantee the absence of transmissible pathogenic agents. It is therefore recommended that these products be treated as potentially infectious, and handled observing the usual safety precautions (do not ingest or inhale).
- All specimens, microbial cultures and inoculated products should be considered infectious and handled appropriately. Aseptic technique and usual precautions for handling the bacterial group studied should be observed throughout this procedure. Refer to "NCCLS M29-A, *Protection of Laboratory Workers from Instrument Biohazards and Infectious Disease Transmitted by Blood, Body Fluids, and Tissue; Approved Guideline* - December 1997". For additional handling precautions, refer to "Biosafety in Microbiological and Biomedical Laboratories, HHS Publication No. (CDC) 93-8395, 3rd Edition (May 1993)", or to the regulations currently in use in each country.
- Do not use reagents past the expiration date.
- Before use, check that the packaging and components are intact.
- Do not use strips which have been damaged : cupules deformed, etc.
- Open ampules carefully as follows :
  - Place the ampule in the ampule protector.
  - Hold the protected ampule in one hand in a vertical position (white plastic cap uppermost).
  - Press the cap down as far as possible.
  - Cover the flattened part of the cap with the upper part of the thumb.
  - Apply thumb pressure in an outward motion to the base of the flattened part of the cap to snap off the top of the ampule inside the cap.
  - Take the ampule out of the ampule protector and put the protector aside for subsequent use.
  - Carefully remove the cap.
- The performance data presented were obtained using the procedure indicated in this package insert. Any change or modification in the procedure may affect the results.
- Interpretation of the test results should be made taking into consideration the patient history, the source of the specimen, colonial and microscopic morphology of the strain and, if necessary, the results of any other tests performed, particularly the antimicrobial susceptibility patterns.

bioMérieux® sa English - 1

STORAGE CONDITIONS

The strips and media should be stored at 2-8°C until the expiration date indicated on the packaging.

SPECIMENS (COLLECTION AND PREPARATION)

API 20 NE is not for use directly with clinical or other specimens.
The microorganisms to be identified must first be isolated on a suitable culture medium (e.g., Trypticase Soy agar) according to standard microbiological techniques.

INSTRUCTIONS FOR USE

Oxidase test

The oxidase test must be performed according to the manufacturer's instructions for use. The result should be recorded on the result sheet as it is an integral part of the final profile (21st identification test).

Selection of colonies

API 20 NE should only be used with non-fastidious Gram-negative rods which do not belong to the *Enterobacteriaceae*.

NOTE 1 : Some non-enteric Gram-negative rods are oxidase negative (*S. maltophilia*, *Acinetobacter*...). These microorganisms may also be identified with API 20 NE but their selection must be based on other bacteriological or clinical criteria.

NOTE 2 : Fastidious organisms having demanding nutritional requirements and requiring appropriate handling precautions (i.e. *Brucella* and *Francisella*) are not included in the API 20 NE database. Alternative procedures must be used to exclude or confirm their presence.

Preparation of the strip

- Prepare an incubation box, tray and lid, and distribute about 5 ml of distilled water or demineralized water [or any water without additives or chemicals which may release gases (e.g. Cl_2, CO_2, etc.)] into the bottom of the tray to create a humid atmosphere.
- Record the specimen number on the elongated flap of the tray. (Do not record the number on the lid as it may be misplaced during the procedure.)
- Remove the strip from its individual packaging.
- Place the strip in the incubation box.

Preparation of the inoculum

- Open an ampule of API NaCl 0.85 % Medium (2 ml) as indicated in the paragraph "Warnings and Precautions" of the package insert for this product, or use any tube containing 2 ml of 0.85 % physiological saline without additives.
- Using a pipette or PSIpette, pick up 1-4 colonies of identical morphology from the agar plate, either by suction or by successive touches. It is recommended to use young cultures (18-24 hours old).
- Prepare a suspension with a turbidity equivalent to 0.5 McFarland. This suspension must be used immediately after preparation.

NOTE : It is very important that the density of the inoculum be adjusted to 0.5 McFarland ; the API 20 NE strip tests may otherwise not function correctly. In particular, a weaker inoculum may lead to false negative results. Do not touch the cupules while working with the strip and do not leave the strip exposed to air for a long period of time after inoculation.

Inoculation of the strip

- Inoculate tests NO_3 to PNPG by distributing the saline suspension into the tubes (and not the cupules) using the same pipette. To avoid the formation of bubbles at the base of the tubes, tilt the strip slightly forwards and place the tip of the pipette or PSIpette against the side of the cupule.
- Open an ampule of API AUX Medium as indicated in the paragraph "Warnings and Precautions" and add approximately 200 µl of the remaining saline suspension to the ampule. Homogenize well with the pipette, avoiding the formation of bubbles.
- Fill the tubes and cupules of tests |GLU| to |PAC| with the suspension. Take care to leave a flat or slightly convex, but not concave, meniscus. Cupules under or overfilled may give incorrect results.
- Add mineral oil to the cupules of the 3 underlined tests (GLU, ADH and URE) until a convex meniscus is formed.
- Close the incubation box and incubate at 29°C ± 2°C for 24 hours (± 2 hours).

READING AND INTERPRETATION

Reading the strip

- After the incubation period, read the strip by referring to the Reading Table.
- Record all spontaneous reactions (GLU, ADH, URE, ESC, GEL and PNPG) on the result sheet.
- The reading of the two tests NO_3 and TRP should be performed whilst protecting the assimilation tests from airborne contamination. To do this, cover the assimilation tests with the incubation box lid during the reading of the NO_3 and TRP tests.
- **NO_3 test :**
  - Add 1 drop of NIT 1 and 1 drop of NIT 2 reagents to the NO_3 cupule.
  - After 5 minutes, a **red** color indicates a **positive** reaction to be recorded on the result sheet.
  - A negative reaction may be due to the production of nitrogen (indicated by the presence of tiny bubbles) : add 2-3 mg of Zn reagent to the NO_3 cupule.
  - After 5 minutes, a cupule remaining **colorless** indicates a **positive** reaction to be recorded on the result sheet. If the cupule turns **pink-red**, the reaction is **negative** as nitrates were present in the tube and were reduced to nitrite by the zinc.

  The reaction used for the identification of the bacterium is the reduction of nitrates. It is positive when either of the above reactions (production of NO_2 or N_2) is positive.

  The production of N_2 may, however, be useful alone as a supplementary test (refer to the Analytical Profile Index).
- **TRP test :**
  Add 1 drop of JAMES reagent. The reaction takes place immediately : a **pink** color which develops in the whole cupule indicates a **positive** reaction to be recorded on the result sheet.

- **Assimilation tests :**
  Observe the bacterial growth. An **opaque** cupule indicates a **positive** reaction.
  Occasionally, a cupule may show weak growth. In this case, the results should be recorded as ∓ or ± by comparing the intensity to that of the other tests on the strip.
  Once these readings have been made, identification should be possible as indicated in the paragraph "Interpretation". However, in the following cases, the strip must be reincubated :
  - if the profile cannot be found in the API 20 NE Analytical Profile Index
  - if the following note is indicated for the profile obtained :

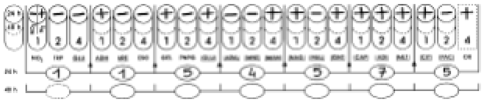
IDENTIFICATION NOT VALID
BEFORE 48-HR INCUBATION

Using a pipette or PSIpette, remove the NIT 1, NIT 2 and JAMES reagents by suction and immediately cover tests NO_3 and TRP with mineral oil so that a convex meniscus is formed. Reincubate the strip at 29°C ± 2°C for a further 24 hours and read the all the tests again, except the first 3 (NO_3, TRP and GLU) which should only be read once at 24 hours.

Interpretation

Identification is obtained with the **numerical profile**.

- Determination of the numerical profile :
  On the result sheet, the tests are separated into groups of 3 and a number 1, 2 or 4 is indicated for each. By adding the values corresponding to positive reactions within each group, a 7-digit number is obtained ; the oxidase reaction constitutes the 21st test and has a value of 4 if it is positive.
- Identification :
  This is performed using the database (V6.0)
  * with the Analytical Profile Index :
    -Look up the numerical profile in the list of profiles.
  * with the identification software :
    -Enter the 7-digit numerical profile manually via the keyboard.



1 154 575 *Pseudomonas aeruginosa*

QUALITY CONTROL

The media, strips, and reagents are systematically quality controlled at various stages of their manufacture. For those who wish to perform their own quality control tests with the strip, it is preferable to use the strain **1. *Sphingobacterium multivorum* ATCC 35656** or else one of the following strains :

2. *Aeromonas hydrophila*	ATCC 35654	4. *Alcaligenes faecalis*	ATCC 35655
3. *Pseudomonas aeruginosa*	ATCC 27853		

ATCC : American Type Culture Collection, 10801 University Boulevard, Manassas, VA 20110-2209, USA.

	NO_3	TRP	GLU	ADH	URE	ESC	GEL	PNPG	⌊GLU⌋	⌊ARA⌋	⌊MNE⌋	⌊MAN⌋	⌊NAG⌋	⌊MAL⌋	⌊GNT⌋	⌊CAP⌋	⌊ADI⌋	⌊MLT⌋	⌊CIT⌋	⌊PAC⌋	OX
1.	–	–	–	–	+	+	–	+	+	+	+	–	+	+	–	–	–	–	–	–	+
2.	+	+	+	+	–	+	+	+	+	+	+	+	+	+	+	+	–	+	–*	–	+
3.	+	–	–	V	V	–	+	–	+	–	–	+	+	–	+	+	+	+	+	–	+
4.	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	+	–	+	+	+	+

* Weak reactions may occur.

Profiles for tests ADH to ⌊PAC⌋ obtained after 48 hours of incubation after culture of the colonies on Trypticase Soy agar.

It is the responsibility of the user to perform Quality Control in accordance with any local applicable regulations.

