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Investigation of engine performance and exhaust gas emissions by using bio-diesel in compression ignition engine and optimisation of bio-diesel production from feedstock by using response surface methodology

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ABSTRACT

Bio-diesel, derived from the transesterification of vegetable oils or animal fats with simple alcohols, has attracted more and more attention recently. As a cleaner burning diesel alternative, bio-diesel claims to have many attractive features including: biodegradability, nontoxicity, renewability and low emission profiles. Free fatty acid (FFA) esterification and triglyceride (TG) transesterification with low alcohols molar ratio are the central reactions for the bio-diesel production. This study presents an experimental investigation into the effects of running biodiesel fuel and its blends on conventional diesel engines. Bio-fuels provide a way to produce fuels without redesigning any of the engine technology present today, yet allowing for green house emissions to decrease.

Bio-diesel is one of these types of emerging bio-fuels, which has an immediate alternative fuel, while providing a decrease in green house gas emissions, as well as a solution to recycling used Waste Vegetable Oils which are otherwise disposed. This study shows how by blending bio-diesel with petroleum diesel at intervals of B5, B10, B15, and B20 decrease green house gas emissions significantly while maintaining similar performance output and efficiency with respect to 100% petroleum diesel.

The focus of this research is to optimize the biodiesel production from crude sunflower oil. The effect of variables including methanol/oil molar ratio, NaOH catalyst concentration, reaction time, reaction temperature, and rate of mixing on the bio-diesel yield was examined and optimized by response surface methodology (RSM). Besides, a second-order model was deduced to predict the biodiesel yield. Confirmation experiment was further conducted, validating the efficacy of the model.

Transesterification of sunflower oil was carried out using low molecular weight alcohols and sodium hydroxide. For sunflower oil, a central composite design with eight factorial, six center and six axial points was used to study the effect of catalyst concentration, molar ratio of methanol to sunflower oil and reaction temperature on percentage yield of the biodiesel. Catalyst concentration and molar ratio of methanol to sunflower oil were the most influential variables affecting percentage conversion and percentage initial absorbance. Maximum percentage yield of 95 % is predicted at a catalyst concentration of 1.1 % (wt/wt) and methanol to sunflower oil molar ratio of 6.8:1 at reaction time of 66 min and temperature of 35°C. In general, the sunflower oil biodiesel exhibited friendly environmental benefits and acceptable stability, demonstrating its feasibility as an alternative fuel.

DEDICATION

I would like to dedicate my dissertation to my beloved parents, my wife and my children. To my parents, Nuor Abualkhair and Ali Abuhabaya who made all of this possible through the endless words of encouragement and undoubted confidence in me. Particularly, to my considerate wife, Aziza Ali, whose love, support, and inspiration have enlightened and entertained me throughout the course of this journey. To my children Omar, Nora, Salma, Halah, Abdulrahman, Aesha, Khadijah, Abdulaziz and Abdulmalek for bright future.

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PUBLICATIONS

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TERMINOLOGY

BDC	Bottom-dead-centre
BP	Brake power, kW
$BSFC$	Brake specific fuel consumption, g/kW/h
BUT	British thermal unit (1.06 kilojoules)
B5, B10, B15, B20	Bio-diesel and standard diesel blend of 5, 10, 15 and 20% bio-diesel by volume
CC	Cubic centimetre
CI	Compression ignition engine
CO	Carbon monoxide, percentage (%)
CO_2	Carbon dioxide, percentage (%)
C_2H_5OH	Ethanol
CV_f	Calorific value, MJ/kg
Eff	Brake thermal efficiency, %
EISA	Energy Independence and Security Act
ETBE	Ethyl tertiary butyl ether
FAAE	Fatty acid alkyl ester
FAEE	Fatty acid ethyl ester
FAME	Fatty acid methyl ester
FFA	Free fatty acid
gal	Gallon
GLY	Glycerol
h	Hour
THC	Total Hydrocarbon emission, part per million (ppm)
H_2SO_4	Sulphuric acid
HVO	Hydrogenated vegetable oil
IC	Internal combustion engine
KOH	Potassium hydroxide
M/O	Methanol to Oil molar ratio, 1 mol Methanol = 32g and 1 mol Oil = 91g
MeOH	Methanol
$\dot{m}_f$	Fuel consumption, g/sec
MG	Monoglyceride
min	Minute
N	Engine speed, revolutions per minute (rpm)
NaOH	Sodium hydroxide
NO_x	Oxide of nitrogen
O_2	Oxygen, %
ppm	Part-per-million
RPM	Revolution-per-minute
RSM	Response surface methodology
SI	Spark ignition engine
SOx	Sulphur oxide
T	Torque, Nm
TDC	Top-dead-centre
TG	Triglyceride
V_{st}	Stroke volume, m^3
ρ_f	Fuel density, kg/m^3
μ	Dynamic viscosity, Pa/s
v	Kinematic viscosity, mm^2/s
wt. %	Weight percentage

CHAPTER - 1

INTRODUCTION

1.1 Global perspective

Energy is very important for society as it is used to sustain and improve well-being. It exists in various forms, from many different sources. Historically, with economic development, energy needs grew, utilizing natural resources such as wood, hydro, fossil fuels, and nuclear energy in the preceding century. However, rising concerns on energy security, economic development, and climate change in the recent past have focused attention on using alternative sources of energy such as bio-fuels. Bio-fuels are the fuels produced from renewable resources, particularly plant derived materials. There are mainly two types of bio-fuels, first generation and second generation bio-fuels. The first generation bio-fuel is bio-diesel and bio-ethanol. Bio-diesel produced by transeseterifiction or reforming of vegetable oils and bio-ethanol produced by sugars/starch fermentation. On the other hand, second generation bio-fuel from lignin and cellulose such as wood straw etc. by hydrolysis to liquid fuel (not yet viable).

The drive towards low carbon emissions, and the recognition that current fossil fuel supplies are predicted to last possibly only 40 years, has focussed the attention of the automotive industry to towards alternative fuels supplies. Figure 1.1 shows the general energy distribution where it is seen that road transportation demands almost 16% of the available fuel sources. This is distributed between commercial vehicles and domestic vehicles as indicated in Figure 1.2. It can be seen that in general terms the industry is producing some 90 million units per year into a global market that already supports some one billion (10^9) units. Based on fundamental and conservative figures of 10,000 miles/year per unit this gives 10×10^{12} miles per year. If a consumption of 7 miles/litre is assumed then this represents a fuel demand of 1.4×10^{12} litres per year. Clearly with such demands, and increasing, then there is a need to seek an alternative fuel source to fossil fuels [254].

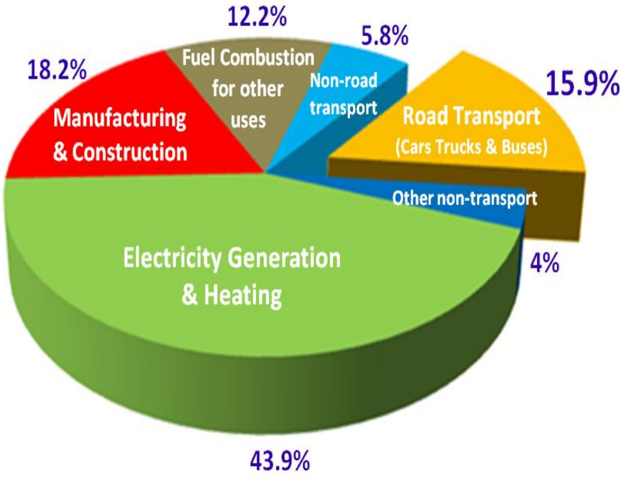
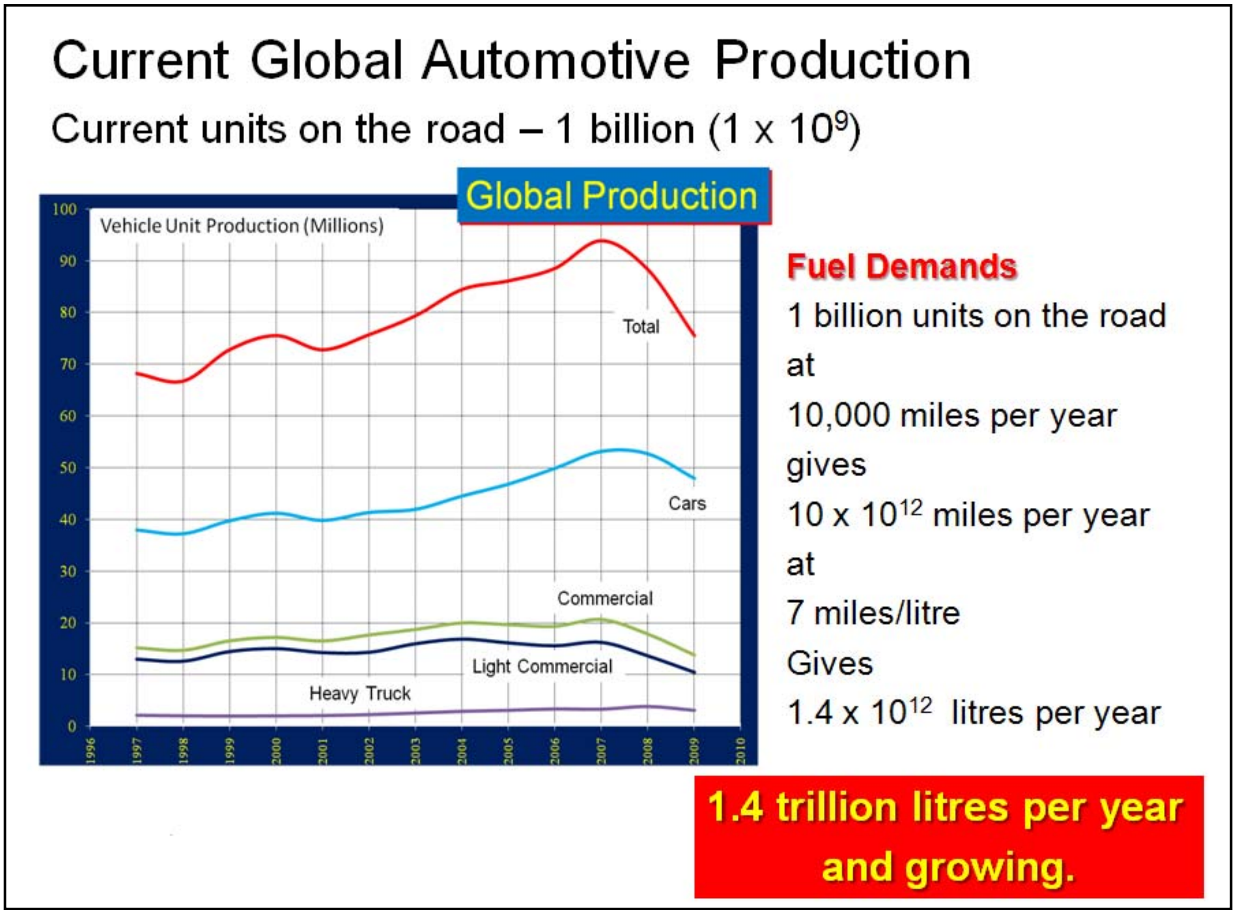


Figure 1.1: General energy distribution



Current Global Automotive Production

Current units on the road – 1 billion (1 x 10^9)

Fuel Demands

1 billion units on the road

at

10,000 miles per year

gives

10 x 10^{12} miles per year

at

7 miles/litre

Gives

1.4 x 10^{12} litres per year

1.4 trillion litres per year and growing.

Figure 1.2: Current Global Automotive Production

Bio-fuels have become a high priority in the European Union, Brazil, the United States and many other countries, due to concerns about oil dependence and interest in reducing greenhouse gas emissions. All these regions have provided massive subsidies, tax credits, tariff imposition and/or mandates for renewable energy production from agricultural sources. The impacts of these incentives and mandates reach far beyond the borders of these economies. In 2009, Brazil and the United States were the leading producers of ethanol, and their production is expected to reach 6.5 and 10.5 billion gallons, respectively, which accounts for more than 90 percent of the world's production, in 2008. As seen in Figure 1.3, world ethanol production has grown at a compound growth rate of 10 percent per annum since 1975, and it grew rapidly at 19 percent per annum from 2001 through 2008, which is attributed to the push towards ethanol in the United States. Similarly, world bio-diesel production has grown at a rate of 42 percent per annum since 1991; the majority of the boom coming from the bio-fuel initiative in the European Union countries [1-3].

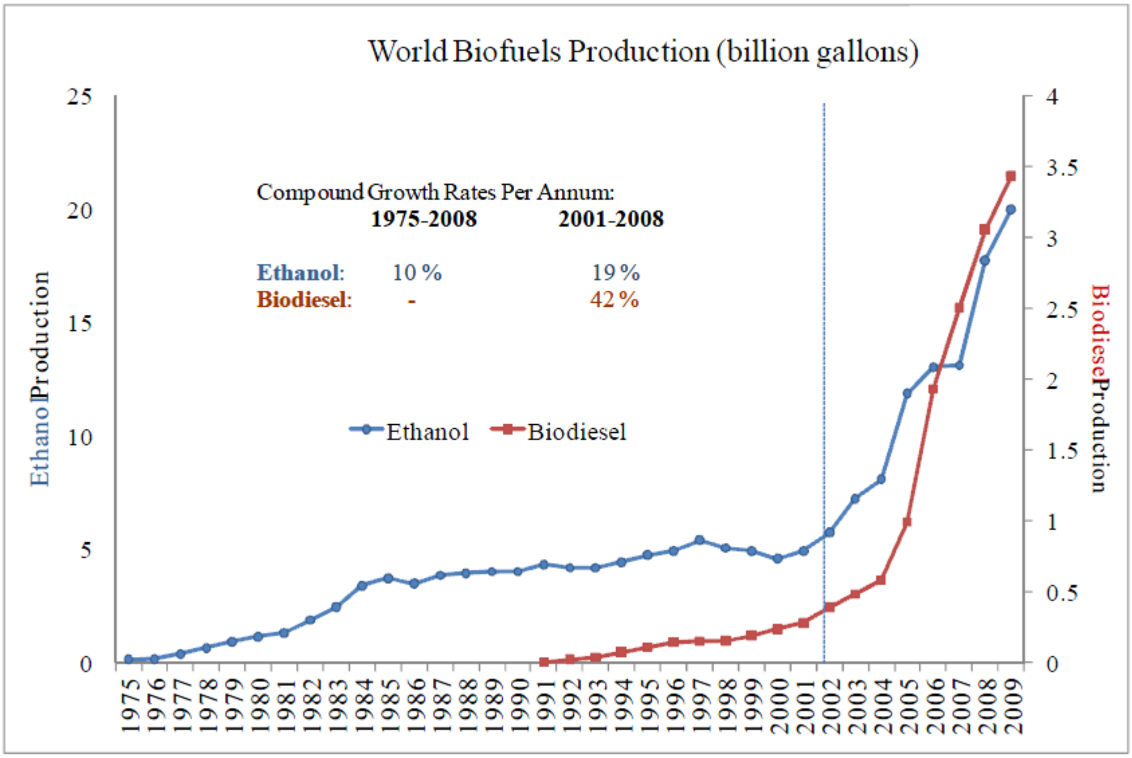


Figure 1.3: World Production of Ethanol and Bio-diesel (billion gallons) [1-3]

The passing of bio-fuel-friendly legislation in several countries has resulted in an exponential growth in global bio-fuel production. For instance, the "Energy Independence and Security Act (EISA) of 2007" in the United States, mandates a 'renewable fuels standard (RFS)' to use 36 billion gallons of renewable fuels per year by 2022. This includes a cap on corn starch-derived ethanol at 15 billion gallons and a 3 billion gallon increment of advanced bio-fuels every year starting 2015 until 2022 [4].

The European Union Bio-fuels Directive required that member states realize a 10% share of bio-fuels (on energy basis) in the liquid fuels market by 2020 [5]. The Renewable Energy Directive set an important framework for the future growth of the industry and paves the way for a stable investment climate. New technologies and applications of bio-fuels will be developed and marketed up to 2020. With this stimulation of the industry and a further coordinated development of bio-fuels throughout the EU and the possibilities of significantly reducing the oil dependence in the transport sector over the next years, the European bio-fuels industry is committed to reach the share of 10 % bio-fuels by 2020 [246].

However many member states such as Germany and France are marching towards greater use of bio-fuels. As seen from Table 1.1, Germany is the leading producer of bio-diesel (36% share in EU market) with the production of 851 million gallons during 2008, followed by the United States (700 mgy), France (540 mgy), Italy (180 mgy) and other countries (561 mgy). Also, the Table 1.1 shows bio-fuel as a proportion of fuel used.