LIMITATIONS OF THE METHOD

- The API 20 NE system is intended uniquely for the identification of those non-fastidious, non-enteric Gram-negative rods included in the database (see Identification Table at the end of this package insert). It cannot be used to identify any other microorganisms or to exclude their presence.
- Only pure cultures of a single organism should be used.

RANGE OF EXPECTED RESULTS

Consult the Identification Table at the end of this package insert for the range of expected results for the various biochemical reactions.

PERFORMANCE

5728 collection strains and strains of various origins belonging to species included in the database were tested :

- 92.53 % of the strains were correctly identified (with or without supplementary tests).
- 3.13 % of the strains were not identified.
- 4.34 % of the strains were misidentified.

WASTE DISPOSAL

Unused ampules of API AUX Medium may be considered as non hazardous waste and disposed of accordingly.

Dispose of all used or unused reagents (other than the ampules of API AUX Medium) as well as any other contaminated disposable materials following procedures for infectious or potentially infectious products.

It is the responsibility of each laboratory to handle waste and effluents produced according to their type and degree of hazardousness and to treat and dispose of them (or have them treated and disposed of) in accordance with any applicable regulations.

WARRANTY

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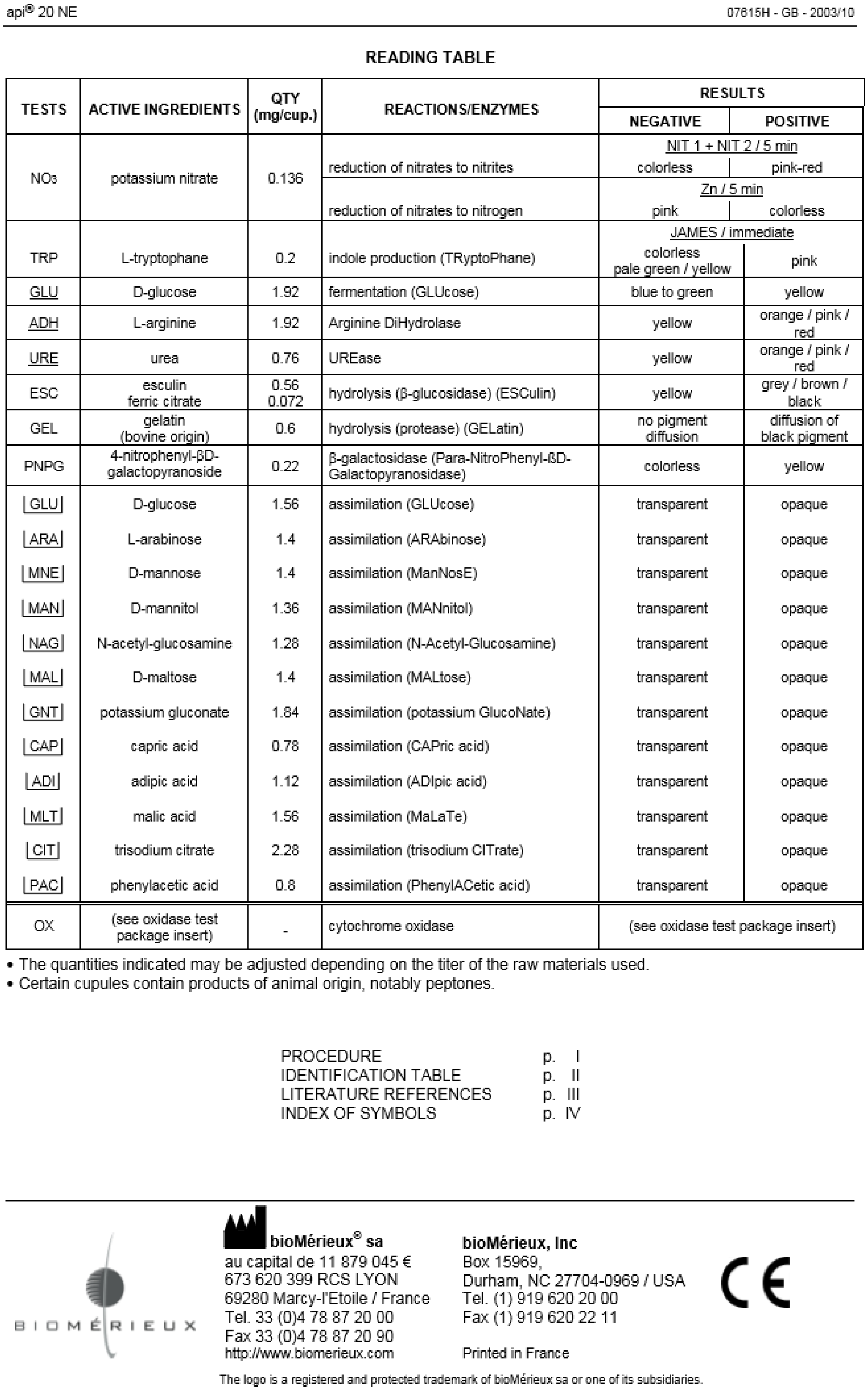

READING TABLE

TESTS	ACTIVE INGREDIENTS	QTY (mg/cup.)	REACTIONS/ENZYMES	RESULTS	
				NEGATIVE	POSITIVE
NO_3	potassium nitrate	0.136		NIT 1 + NIT 2 / 5 min	
			reduction of nitrates to nitrites	colorless	pink-red
				Zn / 5 min	
			reduction of nitrates to nitrogen	pink	colorless
TRP	L-tryptophane	0.2		JAMES / immediate	
			indole production (TRyptoPhane)	colorless pale green / yellow	pink
GLU	D-glucose	1.92	fermentation (GLUcose)	blue to green	yellow
ADH	L-arginine	1.92	Arginine DiHydrolase	yellow	orange / pink / red
URE	urea	0.76	UREase	yellow	orange / pink / red
ESC	esculin ferric citrate	0.56 0.072	hydrolysis (β-glucosidase) (ESCulin)	yellow	grey / brown / black
GEL	gelatin (bovine origin)	0.6	hydrolysis (protease) (GELatin)	no pigment diffusion	diffusion of black pigment
PNPG	4-nitrophenyl-βD-galactopyranoside	0.22	β-galactosidase (Para-NitroPhenyl-ßD-Galactopyranosidase)	colorless	yellow
⌊GLU⌋	D-glucose	1.56	assimilation (GLUcose)	transparent	opaque
⌊ARA⌋	L-arabinose	1.4	assimilation (ARAbinose)	transparent	opaque
⌊MNE⌋	D-mannose	1.4	assimilation (ManNosE)	transparent	opaque
⌊MAN⌋	D-mannitol	1.36	assimilation (MANnitol)	transparent	opaque
⌊NAG⌋	N-acetyl-glucosamine	1.28	assimilation (N-Acetyl-Glucosamine)	transparent	opaque
⌊MAL⌋	D-maltose	1.4	assimilation (MALtose)	transparent	opaque
⌊GNT⌋	potassium gluconate	1.84	assimilation (potassium GlucoNate)	transparent	opaque
⌊CAP⌋	capric acid	0.78	assimilation (CAPric acid)	transparent	opaque
⌊ADI⌋	adipic acid	1.12	assimilation (ADIpic acid)	transparent	opaque
⌊MLT⌋	malic acid	1.56	assimilation (MaLaTe)	transparent	opaque
⌊CIT⌋	trisodium citrate	2.28	assimilation (trisodium CITrate)	transparent	opaque
⌊PAC⌋	phenylacetic acid	0.8	assimilation (PhenylACetic acid)	transparent	opaque
OX	(see oxidase test package insert)	-	cytochrome oxidase	(see oxidase test package insert)	

- The quantities indicated may be adjusted depending on the titer of the raw materials used.
- Certain cupules contain products of animal origin, notably peptones.

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Appendix B – Diesel and Biodiesel Microbial Contamination

Table 0-1: Variation of bacteria, fungi and pH for diesel samples (B0 1/2 and B0 2/2) during of ten weeks of incubation

cfu B0 1/2				**cfu B0 2/2**			**AVG cfu B0**		
week	bacteria	fungi	pH	bacteria	fungi	pH	bacteria	fungi	pH
2	6.18	5.36	7	6.18	5.06	7	6.18	5.21	7.00
4	6.48	6.7	7.18	6.48	6.4	7.09	6.48	6.55	7.14
6	7.36	3.84	7.52	7.36	4.02	7.26	7.36	3.93	7.39
8	7.45	4.28	7.27	7.45	3.21	7.32	7.45	3.75	7.30
10	7.58	4.69	7	7.58	4.7	7.01	7.58	4.70	7.01

Table 0-2: Variation of bacteria, fungi and pH for Sheffield biodiesel samples (SB100 1/2 and SB100 2/2) during of ten weeks of incubation

cfu SB100 1/2				**cfu SB100 2/2**			**AVG cfu SB100**		
week	bacteria	fungi	pH	bacteria	fungi	pH	bacteria	fungi	pH
2	6.18	1.18	7	4.98	1	7	5.58	1.09	7.00
4	5.42	5.17	7.11	4.92	4.54	7.23	5.17	4.86	7.17
6	6.90	ND	7.24	6.81	ND	7.19	6.86	0.00	7.22
8	6.35	1	7.37	6.02	ND	7.42	6.19	0.50	7.40
10	5.95	ND	7.1	7.35	ND	7.05	6.65	0.00	7.08

Table 0-3: Variation of bacteria, fungi and pH for Sheffield biodiesel samples (SB50 1/2 and SB50 2/2) during of ten weeks of incubation

cfu SB50 1/2				**cfu SB50 2/2**			**AVG cfu SB50**		
week	bacteria	fungi	pH	bacteria	fungi	pH	bacteria	fungi	pH
2	6.18	5.99	7	6.18	4.49	7	6.18	5.24	7.00
4	6.48	4.65	7.05	6.48	4.53	7.16	6.48	4.59	7.11
6	6.60	3.27	7.09	7.06	ND	7.27	6.83	1.64	7.18
8	7.76	4.88	7.13	7.76	5.3	7.45	7.76	5.09	7.29
10	6.96	4.83	6.59	7.47	0.52	7.1	7.22	2.68	6.85

Table 0-4: Variation of bacteria, fungi and pH for Sheffield biodiesel samples (SB20 1/2 and SB20 2/2) during of ten weeks of incubation

cfu SB20 1/2				**cfu SB20 2/2**			**AVG cfu SB20**		
week	bacteria	fungi	pH	bacteria	fungi	pH	bacteria	fungi	pH
2	6.18	4.98	7	6.18	5.45	7	6.18	5.22	7.00
4	6.48	4.46	7.05	6.48	4.79	7.08	6.48	4.63	7.07
6	7.01	3.5	7.06	7.16	5.16	7.03	7.09	4.33	7.05
8	6.95	4.56	7.03	7.30	4.93	7.21	7.13	4.75	7.12
10	7.54	2.77	6.58	7.31	ND	6.85	7.43	1.39	6.72

Table 0-5: Variation of bacteria, fungi and pH for Bolton biodiesel samples (BB100 1/2 and BB100 2/2) during of ten weeks of incubation

cfu BB100 1/2				**cfu BB100 2/2**			**AVG cfu BB100**		
week	bacteria	fungi	pH	bacteria	fungi	pH	bacteria	fungi	pH
2	3.83	ND	7	2.7	ND	7	3.265	ND	7
4	4.97	3.78	6.86	3.60	3	6.81	4.285	3.39	6.835
6	2.36	ND	6.9	ND	ND	6.9	1.18	ND	6.9
8	ND	ND	7.11	2.70	ND	7.1	1.35	ND	7.105
10	ND	ND	6.78	5.00	ND	6.76	2.5	ND	6.77

Table 0-6: Variation of bacteria, fungi and pH for Bolton biodiesel samples (BB50 1/2 and BB50 2/2) during of ten weeks of incubation

cfu BB50 1/2				**cfu BB50 2/2**			**AVG cfu BB50**		
week	bacteria	fungi	pH	bacteria	fungi	pH	bacteria	fungi	pH
2	6.18	3.01	7	6.18	0.4	7	6.18	1.71	7.00
4	6.06	5.21	7.29	5.47	5.13	7.38	5.77	5.17	7.34
6	6.80	0.52	7.26	6.70	ND	7.21	6.75	0.26	7.24
8	5.78	ND	7.34	6.01	5	7.42	5.90	2.50	7.38
10	6.22	ND	7.07	6.72	3.3	7.14	6.47	1.65	7.11

Table 0-7: Variation of bacteria, fungi and pH for Bolton biodiesel samples (BB20 1/2 and BB20 2/2) during of ten weeks of incubation

cfu BB20 1/2				**cfu BB20 2/2**			**AVG cfu BB20**		
week	bacteria	fungi	pH	bacteria	fungi	pH	bacteria	fungi	pH
2	6.18	4.36	7	6.18	4.17	7	6.18	4.27	7.00
4	6.48	6.47	7	6.48	6.34	7.01	6.48	6.41	7.01
6	7.70	0	6.99	7.59	1.75	6.96	7.65	0.88	6.98
8	7.55	0	7.26	7.68	1.9	7.12	7.62	0.95	7.19
10	7.74	0	6.96	7.83	2.92	6.57	7.79	1.46	6.77

Table 0-8: Dry biomass average of diesel, Sheffield biodiesel (SB) and Bolton biodiesel (BB)

Sample	**B0**	**SB20**	**SB50**	**SB100**	**BB20**	**BB50**	**B100**
AVG dry biomass [g/l]	2.044	2.611	2.061	1.798	0.864	2.373	2.323

Appendix C – Evaluation of Biodiesel Combustion in Continuous Combustion Rig (CCR)

Table 0-1: CO_2, CO, HC, NO emissions measured at equivalence ratio 0.29, at 0.425m from the ignition point

Sample	**T_2 [°C]**	**CO_2 [%vol]**	**ex. O_2 [%vol]**	**NO [ppm]**	**$\tau_{0.425m}$ [s]**	**HC [ppm]**	**CO [%vol]**
B0	622.33	8.97	2.70	41.33	0.08	26.00	0.06
B25	632.33	9.26	2.45	51.52	0.10	19.46	0.04
B50	676.14	9.58	2.54	55.88	0.10	9.96	0.04
B75	678.29	9.67	2.28	57.56	0.11	10.79	0.03
B100	779.80	9.77	2.54	64.95	0.11	11.92	0.03
B25 % change from B0	101.61	3.20		24.63		-25.17	-30.00
B50 % change from B0	108.65	6.82		35.20		-61.71	-36.67
B75 % change from B0	108.99	7.74		39.26		-58.51	-43.33
B100 % change from B0	125.30	8.91		57.15		-54.14	-43.33

Table 0-2: CO_2, CO, HC, NO emissions measured at equivalence ratio 0.16, at 0.425m from the ignition point

Sample	**T_2 [°C]**	**CO_2 [%vol]**	**ex. O_2 [%vol]**	**NO [ppm]**	**$\tau_{0.425m}$ [s]**	**HC [ppm]**	**CO [%vol]**
B0	635.50	9.66	5.44	45.14	0.05	23.64	0.05
B25	637.67	9.90	5.69	55.02	0.05	17.02	0.04
B50	672.17	10.49	5.81	65.51	0.05	6.40	0.03
B75	679.50	10.50	4.71	70.53	0.06	9.03	0.03
B100	781.20	10.62	5.15	73.48	0.06	9.17	0.03
B25 % change from B0	0.34	2.48		21.88		-28.01	-16.98
B50 % change from B0	5.77	8.54		45.13		-72.93	-39.62
B75 % change from B0	6.92	8.70		56.25		-61.79	-50.94
B100 % change from B0	22.93	9.94		62.79		-61.21	-50.94

Table 0-3: CO_2, CO, HC, NO emissions measured at equivalence ratio 0.14, at 0.425m from the ignition point

Sample	**T_2 [°C]**	**CO_2 [%vol]**	**ex. O_2 [%vol]**	**NO [ppm]**	**$\tau_{0.425m}$ [s]**	**HC [ppm]**	**CO [%vol]**
B0	636.67	10.20	6.40	48.78	0.04	21.22	0.04
B25	639.67	10.95	6.37	58.98	0.05	9.92	0.03
B50	676.17	11.03	6.38	70.50	0.05	6.75	0.02
B75	691.90	11.2	5.74	74.32	0.05	9.46	0.02
B100	783.50	11.32	6.45	76.43	0.05	7.92	0.02
B25 % change from B0	0.47	7.36		20.91		-53.27	-28.57
B50 % change from B0	6.20	8.14		44.53		-68.20	-31.43
B75 % change from B0	8.68	9.80		52.36		-55.40	-37.14
B100 % change from B0	23.06	10.98		56.69		-61.21	-85.94

Table 0-4: CO_2, CO, HC, NO emissions measured at equivalence ratio 0.11, at 0.425m from the ignition point

Sample	**T_2 [°C]**	**CO_2 [%vol]**	**ex. O_2 [%vol]**	**NO [ppm]**	**$\tau_{0.425m}$ [s]**	**HC [ppm]**	**CO [%vol]**
B0	636.80	10.32	8.57	51.52	0.03	19.200	0.020
B25	641.57	10.98	7.63	65.51	0.04	4.878	0.015
B50	679.14	11.28	8.40	72.19	0.04	4.571	0.013
B75	690.33	11.38	7.28	79.28	0.04	4.480	0.013
B100	786.80	11.39	7.60	78.46	0.05	3.444	0.008
B25 % change from B0	0.75	6.40		27.17		-74.59	-25.00
B50 % change from B0	6.65	9.30		40.14		-76.19	-35.00
B75 % change from B0	8.41	10.30		53.90		-76.67	-33.67
B100 % change from B0	23.56	10.37		52.30		-82.06	-60.00

Table 0-5: Emission variations from diesel and biodiesel sample at residence time of 0.22seconds.

Sample	**CGT [°C]**	**CO_2 [%vol]**	**CO [%vol]**	**HC [ppm]**	**ex. O_2 [%vol]**	**NO [ppm]**	**$\tau_{0.425m}$ [s]**	**Φ**
B0	**564.83**	**9.33**	**3.47**	**61.00**	**4.46**	**66.93**	**0.22**	**0.01**
B25	**578.18**	**11.49**	**1.20**	**32.70**	**4.29**	**86.67**	**0.22**	**0.01**
B50	**592.50**	**10.97**	**1.01**	**24.85**	**5.02**	**85.96**	**0.22**	**0.01**
B75	**592.67**	**14.09**	**0.74**	**8.80**	**0.83**	**114.80**	**0.22**	**0.07**
B100	**595.00**	**11.71**	**0.92**	**10.32**	**4.36**	**139.17**	**0.22**	**0.01**

Combustion products from red diesel test on CCA & residence time of combustion gases

Fuel Type: B0

Fuel Flow Rate: 25cc/min

D0 =0m

Port sample D2 = 0.425m (distance from the ignition point)

Nr. Crt.	T_2 [dgr C]	CO_2 [%vol]	O_2 [%vol]	NO [ppm]
1	711.85	10.214	0.345	29.696
2	779.80	13.870	1.651	61.517
3	779.80	13.144	2.703	60.000
4	779.80	12.600	3.400	58.000
5	779.80	11.898	4.716	52.767
6	781.20	10.933	5.441	48.778
7	781.20	10.022	6.401	45.139
9	781.20	9.667	8.567	41.333
10	781.20	8.733	9.197	38.000

Calculation of residence time of combustion gas

I. Calculation of Stoichiometric Air

Fuel specifications from lab analyses for 100kg diesel:

Constituents	% by wt
Carbon	86.9
Hydrogen	12.9
Oxygen	0.07
Nitrogen	0.02
Sulphur	0.09
H_20	0.02

Diesel calorific value: 41098.325 KJ/kg

Calculation for Requirement of Theoretical Amount of Air

Consider a sample of 100kg of diesel. The chemical reactions are:

Element	Molecular weight [Kg/kg mole]
C	12.011
O_2	31.998
H_2	2.0158
S	32.065
N_2	28.014
CO_2	44.009
SO_2	64.063
H_2O	18.0148

$C + O_2 \rightarrow CO_2$

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

$S + O_2 \rightarrow SO_2$

Constituents of fuel:

$C + O_2 \rightarrow CO_2$

$12.011 + 31.998 \rightarrow 44.009$

12.011kg of C requires 31.998kg of O_2 to form 44.009kg of CO_2, therefore 1kg of C requires:

$$\frac{31.998}{12.011} \text{ kg} = 2.664 \text{ kg of } O_2$$

$86.9\ C + 86.9 \times 2.664\ O2 \rightarrow 318.407 \qquad CO_2$

$2\ H_2 + O_2 \rightarrow 2H_2O$

$2 \times 2.0158 + 31.998 \rightarrow 36.0296$

4.0316 kg of H_2 requires 31.998kg of O_2 to form 36.0296kg of H_2O, therefore 1kg of H_2 requires:

$$\frac{31.998}{4.0316}\text{kg} = 7.9368 \text{ kg of } O_2$$

$12.9\ H_2 + 12.9 \times 7.9368\ O_2 \rightarrow 115.285\ H_2O$

$S + O_2 \rightarrow SO_2$

$31.998 + 32.065 \rightarrow 64.063$

31.998kg of S requires 32.065kg of O_2 to form 64.063kg of SO_2, therefore 1kg of S requires:

$$\frac{31.998}{32.065}\ \text{kg} = 0.9979 \text{ kg of } O_2$$

$0.09 + 0.09 \times 0.9979\ O_2 \rightarrow 0.180\ SO_2$

Gas Density	
N_2 =	1.165 kg/m^3
O_2 =	1.331 kg/m^3
CO_2 =	1.842 kg/m^3
H_2O =	0.804 kg/m^3
SO_2 =	2.279 kg/m^3
Air =	1.205 kg/m^3

Total O_2 required for 100 kg diesel = 231.507 + 102.3847 + 0.0898=

Total O_2 required for 100 kg diesel is 333.981 kg of O_2

Flue gases without excess air = CO2 + H_2O + SO_2 [kg]

CO_2 [kg] = 318.41 [kg]
density of CO_2 = 1.842 [kg/m^3]
→ CO_2 = 172.86 m^3

H_2O [kg] = 115.2847108 [kg]
density of H_2O = 0.804 [kg/m^3]
→ H_2O = 143.39 m^3

SO_2 [kg] = 0.179811944 [kg]
density of SO_2 = 2.279 [kg/m^3]
→ SO_2 = 0.08 m^3

O_2 required for 100kg diesel= 333.981 - 0.07 = 333.911 kg

O_2 required = 333.911kg

Oxygen required for 100kg diesel:

O_2 [kg] = 333.911 [kg]
density of O_2 = 1.331 [kg/m^3]
→ O_2 = 250.87 m^3

Air contains 21% by volume O_2.

Therefore, the quantity of air required = 1194.63 m^3 for 100kg diesel

N2 [kg] = 1194.63 - 250.87 m^3 →

N_2 [kg] = 943.76 m^3

Air [kg] = 1194.63 m^3

Total combustion gases:

$CO_2 + H_2O + SO_2 + N_2$ = 172.86 + 143.39 + 0.08 + 943.76 [m3]

Total c.g. = 1260.09 m^3 at NTP from 1kg diesel

Total combustion gases from 1kg diesel = 12.60 [m^3]

Air required for 1kg diesel = 11.95 [m^3]

Rate of diesel flow = 25 cc/min

Density of diesel = 0.834 g/cm^3

Mass of diesel = 0.834 × 25 [kg] = 20.85 [g]

Volume of diesel = 0.000025 [m^3]

Therefore, combustion gases produced at NTP = 12.60 × 0.000025 [m^3/min]

Total C.G. at NTP from 0.000025 [m^3] diesel is 0.000315 [m^3/min]

Theoretical combustion Air required for burning 0.000025 m3 diesel at NTP=0.000299 m^3 air; with excess air:

Crt. No.	**ex. O_2 [%vol]**	[1]**Th. Comb Air with ex. air** [m^3/kg fuel]	[2]**Actual ex. air** [m^3]	[3]**Total CG at ex air** [m^3/kg diesel]
1	0.35	0.000402	0.000103	0.000418
2	1.65	0.000792	0.000493	0.000808
3	2.70	0.001106	0.000807	0.001122
4	3.40	0.001314	0.001015	0.001330
5	4.72	0.001707	0.001408	0.001723
6	5.44	0.001924	0.001625	0.001940
7	6.40	0.002210	0.001912	0.002227
9	8.57	0.002857	0.002559	0.002874
10	9.20	0.003045	0.002747	0.003062

[1] For excess air calculation consider O_2 measured and the fact that 21% by vol is air:

[2] Actual excess air at NTP conditions is presented in table above:

[3] Total Volume of Combustion Gases using Excess Air is presented above

Calculation of Volume of Combustion Gases at the Temperature measured:

Normal temperature: T1 = 273 K

Sample temperature: Ti, where i = 1..5 [K]

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \& \quad P_1=P_2$$

$$V_2 = \frac{T_2}{T_1} \text{ x } V_1$$

Volume of air at temperature T_i $\quad {}^{4)}V_{ti} = \frac{T_i}{273} \times {}^{3)}V_{NTP\_real}$ [m^3/min]

Table below presents the Volume of Combustion Temperature at the measured Temperature:

Crt. No.	**T_2** [K]	$^{4)}$ **Vol_C.G$_{T2}$** [m^3/min]	$^{5)}$ **v_{T2}** [m/s]	**$\tau_{0.425m}$** [s]	**NO** [ppm]
1	984.85	0.420	1.93	0.22	29.70
2	1052.80	0.860	3.95	0.11	61.52
3	1052.80	1.191	5.46	0.08	60.00
4	1052.80	1.410	6.47	0.07	58.00
5	1052.80	1.824	8.37	0.05	52.77
6	1054.20	2.054	9.43	0.05	48.78
7	1054.20	2.357	10.81	0.04	45.14
9	1054.20	3.038	13.94	0.03	41.33
10	1054.20	3.237	14.85	0.03	38.00

Cross sectional area of the combustion tube A_t:

Tube i.d = 68 mm

$$A_t = \frac{\pi d^2}{4} = \frac{\pi}{4} \times 68^2 \text{ x } 10^{-6} = 0.0036 \text{ [m}^2\text{]}$$

Cross section area At = 0.0036 m^2

Velocity of combustion gases at the temperature measured (vT2):

$$v_{T2} = \frac{Vol\_C.G_{T2}}{A_t*60}$$ [m/sec] the values are presented in [5)] table above.

$$\tau_{0.425m} = \frac{D_2}{v_{T2}}$$ The values are presented in [6)] table above.

$D_2 =$ 0.425[m]

Calculations to determine equivalence ratio, Φ:

The equivalence ratio is defined as the fuel/air ratio normalized with respect to the stoichiometric fuel/air ratio.

$$\Phi = \frac{m_f/m_a}{(m_f/m_a)_{st}}$$ [wt/wt]

$m_f =$ 0.000025 [m^3/min]

$m_{a\_st} =$ 0.000299 [m^3]

Nr crt.	**ex. O_2 [%vol]**	**[1)]Th. Comb Air with ex. air** [m^3/kg fuel]	Φ
1	0.35	0.000402	0.74
2	1.65	0.000792	0.38
3	2.70	0.001106	0.27
4	3.40	0.001314	0.23
5	4.72	0.001707	0.17
6	5.44	0.001924	0.16
7	6.40	0.002210	0.14
9	8.57	0.002857	0.10
10	9.20	0.003045	0.10

Appendix C – Evaluation of Biodiesel in Land Rover VM2400 Diesel Engine

Appendix C presents the results of the experimental work performed on Land Rover VM2400 diesel engine.

Table 0-1: Engine performance and exhaust emissions from B0, B25, B50, B75 and B100 fuel at 2000rpm