Table 1.1: The World's Major Bio-fuel Producers During 2008 [1, 3, 247-250]

Ethanol Production			**Bio-diesel Production**			**Fuel used**		**Bio-fuel to Fuel used**
Country	Million gallon	World Share (%)	Country	Million gallon	World Share (%)	Country	Million gallon	Proportion (%)
USA	9,000	51.9	USA	700	19.4	Brazil	37,573	17.23
Brazil	6,472	37.3	EU-27	2,342	65.0	USA	294,809	3.29
EU-27	734	4.2	Germany	851(36%)		Germany	38,847	2.19
China	502	2.9	France	548(23%)		Colombia	4,127	1.91
Canada	238	1.4	Italy	180(8%)		Portugal	4,369	1.85
Thailand	90	0.5	Belgium	84(4%)		France	30,032	1.82
Colombia	79	0.5	Poland	83(4%)		Italy	24,781	0.73
India	66	0.4	Portugal	81(3%)		Canada	34,191	0.70
Australia	26	0.2	other EU	515(22%)		Thailand	14,106	0.64
Other	128	0.7	other	561	15.6	China	118,404	0.42
World	17,335	100		1,929	100	India	44,785	0.15

Brazil invested heavily in ethanol production during the energy crisis of 1970s and now has one of the world's most advanced production and distribution systems. Brazil is aiming to replace 10% of bio-fuel consumed worldwide by 2012, which requires it to export 20% of its current production [6]. For production of ethanol, France, Germany, Russia, United States, China, and Canada mainly use corn as their main feedstock, whereas, Brazil and India use sugarcane, which is more energy efficient as their production with 645 million tonnes and 348 million tonnes in 2011 respectively [251]. In China, about 80% of the ethanol is corn-based, with the remainder produced from cassava and wheat and in the United States, about 90% of the ethanol is produced from corn (about 22% of total corn production in 2007) [7].

For bio-diesel production, most of the European countries use rapeseed and sunflower oil as their main feedstock, soybean oil is the main feedstock in the United States. Palm oil in South-east Asia (Malaysia and Indonesia) and coconut oil in the Philippines are being considered. In addition, some species of plants yielding non-edible oils, e.g. jatropha, karanji and pongamia may play a significant role in providing resources.

1.2 Fuel demands past present and future

Due to the increasing global energy demand and limited fossil fuel reserves, one of the most daunting challenges facing science in the 21st century is to deliver solutions for future global energy needs in a sustainable manner [12]. There is also an increasing awareness that the utilization of fossil raw materials and fuels increases the net discharge of carbon dioxide (CO_2) into the atmosphere and contributes to the "green house effect" [13]. Thus, beside the energy problem, the other important challenge is to predict how Earth's ecosystems will respond to global climate change. On the other hand methane (CH_4) is considered to be the most prevalent greenhouse gas, and the build up of CH_4 causes global climate change [14]. The concentration of methane in Earth's atmosphere in 1998, was 1745 ppb (part per billion), up from 700 ppb in 1750. By 2008, however, global methane levels, which had stayed mostly flat since 1998, had risen to 1,800 ppb [14]. The desire to maintain sustainable development has led to an increasing interest in society for bio-fuels and the conversion of renewable biomass resources to liquid fuels.

Bio-fuels are biomass-based components of transport fuels, and are an interesting sustainable option for the transport sector. Unlike the combustion of fossil fuels which releases CO_2 that was captured several hundred million years ago, CO_2 released by during the utilization of a biomass based fuel is balanced by CO_2 captured in the recent growth of the biomass, resulting in far less net impact on greenhouse gas levels such as cellulosic materials, mostly wood, feedstock [15]. Since biomass utilization can be considered as a closed carbon cycle, the production and usage of bio-fuels is expected to reduce the net CO_2 emission significantly.

Generally, until recently, the need for bio-fuels remained a low priority, as petroleum supply and demand curves were satisfactorily addressed. Nonetheless, global petroleum demands have increased steadily from 56.2×10^6 barrels/day in 1975 to 85.9×10^6 barrels/day in 2007 [16]. The impact of this growth in demand, and limited global production capacity has been foretold by several organizations and individuals [12,17]. Coupled with these concerns, the contribution of combustion CO_2 from fossil fuels to climate change has been noted in several recent reviews [18,19], not to mention the use of fossil fuels also contributes to water pollution.

As described by Hoffert et al. [20], future reductions in the ecological footprint of energy will require a multi-faceted approach that includes the use of hydro, wind, nuclear, solar power, and fossil fuels (from which carbon is sequestered) and bio-fuels. In addition to the need to develop novel green technologies to reduce carbon emission in the future, existing green and low impact energy generation technologies should be implemented in existing industrial practices. A review by Pacala and Socolov [18], shed light on a portfolio of existing technologies capable of meeting the world's energy needs over the next 50 years and of limiting atmospheric CO_2 to a trajectory that avoids a doubling of the preindustrial concentration. By upgrading current industrial practices while implementing already existing green technologies at an industrial scale or increasing the amount and quality of implementation in industry, it is proposed that over the next fifty years the atmospheric CO_2 concentration can be limited to 500±50 ppm to prevent the most damaging climate change [18].

To be able to cover our global energy needs, the chosen renewable resources must have high energy content, be available in high volumes and be easily accessible at an affordable cost. Without meeting these four requirements the economical viability of any proposed renewable resource is questionable [12].

1.3 Current primary sources of fuel

Fossil fuels such as gasoline and diesel fuel are the most important source of energy for our society today, providing the bulk of global energy requirements for transportation, construction, heating, and agriculture. The excessive use of energy resources was a result of the belief that our energy resources would last for a considerably long period. This has resulted in the abusive use of our non-renewable energy sources like fossil fuels. The machines that use the non-renewable energy were not designed to use fuels efficiently and hence ended up accelerating the consumption of these resources. Given the finite amount of non-renewable energy, it is imperative to conserve the current sources or to use renewable sources to compliment the use of the non-renewable resources.

Many new developments in technology have made alternative sources of energy more economically feasible including advances in solar, wind, geothermal and nuclear energy. The advancement of technology has consistently increased the viability of these alternative sources as serious supplements to the world's energy needs [21].

Renewable energy is consumed across all energy use sectors - residential, commercial, industrial, transportation and the electric power industry as shown in Figure 1.1. The two sectors which consume the most are electric power and industrial, though patterns are changing. In 2008, the electric power sector accounted for 51% of renewable energy consumption and the industrial sector 28%, down from 56% and 30%, respectively, in 2004. This was due in some measure to the substantial change in the transportation sector, whose share rose from 5% to 11% between 2004 and 2008. The increase was due to increased consumption of bio-fuels, primarily ethanol derived from corn, but also to a lesser extent bio-diesel.

Table 1.2: Oil Yield for Various Products

Crop	Yield - US gallons/acre	Estimation of Water Requirement inches/acre
Corn	18	20-25
Cashew nut	19	15-20
Oats	23	15-20
Cotton	35	30-40
Soybean	48	15-20
Coffee	49	30-45

pumpkin seed	57	25-30
mustard seed	61	25-30
Rice	88	30-40
sunflowers	102	20-30
Cocoa	110	35-45
Peanuts	113	20-30
Rapeseed	127	25-30
Olives	129	15-20
castor beans	151	15-20
pecan nuts	191	15-20
Jatropha	202	20-30
macadamia nuts	240	15-20
brazil nuts	255	15-20
Coconut	287	30-40
Oil palm	635	20-30

Bio-diesel is a type of bio-fuel that is derived from vegetable oils, animal fats or recycled grease. However, as many people have already realized, using corn as a fuel source - when so many people in the world are starving - is not the wisest solution to meet the need for renewable energy. In addition the yield from edible food-stock is not really the best to use unless there is surplus stock – see Table 1.2.

1.3.1 Solar Energy

Concentrated solar thermal power plants produce power by converting the sun's energy into electricity. High temperatures are generated through concentration of the sun’s rays via mirrors. Solar thermal plants then transfer this energy through some heat transfer medium which in turn is used to rotate a turbine and generate electricity. The concept of using the sun's electromagnetic radiation to convert to other forms of energy has been used for many centuries. The sun supplies a significant amount of energy to the surface of the earth, and forty minutes of irradiance is enough to match the world's annual needs. The solar constant is the amount of incoming solar electromagnetic radiation per unit area, measured on the outer surface of Earth's atmosphere. The Solar constant is 1367 Watts.m^{-2} [22].

1.3.2 Wind Energy

Wind energy has been used since early history, propelling boats in 5000 B.C. along the Nile River. The popularity of wind energy tends to rise with the rise in oil prices. Wind is a form of solar energy, as they result from uneven heating of the atmosphere by the sun, the irregularities of the earth's surface, and rotation of the earth. Modern wind turbines fall into two basic groups: the horizontal-axis variety and the vertical axis design. Horizontal-axis wind turbines typically either have two or three blades. These three-bladed wind turbines are operated upwind, with the blades facing into the wind. Utility-scale turbines range in size from 100 kilowatts to as large as several megawatts. Larger turbines are grouped together into wind farms, which provide bulk power to the electrical grid.

Wind turbines don't produce emissions (except noise) and wind is a domestic source of energy, with an unlimited potential. Wind energy is one of the lowest-priced renewable energy technologies available today, costing between 3.8 and 5.5 pence per kilowatt-hour, depending upon the wind resource and financing of the particular project. Wind turbines can be built on hillsides, thus benefiting the economy in rural areas, where many of the best wind sites are found. Farmers can continue to work the land because the wind turbines use only a fraction of the land. Wind power plant owners make rent payments to the farmer or rancher for the use of the land. The major disadvantage is that wind power must compete with conventional generation sources on a cost basis. Despite technological developments through the years, the cost of production is still relatively expensive. Wind energy is not available at all times and this is a limiting factor, batteries must be used to store energy for times when the wind is unavailable. Other concerns include the production of very loud noise and vibration by the rotor blades, the adverse visual impacts of having wind mills scattered across the land, and many birds killed by flying into the rotors [23].

1.3.3 Standard Diesel Fuel

Diesel fuel is used in high-compression engines. Air is compressed until it is heated above the auto-ignition temperature of diesel. Then the fuel is injected as a high pressure spray. There is no separate ignition source. As a result, diesel is required to have a high flash point and a low auto-ignition temperature. The flashpoint of a fuel is the lowest temperature at which it can form an ignitable mix with air. The high flash point of diesel fuel means that it does not burn as easily as gasoline, which is a safety factor. Too low a flash point is a fire hazard because ignition may continue and lead to explosion. Auto-ignition temperature is the temperature at which a substance can be ignited without any external source, such as a spark or flame.

The problem of generating harmful combustion products such as particulate matter (PM), aldehydes, polycyclic aromatic hydrocarbons (PAHs), CO, NOx, and unburned hydrocarbons is of great health and environmental concern. Although the level of these emissions has been falling with technical improvements, any further reduction of these pollutants through the traditional combustion process requires disproportionately greater efforts and expenditure of resources. Accordingly, a new revolutionary method is required to solve these problems [25].

1.3.4 Bio-diesel Fuel

Bio-diesel, as defined by the American Society for Testing and Materials (ASTM), is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Due to the great molecular similarities between bio-diesel and petroleum-based diesel, this alternative fuel has a chance of fulfilling the technical requirements of diesel fuel [26]. It is a domestic, clean-burning, renewable liquid fuel that can be used in compression-ignition engines instead of petroleum-based diesel with little or no modifications. The dominant bio-diesel production process, namely transesterification, typically involves the reaction of an alkyl-alcohol with a long chain ester linkage in the presence of a catalyst to yield mono-alkyl esters (bio-diesel) and glycerol.

The idea of using vegetable oil as a fuel dates back to 1895, when Dr. Rudolf Diesel developed the first diesel engine with the intention of running it on a variety of fuels [27]. The engine was demonstrated at the World Exhibition in 1900 in Paris operating on oil extracted from peanuts. Since his death in 1913, his engine has been modified to run on petroleum-based diesel fuel and it was not until the 1970's that interest in bio-diesel was instigated. Today, bio-diesel fuels have been commercialised in many countries, including Austria, Czech Republic, Germany, France, Italy, Slovakia, Spain, and the USA.

The difference between bio-diesel and petroleum diesel lies in the name itself. Petroleum diesel is 100% petroleum based and considered as a fossil fuel. On the other hand bio-diesel is created from live feedstock such as vegetable oil, peanut oil, coconut oil, even algae oil. Bio-diesel can be used as a direct fuel considered B100, or in its unrefined form of vegetable oil. Many of these vegetable oils are similar in properties to those of petroleum diesel, the main difference is that vegetable oils and bio-diesels have a lower oxidative stability state, a higher viscosity coefficient, and a higher volatility point. These properties make bio-diesel blends a suitable candidate for an immediate alternative energy fuel [28].

Bio-diesel blends are more commonly used than pure B100 fuels. The main reason for this is that running 100% bio-diesel sometimes requires modifications to the engine, due to the higher content of alcohol present in bio-diesel. These modifications require fuel lines to be changed to steel, as alcohol will corrode the rubber lines more commonly used. Because only 1 percent of petrol is toxic enough to prevent the formation of mould it is common to use B99 (99 % bio-diesel and 1% petroleum diesel) instead of B100. The letter "B" designates the type of fuel, in this case Bio-diesel, while the number after it designates the percentage of bio-diesel. B5 contains 5% bio-diesel mixed with 95% petroleum diesel. Following this rule, B20 has 20% bio-diesel and 80% petroleum diesel. Blending the two different diesel fuels, allows the fuel to have the benefits of the lower emissions present in bio-diesel, while allowing for a lower concentration of alcohol which allows for the engine to run without any modifications.

The cost of bio-diesel production, however, is higher than that of petroleum-based diesel production: UK £0.24-0.40 per litre bio-diesel compared to UK £0.17-0.25 per litre petroleum diesel. Commercial scale bio-diesel production utilizes homogeneous base-catalysed technologies requiring highly refined virgin vegetable oils as raw materials. Conversely, acidic-catalysed processes allow for the use of lower cost feedstocks such as waste cooking oils that contain significant amounts of free fatty acid (FFA). Krawczyk [27] stated that almost 70-95% of the total bio-diesel production cost arises from the cost of the raw materials, and that reducing the cost of feedstock is necessary for bio-diesel's long-term viability. Waste cooking oils are a more economically viable source of biomass than pure vegetable oils and are a promising alternative to vegetable oils for bio-diesel production [29]. The advantages of bio-diesel used as diesel fuel are [30]:

- Liquid nature-portability.
- Ready availability.
- Renewability.
- Higher heat content (about 88% of diesel fuel).
- Lower sulphur content.
- Lower aromatic content.
- Bio-degradability.
- Bio-diesel has similar Cetane number to diesel fuel; this indicates a potential for higher engine performance close to that of diesel fuelled engines.
- The superior lubricating properties.

- Their higher flash point makes them safer to store.
- They contain higher amount oxygen (up to 11%) that ensures more complete combustion of hydrocarbons and better auto-ignition processes.
- Bio-diesel almost completely eliminates lifecycle carbon dioxide emissions.

Some of the drawbacks are: [30]

- Bio-diesel tends to affect rubber hoses and gaskets.
- Possible concerns with engine warranties.
- Special measures that must be taken to use Bio-diesel in cold climates.
- Higher cost than petro-diesel.
- Limited commercial availability.
- Higher viscosity.
- Lower volatility.
- The reactivity of unsaturated hydrocarbon chains.
- Under certain load conditions Bio-diesel has higher fuel consumption compared to conventional diesel.

1.3.4.1 Fuel injection equipment (FIE)

Diesel fuel injection equipment (FIE) manufactures fully support the development of alternative sources of fuel for compression ignition engines. In Europe and the United States of America, as well as other countries, fuel resources such as rapeseed methyl ester and soybean methyl ester, collectively known as fatty acid methyl esters (FAME), are being used as alternatives and extenders for mineral oil derived fuels.

The FIE manufactures are aware of issues particular to bio-diesel fuels, and have been active in the generation of standards for these fuels. At the time of first common position statement in 2000 there existed national standards for vegetable oil methyl esters in Austria, Italy, Germany and France. The European FAME standard EN14214 shown in Table 1.3 was ratified in 2003 and supersedes these national standards. EN 14214 provides the minimum requirements for FAME quality whether used as pure FAME or as a blend component.

To date, experience in Europe has been mainly associated with the methyl esters of rapeseed oil. Whether or not the service experience with these fuels will apply/extend to all FAME (like those derived from soybean, tallow and used frying oil) has yet to be determined.

1.3.4.2 FIE manufactures concerns

FAMEs are derived from a wide range of base stocks, resulting in a similarly wide range of fuel characteristics. Amongst the concerns of the FIE manufactures are the following fuel characteristics:

- Free methanol
- Water
- Free glycerine
- Mono, di- and triglycerides
- Free fatty acids
- Total solid impurity level
- Alkali/alkaline earth metals
- Oxidation stability

Table 1.3: European FAME standards EN 14214

EN 14214 - Property	Units	lower limit	upper limit	Test-Method
Ester content	% (m/m)	96,5	-	EN 14103
Density at 15°C	kg/m³	860	900	EN ISO 3675 / EN ISO 12185.
Viscosity at 40°C	mm²/s	3,5	5,0	EN ISO 3104
Flash point	°C	> 101	-	ISO 3679
Sulfur content	mg/kg	-	10	-
Tar remnant (at 10% distillation remnant)	% (m/m)	-	0,3	EN ISO 10370
Cetane number	-	51,0	-	EN ISO 5165
Sulfated ash content	% (m/m)	-	0,02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper band corrosion (3 hours at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Thermal Stability	-	-	-	-
Oxidation stability, 110°C	hours	6	-	EN 14112
Acid value	mg KOH/g	-	0,5	EN 14104
Iodine value	-	-	120	EN 14111
Linolic Acid Methylester	% (m/m)	-	12	EN 14103
Polyunsaturated (>= 4 Double bonds) Methylester	% (m/m)	-	1	-
Methanol content	% (m/m)	-	0,2	EN 14110
Monoglyceride content	% (m/m)	-	0,8	EN 14105
Diglyceride content	% (m/m)	-	0,2	EN 14105

Triglyceride content	% (m/m)	-	0,2	EN 14105
Free Glycerine	% (m/m)	-	0,02	EN 14105 / EN 14106
Total Glycerine	% (m/m)	-	0,25	EN 14105
Alkali Metals (Na+K)	mg/kg	-	5	EN 14108 / EN 14109
Phosphorus content	mg/kg	-	10	EN 14107

All FAMEs are less stable than mineral oil derived fuels. FAMEs are readily “bio-degradable” in the event of accidental spillage or leakage, which is claimed to be a marketing advantage. On the other hand, the reduced thermal oxidative stability is of major concern to the FIE manufactures, as the products of fuel ageing can be potentially harmful to the fuel system, see to the Table 1.4.

Table 1.4: Fuel injection Equipment-Potential Problems with FAME

Fuel characteristic	Effect	Failure mode
Fatty acid methyl ester	Softening, swelling hardening and cracking of some elastomers including nitrile rubbers (physical effect depends upon elastomer composition) Displacement of deposits from diesel operation	Fuel leakage Filter plugging
Free methanol in FAME	Corrosion of aluminium and zinc Low flash point	Corrosion of FIE
FAME process chemicals	Entry of potassium and sodium and water hardness (alkaline earth metals) Entry of free fatty acids hastens the corrosion of non ferrous metals, e.g. zinc Salt formation with organic acids (soaps) Sedimentation	Filter plugging Corrosion of FIE Filter plugging Sticking moving parts
Free water	Reversion (Hydrolysis) of FAME to fatty acid and methanol Corrosion Sustainment of bacterial growth Increase of electrical conductivity of the fuel	Corrosion of FIE Filter plugging
Free glycerine	Corrosion of non-ferrous metals Soaking of cellulose filters Sediment on moving parts and lacquering	Filter plugging Injector coking
Mono-,di- and tri-glyceride	Similar to glycerine	Injector coking
Higher modulus of elasticity	Increase of injection pressure	Injector coking
High viscosity at low temperature	Generation of excessive heat locally in rotary type distributor pumps	Fuel delivery problems Pumps seizures

	Higher stressing of components	Early life failures Poor nozzle spray atomization
Solid impurities / particles	Potential lubricity problems	Reduced service life Nozzle seat wear Blocked nozzles
Ageing products		
Corrosive acids (formic & acetic)	Corrosion of all metal parts May form simple cell	Corrosion of FIE
Higher molecular organic acids	Similar to fatty acid	
Polymerisation products	Deposits, precipitation especially from fuel mixes	Filter plugging Lacquer formation by soluble Polymers in hot areas

1.3.5 Methanol as Fuel

Methanol is an alcohol made from natural gas [31]. The first step in its production uses steam re-forming to convert the natural gas to synthesis gas (syngas). In a second step, and after removal of impurities, carbon monoxide and hydrogen are catalytically removed to give methanol. It can also be produced from biomass, i.e. cellulosic materials, mostly wood [32]. The raw material must first be prepared by milling, grinding and drying, and is then converted into syngas and then into methanol.

1.3.6 Ethanol as Fuel

Ethanol can be produced from biomass (crops rich in sugar, starch or cellulosic material) rather than from natural gas [33]. Its manufacture involves the fermentation of sugar, using yeast. Because sugar (glucose) occurs as such in only very few plants, larger carbohydrate molecules have to be cracked by hydrolysis to fermentable sugar, after the raw material has been size controlled by splintering and milling. Varied hydrolysis techniques reflect the most important differences in production methods required by different feed stocks. Both spark ignition and diesel engines can use ethanol. It can be used mixtured with gasoline, both as a fuel, or after conversion into ETBE (Ethyl Tertiary Butyl Ether), an anti-knock additive. Ethanol yields lower carbon dioxide (CO_2) emissions than gasoline and diesel. It produces low carbon monoxide (CO) and unburned hydrocarbons (HCs) emissions compared with gasoline but higher ones compared with diesel.

1.3.7 Electric Vehicles

Decreased fuel consumption, or the elimination of the direct use fossil fuel all together can be seen as the biggest overall benefit of electric vehicles. This reduction or elimination of combustion potentially reduces overall green house gas emissions and pollution. Electric vehicles have the ability to provide emission free urban transportation. If the power plants that generate the electricity are taken into consideration, overall emissions are still greatly reduced [34]. Electric vehicles also greatly reduce the level of noise pollution. The design of electric vehicles involves the integration of mechanical and electrical systems and, as such, a thorough understanding of the components that make up the vehicles is important.

Electric vehicles come in many forms using many different technologies, but is mainly comprised of three sections: (i) an energy storage device, (ii) an electric drive and (iii) an electric motor. There may also be a mechanical transmission that will link the electric motor to the drive wheels of the vehicle. The electric drive has the job of controlling the flow of energy through to the traction motor. The drive may also have the capability of controlling the flow of energy from the drive tyres through to the energy storage device. This is known as regenerative braking [35].

1.3.8 Fuel Cell

Hydrogen in either a compressed or liquid form can be converted into electrical energy by a hydrogen fuel cell through catalysis. Fuel cells are considered to be the most promising but least developed technology for automobile propulsion. A simple way to describe a fuel cell is as an easily refillable electric battery. Although fuel cells do not store energy, they converted the energy by combining the hydrogen with oxygen. The technology is promising as there are no direct green house gas emissions or by-products. The result of the hydrogen-oxygen catalysis is pure water.

1.4 First and second generation bio-fuel

1.4.1 First Generation bio-fuel

First-generation bio-fuels are produced in two ways. One way is through the fermentation of either a starch-based food product, such as corn kernels, or a sugar-based food product, such as sugar cane, into ethanol, also known as ethyl alcohol, or "gasohol." Another way is by processing vegetable oils, such as soy, rapeseed and palm, into bio-diesel, a nonpetroleum-based diesel fuel. The conventional process is shown in Figure 1.4. The oil is obtained using the conventional techniques of production. Some of the most popular types of first generation bio-fuels are: Bio-diesel: This is the type of bio-fuel most commonly used in

Europe and is mainly produced using a process called transesterification. This fuel if very similar to mineral diesel and is chemically known as fatty acid methyl. This oil is produced after mixing the biomass with methanol and sodium hydroxide in a chemical reaction which produces bio-diesel. Bio-diesel is very commonly used for diesel engines after mixing up with mineral diesel, so much so that in many countries the manufacturers of diesel engines ensure that the engine works well with bio-diesel.

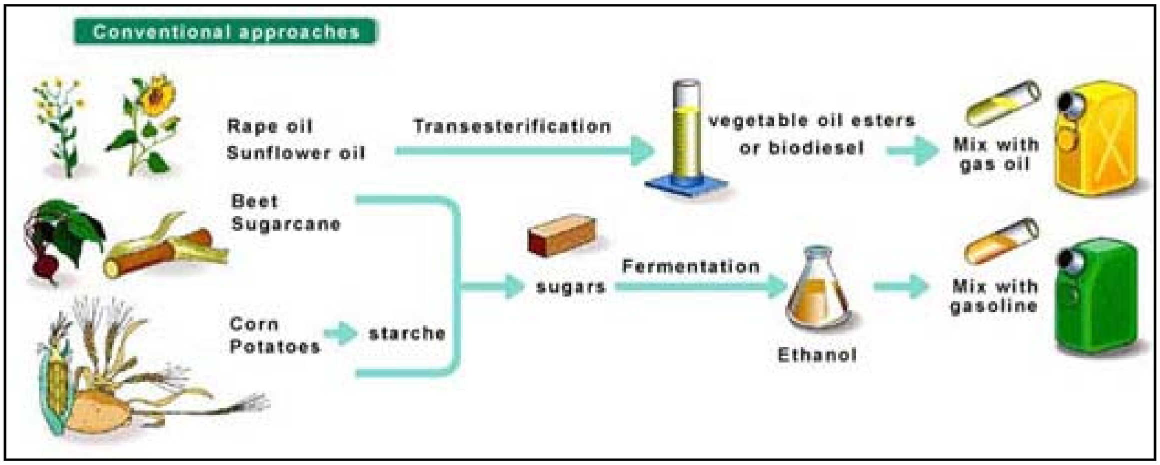


Figure 1.4: Conventional process of producing first generation bio-fuels [36]

Vegetable oil: These kinds of oil can be used not only for cooking purpose but also as fuel. The main fact that determines the usage of this oil is its quality with good quality oil generally retained for cooking purpose. Vegetable oil can be used directly in most old diesel engines, but only in a warm atmosphere. In most countries, vegetable oil is mainly used for the production of bio-diesel, see Figure 1.5.

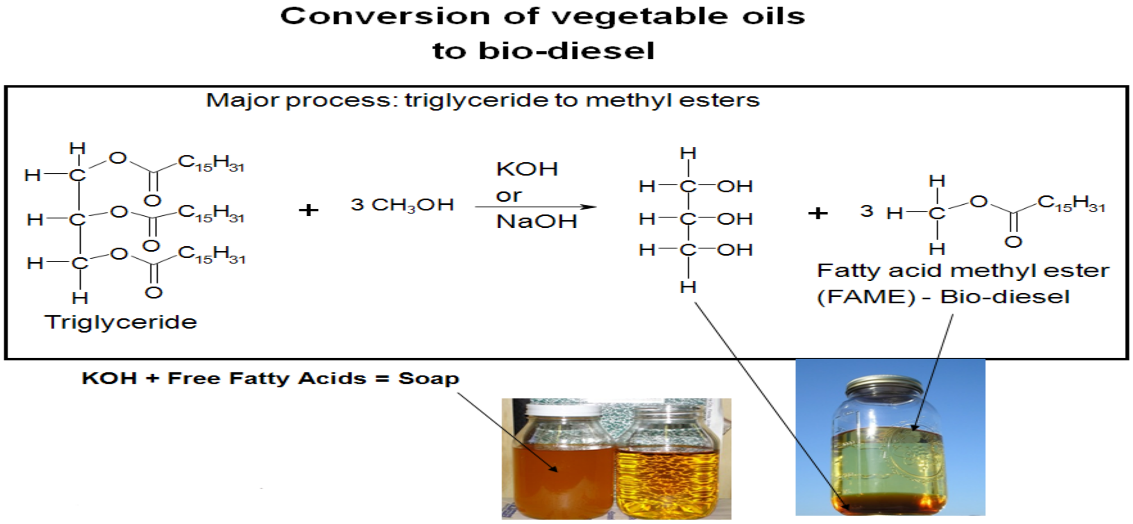


Figure 1.5: Conventional of vegetable oils to bio-diesel

Biogas: Biogas is mainly produced after the anaerobic digestion of organic materials. Biogas can also be produced from the biodegradation of waste materials which are fed into anaerobic digesters and which yield biogas. The residue or the by-product can be used as manure or fertilizers for agricultural use. The biogas produced is very rich in methane which can be easily recovered through the use of mechanical or biological treatment systems. A less clean form of biogas is landfill gas which is produced by the use of naturally occurring anaerobic digesters, but these gases can be a severe threat if they escape into the atmosphere.

Bioalcohols: These are alcohols produced by the use of enzymes and micro organisms through the process of fermentation of starches and sugar. Ethanol is the most common type of bioalcohol whereas butanol and propanol are some of the less common ones. Butanol is produced using the process of acetone-butanol-ethanol (ABE) fermentation, and experiments have demonstrated that butanol is a more energy efficient fuel and can be directly used in the various gasoline engines. Thus biobutanol is sometimes referred to as a direct replacement for gasoline [36].

Syngas: This is a gas that is produce after the combined process of gasification, combustion and pyrolysis. Bio-fuel used in this process is converted into carbon monoxide and then into energy by pyrolysis. During the process, a very little oxygen is supplied to keep the combustion under control. In the last step known as gasification the organic materials are converted into gases such as carbon monoxide and hydrogen. The resulting gas, syngas, can be used as a fuel of internal combustion engines or as an intermediate for the production of other chemicals.

1.4.2 Second Generation bio-fuel

Second-generation bio-fuels (hydrogenated vegetable oil (HVO), synthetic diesel, bioethanol (more advanced than 1st generation) can be produced from ‘plant biomass’ which tends to refers to lignocellulosic materials (whole parts of plants). These second-generation, or "advanced," bio-fuels, are made from non-food sources, and hold significant promise as a low-carbon, renewable transportation fuel that can complement traditional petroleum-based fuels in meeting the world's future some of energy needs. The process of making alcohol from lignocellulosic biomass, in principle, is relatively simple: after hydrolysis and a subsequent fermentation, the ethanol can be refined by distillation as shown in Figure 1.6 [43].

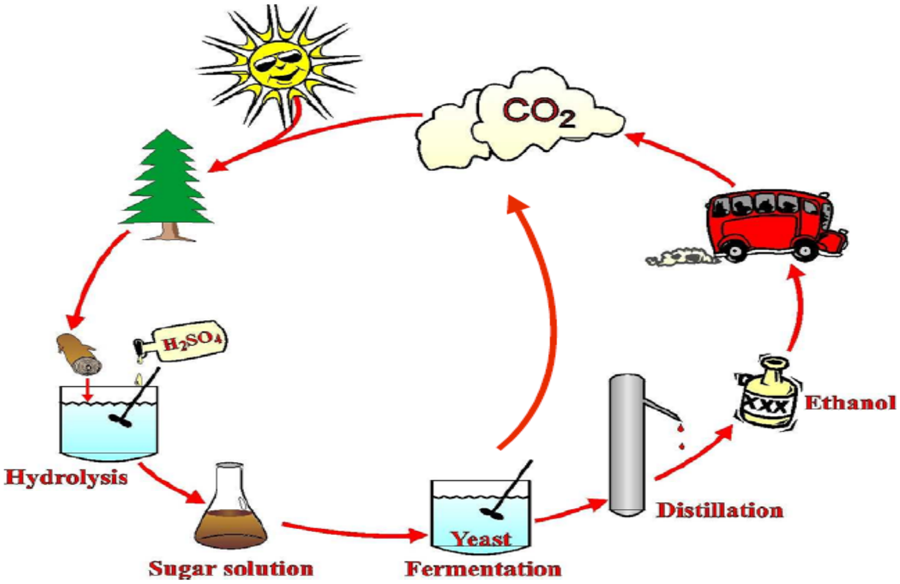


Figure 1.6: Second generation bio-fuel [44]

Although using cellulosic biomass as a source of new transportation fuels has obvious advantages, these materials have different chemical structural bonds than food-based crops and are difficult to break down, especially on a large scale. However, these second-generation fuels may play an important role in diversifying the world's energy sources and curbing greenhouse gas emissions [37].