2000 rpm															
Fuel	Load [%]	AVG Torque [Nm]	AVG Engine speed [rpm]	AVG BSFC [g/kw-h]	AVG Power [kW]	**BMEP [bar]**	**BTE [%]**	Water OUT Temp. [dgr C]	Exhaust Manifold Temp, [dgr C]	BSCO [% vol]	BSHC [ppm]	BSCO2 [% vol]	O2 [%]	BSNOx [ppm]	AVG SFC [L/h]
T1-B0	15	27.4	1996.40	409.75	5.72	143.36	21.38	65.40	185.20	0.19	11.89	3.05	16.09	175.61	2.81
	25	45.6	1997.75	317.75	9.54	238.89	27.57	67.80	225.00	0.16	10.57	3.94	14.96	203.60	3.64
	50	91.3	1999.60	255.92	19.12	478.15	34.23	72.80	357.00	0.15	9.09	6.18	12.13	301.73	5.87
	75	136.8	2000.00	251.81	28.64	716.02	34.79	78.20	509.60	0.15	8.14	8.54	9.18	361.37	8.65
	100	182.1	2001.33	250.65	38.16	953.47	34.95	83.60	666.60	0.14	7.47	10.74	6.32	403.24	11.47
B25	15	26.9	1994.50	444.12	5.61	140.66	21.10	64.40	186.52	0.09	10.28	3.16	16.19	187.46	2.89
	25	44.7	1995.33	336.67	9.34	234.05	27.35	68.00	226.28	0.08	9.99	3.98	15.11	224.58	3.71
	50	88.9	1997.50	268.07	18.59	465.35	34.29	74.00	360.25	0.07	8.32	6.29	12.03	328.04	5.89
	75	133.2	2000.00	263.24	27.90	697.43	33.80	81.80	514.72	0.07	7.62	8.62	8.91	384.72	8.97
	100	176.8	2001.00	262.86	37.05	925.72	34.62	85.25	675.25	0.07	6.61	10.98	6.22	428.05	11.63
T2-B0	15	27.4	1996.40	409.75	5.72	143.36	21.30	68.40	186.00	0.19	11.69	3.08	16.14	175.69	2.82
	25	45.6	1997.75	317.75	9.54	238.89	27.29	73.00	224.40	0.15	10.38	3.99	14.99	203.56	3.67
	50	91.3	1999.60	255.92	19.12	478.15	34.26	76.80	358.20	0.15	8.88	6.23	12.10	301.80	5.86
	75	136.8	2000.00	251.81	28.64	716.02	34.66	78.60	510.40	0.14	7.73	8.58	9.05	362.90	8.68
	100	182.1	2001.33	250.65	38.16	953.47	34.98	84.00	667.02	0.13	7.17	10.76	6.23	403.20	11.46
B50	15	26.5	1997.00	472.57	5.55	138.98	20.71	65.40	188.40	0.09	9.87	3.22	16.29	212.83	3.02
	25	44.0	1999.00	360.61	9.22	230.56	26.81	67.40	227.08	0.07	8.53	4.06	15.09	257.03	3.87
	50	87.6	1998.33	290.47	18.34	458.88	33.54	71.80	364.16	0.07	7.59	6.38	11.99	374.68	6.16
	75	130.9	2001.00	285.06	27.43	685.39	34.18	79.80	518.28	0.06	6.43	8.71	8.67	445.96	9.04
	100	172.9	2002.00	284.89	36.24	905.11	34.06	82.20	679.60	0.06	5.20	11.08	5.52	518.38	11.99
T3-B0	15	27.4	1996.40	409.75	5.72	143.36	21.29	66.20	185.60	0.19	11.72	3.08	16.11	175.60	2.82
	25	45.6	1997.75	317.75	9.54	238.89	27.44	68.80	224.70	0.16	10.54	3.96	14.97	204.00	3.65
	50	91.3	1999.60	255.92	19.12	478.15	34.27	71.50	357.86	0.15	8.99	6.21	12.11	301.64	5.86
	75	136.8	2000.00	251.81	28.64	716.02	34.72	76.50	509.44	0.14	8.16	8.56	9.12	361.42	8.66
	100	182.1	2001.33	250.65	38.16	953.47	34.99	81.33	667.42	0.14	7.57	10.75	6.27	403.30	11.46
B75	15	26.1	1997.67	488.48	5.47	136.82	20.74	63.40	189.26	0.08	8.42	3.24	16.26	234.66	3.09
	25	43.4	1999.33	376.79	9.08	227.07	27.13	66.20	228.42	0.07	9.03	4.07	15.14	277.03	3.92
	50	86.7	2000.00	298.85	18.16	453.96	34.01	71.20	366.10	0.06	8.26	6.42	12.04	420.82	6.26
	75	129.2	2000.00	290.52	27.07	676.70	34.79	79.25	520.68	0.06	8.02	8.79	8.80	502.22	9.12
	100	170.3	2001.00	290.23	35.68	891.51	35.13	81.80	683.96	0.06	8.08	11.21	5.63	578.85	11.90
T4-B0	15	27.4	1996.40	409.75	5.72	143.36	21.38	66.80	185.40	0.19	11.80	3.06	16.10	175.66	2.81
	25	45.6	1997.75	317.75	9.54	238.89	27.57	70.20	224.85	0.16	10.56	3.95	14.96	203.86	3.64
	50	91.3	1999.60	255.92	19.12	478.15	34.23	73.80	357.80	0.15	9.04	6.19	12.12	301.50	5.87
	75	136.8	2000.00	251.81	28.64	716.02	34.79	77.80	510.30	0.15	8.02	8.55	9.15	361.38	8.65
	100	182.1	2001.33	250.65	38.16	953.47	34.98	83.20	667.38	0.15	7.41	10.75	6.30	403.44	11.46
B100	15	25.1	1995.67	539.98	5.24	131.25	19.98	57.50	190.06	0.08	8.88	3.26	16.26	252.87	3.21
	25	42.0	1996.00	396.72	8.77	219.74	27.19	60.40	230.54	0.07	9.18	4.09	15.02	306.24	3.95
	50	83.4	1998.67	309.80	17.46	436.86	34.82	73.00	367.44	0.06	9.44	6.46	11.94	456.97	6.13
	75	124.5	1999.67	297.17	26.08	652.06	36.30	75.40	523.68	0.06	8.51	8.88	8.77	558.31	8.79
	100	165.1	2001.00	296.07	34.60	864.46	36.43	81.67	686.36	0.06	8.44	11.29	5.63	618.03	11.61

Table 0-2: Performance and exhaust emissions % difference from baseline for engine at 2000rpm

% Difference from base B0 - 2000rpm															
Fuel	Load [%]	Torque [%]	Engine speed [rpm]	BSFC [%]	Power [%]	BMEP [%]	BTE [%]	Water OUT Temp. [%]	Exhaust Manifold Temp, [%]	BSCO [%]	BSHC [%]	BSCO2 [%]	O2 [%]	BSNOx [%]	SFC [%]
B25	15	-1.88	-0.10	8.39	-1.98	-1.88	-1.30	-1.53	0.71	-50.63	-13.48	3.61	0.61	6.75	2.73
	25	-2.03	-0.12	5.95	-2.15	-2.03	-0.78	0.29	0.57	-52.07	-5.53	1.02	1.05	10.31	2.01
	50	-2.68	-0.11	4.75	-2.78	-2.68	0.18	1.65	0.91	-51.34	-8.47	1.72	-0.82	8.72	0.39
	75	-2.60	0.00	4.54	-2.60	-2.60	-2.84	4.60	1.00	-53.85	-6.40	0.94	-2.95	6.46	3.71
	100	-2.91	-0.02	4.87	-2.93	-2.91	-0.95	1.97	1.30	-52.42	-11.48	2.23	-1.61	6.15	1.38
B50	15	-3.06	0.03	15.33	-3.03	-3.06	-2.79	-4.39	1.29	-52.38	-15.59	4.52	0.95	21.14	7.02
	25	-3.49	0.06	13.49	-3.43	-3.49	-1.76	-7.67	1.19	-53.14	-17.84	1.95	0.67	26.27	5.46
	50	-4.03	-0.06	13.50	-4.09	-4.03	-2.09	-6.51	1.66	-53.50	-14.52	2.47	-0.87	24.15	5.09
	75	-4.28	0.05	13.20	-4.23	-4.28	-1.38	1.53	1.54	-54.08	-16.73	1.48	-4.28	22.89	4.18
	100	-5.07	0.03	13.66	-5.04	-5.07	-2.62	-2.14	1.89	-53.66	-27.45	2.99	-11.32	28.56	4.61
B75	15	-4.57	0.06	19.21	-4.50	-4.57	-2.56	-4.23	1.97	-56.45	-28.18	5.25	0.88	33.63	9.36
	25	-4.95	0.08	18.58	-4.87	-4.95	-1.11	-3.78	1.66	-57.90	-14.37	2.70	1.15	35.80	7.34
	50	-5.06	0.02	16.77	-5.04	-5.06	-0.76	-0.42	2.30	-58.68	-8.11	3.51	-0.64	39.51	6.77
	75	-5.49	0.00	15.37	-5.49	-5.49	0.20	3.59	2.21	-59.03	-1.66	2.64	-3.49	38.96	5.25
	100	-6.50	-0.02	15.79	-6.51	-6.50	0.42	0.57	2.48	-59.20	6.82	4.27	-10.22	43.53	3.89
B100	15	-8.45	-0.04	31.78	-8.48	-8.45	-6.55	-13.92	2.51	-58.70	-24.75	6.41	0.96	43.95	14.03
	25	-8.02	-0.09	24.85	-8.10	-8.02	-1.36	-13.96	2.53	-58.86	-13.03	3.48	0.34	50.22	8.49
	50	-8.64	-0.05	21.05	-8.68	-8.64	1.73	-1.08	2.69	-60.43	4.45	4.32	-1.49	51.57	4.53
	75	-8.93	-0.02	18.01	-8.95	-8.93	4.35	-3.08	2.62	-60.20	6.05	3.86	-4.12	54.49	1.60
	100	-9.34	-0.02	18.12	-9.35	-9.34	4.17	-1.84	2.84	-61.11	13.95	5.11	-10.58	53.19	1.33

Table 0-3: Engine performance and exhaust emissions from B0, B25, B50, B75 and B100 fuel at 2500rpm