1.4.3 Recycled Fuels

Waste vegetable oil (WVO) is known as a second generation bio-diesel. WVO is collected from restaurants, and while usually is free to the user requires extensive cleaning and refining before it can be turned into a bio-diesel fuel. One of the main advantages to WVO is the ability to recycle a product. Waste vegetable oil needs to be disposed of properly and usually requires an added cost to the restaurant to do so. By using these base oils as a fuel the restaurants save money, and the oil is further utilized. Production of bio-diesel using pure vegetable oil means that large quantities of agricultural resources like corn, palm, and canola are required. This usually causes, on larger scales, a fight for the rights to these agricultural products. These pure vegetable oils are extracted from food, and as bio-diesel becomes more popular and its price rises, farmers tend to reserve their crops for the fuel industry to obtain a steady income.

1.5 Crop yield

There is growing concern that diversion of agricultural land for biomass plantations or the direct conversion of food to fuel could lead to decreased availability of land for food production, particularly in low-income countries [38,39]. In particular, the use of arable land for production of food crops as a feedstock for bio-fuels has received widespread international criticism. A United Nations spokesperson on the right of food, Jean Siegler, reported by the BBC, recently characterized the practice of using land to grow bio-fuel crops as a "crime against humanity" that would bring more hunger to the world [41]. Such analyses are increasingly common as global food price rise sharply, in part due to the use of arable land for bio-fuel crop production as shown in Figure 1.7.

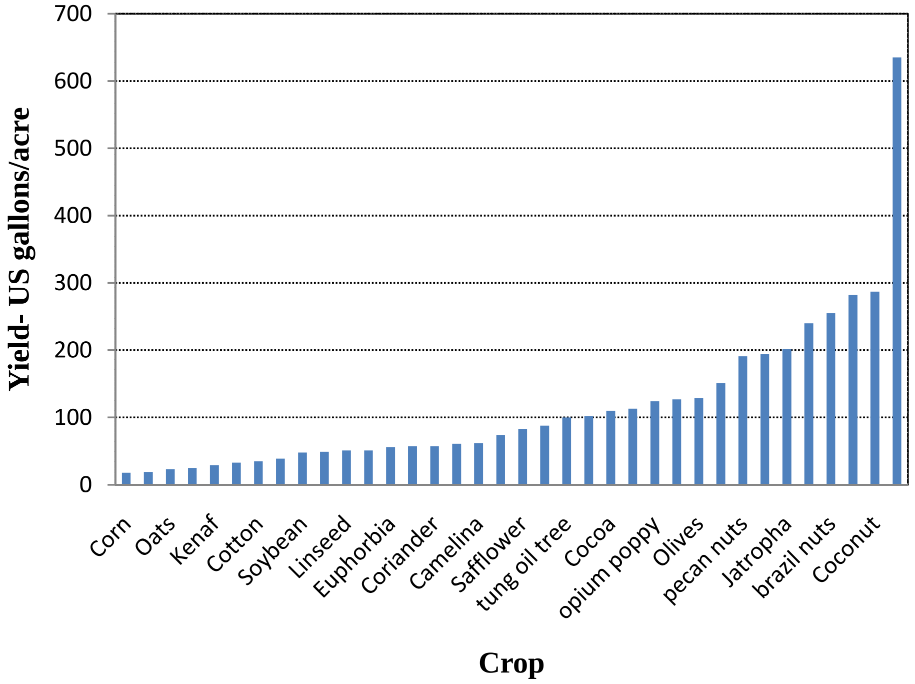


Figure 1.7: Oil Yield for Various Products

Nonhebel [40] showed that in developing countries there is insufficient land to meet the needs for both food and energy when biomass plantations are substituted for arable land. He does, however, conclude that biomass energy will be the most likely renewable energy source in the near future; therefore, there is a need for research to find a way to resolve this tension.

Virgin oil feedstock, rapeseed and soybean oils are commonly used for bio-diesel production. Soybean oil alone accounts for about ninety percent of all relevant fuel stocks in the United States [45]. At the same time, the positive attributes of pure vegetable oil need to be balanced against the limited global production of plant oils since the production of vegetable oils for use as fuels is limited by the agricultural capacity of a given economy. It is important to note that soybeans are also a food resource; if not used to produce bio-diesel, 81% of the soybean's yield is protein such as textured vegetable protein (soybeans produce significantly more protein per acre than most other uses of land) will be used for either human consumption or animal feed [46]. Due to production limitations of feedstock, there is a constant search for next generation technologies that may address these problems by technological advances and/or increase soybean yields from existing acreage [47].

1.6 Properties of Vegetable Oils

The physical fuel properties of vegetable oils are listed in Table 1.5. This table indicates that the kinematic viscosity of vegetable oils varies from 30-40 mm/s^2 at 38^{o}C. The high viscosity of these oils is due to their larger molecular mass than that of diesel fuel. The flash point of vegetable oils is very high (above 200^{o}C). The calorific heating values are in the range of 39-40 MJ/kg, while diesel fuel is about 44 MJ/kg. This explains the higher fuel consumption with bio-diesel under some operating conditions. The presence of chemically bound oxygen in vegetable oils lowers their heating values by about 10%. The Cetane numbers are in the range of 32-40, which is close to that of diesel [15].

Table 1.5: Properties of vegetable oils [15]

Vegetable Oil	Kinematic Viscosity At 38^{o}C (mm^2/s)	Cetane Number	Heating Value (MJ/kg)	Cloud Point (^{o}C)	Pour Point (^{o}C)	Flash Point (^{o}C)	Density (kg/l)
Corn	34.9	37.6	39.5	-1.1	-40.0	277	0.9095
Cottonseed	33.5	41.8	39.5	1.7	-15.0	234	0.9148
Crambe	53.6	44.6	40.5	10.0	-12.2	274	0.948
Linseed	27.2	34.6	39.3	1.7	-15.0	241	0.9236
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026
Rapeseed	37	37.6	39.7	-3.9	-31.7	246	0.9115
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144

Sesame	35.3	40.2	39.3	-3.9	-9.4	260	0.9133
Soya Bean	32.6	37.9	39.6	-3.9	-12.2	254	09138
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161
Palm	39.6	42	-	31.0	-	267	0.9180
Babasu	30.3	38	-	20.0	-	150	0.9460
Diesel	3.06	50	43.8	-	-16.0	76	0.8550

The biggest and probably most important difference in properties is the high viscosity coefficient of vegetable oil, typically about ten times the value for diesel. This property alone makes bio-diesel a superior fuel than its petroleum counterpart, and suggests that bio-diesel can prevent wear and tear on engine parts and components, while decreasing harmful emissions. The coefficient of viscosity is a number that refers to the capability of a liquid to drain by gravity. This is further explained as a fluid's internal resistance to flow or considered to be fluid friction. The coefficient of viscosity is known either as kinematic viscosity (v) [mm^2/s], or dynamic viscosity (μ) [Pa.s]. Figure 1.8 shows this phenomenon more clearly. Consider a liquid flowing steadily over a smooth horizontal surface. It will be observed that the liquid flows in layers or planes parallel to the bottom. The layer which is in immediate contact with the bottom surface is at rest. The velocity of the different layers increases gradually (Laminar flow) as the reference plane moves away from the bottom (static surface) towards the top of the fluid (main flow plane), where it is a maximum. The viscous or drag force on a fluid layer is proportional to the viscosity of the fluid and difference in velocity between the top and bottom of the layer. The velocity profile shown in Figure 1.8 will generally be parabolic.

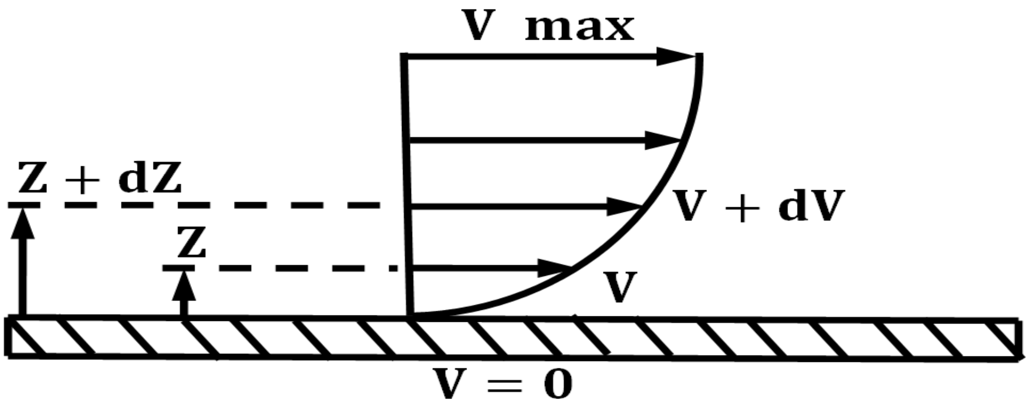


Figure 1.8: Example of a fluid flow into a line [16]

Dynamic viscosity μ provides the properties observed in bio-diesel fuels which prevent high friction between the fuel and the engine. Lower friction means less frictional force to be converted to heat, and thus less wear and tear. Dynamic viscosity is given by the Equation (1.1):

$$F = \mu S\, dv/dz \tag{1.1}$$

Where:

$F = frictional\ drag\ force\ (N)$

$\mu = Dynamic\ viscosity\ \left(\frac{N.s}{m^2}\right)$

$S = Area\ of\ the\ layer\ being\ considered\ (m^2)$

$\frac{dv}{dz} = Shear\ velocity\ (fraction\ velocity) where\ v\ \left(\frac{m}{s}\right) and\ z\ (m) as\ shown\ the\ figure$

The Kinematic viscosity is as shown in Equation (1.2):

$$v = \mu/\rho \tag{1.2}$$

Where:

$v = Kinamatic\ viscosity\ \left(\frac{m^2}{s}\right)$

$\mu = Dynamic\ viscosity\ \left(\frac{N.s}{m^2}\right)$

$\rho = Density\ of\ the\ fluid\ \left(\frac{kg}{m^3}\right)$

Bio-diesel is created by a process which the industry refers to as esterification or transesterification: here the chemical properties of the base vegetable oil are modified. Transesterification leads to engine combustion benefits which include a reduced viscosity, a complete removal of glycerin, a higher boiling point, a higher flash point and a lowered pour point [17]. All benefits which provide a more stable fuel and allow the diesel engine to have a more complete air fuel mixture before combustion.

1.6.1 Types of base vegetable oil for bio-diesel production

First-generation bio-diesel can be produced straight from vegetable oil, also called pure plant oil, a refined oil which has not been used for cooking. This allows for the bio-diesel to be produced in less time, since refining and cleaning are eliminated. The pure base vegetable oil also has a lower acidic level which, in turn, requires less methanol and catalyst for a successful chemical reaction. The second type of base vegetable oil is known as a second generation of bio-diesel and is made from WVO which requires extensive cleaning and refining before it can be turned into a bio-diesel fuel. One of the main advantages to WVO is that a product is recycled.

1.6.2 Transesterification process

Due to their high viscosity and low volatility, vegetable oils do not burn completely and tend to form deposits in the fuel injector of diesel engines. Different ways have been considered to reduce the high viscosity of vegetable oils:

- Dilution using regular diesel.
- Micro emulsions with short chain alcohols such as ethanol or methanol.
- Thermal decomposition, which produces alkanes, alkenes, carboxylic acids and aromatic compounds.
- Catalytic cracking, which produces alkanes, cyclo alkanes and alkyl benzenes.
- Transesterification with ethanol or methanol.

In order to reduce the higher viscosity of bio-fuels and enhance its performance, the most effective method is a process called transesterification. In this process glycerol, which makes the fuel denser, is extracted to obtain a fuel that is less viscous. There are three basic routes to ester production from oils and fats:

- Base catalyzed esterification of the oil with alcohol.
- Direct acid catalyzed esterification of the oil with methanol.
- Conversion of the oil to fatty acids, and then to alkyl esters with acid catalysis.

For several economic reasons, the majority of alkyl esters produced today is by the base catalysed reaction. Some of the reasons for this are:

- Low temperature (65°C) and pressure (2 bar) required for the process.
- High conversion rate with (98%) minimal reaction time.
- Direct conversion to methyl ester without any intermediate steps.
- Reactants required are readily available.

Figure 1.9 shows the effectiveness of the process. As seen, the conversion rate of this reaction is almost 100% i.e. no reactants are wasted. For the transesterification process shown in Figure 1.10, 1 kg of pure bio-fuel oil is taken in a round bottom flask; a separately prepared mixture of 8 gm of sodium hydroxide (NaOH) is dissolved in 240 gm of methanol and is added to this round bottom flask. The mixture is stirred and maintained at 65°C for 1 hour and then allowed to settle under gravity in a separating funnel. Ester forms the upper layer in the separating funnel and glycerol forms the lower layer. The separated ester is mixed twice with 0.25 kg of hot water and allowed to settle under gravity for 24 hours. The catalyst dissolved in water, forms the lower layer and can be separated. Moisture is removed from this ester using silica gel crystals. About 0.905 kg of purified ester was obtained at the end. The entire process takes 48 hours. The purified bio-fuel oil methyl ester is then blended with petroleum diesel fuel in various concentrations for preparing bio-diesel blends to be used in the engine [15].

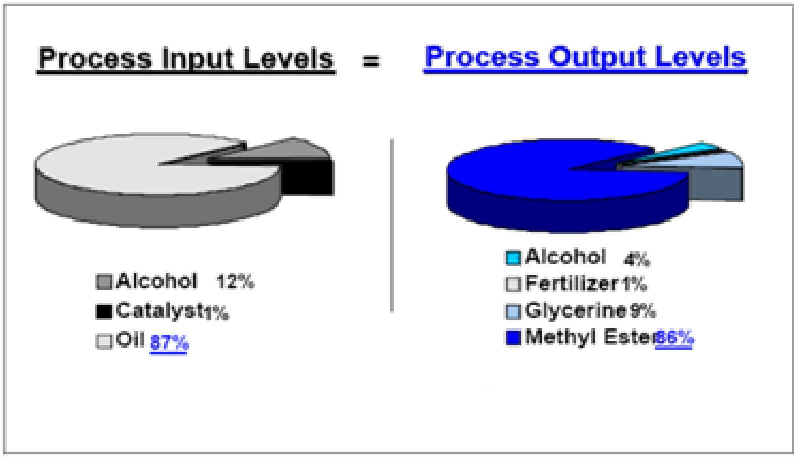


Figure 1.9: General overview of transesterification process [www.bio-diesel.org]

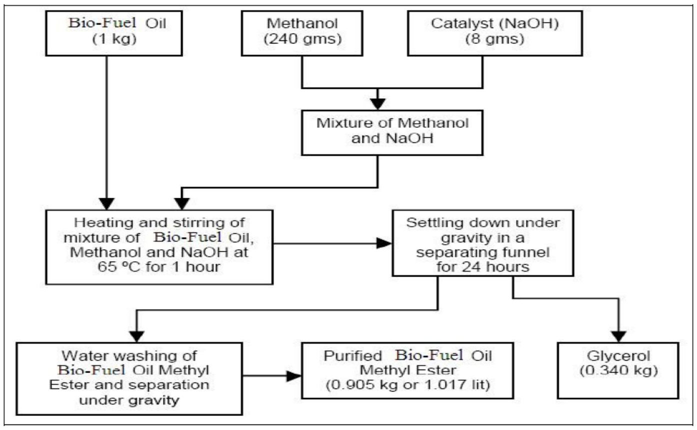


Figure 1.10: Flow chart for transeseterification process [15]

1.6.3 Reactants and Product of Transesterification Process

The process of transesterification yields two reactants. The first of these is the triglycerides found in the vegetable oil while the second of these reactants is alcohol. Triglycerides can have different alkyl groups as bio-diesel can be made out of different kinds of straight or waste vegetable oils. In order to have the triglycerides react a compatible alcohol must be used. For production of bio-diesel the alcohol is likely to be either methanol or ethanol. These two alcohols are used in particular for this chemical reaction because there is very little space between triglycerides atoms for the alcohol to react [17].

When these two reactants are in contact they yield two products: glycerin and methyl ester or ethyl ester depending whether methanol or ethanol was used as an alcohol. Glycerin is seen as a by-product and considered waste, though it is usually recycled by other companies for their products. The resulting product is considered the fuel, in this case bio-diesel. Since the glycerin is denser than the bio-diesel fuel, when it separates it sinks, allowing for its easy extraction from the fuel. This reaction can be seen by the following Equation (1.3):

$$\boldsymbol{Vegetable\ oil + Alcohol \rightarrow Glycerin + Bio - diesel} \tag{1.3}$$

As stated above the use of this transesterification process yields a 79% efficient reaction. This means that the following statement holds true for most bio-diesel productions.

$$\boldsymbol{80\%\ Vegetable\ oil + 20\%\ Alcohol\ \rightarrow 79\%\ Biodiesel + 21\%\ Glycerin} \tag{1.4}$$

Under ideal conditions almost all of the base fuel will be converted to a bio-fuel. The glycerin accounts for only a small part of the reaction. When the reaction is complete, the reactants used to produce glycerin and bio-diesel can return themselves into reactants and allow a chemical reaction to produce triglycerides and alcohol. Since the use of WVO is common, it should be noted that WVO contains some free fatty acids (FFAs) that have been dislocated during the cooking processes. As with the base oil these FFAs have to be neutralized because they can lead to undesired reactions, which could make the bio-diesel unusable.

The catalyst and methanol must be added in exact quantities to neutralize the acidic levels of the reactants. If this is not done, the reaction results in high quantities of glycerine or soaps and no usable fuel will be obtained. The catalyst used in this reaction can be one of two types: sodium hydroxide (NaOH) or potassium hydroxide (KOH). Since these catalysts have high base levels, they help speed-up the reaction, and allow for bio-diesel to begin to be produced in as little as 15 minutes [13]. In order to find the right ratio of catalyst to be used a titration process is required, which will be considered later on. Having a strong base catalyst allows for the neutralization of the free fatty amino acids and will deprotonate the alcohol and consequently allow the transesterification process to occur.

Since the reaction needs to find an equilibrate state, addition of excess alcohol is added to the base oil, which guarantees a complete reaction. The excess alcohol will be removed and can be used for another batch of bio-diesel production. To ease the reaction, a heated element is added to the batch to maintain a temperature of 50-65°C. This allows for the transesterification process to speed-up, and is why bio-diesel production can be created in a short period of time. This heated element is usually hot water circulating through a copper coil submerged in the batch.

1.6.4 Chemical Reaction of the Base Catalyzed Transesterification Process

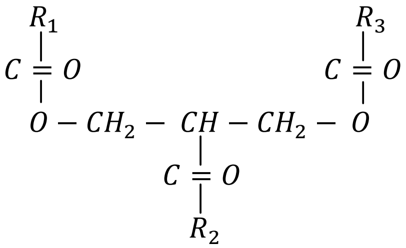
Transesterification refers to a chemical process of transformation of an ester. This reaction finds an equilibrate state, requiring the base catalyst to be efficient. The production of bio-diesel for this study is based on methanol only which yields methyl ester, for this reason only the reaction of this fuel will be considered. An ester is a class of chemical compounds and functional group, usually acids, in which at least one -OH group is be replaced by an -o-alkyl group. Alkyls are chemical compounds that consist of carbon and hydrogen atoms arranged in a chain [18].

The chemical formula of methanol is CH_4O and its semi-developed formula is CH_3-OH. The chemical formula for the methyl group is CH_3. Since the base catalyst deprotonates the alcohol, a reaction between the two reactants can take place. Deprotonate refers to the removal of a proton (hydrogen H+) from a molecule, forming the conjugate base [18]. In the presence of NaOH, methanol deprotonate in the form shown in Equation (1.4):

$$CH_3 \ - OH + NaOH \rightarrow CH_3\,O^- + H^+$$
$$CH_3 - O = CH_3O^- \tag{1.4}$$

Once the methanol is deprotonated and converted into methoxide, it has a slight negative charge. This is important for the reaction to continue. From Equation 1.4 it is clear that the dissolution of the lye (NaOH) and the methanol will yield the first product and a Hydrogen atom with an extra positive charge.

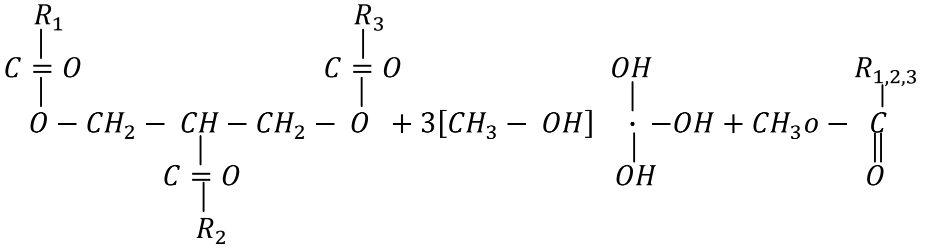
The second stage of this reaction depends on the chemical composition of the base oil being used. Since a diverse group of oils can be used, the equation shown is generalized to represent the triglycerides present in these oils. The main difference between one oil to another will be in the different types of alkyl groups. For simplification the different alkyl groups are denoted by R₁, R₂ and R₃. Equation 1.5 shows the chemical composition of this oil:



$$\begin{array}{ccccc} R_1 & & & & R_3 \\ | & & & & | \\ C=O & & & & C=O \\ | & & & & | \\ O & -CH_2- & CH & -CH_2- & O \\ & & | & & \\ & & C=O & & \\ & & | & & \\ & & R_2 & & \end{array} \qquad (1.5)$$

Note that C=O has a slight positive charge.

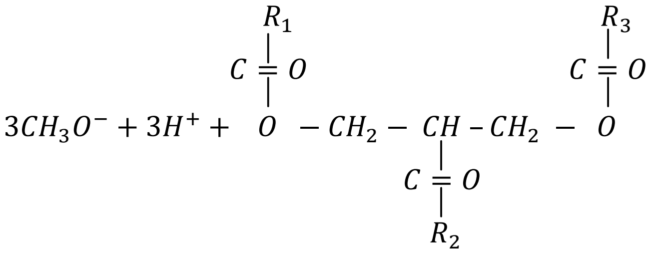
After deprotonisation of methanol in the presence of lye the methoxide will be added to the triglyceride and the transesterification process can begin. Equation 1.6 shows the reaction based on the catalyzed transesterification of triglycerides with the alkyl groups specified previously as R₁, R₂ and R₃, with methanol. The catalyst used here is NaOH, and the product of this chemical reaction is the bio-diesel: methyl ester, and the by-product glycerin.



$$\begin{array}{cccccccc} R_1 & & & & R_3 & & & \\ | & & & & | & & & \\ C=O & & & & C=O & & OH & R_{1,2,3} \\ | & & & & | & & | & | \\ O & -CH_2- & CH & -CH_2- & O & +3[CH_3-OH] & \cdot\ -OH+CH_3o- & C \\ & & | & & & & | & \| \\ & & C=O & & & & OH & O \\ & & | & & & & & \\ & & R_2 & & & & & \end{array} \qquad (1.6)$$

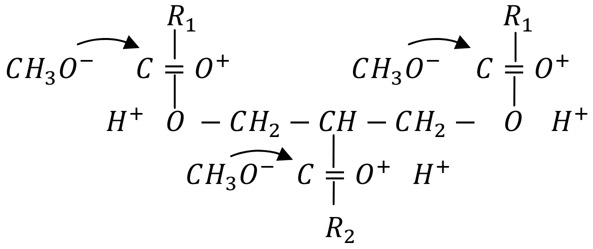
$$Triglyceride \qquad Methanol \qquad Glycerin \qquad Methyl\ Ester$$

Since the methanol has been deprotonated it now contains some particles with a slight negative charge, while some of the elements of the triglycerides have a slightly positive charge as noted previously. Electrostatic forces cause the negative charged particles to attach themselves to the positive charged particles. Equation 1.7 shows the reactants before the transesterification process:



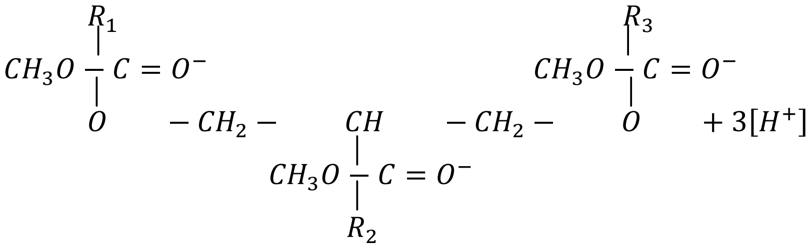
$$3CH_3O^- + 3H^+ + \overset{\substack{R_1\\|\\C = O\\|}}{O} - CH_2 - \underset{\substack{|\\C = O\\|\\R_2}}{CH} - CH_2 - \overset{\substack{R_3\\|\\C = O\\|}}{O} \tag{1.7}$$

The first step of this reaction has the particles of the triglycerides charged positively, which attracts the negative charged particle present in the deprotonisation of the methanol. This can be seen by Equation 1.8:



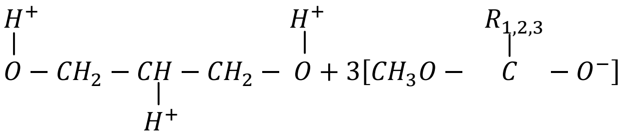
$$\overset{\substack{R_1\\|\\CH_3O^- \curvearrowright C = O^+\\|}}{H^+\ O} - CH_2 - \underset{\substack{|\\CH_3O^- \curvearrowright C = O^+\ H^+\\|\\R_2}}{CH} - CH_2 - \overset{\substack{R_1\\|\\CH_3O^- \curvearrowright C = O^+\\|}}{O}\ H^+ \tag{1.8}$$

After this step because the oxygen has a pair of electrons and carbon cannot contain more than it has, it will break the double bond it contains with the oxygen. This is seen in Equation 1.9.



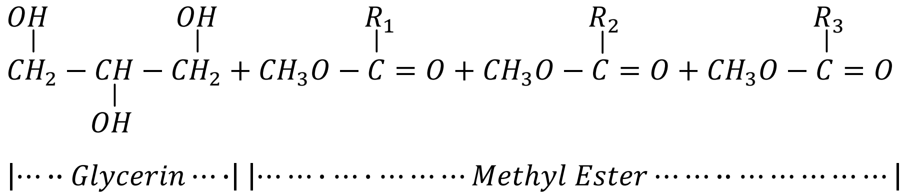
$$\overset{\substack{R_1\\|\\CH_3O - C = O^-\\|}}{O} - CH_2 - \underset{\substack{|\\CH_3O - C = O^-\\|\\R_2}}{CH} - CH_2 - \overset{\substack{R_3\\|\\CH_3O - C = O^-\\|}}{O} + 3[H^+] \tag{1.9}$$

The three H^+ (positively charged hydrogen atoms) from the deprotonisation of methanol are attracted to the oxygen atom which is negatively charged. This reaction seen in Equation 1.10 and accounts for the formation of glycerine.



$$\overset{\substack{H^+\\|}}{O} - CH_2 - \underset{\substack{|\\H^+}}{CH} - CH_2 - \overset{\substack{H^+\\|}}{O} + 3[CH_3O - \overset{\substack{R_{1,2,3}\\|}}{C} - O^-] \tag{1.10}$$

From the reaction two final products are produced, one is of highest interest; the methyl ester - the bio-diesel fuel and the second is the glycerin by-product which will be discarded. This glycerin has a dark brown colour while the bio-diesel fuel is a light caramel yellow, similar in colour to apple juice. Equation 1.11 shows the chemical reactions for these two final products:



$$\overset{\overset{OH}{|}}{CH_2} - \underset{\underset{OH}{|}}{CH} - \overset{\overset{OH}{|}}{CH_2} + CH_3O - \overset{\overset{R_1}{|}}{C} = O + CH_3O - \overset{\overset{R_2}{|}}{C} = O + CH_3O - \overset{\overset{R_3}{|}}{C} = O \qquad (1.11)$$

$$|\cdots\cdots Glycerin \cdots\cdot| \; |\cdots\cdots\cdots\cdots\cdots\cdots\ Methyl\ Ester \cdots\cdots\cdots\cdots\cdots\cdots\cdots|$$

This is the final reaction plus some excess alcohol which was added to ensure a complete reaction. The alcohol can also be removed and then recycled. Leaving the final product of methyl ester or 100% bio-diesel, B100, this can be used directly or mixed with petroleum diesel [17].

1.6.5 Physical Properties of Bio-diesel

The properties of bio-diesel and diesel fuels, see Table 1.6, are very similar to each other and therefore bio-diesel rates as a strong candidate as an alternative or extender for diesel. This is due to the fact that the conversion of triglycerides into methyl or ethyl esters improves the properties of base oil by decreasing its density and viscosity. The cetane numbers for bio-diesel is close that of diesel, suggesting similar combustion behaviour as that of diesel.

Table 1.6: Physical properties of bio-diesel [15]

Vegetable Oil Methyl Ester (Bio-diesel)	Kinematic Viscosity (mm^2/s)	Cetane Number	Heating Value (MJ/kg)	Cloud Point (^{o}C)	Pour Point (^{o}C)	Flash Point (^{o}C)	Density (kg/l)
Peanut	4.9	54	33.6	5	-	176	0.883
Soya Bean	4.5	45	33.5	1	-7	178	0.885
Palm	4.7	62	33.5	13	-	164	0.880
Sunflower	4.6	49	33.5	1	-	173	0.860
Tallow	-	-	-	12	9	96	-
Diesel	3.06	50	43.8	-	-16	76	0.855
20% Blend Bio-diesel	3.2	51	43.2	-	-16	128	0.859

1.7 Aims

The aim of this research is to investigate the viability of using bio-diesel as an alternative, or additive, to basic diesel fuel. The engine performance is to be evaluated along with the emission characteristics for an engine running with bio-diesel and traditional fuels. Also, the research will study the effect of reaction temperature, catalyst concentration (wt.%), molar ratio of alcohol:oil (mol/mol) and reaction time on the percentage conversion. The response surface methodology (RSM) was used to optimize the conditions for the maximum conversion to bio-diesel and understand the significance and interaction of the factors affecting the bio-diesel production.

1.8 Objectives

The objective of this research was to find an immediate alternative energy solution, which does not involve a drastic overhaul of the world's engine structure. Obtaining a viable solution is one which can reduce the global green house emissions over the petroleum diesel counterpart, while maintaining a similar output in performance, and efficiency. It should also be noted that this study will look at how these bio-fuels compare in cost to petroleum diesel, and what benefits are provided by recycling used vegetable oil (WVO). Further objective of this research was to optimize bio-diesel production from crude sunflower oil by using conventional transesterification method. The use of crude sunflower oil as raw material for bio-diesel production will enhance the viability of the sunflower oil industry, making sunflower oil preferred renewable bio-base ingredients for existing or new industrial application.

1.9 Outline of Thesis

An introduction to the problem, description of alternative fuels used in the study, some of their associated advantages and disadvantages will be discussed, global perspective, and automotive industry, fuel demand past present and future, and discussion of the aims and the objectives is given Chapter 1.

Chapter 2 presents the literature survey; description of impact of used bio-fuels on agriculture and environment and presents the methods of bio-fuel production from feedstock and non feedstock by using transesterification process.

Chapter 3 presents the experimental techniques and instrumentation used in the bio-diesel production by “Fuelpod” for transesterifying oil at non-optimize conduction. The details validation of the experimental setup and, material and method to characterize the oil properties tested fuels and describes the results for the oils and fuels properties. This includes viscosity, free fatty acid content and perhaps degree for the oils and viscosity, cloud point and pour point for the fuels.

Chapter 4 presents the experimental techniques used in bio-diesel production at optimize conduction by using RSM strategy. The chapter describes the optimisation of the fuel manufacture process and discussion the results for the bio-diesel optimal production yield. This includes, alcohol to oil molar ratio, concentration of catalyst, rate of mixing and, reaction time and temperature.

Chapter 5 presents the experiment setup used in the compression ignition engine investigation, the results and discussion for the experimentally obtained data involving the engine performance and exhaust gas emissions. This includes measured brake power, torque and fuel consumption, concentration of exhaust gas emissions such as carbon monoxide, oxide of nitrogen, hydrocarbon and carbon dioxide. The cost analysis for bio-diesel blends as fuel discusses as well in this chapter.

Finally, in Chapter 6 a general discussion of the dissertation is given followed by recommendations for future studies.

1.10 Conclusions

In summary, with economic development, energy needs grew, utilizing natural resources such as hydro, fossil fuel, wood, and nuclear energy in the preceding century. Bio-fuels were suggested alternative resource as fuel in internal combustion engines. There are two types of bio-fuels, first generation bio-fuel, such as bio-diesel and bio-ethanol. Bio-diesel produced by transesterification or reforming of vegetable oil and bio-ethanol produced by fermentation of sugars or starch. However, second generation bio-fuel produced from lignin and cellulose such as wood, straw.