2500 rpm															
Fuel	Load [%]	AVG Torque [Nm]	AVG Engine speed [rpm]	AVG BSFC [g/kw-h]	AVG Power [kW]	**BMEP [bar]**	**BTE [%]**	Water OUT Temp. [dgr C]	Exhaust Manifold Temp, [dgr C]	BSCO [% vol]	BSHC [ppm]	BSCO2 [% vol]	O2 [%]	BSNOx [ppm]	AVG SFC [L/h]
T1-B0	15	28.26	2498	422.91	7.39	147.97	20.62	75.20	202.52	0.17	9.48	3.26	15.94	206.37	3.77
	25	46.30	2498	337.38	12.11	242.43	26.15	75.40	234.60	0.17	8.75	3.92	14.81	242.06	4.86
	50	90.68	2499	282.23	23.73	474.80	30.74	78.40	338.88	0.1699	7.63	5.72	12.15	339.77	8.11
	75	136.90	2500	265.24	35.84	716.81	33.04	82.40	476.65	0.16	6.28	7.98	9.67	418.16	11.39
	100	176.87	2500	252.13	46.30	926.09	32.96	87.20	598.98	0.16	5.94	9.56	7.45	476.36	14.75
B25	15	27.80	2498	455.82	7.27	145.56	20.88	74.80	202.92	0.11	8.20	3.28	16.06	225.54	3.78
	25	45.48	2498	345.17	11.90	238.13	26.46	75.20	236.24	0.10	7.23	3.98	14.99	258.66	4.88
	50	89.02	2499	276.08	23.30	466.09	32.69	78.80	340.08	0.10	6.67	5.76	12.34	362.10	7.74
	75	133.76	2500	261.94	35.02	700.37	34.94	81.80	478.24	0.09	5.59	8.08	9.76	442.91	10.89
	100	173.22	2500	265.96	45.35	906.98	34.14	85.25	603.18	0.09	4.03	9.92	7.46	516.33	14.43
T2-B0	15	28.24	2497	422.91	7.38	147.86	20.60	76.20	202.76	0.18	9.57	3.25	16.05	207.17	3.77
	25	46.00	2497	337.38	12.03	240.86	26.06	76.60	234.90	0.17	8.75	3.94	14.92	241.04	4.85
	50	90.77	2496	282.23	23.73	475.27	30.73	79.60	338.54	0.17	7.63	5.79	12.24	339.90	8.11
	75	136.87	2499	265.24	35.82	716.63	33.03	82.60	476.86	0.16	6.28	7.90	9.69	417.35	11.39
	100	177.24	2500	250.34	46.40	928.04	33.05	87.00	597.88	0.16	5.94	9.58	7.26	475.53	14.75
B50	15	27.56	2498	486.85	7.21	144.30	20.45	77.00	206.04	0.08	6.65	3.43	16.23	234.45	3.97
	25	44.84	2499	374.29	11.73	234.78	25.85	76.40	239.16	0.07	5.73	4.20	15.09	276.77	5.11
	50	88.22	2499	292.98	23.09	461.92	32.73	78.40	342.36	0.07	4.74	6.18	12.47	400.96	7.95
	75	132.40	2499	278.53	34.65	693.24	34.45	83.80	484.14	0.07	4.19	8.52	10.03	490.78	11.33
	100	171.22	2500	271.19	44.82	896.49	34.92	85.80	610.28	0.06	4.03	10.42	7.56	562.16	14.47
T3-B0	15	28.30	2499	414.66	7.40	148.18	20.64	74.00	202.14	0.18	9.48	3.26	15.99	206.77	3.77
	25	45.85	2497	330.97	11.99	240.07	25.97	74.00	235.20	0.17	8.75	3.93	14.86	241.55	4.85
	50	90.87	2497	263.11	23.76	475.78	30.72	77.67	339.12	0.17	7.63	5.76	12.19	339.83	8.12
	75	136.46	2499	251.51	35.71	714.50	32.95	82.75	476.72	0.16	6.28	7.94	9.68	417.75	11.38
	100	177.46	2500	249.80	46.46	929.20	33.12	86.33	598.93	0.16	5.94	9.57	7.35	475.95	14.73
B75	15	27.38	2498	514.50	7.16	143.36	20.40	76.40	206.82	0.07	8.83	3.55	16.26	244.95	4.11
	25	44.46	2498	392.64	11.63	232.80	25.91	76.80	243.64	0.06	8.49	4.28	15.21	292.00	5.26
	50	87.86	2499	304.11	22.99	460.03	33.29	79.20	348.12	0.06	8.24	6.34	12.60	418.91	8.10
	75	131.46	2502	291.85	34.44	688.32	34.57	84.60	491.32	0.05	6.95	8.87	10.37	518.38	11.68
	100	170.54	2502	290.19	44.68	892.95	34.32	86.20	621.60	0.05	7.06	10.72	7.76	598.95	15.26
T4-B0	15	28.22	2496	416.23	7.38	147.76	20.56	75.40	203.12	0.18	9.35	3.24	16.15	207.03	3.77
	25	45.98	2497	333.82	12.02	240.75	26.00	75.20	234.82	0.17	8.70	3.90	15.03	242.02	4.86
	50	90.83	2497	263.21	23.75	475.60	30.62	78.80	338.96	0.17	7.46	5.86	12.33	339.80	8.15
	75	136.20	2499	251.81	35.65	713.14	32.84	82.60	476.54	0.16	6.28	7.98	9.71	418.10	11.40
	100	177.82	2500	250.45	46.55	931.06	33.15	86.80	598.90	0.16	5.94	9.58	7.07	476.32	14.75
B100	15	27.18	2496	540.84	7.10	142.31	20.48	73.20	211.64	0.03	9.54	3.58	16.15	250.95	4.24
	25	44.20	2497	407.76	11.56	231.43	26.31	74.50	246.02	0.02	9.23	4.30	15.04	302.67	5.37
	50	87.20	2498	314.73	22.81	456.60	33.78	74.00	352.10	0.02	8.42	6.52	12.50	438.10	8.26
	75	130.64	2500	299.06	34.21	684.03	35.59	82.60	498.62	0.02	8.39	8.96	10.02	542.72	11.75
	100	170.28	2501	298.55	44.59	891.58	34.38	83.40	627.80	0.01	8.15	10.89	7.35	626.16	15.86

Table 0-4: Performance and exhaust emissions % difference from baseline for engine at 2500rpm

% Difference from base B0 - 2500rpm															
Fuel	Load [%]	Torque [%]	Engine speed [rpm]	BSFC [%]	Power [%]	BMEP [%]	BTE [%]	Water OUT Temp. [%]	Exhaust Manifold Temp, [%]	BSCO [%]	BSHC [%]	BSCO2 [%]	O2 [%]	BSNOx [%]	SFC [%]
B25	15	-1.63	0.00	7.78	-1.63	-1.63	1.25	-0.53	0.20	-37.00	-13.46	0.61	0.73	9.29	0.50
	25	-1.77	0.00	2.31	-1.77	-1.77	1.20	-0.27	0.70	-42.69	-17.46	1.53	1.26	6.86	0.41
	50	-1.84	0.00	-2.18	-1.84	-1.84	6.33	0.51	0.35	-42.27	-12.63	0.70	1.57	6.57	-4.50
	75	-2.29	0.00	-1.24	-2.29	-2.29	5.74	-0.73	0.33	-44.42	-10.98	1.25	0.94	5.92	-4.42
	100	-2.06	0.00	5.48	-2.06	-2.06	3.57	-2.24	0.70	-43.75	-32.17	3.77	0.10	8.39	-2.18
B50	15	-2.41	0.03	15.12	-2.38	-2.41	-0.72	1.05	1.62	-55.70	-30.49	5.48	1.11	13.17	5.49
	25	-2.52	0.09	10.94	-2.44	-2.52	-0.80	-0.26	1.81	-59.11	-34.51	6.62	1.17	14.82	5.51
	50	-2.81	0.12	3.81	-2.69	-2.81	6.51	-1.51	1.13	-58.81	-37.92	6.77	1.87	17.96	-1.99
	75	-3.26	0.00	5.01	-3.27	-3.26	4.32	1.45	1.53	-56.51	-33.28	7.91	3.49	17.60	-0.52
	100	-3.40	0.00	8.33	-3.40	-3.40	3.45	-1.38	2.07	-60.93	-32.18	8.80	4.15	18.22	-1.90
B75	15	-3.25	-0.03	24.08	-3.28	-3.25	-1.16	3.24	2.32	-61.27	-6.88	9.03	1.66	18.46	9.20
	25	-3.03	0.07	18.63	-2.96	-3.03	-0.24	3.78	3.59	-65.03	-3.01	9.01	2.34	20.89	8.55
	50	-3.31	0.08	15.58	-3.23	-3.31	8.37	1.97	2.65	-64.68	7.93	10.20	3.32	23.27	-0.35
	75	-3.66	0.13	16.04	-3.54	-3.66	4.90	2.24	3.06	-68.74	10.63	11.69	7.18	24.09	2.62
	100	-3.90	0.08	16.17	-3.82	-3.90	3.62	-0.15	3.79	-69.69	18.84	12.07	5.50	25.84	3.58
B100	15	-3.69	-0.01	29.94	-3.70	-3.69	-0.39	-2.92	4.19	-85.81	2.09	10.51	-0.01	21.22	12.57
	25	-3.87	-0.01	22.15	-3.88	-3.87	1.18	-0.93	4.77	-87.63	6.07	10.26	0.03	25.06	10.62
	50	-4.00	0.01	19.58	-3.98	-4.00	10.32	-6.09	3.88	-88.24	12.94	11.33	1.43	28.93	1.35
	75	-4.08	0.04	18.76	-4.04	-4.08	8.36	0.00	4.63	-87.96	33.69	12.28	3.13	29.81	3.11
	100	-4.24	0.03	19.21	-4.21	-4.24	5.71	-3.92	4.83	-93.41	37.15	13.64	4.03	31.46	7.55

Table 0-5: Engine performance and exhaust emissions from B0, B25, B50, B75 and B100 fuel at 3000rpm