The physical properties of vegetable oils, bio-diesel and standard diesel were showed in this chapter. The greatest difference between vegetable and diesel oil was their viscosity, typically about 10 times the value for diesel. The high viscosity of the vegetable oil may contribute to formation of carbon deposits in engines, incomplete combustion and reduced life of an engine. Thus, it is important to know the properties of vegetable oil before use it in the engine. The viscosity of vegetable oils were varies from 30-40 mm2/s and 38^o, whereas it was just 4.7 mm^2/s in average for bio-diesel and 3.06 mm^2/s for diesel fuel. The calorific heating values for vegetable and bio-diesel oils were in the range of 39-40 MJ/kg, while diesel fuel was about 44 MJ/kg. The Cetane numbers were in the range of 32-40, which is close to that of diesel fuel.

The next chapter presents the literature survey, which will be description of impact of used bio-fuels on agriculture and environment and presents the methods of bio-fuel production from feedstock and non feedstock by using transesterification process.

CHAPTER - 2

LITERATURE SURVEY

2.1 Introduction

Nowadays, the world energy demand has increased significantly due to the global industrialization and increase of population. As a result, the current limited reservoirs will soon be depleted at the current rate of consumption. The Oil and Gas Journal (O&GJ) estimates that at the beginning of 2004, the worldwide reserves still had 1.27 trillion barrels of oil and 6,100 trillion cubic feet of natural gas left. However, at today's consumption level of about 85 million barrels of oil per day and 260 billion cubic feet of natural gas per day, the current reserves can only be used for another 40 years for the oil and 64 years for the natural gas [59].

Moreover, increase of pollutant emissions from the use of petroleum fuel will affect human health, such as respiratory system, nervous system and skin diseases etc. Both the increased energy needs and environmental consciousness have stimulated the research of searching an alternative fuel. Bio-diesel may be the best answer due to its following advantages:

- Reduces the country's dependence on imported petroleum.
- Being renewable and it contributes less to global warming than petroleum fuel due to its closed carbon cycle. The primary feedstocks are sustainable and most of the carbon in the fuel can be removed from the air by the plant.
- Provides good engine performance and can be used without engine modification.
- Provides the market with bio-diesels from sufficient production of vegetable oils and animal fats, thus enhancing the rural economies.
- Biodegradable and nontoxic.
- Exhibits lower combustion profile, especially sulphur oxide (SOx).

2.2 Impacts of Bio-fuels on Agriculture and Environment

Since bio-fuels are produced from agricultural sources their production impacts on food security, the environment, natural resources, ecosystems, and the livelihood of possibly billions of people. Traditionally, agriculture has been the source of food, animal feed and fibre, but the connection between energy and agriculture was weak and largely confined to links through production costs of diesel and fertilizer and other agro-chemicals, which are all energy intensive. This linkage was a concern mainly in the developed countries. But now a new linkage is being established through a demand-pull from the energy sector. It is being pulled by the opportunity to gain massive bio-fuel subsidies due to high oil prices. This new link has led to higher commodity prices with the growth in bio-fuel production.

The growing popularity of bio-fuels has fuelled the debate on the price of food. For instance, the United States bio-fuel boom has led to a rapid increase in the price of corn, from \$2.20/bushel in September 2006 to a peak of \$7.40/bushel in June 2008. In the same period, soybean prices also experienced rapid increase from \$5.20/ bushel to \$16.40/bushel. Since corn and soybeans are major ingredients in livestock feed, their higher prices increase the cost of milk, meat, eggs, etc., which are all passed on to consumers. In terms of annual food bill, it has been estimated that United States consumers paid \$22 billion more for food in 2007, of this two thirds was due to bio-fuels [60]. Food grains and oilseeds form the major source of bio-fuel feedstock and this competes directly with their use as food and feed, and indirectly for land, water, and other resources.

Since both agricultural supply and the demand for food are highly inelastic in the short-run, any surge in demand for bio-fuel feedstock puts upward pressure on commodity prices in global agricultural markets. Higher commodity prices can benefit farmers and improve their well-being depending on whether they are net-sellers or net-buyers of food, and the impact of higher commodity prices on those earning rural wages. Growing food crops for energy purposes can foster rural economic activities and generate employment and income sources for the poor, but higher food prices can also severely affect the purchasing power of smallholder farmers, landless labourers, and the urban poor. Bio-fuels are promising but pose serious challenges.

Advocates for bio-fuels argue that they are a suitable strategy for improving energy security of a country, especially when that country depends largely on geo-politically unstable energy suppliers [61, 62]. Several studies have shown that greater use of bio-fuels and other liquid and gaseous fuels for transport could reduce green house gas emissions, improve vehicle performance and protect ecosystems [63-66]. Hill et al. [67] by using life-cycle analysis (Life-cycle analysis is an emerging popular technique particularly for analyzing environmental aspects of, for example, green house gas emissions of a product by accounting for all stages of its life cycle), they found that the corn-ethanol yields 25% more energy and generates 12% less greenhouse gas emissions, and soybean bio-diesel yields 93% more energy and generates 41% less greenhouse gas emissions, relative to fossil fuels. However, several studies in the recent past have argued that bio-fuels produced on converted land can be much greater net emitters of greenhouse gas emissions than fossil fuels because use of the land for bio-fuels leads to land conversion elsewhere in the world, and that land conversion releases carbon and reduces future carbon sequestration [68, 69].

Growing demand for bio-fuel feedstock particularly in EU and the U.S. has resulted in soaring feedstock prices, which have been partially transmitted to many developing countries. Apart from hurting the net purchasers of food, higher prices also lead to deforestation in places such as Brazil [70], Indonesia and Malaysia [71]. Worry is being expressed at the potential land degradation in the develop countries due to withdrawal of land from agriculture [72]. Though there are various views on the beneficial aspects of different types of bio-fuels, Pagel [73] reports that the United Nations supports the Brazilian bio-fuel model as it wins both environmentally and commercially, as well as from a developmental perspective.

2.3 Land Use Change

Bio-fuel production removes CO_2 from the atmosphere and thus reduces greenhouse gas emissions relative to fossil fuels, which take carbon from the ground. However, some researchers argue that whether or not bio-fuels offer carbon savings depends on how they are produced. They argue that the increasing demand of bio-fuel production will lead to increase in demand for feedstock, which in turn will either require bringing undisturbed land into cultivation (e.g. forest, grassland) or to divert existing croplands into bio-fuels. A direct land use change converts native land cover, such as forests or grasslands or other natural ecosystems, to bio-fuel production. The expansion of bio-fuel production into forests and grasslands releases carbon stored in the plants and soil into the atmosphere through decomposition or burning, which will result in a net increase in greenhouse gas emissions. Indirect land use change diverts existing food and feed croplands into bio-fuels, which may result in clearing more forests or grasslands elsewhere to replace crops for animal feed and food [69].

2.4 Bio-diesel production Methods

There are four primary options for making bio-diesel from fats and oils.

2.4.1 Direct use and blending

The possibility of direct use of vegetable oils as fuel has been recognized since the beginning of the diesel engine. In 1893, Rudolf Diesel successfully demonstrated his innovation, the diesel engine, by running it on peanut oil (a biomass fuel), and for the first time, the possibility of utilizing biomass as for engine fuels was established. However, the straight use of vegetable oils to replace conventional fuels meets operational problems due to its high viscosity. Polymerization, as a result of reactivity of C-C double bonds that may be present, lower its volatility which causes the formation of carbon deposits in engines due to incomplete combustion, and oil ring sticking, due to thickening and gelling of the lubricating oils as a result of contamination [74].

The great advancement in petroleum industry technologies meant fossil fuels could be produced much cheaper than the biomass alternatives, resulting in, for many years, the near elimination of the biomass fuel production infrastructure. However, interest in the use of vegetable oils for engine fuels has been reported periodically. For instance, during the World War II, vegetable oils were used and tested in diesel engines in several countries, e.g., Belgium, France, the United Kingdom, Germany, Japan, etc. Vegetable oils can be used by blending with the diesel fuel, given rise to improvement in the physicochemical properties of the former. Nevertheless, the long term use of this blending in a modern diesel engine has become impractical because of the reduction in power output and thermal efficiency by carbon deposits [74, 75].

2.4.2 Microemulsions

A microemulsion is technically defined as a stable dispersion of one liquid phase into another, which has a droplet diameter approximately 100 nm or less. Microemulsion processes have been studied for bio-diesel production as a means to improve the viscosity of vegetable oils by blending with a simple alcohol such as methanol or ethanol [76, 77]. However, significant carbon deposits, incomplete combustion, increase in the viscosity of lubricating oils, and sticking of the injector needle are all reported as long term consequences of using fuel produced by this process [77].

2.4.3 Thermal cracking (pyrolysis)

Pyrolysis is defined as the conversion of one substance into another by means of heat in the absence of air or oxygen at temperatures ranging from 450 °C to 850 °C or by heat with the aid of a Lewis acid catalyst. The Lewis acid catalysts used in this process include zeolites, clay montmorrilite, aluminum choride, aluminum bromide, ferrous choride, and ferrous bromide. However, the removal of oxygen during thermal processing also eliminates the environmental benefits associated with using an oxygenated fuel [75]. In addition, these fuels are produced more like gasoline than diesel.

2.4.4 Transesterification (Alcoholysis)

Among the present methodologies, transesterification is considered as the best process. Transesterification reactions are reversible reactions that involve the transformation of one ester into another different ester. For manufacturing bio-diesel, transesterification is performed to lower the viscosity of vegetable oils. Specifically, a triglyceride (TG) molecule (primary compound in vegetable oils) reacts with a low molecular weight alcohol, yielding a mono alkyl ester and by-product glycerine, which is used in pharmaceutical and cosmetic industries. The transesterification reaction for bio-diesel synthesis is shown in Figure 2.1.

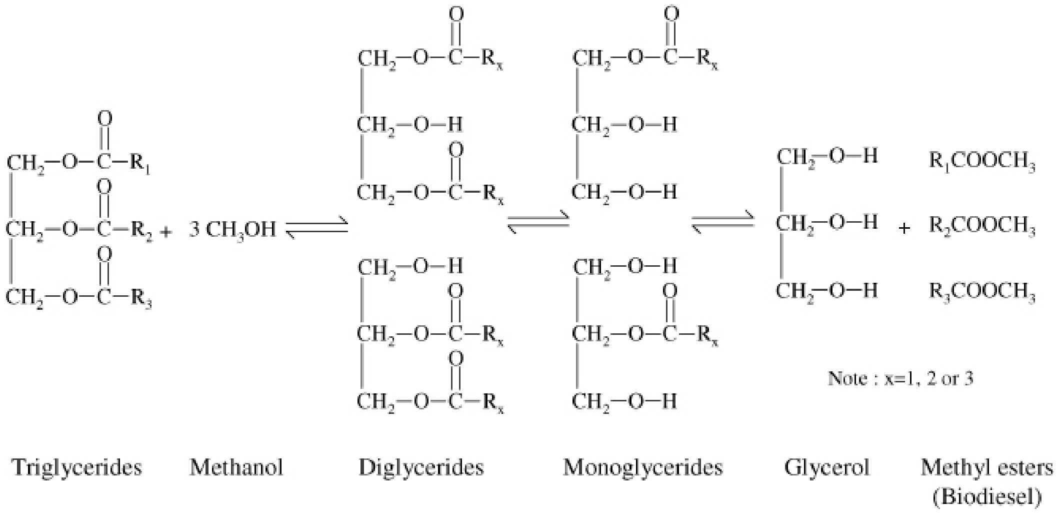


Figure 2.1: Triglyceride transesterification reaction

Since transesterification is a reversible reaction, alcohols are usually present in excess to assist in rapid TG conversion and ensure complete conversion. Methanol and ethanol are commonly used, especially methanol because of its low cost. The rate of the reaction can be significantly improved by the presence of acid or basic catalysts. In general, the use of basic catalysts is more desirable since it provides satisfactory conversion within a short time.

Currently, most commercial bio-diesel production is performed by alkali-catalyzed transesterification since it can be operated under mild conditions to achieve significant conversion with minimal reaction time and side reactions. However, the standard bio-diesel production suffers from the presence of water and free fatty acids (FFAs) in feedstocks. The presence of water favours the formation of FFAs by hydrolysis of TGs and esters products (bio-diesel). Formation of FFA in the presence of basic homogeneous catalysts gives rise to soap, creating serious problems for product separation and ultimately hindering catalytic activity. As a result, highly refined vegetable oils are required for the process otherwise pre-treatment is required for the feedstocks to reduce the acid and water concentrations to below optimum threshold limits, i.e., FFAs < 1 wt% and water < 0.5 wt% [78]. Various factors affect the process of transesterification, and the more important ones are described in the next section.

2.4.4.1 Catalyst type and concentration

Catalyst type and catalyst concentration are the most important factors in the transesterification reaction. Commonly used and very effective alkali catalysts are sodium hydroxide (NaOH), sodium methoxide (NaOCH3), potassium hydroxide (KOH), and potassium methoxide (KOCH3) [97]. A previous study investigated the methanolysis of beef tallow with catalysts NaOH and NaOMe [98]. The results indicated that NaOH was significantly better than NaOCH3. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are generally used for alkaline transesterification in concentrations from 0.4 to 2% (wt/wt) of oil. Methanolysis or ethanolysis of most vegetable oils with 1% (wt/wt) of potassium hydroxide gives the best yields and lowest viscosities of the esters [43]. Generally, increasing catalyst concentration (in range 0.5 to 1.5% wt/wt) has a curvilinear effect on the conversion obtained, with yield inhibited at high catalyst concentration [99]. The best yield is obtained at about 1% (wt/wt) catalyst concentration and a reduction in yield is observed as catalyst concentration is increased. The reduction in yield is due to reversible reactions being favoured at high catalyst concentrations [99].

Meka et al. [105] studied the effect of catalyst (NaOH) concentration on reaction time at two temperatures 50 and 60 ºC for safflower oil, when the methanol/oil molar ratio was kept at 6:1. The authors found that in both cases, reaction time decreased proportionally with increase in catalyst concentration from 1% to 2%, but soap was formed when catalyst concentration was above 2%. Ataya et al. [106] performed canola oil transesterification experiments and found TG conversion increased when the catalyst (NaOH) concentration increased from 1% to 3%.

Rashid et al. [107] evaluated the effect of catalyst type and concentration on the rapeseed oil ester yields, and observed that the hydroxides gave rise to higher yield than the counterpart methoxides. The results showed that 1% KOH was the optimal value when the concentration was varied between 0.25% and 1.5%. This was in accordance with the result obtained by Tomasevic et al. [99] and Meher et al. [104]. The same trends were observed when varying the concentration of NaOH from 0% to 1.5%. The best ester yield was achieved for NaOH concentration of 1%, which was also recommended by Freedman et al. [101]. In contrast, Vicente et al. [109] drew a conclusion that bio-diesel yields after separation and purification steps were higher for methoxide catalysts (NaOCH3, KOCH3) than for hydroxide catalysts (NaOH, KOH) when methanolysis of sunflower oil was performed. This phenomenon of yield loss was ascribed to the fact that hydroxide catalysts could cause more TG saponification and methyl ester dissolution in glycerol. Moreover, among these catalyzed transesterifications, the reactions using NaOH were fastest.

Alkaline catalysts are more sensitive to the presence of free fatty acid and water. Their application in vegetable oil transesterification can cause soap formation by neutralizing the free fatty acid in the oil, which can partially consume the catalyst, thus decreasing the bio-diesel yield. Usually in basic conditions, the acceptable total FFA and water content are 0.5% and 0.1%-0.3%, respectively [110]. Acid catalysts were preferred for bio-diesel production when the FFA content is high. The acids could be sulphuric acid (H2SO4), phosphoric acid, hydrochloric acid (HCl) or organic sulphonic acid. H2SO4 and HCl are commonly preferred. Goff et al. [111] studied a single step acid-catalyzed alcoholysis of soybean oil using sulphuric, hydrochloric, formic, acetic, and nitric acids at 0.1 and 1 wt.% loadings and temperatures of 100 °C and 120 °C in sealed ampules, only sulphuric acid was found to be effective. Further kinetic studies demonstrated that at 100 °C, 0.5 wt.% sulphuric acid catalyst, and nine times methanol stoichiometry, >99 wt.% conversion of TG was achieved in

8 h. The same conversion could be obtained at less than 4 h if FFA concentrations were less than 0.8 wt%. Reaction conditions near 100 °C at 0.1 to 0.5 wt.% were identified as providing the necessary conversions in a 24 h batch cycle.

Zullaikah et al. [91] undertook a two-step acid-catalyzed process for the production of bio-diesel from rice bran oil. The first step was carried out at 60 ºC and the second step at 100 ºC. In their work, the organic phase of the first step reaction product was used as the substrate for a second acid-catalyzed methanolysis. By this two-step sulphuric acid catalyzed reaction, the yield could be more than 98% in less than 8 h. Williams et al. [110] successfully prepared bio-diesel from waste vegetable oil by 1% sulphuric acid catalyzed reaction at 117 ºC in which butanol was selected as the alcohol. Al-Widyan et al. [112] evaluated the effect of different concentrations of HCl, H2SO4, and excess ethanol on the transesterification of waste palm oil. The authors reported that higher catalyst concentrations (1.5-2.25 M) produced bio-diesel with lower specific gravity in a much shorter reaction time than lower concentrations. The specific gravity served as an indicator for the effectiveness and completeness of the conversion process. Lower values meant more complete reaction since more of the heavy glycerol was removed. At 2.25 M, the H2SO4 performed better than HCl.

2.4.4.2 Molar ratio of alcohol to oil and type of alcohol

The molar ratio of alcohol to oil is another important variable affecting the yield of bio-diesel from oil (A molar ratio is ratio between the amounts in moles of any two compounds involved in a chemical reaction, one mole of methanol = 32 grams and one mole of oil = 900 grams). Based on reaction stoichiometry, only three moles of alcohol are required to transesterify a molecule of triglyceride and produce three moles of fatty acid alkyl esters (bio-diesel) and a mole of glycerol. Generally, 100-200% excess alcohol is used, which drives the reaction in the forward direction and favours bio-diesel production. However, a very high molar ratio of alcohol to vegetable oil is avoided because it might interfere with the phase separation of bio-diesel and glycerol post transesterification reaction. Additionally, when high molar ratios are used, the reverse reaction is favoured, lowering the yield of esters.

In a previous study, the transesterification of cynara oil with ethanol as an alcohol source was studied at molar ratios of alcohol to oil between 3:1 and 15:1. The conversion increased as the molar ratio increased up to a value of 12:1. The best conversions were obtained at molar ratios between 9:1 and 12:1. For lower molar ratios, the reaction was not completed and for higher molar ratios, the yield of esters decreased because of improper phase separation [100]. However, the optimal molar ratio will vary from one oil source to another.

Zhou et al. [103] studied the effect of alcohol/oil molar ratio on the single-phase base-catalyzed ethanolyses of sunflower oils. In that study, four molar ratios of ethanol to sunflower oil (6:1, 20:1, 25:1, and 30:1) were examined. The authors found that at ethanol/oil molar ratios of 20, 25, and 30:1, equilibrium was reached in 6 to 10 min at 23 ºC when 1.4% of potassium hydroxide was used; While at the molar ratio of 6:1, equilibrium could not be reached even after 30 min. Increasing the molar ratio did favour the formation of esters, but the difference for the range of molar ratios from 25:1 to 20:1 was small.

Meher et al. [104] concluded that the reaction was faster with higher molar ratio of methanol to oil whereas a longer time was required for a lower molar ratio (6:1) to get the same conversion. In their research, the molar ratio of methanol to oil, i.e., 6:1, 9:1, 12:1, and 24:1, were investigated for optimizing bio-diesel production from Karanja oil.

Canakci et al. [65] investigated the effect of different alcohol types on transesterification. Methanol, ethanol, 2-propanol, and 1-butanol were tested for a 48-h test period, with sulphuric acid catalyst concentration equal to 3% and the molar ratio of alcohol to oil at 6:1. The conversion was 87.8%, 95.8%, 92.9%, and 92.1% for methyl ester, ethyl ester, 2-propyl ester, and 1-butyl ester, respectively. A higher conversion rate was observed for the longer chain alcohols compared with methanol. The authors attributed this to the fact that higher reaction temperatures were chosen due to the higher boiling point of the long chain alcohols. Also, long chain alcohols can increase the solubility between the oil and alcohol since they are more non-polar than shorter chain alcohols.

2.4.4.3 Effect of temperature and reaction time

Temperature influences the rate of the reaction and percentage conversion [99]. In one study refined oil was transesterified with methanol, with a 6:1 molar ratio of methanol to oil, 1% (wt/wt) NaOH, and three different reaction temperatures [60]. After 6 minutes, yields of 94, 87 and 64% were obtained respectively for 60, 45 and 32 °C. However, after an hour, yields were similar at 60 and 45 °C and only slightly lower at 32°C. As expected conversion increases with reaction time. In the same study, the effect of reaction time on conversion was also studied. For cottonseed, soybean, sunflower and transesterified peanut oil, with methanol to oil molar ratio 6:1, 0.5% (wt/wt) sodium methoxide catalyst, and 60 °C reaction temperature, an approximate percentage yield of 80% was obtained after a minute for sunflower and soybean oils. After 60 minutes, the yield was similar (93 to 98%) for all four oils studied [101].

With beef tallow, the reaction was slow during the first minute possibly due to initial mass transfer limitations of methanol in the beef tallow. However, the reaction proceeded at a faster rate from 1 to 5 minutes, with the highest conversion reached at about 15 minutes [113]. The boiling point of methanol is 64.8 °C. At reaction temperatures higher than this the alcohol will burn and this will cause reduced yield. Leung et al. [114] indicated that reaction temperature higher than 50 °C had a negative impact on the product for neat oil.

2.4.4.4 Mixing intensity

Mixing is an important transesterification factor as low molecular weight alcohols like methanol and ethanol are immiscible with oil at the room temperature. Hence, the reaction mixtures are often agitated mechanically to facilitate mass transfer of alcohol into the oil. In a prior study, the effect of mixing on transesterification of beef tallow was studied [61]. The results showed that the reaction did not proceed without mixing the two reactants, however, when NaOH-methanol mixture was added to the melted beef tallow in the reactor with continuous mixing, stirring speed was found to be insignificant suggesting that the mixing speeds studied were way above the threshold requirement for mixing. A mixing speed of 600 rpm was concluded as optimum in some previous studies.

2.5 The challenge for the current bio-diesel production

The major obstacles to current bio-diesel production are the cost and limited availability of fat and oil resources. There are two aspects relevant to the cost of bio-diesel synthesis; the raw material cost and the processing cost. In term of the processing cost, the current bio-diesel synthesis involves the use of homogeneous alkali catalysts operating in a batch-type process followed by an additional effort to remove the liquid catalysts and saponified products. To make bio-diesel commercially viable and compete with petroleum-based diesel, a continuous process needs to be developed to replace the time-consuming batch process since the latter presents high capital costs, is labour intensive, and it is difficult to control the process and product quality. In addition, replacing liquid catalysts with heterogeneous catalysts would minimize the separation steps, and other benefits; for instance, it is environmentally friendly, easily recovered, and can potentially be re-used. Eventually, the production costs can be substantially reduced.

Regarding raw material costs, the cost of highly refined vegetable oils, which accounts for 80% of total production cost [79], can be significantly lowered by substituting with more economical feedstocks such as restaurant waste and animal fats. However, the quality of these low-cost feedstocks can generate processing problems in standard bio-diesel production because the alkali-catalyzed system is very sensitive to water, free fatty acids and other impurities. Even refined oils and fats could contain small amounts of free fatty acids [75].

Moreover, the current increased production of animal fats, waste cooking oils (WCOs), and greases from household and industrial sources is a growing problem and an opportunity. According to the National Renderers Association, about 9.3 billion tons of fats and greases, including inedible tallow, yellow grease, edible tallow, lard, and poultry fat, are processed by the rendering industry annually [80]. All these waste greases and fats can be sold commercially for inclusion in livestock feed. However, since 2002, the European Union has enforced a ban on feeding such rendered by-products to certain animals, because it has the potential to pass animal diseases such as Bovine Spongiform Encephalopathy to other animals or humans.

Since these feedstocks are readily available at a low price, the use of such biomass for the synthesis of bio-diesel provides a means to convert waste fats and oils into a more valuable product. However, the use of such feedstocks in the standard process is challenging due to high concentrations of FFAs, water, and other impurities. Pre-treatment stages, acid-catalyzed esterification integrated with water separation, are necessary to minimize the acid and water content to less than the threshold limits set by the subsequent alkali-catalyzed transesterification.

2.6 Lower-cost Feedstocks for Bio-diesel Production and using it as Fuel

Though bio-diesel has many advantages compared with petroleum diesel, its high production cost has become the primary barrier to its commercialization. Currently, bio-diesel unit price is 1.5-3.0 times higher than that of petroleum derived diesel fuel depending on feedstock [78, 79].

Bio-diesel can be produced from TGs present in naturally occurring fats and oils by transesterification with alcohol, usually methanol, in the presence of catalyst. Transesterification is a reversible process and glycerol is the by-product. The feedstocks used for bio-diesel production currently are mainly high quality food-grade vegetable oils, such as sunflower oil and rapeseed oil in European, soybean oil in United States, and palm oil in Malaysia [115]. However, to compete with diesel fuel and survive in the market, lower-cost feedstocks are required, including WCO, grease, soapstocks, as feedstock costs are more than 85% of the total cost of bio-diesel production [79]. Non-edible oils, like Jatropha, can also be used to produce bio-diesel [155,156]. In addition, growing interest has arisen concerning algae-based bio-diesel [123].

2.6.1 Bio-diesel Production from Waste Cooking Oil

Waste vegetable oils are generally low cost. They usually can be collected from large food processing and service facilities. However, due to the very high temperature that occurs during the food frying process, chemical reactions such as hydrolysis, polymerization and oxidation will have taken place, and these can lead to an increase of free fatty acid (FFA) level. Hence, acid catalysis is preferred since it is insensitive to FFA [101].

Zheng et al. [95] studied the reaction kinetics of acid-catalyzed transesterification of waste frying oil. They found that at the methanol/oil molar ratio of 250:1 at 70 ºC or in the range 74:1-250:1 at 80 ºC, the reaction was a pseudo-first-order reaction. High yield of 99±1% could be achieved at both 70 ºC and 80 ºC and a stirring rate of 400 rpm, using a feed molar ratio oil:methanol:acid of 1:245:3.8. In contrast, Wang et al. [88] investigated a two-step catalyzed processes for synthesis of bio-diesel by using WCO from Chinese restaurants. In the first step, ferric sulphate-catalyzed methanolysis was carried out, while potassium hydroxide catalysis was performed in the second step. The authors concluded that compared with one-step sulphur acid catalysis the two-step catalyzed process provided a simpler and more economic method to produce bio-diesel from WCO.

Moreover, the by-products of glycerol and soapstock in this process could be easily handled. Similarly, Issariyakul et al. [125] also used the two-step process to transesterify WCO, except that sulphuric acid was selected as acid catalyst and mixtures of methanol and ethanol were used for transesterification in order to use the better solvent properties of ethanol and a more rapid equilibrium using methanol. More than 90% ester was obtained by using the two-stage method compared with yield of ~50% ester by using the single stage alkaline catalyst.

In the above mentioned two-step process that was developed by Canakci et al. [90], acid catalyst (usually sulphuric acid) was first chosen to reduce the FFA to less than 1%, then the pre-treated feedstock was transesterified under alkaline catalysis. The advantage of this two-step process relies on the fact that it can increase the reaction rate by using alkaline catalyst and avoid soap formation by applying acid catalyst.

The performances of bio-diesel obtained from WCO in terms of engine performance and emissions have been studied by many researchers. Çetinkaya et al. [126] investigated the engine performance of bio-diesel fuel originated from used cooking oil in a Renault Mégane automobile with four stroke, four cylinder, 75 kW diesel engine in winter conditions for 7500 km road tests in urban and long distance traffic. The results showed that the torque and brake power output obtained from the used cooking oil bio-diesel were 3-5% less than those of No. 2 diesel fuel. The engine exhaust gas temperature at each engine speed of bio-diesel was less than that of No. 2 diesel fuel. Higher values of exhaust pressures were found for No. 2 diesel fuel at each engine speed. The injection pressures of both fuels were similar. Based on the experimental results, the authors concluded that used cooking oil bio-diesel could be recommended as a No. 2 diesel fuel alternative for winter conditions.

Lin et al. [127] also used WCO to prepare bio-diesel and then conducted a study in which the exhaust tail gas of bio-diesels were compared when the engine was operated using different fuel types, including neat bio-diesel, bio-diesel/diesel blends, and normal diesel fuels. Among the collected data, the authors found that B20 and B50 were the optimum fuel blends.

Al- Widyan et al. [128] used the ethyl ester of waste vegetable oils as a fuel in diesel engines and initiated a study to investigate its potential to substitute oil-based diesel fuel. The fuels evaluated included 100% ester, several ester/diesel blends and diesel fuel as the baseline fuel. The tests were run on a standard test rig of a single-cylinder, direct-injection diesel engine. The results indicated that the blends burned more efficiently with less specific fuel consumption, resulting in higher thermal efficiency. Moreover, less CO and unburned hydrocarbons (HCs) than diesel fuel were produced by the blends. The blends and 100% ester surpassed the diesel fuel in essentially all aspects of engine performance considered. Overall, 100% ester and 75:25 ester/diesel gave the best results regarding performance, while for emissions the 50:50 blends exhibited the best results. The ester fuel demonstrated a good potential as fuel for diesel engines.

Similar trends for emission results were observed by Dorado et al. [129], who characterized exhaust emissions from a diesel engine fuelled with transesterified waste olive oil and found lower emissions of CO, carbon dioxide (CO2), nitrogen oxides (NOx), and SO2. The particulate emissions from used cooking oil bio-diesel were also evaluated by another research group [130]. The bio-diesel fuels were tested in a DI diesel commercial engine either pure or in 30% and 70% v/v blends with a reference diesel fuel. A sharp decrease was observed in both smoke and particulate matter (PM) emissions as the bio-diesel concentration increased. This was attributed to the fact that the oxygen content of the bio-diesel improved the oxygen availability in rich-zone flames in the combustion chamber.

Recently, an environmental approach was suggested by Nas et al. [131], who presented an overview of energy potential of bio-diesel generated from WCO. The authors finally drew a conclusion that bio-diesel could reduce nearly all forms of air pollution, especially air toxics and cancer-causing compounds.

2.6.2 Bio-diesel Production from Waste Grease

Esterification is the central reaction to reduce the levels of FFA in the low-cost feedstock to an acceptable range, making the feedstock suitable for further processing in the standard bio-diesel synthesis. Esterification is a reversible reaction between carboxylic acids and alcohols in the presence of strong acid catalyst, resulting in the formation of water and at least one ester product, see Figure 2.2. The mechanism of homogeneous catalyzed esterification has long been established; a protonated carboxylic acid is nucleophilically attacked by an alcohol molecule from the bulk phase yielding an ester and water. Esterification can be carried out by a catalyst free method, enzymatic method, or use of homogeneous and heterogeneous acid catalysts.

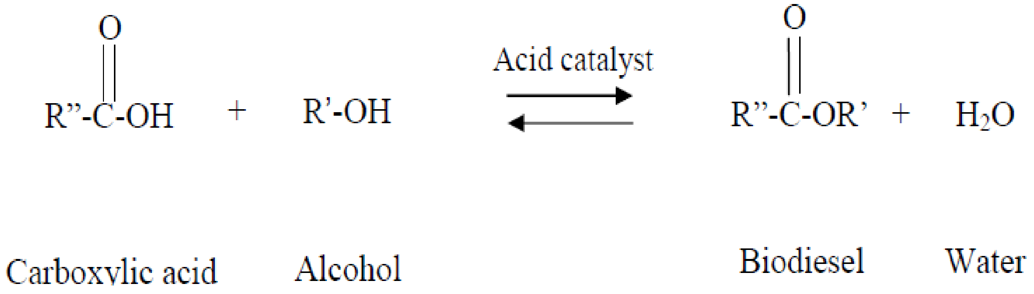


Figure 2.2: Carboxylic acid esterification.

Non-catalytic esterification is normally performed under supercritical conditions for alcohol, i.e., the critical temperature and pressure of methanol are 239 °C and 8.09 MPa. Under such reaction conditions, the alcohol itself starts acting as a catalyst [24], the degree of alcohol solubility in oil is increased, thereby favouring the transition from a solubility-limited reaction to a rate-limited reaction [82,83]. As a result, transesterification of TGs with ethanol can be simultaneously performed. Additional benefits from a supercritical alcohol method are the separation of esters and glycerol from the reaction mixture becomes much easier since in the presence of water and glycerol will be in the water portion while esters are in the upper portion. Saka and Kusdiana [26] reported a fast and high conversion of rapeseed oil into methyl esters by using supercritical methanol without the aid of any catalyst. However, in this process, high energy intensity is required with additional safety hazards.