3000 rpm															
Fuel	Load [%]	AVG Torque [Nm]	AVG Engine speed [rpm]	AVG BSFC [g/kw-h]	AVG Power [kW]	BMEP [bar]	BTE [%]	Water OUT Temp. [dgr C]	Exhaust Manifold Temp, [dgr C]	BSCO [% vol]	BSHC [ppm]	BSCO2 [% vol]	O2 [%]	BSNOx [ppm]	AVG SFC [L/h]
T1-B0	15	26.87	3002	468.98	8.45	140.67	18.68	69.40	226.20	0.07	8.93	3.34	15.93	288.47	4.75
	25	43.93	3003	361.35	13.82	230.03	24.24	70.20	265.40	0.06	7.14	4.01	14.87	316.26	5.99
	50	88.10	3004	275.75	27.72	461.29	32.13	74.40	371.60	0.06	6.57	5.59	12.80	453.72	9.06
	75	129.47	3006	260.41	40.75	677.89	33.64	80.40	489.00	0.06	5.32	7.14	10.81	497.68	12.72
	100	175.12	3007	259.80	55.14	916.93	35.22	85.20	629.60	0.06	4.82	9.33	7.97	502.36	16.44
B25	15	26.42	2996	504.53	8.29	138.34	18.42	68.20	226.90	0.06	5.86	3.42	15.89	296.01	4.89
	25	43.20	2997	377.03	13.56	226.19	24.38	70.00	265.84	0.05	5.29	4.10	14.93	319.56	6.04
	50	86.88	3000	285.55	27.29	454.90	32.40	76.00	372.23	0.04	3.58	5.64	12.77	481.07	9.15
	75	127.03	3002	266.85	39.93	665.14	33.91	80.40	490.44	0.04	4.73	7.57	10.92	565.81	12.79
	100	171.23	3002	262.02	53.84	896.58	35.29	84.00	632.25	0.04	4.02	10.13	8.03	561.48	16.57
T2-B0	15	26.90	3002	477.26	8.46	140.85	18.74	69.40	226.52	0.06	8.78	3.34	16.38	288.50	4.74
	25	44.03	3003	366.25	13.85	230.56	24.24	71.80	266.04	0.06	7.07	4.01	15.32	316.66	6.00
	50	88.02	3004	285.22	27.69	460.87	32.03	75.40	372.18	0.06	6.57	5.59	13.02	453.82	9.08
	75	130.20	3004	268.31	40.96	681.73	33.88	80.00	489.62	0.05	5.57	7.14	10.98	498.04	12.70
	100	178.97	3007	259.65	56.36	937.08	36.05	85.20	630.02	0.04	5.07	9.33	7.89	502.44	16.42
B50	15	26.02	2998	544.41	8.17	136.26	17.75	70.00	228.68	0.04	7.22	3.55	15.84	324.37	5.19
	25	42.64	2999	403.10	13.39	223.28	24.10	71.80	268.64	0.04	6.24	4.22	14.86	368.67	6.26
	50	85.68	3000	308.46	26.91	448.62	31.13	75.50	375.66	0.04	5.24	6.06	12.78	548.01	9.74
	75	125.87	3000	287.24	39.54	659.04	33.39	78.20	495.75	0.03	4.84	7.82	10.73	638.33	13.34
	100	171.96	3000	284.83	54.02	900.40	34.20	83.25	638.54	0.02	4.45	10.42	8.26	642.32	17.80
T3-B0	15	26.90	3001	468.51	8.45	140.85	18.70	66.00	226.34	0.06	8.93	3.34	15.77	286.48	4.75
	25	44.00	3002	357.63	13.83	230.38	24.27	67.25	266.10	0.06	7.19	4.01	14.74	316.84	5.99
	50	88.10	3003	286.86	27.70	461.29	32.11	72.50	372.26	0.05	6.63	5.59	12.75	453.78	9.06
	75	130.43	3006	265.72	41.05	682.95	33.89	78.50	490.25	0.05	5.74	7.14	10.64	496.76	12.72
	100	179.88	3007	258.84	56.64	941.85	36.18	83.75	629.98	0.05	5.44	9.33	7.56	500.98	16.44
B75	15	25.86	2996	560.63	8.11	135.39	17.88	71.25	230.02	0.04	8.48	3.58	16.11	364.63	5.32
	25	42.20	2997	428.89	13.24	220.96	23.78	71.00	269.98	0.04	7.22	4.38	15.10	420.30	6.53
	50	85.22	2997	321.43	26.75	446.21	31.40	76.50	378.74	0.03	7.03	6.24	13.05	614.18	9.98
	75	124.46	2999	303.17	39.08	651.67	33.16	80.25	499.32	0.03	6.27	8.12	10.96	687.50	13.81
	100	171.23	3000	294.01	53.79	896.58	34.74	83.25	643.25	0.03	6.15	11.02	8.13	709.88	18.15
T4-B0	15	26.73	3000	471.53	8.40	139.98	18.58	68.80	226.68	0.07	8.94	3.34	16.03	286.52	4.75
	25	43.73	3002	363.08	13.75	228.99	24.13	70.40	266.08	0.06	7.17	4.01	14.97	316.54	5.99
	50	88.02	3003	279.65	27.68	460.87	32.08	72.40	372.48	0.06	6.68	5.59	12.86	453.74	9.06
	75	129.57	3004	260.32	40.76	678.41	33.65	79.80	490.16	0.06	6.02	7.14	10.81	496.88	12.72
	100	178.60	3007	258.87	56.24	935.15	35.92	84.80	630.10	0.06	5.57	9.33	7.81	502.26	16.44
B100	15	25.57	2999	582.70	8.03	133.87	18.51	70.80	231.54	0.03	8.94	3.56	16.13	406.48	5.30
	25	41.68	2998	441.47	13.09	218.24	24.36	72.20	270.46	0.02	7.80	4.24	15.10	466.41	6.57
	50	84.62	2998	320.65	26.57	443.07	33.37	79.60	380.08	0.02	7.49	6.23	12.96	704.19	9.73
	75	122.68	2998	303.88	38.52	642.35	34.59	81.50	502.04	0.02	6.93	8.25	10.89	754.35	13.62
	100	168.63	3000	293.77	52.98	882.96	36.24	84.25	646.25	0.02	6.76	11.20	8.01	750.58	17.88

Table 0-6: Performance and exhaust emissions % difference from baseline for engine at 2500rpm

% Difference from base B0 - 3000rpm															
Fuel	**Load [%]**	**Torque [%]**	**Engine speed [rpm]**	**BSFC [%]**	**Power [%]**	**BMEP [%]**	**BTE [%]**	**Water OUT Temp. [%]**	**Exhaust Manifold Temp, [%]**	**BSCO [%]**	**BSHC [%]**	**BSCO2 [%]**	**O2 [%]**	**BSNOx [%]**	**SFC [%]**
B25	15	-1.66	-0.18	7.58	-1.83	-1.66	-1.37	-1.73	0.31	-14.32	-34.39	2.47	-0.27	2.61	2.96
	25	-1.67	-0.19	4.34	-1.85	-1.67	0.58	-0.28	0.17	-25.41	-25.93	2.24	0.43	1.04	0.94
	50	-1.38	-0.14	3.55	-1.53	-1.38	0.85	2.15	0.17	-32.53	-45.58	0.93	-0.21	6.03	1.00
	75	-1.88	-0.13	2.47	-2.01	-1.88	0.81	0.00	0.29	-32.55	-11.12	6.02	1.05	13.69	0.54
	100	-2.22	-0.16	0.85	-2.37	-2.22	0.19	-1.41	0.42	-37.10	-16.62	8.51	0.82	11.77	0.80
B50	15	-3.26	-0.12	14.07	-3.38	-3.26	-5.25	0.86	0.95	-28.52	-17.75	6.13	-3.30	12.43	9.41
	25	-3.16	-0.14	10.06	-3.30	-3.16	-0.56	0.00	0.98	-30.00	-11.81	5.30	-3.00	16.43	4.34
	50	-2.66	-0.16	8.15	-2.81	-2.66	-2.82	0.13	0.94	-32.94	-20.24	8.50	-1.89	20.76	7.29
	75	-3.33	-0.14	7.06	-3.47	-3.33	-1.43	-2.25	1.25	-36.72	-13.12	9.55	-2.32	28.17	5.06
	100	-3.91	-0.23	9.70	-4.14	-3.91	-5.12	-2.29	1.35	-40.78	-12.07	11.71	4.65	27.84	8.39
B75	15	-3.88	-0.18	19.66	-4.05	-3.88	-4.36	7.95	1.63	-35.52	-5.06	7.14	2.12	27.28	11.95
	25	-4.09	-0.18	19.93	-4.26	-4.09	-2.05	5.58	1.46	-39.33	0.45	9.23	2.46	32.65	9.07
	50	-3.27	-0.19	12.05	-3.45	-3.27	-2.22	5.52	1.74	-43.40	5.93	11.75	2.35	35.35	10.19
	75	-4.58	-0.24	14.09	-4.81	-4.58	-2.16	2.23	1.85	-42.34	9.25	13.76	2.99	38.40	8.57
	100	-4.81	-0.24	13.59	-5.04	-4.81	-3.97	-0.60	2.11	-43.39	12.97	18.15	7.48	41.70	10.35
B100	15	-4.36	-0.06	23.58	-4.42	-4.36	-0.35	2.91	2.14	-54.58	-0.01	6.60	0.62	41.86	11.69
	25	-4.70	-0.14	21.59	-4.83	-4.70	0.99	2.56	1.65	-60.26	8.89	5.77	0.85	47.35	9.73
	50	-3.86	-0.16	14.66	-4.01	-3.86	4.03	9.94	2.04	-65.50	12.14	11.44	0.79	55.20	7.45
	75	-5.32	-0.20	16.73	-5.50	-5.32	2.80	2.13	2.42	-66.27	15.02	15.54	0.77	51.82	7.04
	100	-5.58	-0.22	13.48	-5.79	-5.58	0.88	-0.65	2.56	-69.90	21.50	20.07	2.63	49.44	8.74

Table 0-7: Engine performance and exhaust emissions from B0, B25, B50, B75 and B100 fuel at 3500rpm

3500 rpm															
Fuel	Load [%]	AVG Torque [Nm]	AVG Engine speed [rpm]	AVG BSFC [g/kw-h]	AVG Power [kW]	**BMEP [bar]**	**BTE [%]**	Water OUT Temp. [dgr C]	Exhaust Manifold Temp, [dgr C]	BSCO [% vol]	BSHC [ppm]	BSCO2 [% vol]	O2 [%]	BSNOx [ppm]	AVG SFC [L/h]
T1-B0	15	24.87	3492	545.86	9.09	130.20	16.05	78.80	262.20	0.08	10.01	3.23	15.66	368.55	5.95
	25	40.73	3497	409.04	14.92	213.28	21.41	76.40	294.80	0.08	9.95	4.10	14.84	394.43	7.32
	50	80.85	3501	306.45	29.64	423.33	28.58	80.40	392.20	0.07	9.09	5.43	13.13	418.47	10.89
	75	121.00	3501	277.58	44.37	633.55	31.56	84.20	507.60	0.07	8.34	7.00	11.03	436.62	14.77
	100	159.60	3502	265.08	58.52	835.66	33.04	87.20	643.20	0.07	6.46	9.02	8.37	446.63	18.60
B25	15	24.80	3498	586.04	9.08	129.85	16.07	75.80	262.46	0.07	9.02	3.44	15.69	412.16	6.14
	25	40.56	3498	430.54	14.86	212.40	21.40	77.20	295.32	0.07	8.98	4.31	14.81	452.50	7.54
	50	79.90	3500	316.40	29.28	418.36	28.78	80.00	392.96	0.06	7.77	5.69	13.06	480.68	11.06
	75	120.17	3502	277.78	44.07	629.19	32.03	83.00	510.04	0.06	6.41	7.35	11.05	506.92	14.95
	100	158.24	3500	267.26	58.00	828.56	33.73	86.67	644.36	0.06	4.99	9.78	8.64	536.24	18.68
T2-B0	15	24.87	3492	545.86	9.09	130.20	16.02	76.40	262.64	0.08	9.88	3.26	16.09	368.20	5.96
	25	40.73	3497	409.04	14.92	213.28	21.34	76.60	295.40	0.08	9.99	4.12	15.21	394.70	7.34
	50	80.85	3501	306.45	29.64	423.33	28.56	81.40	392.98	0.08	9.02	5.48	13.34	418.47	10.90
	75	121.04	3501	277.58	44.38	633.76	31.62	83.20	507.82	0.08	8.25	7.28	10.95	436.72	14.74
	100	159.60	3502	265.08	58.52	835.66	33.05	87.80	643.58	0.07	6.91	9.04	8.09	446.82	18.60
B50	15	24.37	3497	629.27	8.92	127.58	15.49	78.80	264.06	0.07	8.51	3.54	15.74	454.82	6.49
	25	39.80	3498	461.08	14.58	208.40	20.71	76.40	297.48	0.06	8.62	4.44	14.85	504.78	7.93
	50	78.94	3498	338.76	28.92	413.33	28.09	80.40	395.84	0.06	7.55	5.96	13.02	548.69	11.60
	75	118.33	3497	305.95	43.33	619.55	31.20	84.20	511.56	0.06	6.31	7.88	10.87	572.91	15.65
	100	156.00	3498	288.22	57.14	816.81	32.72	87.20	648.62	0.05	4.74	10.12	8.27	586.02	19.68
T3-B0	15	24.87	3492	545.86	9.09	130.20	16.08	75.75	263.10	0.08	9.94	3.23	15.54	367.65	5.94
	25	40.73	3497	409.04	14.92	213.28	21.34	75.25	295.62	0.08	10.05	4.10	14.73	394.04	7.34
	50	80.85	3501	306.45	29.64	423.33	28.62	78.75	393.52	0.08	9.01	5.46	12.91	418.46	10.88
	75	121.00	3501	277.58	44.37	633.55	31.57	83.50	508.16	0.08	8.26	7.21	10.53	436.84	14.76
	100	159.60	3502	265.08	58.52	835.66	33.04	86.25	644.18	0.07	6.46	9.02	7.65	466.78	18.60
B75	15	24.00	3496	657.61	8.79	125.66	15.57	79.50	266.76	0.06	9.88	3.58	15.91	474.12	6.61
	25	39.44	3496	479.40	14.44	206.51	21.10	77.75	299.84	0.05	9.98	4.46	15.00	528.22	8.02
	50	78.26	3500	350.99	28.68	409.77	28.56	80.25	399.02	0.05	9.59	6.10	13.10	586.66	11.77
	75	117.23	3500	310.02	42.97	613.83	31.73	84.75	515.48	0.05	9.82	8.02	11.06	604.51	15.87
	100	154.16	3499	300.43	56.49	807.18	33.39	83.00	654.56	0.05	8.65	10.43	8.44	658.52	19.83
T4-B0	15	24.87	3492	545.86	9.09	130.20	16.05	77.20	263.08	0.08	10.00	3.24	15.76	358.15	5.95
	25	40.73	3497	409.04	14.92	213.28	21.41	76.40	295.38	0.08	10.30	4.11	14.92	384.04	7.32
	50	80.85	3501	306.45	29.64	423.33	28.58	80.60	394.04	0.08	8.95	5.46	13.13	418.46	10.89
	75	121.00	3501	277.58	44.37	633.55	31.56	83.60	508.32	0.07	8.25	7.26	10.84	436.62	14.77
	100	159.60	3502	265.08	58.52	835.66	33.01	87.00	644.42	0.07	6.45	9.02	8.04	466.84	18.62
B100	15	23.86	3432	663.77	8.57	124.93	16.29	76.25	268.16	0.03	11.35	3.60	15.87	482.66	6.44
	25	39.10	3499	502.86	14.33	204.73	21.54	79.20	302.04	0.03	10.85	4.46	15.07	528.89	8.13
	50	77.60	3502	357.53	28.46	406.31	29.69	82.80	402.62	0.02	9.79	6.03	13.18	606.72	11.72
	75	116.04	3499	327.04	42.52	607.60	32.80	85.00	518.98	0.02	10.97	8.11	10.80	624.10	15.85
	100	153.64	3501	312.43	56.33	804.47	34.76	83.60	659.08	0.02	10.05	10.46	8.02	678.57	19.82

Table 0-8: Performance and exhaust emissions % difference from baseline for engine at 3500rpm

% Difference from base B0 - 3500rpm															
Fuel	Load [%]	Torque [%]	Engine speed [rpm]	BSFC [%]	Power [%]	BMEP [%]	BTE [%]	Water OUT Temp. [%]	Exhaust Manifold Temp, [%]	BSCO [%]	BSHC [%]	BSCO2 [%]	O2 [%]	BSNOx [%]	SFC [%]
B25	15	-0.27	0.18	7.36	-0.09	-0.27	0.16	-3.81	0.10	-12.01	-9.84	6.57	0.18	11.83	3.18
	25	-0.41	0.02	5.26	-0.40	-0.41	-0.07	1.05	0.18	-9.91	-9.72	5.16	-0.16	14.72	3.10
	50	-1.18	-0.04	3.25	-1.21	-1.18	0.67	-0.50	0.19	-12.61	-14.56	4.82	-0.52	14.87	1.50
	75	-0.69	0.02	0.07	-0.67	-0.69	1.51	-1.43	0.48	-11.03	-23.18	4.95	0.19	16.10	1.22
	100	-0.85	-0.04	0.82	-0.89	-0.85	2.07	-0.61	0.18	-11.31	-22.83	8.47	3.26	20.06	0.44
B50	15	-2.01	0.16	15.28	-1.85	-2.01	-3.32	3.14	0.54	-15.74	-13.81	8.62	-2.22	23.52	8.91
	25	-2.29	0.03	12.72	-2.26	-2.29	-2.98	-0.26	0.70	-17.26	-13.70	7.79	-2.34	27.89	8.08
	50	-2.36	-0.08	10.54	-2.44	-2.36	-1.66	-1.23	0.73	-19.88	-16.28	8.73	-2.42	31.12	6.43
	75	-2.24	-0.12	10.22	-2.36	-2.24	-1.35	1.20	0.74	-22.61	-23.53	8.22	-0.78	31.18	6.18
	100	-2.26	-0.10	8.73	-2.36	-2.26	-0.99	-0.68	0.78	-22.11	-31.38	11.94	2.19	31.15	5.80
B75	15	-3.49	0.12	20.47	-3.37	-3.49	-3.15	4.95	1.39	-25.16	-0.56	10.84	2.40	28.96	11.34
	25	-3.18	-0.03	17.20	-3.20	-3.18	-1.14	3.32	1.43	-35.40	-0.65	8.80	1.86	34.05	9.26
	50	-3.20	-0.04	14.53	-3.24	-3.20	-0.19	1.90	1.40	-34.31	6.45	11.71	1.45	40.20	8.18
	75	-3.11	-0.04	11.69	-3.15	-3.11	0.49	1.50	1.44	-33.97	18.79	11.29	5.00	38.38	7.55
	100	-3.41	-0.08	13.34	-3.48	-3.41	1.06	-3.77	1.61	-33.02	33.84	15.66	10.42	41.08	6.58
B100	15	-4.05	-1.72	21.60	-5.70	-4.05	1.53	-1.23	1.93	-58.52	13.60	10.97	0.66	34.77	8.15
	25	-4.01	0.07	22.93	-3.95	-4.01	0.60	3.66	2.25	-62.20	5.30	8.62	0.96	37.72	11.18
	50	-4.02	0.01	16.67	-4.01	-4.02	3.88	2.73	2.18	-67.68	9.38	10.30	0.39	44.99	7.60
	75	-3.09	-0.06	17.82	-4.15	-4.10	3.95	1.67	2.10	-71.43	33.02	11.66	-0.35	42.94	7.37
	100	-3.73	-0.02	17.86	-3.75	-3.73	5.31	-3.91	2.27	-75.97	55.81	16.01	-0.16	45.35	6.43

List of Publications

- C. Pisac, DR. R. Calay, DR. Y. Chen, Prof S. Ahmed, Comparative study of NOx formation from biodiesel and diesel. Innovations in fuel economy and sustainable road transport, 2011. http://www.researchandmarkets.com/reportinfo.asp?report_id=2072402&t=t