It is well known and widely documented that lipase, a glycerol ester hydrolase, can be used for various esterification reactions in different fields such as oil and fat restructuring [84-87]. The advantages of using an immobilized lipase as a biocatalyst for esterification reactions include enhanced solubility of hydrophobic substrates, elimination of side reactions caused by water, facilitation of product recovery, and protection from microbial contamination [85]. For instance, using low reaction temperatures, 98% conversion of carboxylic acid was achieved within 12.5 h for methanolysis of oleic acid [86]. The half-life of the lipase used was reported to be 15 days. However, lipase is relatively more expensive, in addition to producing insufficient reaction yields, higher sensitivity to the reaction conditions, as well as, long reaction times when compared to the use of homogeneous or heterogeneous acid catalysts. The use of homogeneous and heterogeneous acid catalysts for FFA esterification has been extensively researched due to its insensitivity to a wide range of feedstocks, high production yields, relatively low cost, and potentially being recoverable for re-use.

The most common approach for processing waste greases in bio-diesel synthesis is a two-step acid pre-treatment before the successive base-catalyzed transesterification [88-91]. By using a two-step sulphuric acid-catalyzed pre-esterification, Canakci and Van Gerpen [90] were able to reduce the acid levels of the high FFA feedstocks (reaction mixtures containing 20-40 wt% FFA) below 1 wt% within 1 h, making the feedstocks suitable for subsequent alkali-catalyzed transesterification. Recently, the two-step catalyzed process was shown to be an economic and practical method for bio-diesel production from WCOs where acid values of 75.9 mg KOH/g were presented [88].

Employing a ferric sulphate catalyzed reaction followed by potassium hydroxide (KOH) catalyzed transesterification, a yield of 97.3% fatty acid methyl ester (FAME) was achieved within 4 h. By integrating the heterogeneous catalyst in the pre-treatment process, several advantages were introduced such as no acidic wastewater, higher efficiency, lower equipment cost, and easy recovery compared to corrosive liquid acids. Another reaction route for a two-step process was proposed and proven by Saka and his co-workers [81,92,93], where the first step involves hydrolysis with subcritical water at 270 °C and subsequently followed by methyl esterification of the oil products at the same temperature. In this process, TGs were hydrolyzed with subcritical water to yield FFAs, which further reacted with supercritical methanol, resulting in a completed reaction within 20 min.

Besides catalyzing the esterification, acid catalysts are able to perform TG transesterification; however, acid catalysts are 3 orders of magnitude slower than basic catalysts [38], thus allowing FFA esterification and TG transesterification to be catalyzed simultaneously [78,79,95,96]. The slow activity can be traded off with a decrease in process complexity, equipment pieces, and the amount of waste stream. For instance, Zhang et al. [78,79] have shown that, in bio-diesel production using WCOs, a one-step acid catalyzed process offered more advantages over the alkali-catalyzed process with regard to both technological and economical benefits. It was also proved to be a competitive alternative to a two-step acid pre-esterification process.

2.6.3 Bio-diesel Production from Soapstock

Soapstock, known as a by-product of refining vegetable oils, is another low value feedstock for bio-diesel production. Soapstock contains a substantial amount of water, which can be emulsified with the lipid constitutes and is difficult to remove. In addition, the presence of both FFA and acylglycerols makes the transesterification reaction more complicated. Alkaline catalysis cannot be utilized due to the high FFA level [90]. Haas et al. [132] developed a simple, high-efficiency method for synthesis of bio-diesel from soybean oil soapstock. The process involved two steps: the first step, alkaline hydrolysis of all lipid-linked fatty acid ester bonds and the second step, acid-catalyzed esterification of the resulting fatty acid sodium salts. In the first step, all glycerides and phosphoglycerides in the soapstock could be completely saponified. After water removal, the resulting FFA sodium salts were rapidly and quantitatively converted into fatty acid methyl ester (FAME) by incubation with methanol and sulphuric acid at 35 ºC and ambient pressure in the second step. The specifications of the FAME produced could meet the current specifications for bio-diesel. This bench-scale method was further developed to the small pilot scale, producing about 2.5 litres of material per run [133].

All variables examined for the ester product, including flash point, water and sediment, carbon residue, sulphated ash, density, kinematic viscosity, sulphur, cetane number, cloud point, copper corrosion, acid number, free glycerin, and total glycerin were within the provisional bio-diesel specifications of the ASTM. Density and iodine values were comparable to those of commercial soy-based bio-diesel. The emission profile was quite similar to that of bio-diesel produced from refined soy oil, showing reductions of total hydrocarbons, particulates and CO, compared with petroleum diesel fuel.

However, Haas et al. [134] found that though this method could achieve the efficient production of high-purity bio-diesel, substantial amounts of solid sodium sulphate were generated as a by-product. The cost related to the disposal of this waste material could be high. Therefore, they only used acid catalyzed esterification to produce bio-diesel from soapstock. The optimal conditions for the maximum esterification were found to be at 65 ºC, 26 h, a molar ratio of total FA/methanol/ sulphuric acid of 1:1.5:1.5. Further economic analysis by Haas [135], suggested that the production cost of soapstock bio-diesel would be approximately US$ 0.41/l, a 25% reduction relative to the estimated cost of bio-diesel produced from soy oil.

Jin et al. [136] developed a three-step process for producing bio-diesel from the mixture of oil sediments (OS) and soapstocks (SS), at the same time, phosphatides were obtained. In the first step, the OS-SS mixture was extracted with ethyl ether and the mixture was divided into three phases. Cooled acetone was chosen to extract the organic top phase, including TGs and phosphatides. Phosphatides were separated from TGs since they were insoluble in the acetone. In the second step, soap phase was acidified with sulphuric acid to yield fatty acid. Then the so called "high acid" oil was efficiently converted into methyl esters by acid-catalyzed esterification. The esterification reaction was carried out with 5:1 methanol/oil (mol/mol) in the presence of 3% sulphuric acid as an acid catalyst at 85 ºC for 5 h. Bio-diesel recovery under these conditions was 92.1% of theoretical. Alkaline catalyzed transesterification process was performed in the third step to convert the TGs into bio-diesel and glycerol. The maximum ester yield of 94% was obtained under the optimal variables: 6/1 methanol/oil (mol/mol), 1% NaOH (wt.%), 65 ºC, and 1 h. Five important fuel properties of bio-diesel from the OS-SS mixture, including density (at 15 ºC), kinematic viscosity (at 40 ºC), flash point, calorific value, and acid value, were found to be comparable to those of the No. 2 diesel fuel and conforming to both the American and German standards for bio-diesel.

Recently, Wang et al. [137] pointed out three major disadvantages of the process developed by Haas [135]: (1) High temperature steam is required since conventional acidulation method is needed to recover acid oil from soapstock; (2) An additional process, saponification of the glycerides, is needed to convert them to free fatty acid salts; (3) The esterification reaction time is too long, leading to low productivity. The authors developed an attractive method to produce bio-diesel from soybean soapstock. Separation of extracted acid oil from soapstock was performed with only sulphuric acid solution under an ambient temperature of 25±2 ºC. A maximum acid oil recovery yield of 97% could be achieved based on the total fatty acids of the soapstock. The acid oil could be directly converted into bio-diesel at 95 ºC in a pressurized reactor within 5 h and the yield of purified bio-diesel was 94% based on the total fatty acids of the soapstock. The optimal esterification conditions were determined to be a weight ratio of 1:1.5:0.1 of acid oil/methanol/sulphuric acid.

Besides soybean oil soapstock, other soapstocks are also of interest to be utilized to produce bio-diesel, thus increasing the potential supply of this fuel. Usta et al. [138] first used hazelnut soapstock/waste sunflower oil mixture to produce bio-diesel. The process involved two steps, including acid (sulphuric acid) and base (sodium hydroxide) catalysis. The hazelnut soapstock/waste sunflower oil mixture was first heated to 100 ºC to remove the water. Then, the mixture was cooled down to 35 ºC before the 2nd-step catalysis. The effects of the bio-diesel addition to the diesel fuel on the performance and emissions of a four cycles, four cylinder, turbocharged indirect injection diesel engine were investigated at both full and partial loads. Experimental results indicated that the hazelnut soapstock/waste sunflower oil methyl ester could be partially substituted for diesel fuel at most operating conditions without any engine modification and preheating of the blends.

Keskin et al. [139] used cottonseed oil soapstock to produce bio-diesel. The cottonseed oil soapstock bio-diesel was blended with diesel fuel and the blends were tested in a single cylinder direct injection diesel engine. It was reported that high calorific value and cetane number, low sulphur and aromatic content, and similar characteristics were observed for the blends. The power output and torque of the engine with blends decreased by 6.2% and 5.8%, respectively. Particulate material emission of the engine with blends at maximum torque speed was decreased by 46.6%. It was concluded that blends of cottonseed oil soapstock bio-diesel and diesel fuel could be used as alternative fuels in conventional diesel engines without any major changes. However, since bio-diesel has a solvent effect that may release deposits accumulated on tank walls and pipes from previous diesel fuel usage, which may end up in fuel filters, these would need to be checked more frequently.

In summary, WCO, grease, and soapstock are potential feedstocks for bio-diesel production, which can lower the cost of bio-diesel since they are inexpensive. However, since all these feedstocks contain high FFA, it will cause soap and water formation when using an alkaline catalyst, which could decrease the ester yield and make the separation of ester, glycerol, and wash water more difficult. Acid catalysts can convert FFAs into esters, but the reaction rate is too slow. Moreover, this process requires more alcohol and large reactors and is corrosive [65]. The two-step process, of which the first step serves as a pre-treatment, is usually preferred. However, this will increase the unit's cost. Supercritical transesterification process can be an alternative method because of the following advantage: the pre-treatment step, soap and catalyst removal are not necessary since a catalyst is not required [134-137]. The reaction duration is significantly shorter than traditional transesterification reaction [26]. The reaction is not sensitive to either FFA or water [81,136]. However, this method requires a high molar ratio of alcohol to feedstock [26,134.135] and high reaction pressure and temperature, which will cause higher operating costs.

2.6.4 Bio-diesel Production from Jatropha Oil

There is growing interest for bio-diesel production from non-edible oil sources, like Jatropha curcas L. (JCL). JCL is a plant belonging to Euphorbiaceae family, which is a non-edible oil-bearing plant widespread in arid, semi-arid and tropical regions of the world [88]. JCL has an estimated annual production potential of 200 000 metric tonnes in India and can be grown in waste land [74]. Singh et al. [145] gave detailed information on the use of different components of JCL fruit for energy purposes. It was found that the shell could be for combustion, hull/husk for gasification, cake for production of biogas, spent slurry as manure, oil and bio-diesel (made from Jatropha oil) for running CI engines. The kernels of JCL contain about 50% oil. The oil recovery in a mechanical expeller was about 85%, while more than 95% recovery of oil could be achieved when extracted by solvent method. The bio-diesel from JCL oil has a great potential because of its comparable properties to diesel, such as calorific value and cetane number [146]. Therefore, many researchers have shown great interest in using Jatropha oil to produce bio-diesel.

Azam et al. [147] found FAME of Jatropha curcas were most suitable for use as bio-diesel and met the major specification of bio-diesel standards of the European, Germany and USA Standards Organization. Sarin et al. [148] made appropriate blends of Jatropha and palm bio-diesel to improve oxidation stability and low temperature properties because Jatropha bio-diesel has good low temperature property and palm bio-diesel has good oxidative stability. It was found that antioxidant dosage could be reduced by 80-90% when palm oil bio-diesel is blended with Jatropha bio-diesel at about 20-40%. Tiwari et al. [117] used response surface methodology to optimize three important reaction variables, including methanol quantity, acid concentration, and reaction time. The optimum combination for producing bio-diesel and reducing the FFA of Jatropha oil from 14% to less than 1% was found to be 1.43% v/v sulphuric acid catalyst, 0.28 v/v methanol-to-oil ration and 88 min reaction time at 60 ºC. The properties of Jatropha oil bio-diesel conform to European and American standards.

Berchmans et al. [118] developed a two-step pre-treatment process in which the high FFA (15%) of Jatropha curcas seed oil was reduced to less than 1%. In the first step, the reaction was carried out with 0.60 w/w methanol-to-oil ratio in the presence of 1 wt.% sulphuric acid as an acid catalyst in 1 h at 50 ºC. In the second step, the transesterification reaction was performed using 0.24 w/w methanol-to-oil ratio and 1.4 wt% sodium hydroxide

(NaOH) as alkaline catalyst to produce bio-diesel at 65 ºC. A final bio-diesel yield of 90% in 2 h was reported. As well as experimental studies, theoretical studies of reaction mechanism have been conducted regarding base-catalyzed transesterification of the glycerides of the Jatropha oil [119]. In that study, semi-empirical AM1 molecular orbital calculations were used to investigate the reaction pathways of base catalyzed transesterification of glycerides of palmitic, oleic and linoleic acid. The researchers concluded that the reaction mechanism included three steps: Step 1- Nucleophilic attack of the alkoxide anion on the carbonyl group of the glyceride to form a tetrahedral intermediate. Step 2-Breaking of the tetrahedral intermediate to form the alkyl ester and the glyceride anion. Step 3-Regeneration of the active catalyst, which may start another catalytic cycle. This study suggested that the Step 2, decomposition of the tetrahedral intermediate, determined the rate of base-catalyzed transesterification of glycerides.

Meanwhile, many researchers have attempted to evaluate the performance, emission, and combustion characteristics of Jatropha oil and Jatropha oil bio-diesel in a diesel engine [130, 134-136]. Haldar et al. [150] found that Jatropha oil gave the best results related to the performance and emissions, such as CO, CO2, HC, smoke and particulates, at high loads when injected 45º before Top Dead Center when compared with non-edible straight vegetable oils of Putranjiva, Jatropha and Karanja. Kumar et al. [151] used Jatropha oil and methanol in various methods, such as blending, transesterification and dual fuel operation (methanol/Jatropha oil=3:7, v/v) to compare with performance, emission and combustion parameters. Experimental results indicated that Jatropha oil and methyl ester showed higher diffusion combustion compared to standard diesel operation. Jatropha oil could be used as fuel in diesel engines directly and by blending it with methanol. Use of methyl ester of Jatropha oil and dual fuel operation with methanol induction could give better performance and reduced smoke emissions than the blend.

Similar observations have been reported by other researchers [145], who found that bio-diesel from Jatropha oil offered higher brake thermal efficiency than blended de-waxed de-gummed Jatropha oil or even diesel. Jatropha oil bio-diesel could be blended with diesel in any proportion or could be used as pure bio-diesel successfully in CI engine without any problem. In spite of above-mentioned advantages related to engine emissions, higher NOx exhaust levels with Jatropha based bio-diesel have been reported by several researchers [146,147]. To solve this, Pradeep et al. [98] effectively employed a low cost technique, hot exhaust gas recirculation (HOT EGR). Compared with COOLED EGR, this method was cost-effective and easy to implement. The optimal EGR level was 15%, based on adequate reduction in nitric oxide emissions, minimum possible smoke, CO, HC emissions and reasonable brake thermal efficiency.

Though attracting substantial interest due to its general characteristics and potential, it is recommended by some researchers that more and better data are urgently needed to guide investment since uncertainties do exist, based on the fact that Jatropha curcas is a wild plant which exhibits a lot of variability in yield, oil content and oil quality [155]. An extensive study on Jatropha bio-diesel fuel sustainability, including the three inseparable dimensions: environmental, economic and social, emphasized the situation-specific interactions between different sustainability dimensions and consideration of the political and ethical side of bio-energy production [156]. Achten et al. [156] pointed out that based on the available information it is still difficult to conclude whether JCL bio-diesel will meet the two essential minimum requirements for bio-fuels: to be a more sustainable alternative than fossil fuels (i.e. produced from renewable raw material and that their use has a lower negative environmental impact.

2.7 Conclusions

In summary, several studies have shown that use of bio-fuels for transport could reduce exhaust gas emissions and improve engine performance. There were four primary options for making bio-diesel from vegetable oils. In a previous study, the best option to conversion the vegetable oils to bio-diesel was transesterification process. For making bio-diesel, transesterification process is performed to lower viscosity of vegetable oils and complete conversion.

Various factors affect on the transesterification process, and the more important ones were described in this chapter. Catalyst type and its concentration, molar ratio of alcohol to oil and type of alcohol, effect of temperature and reaction time, and rate of mixing are the most important factors affect in the transesterification reaction. Commonly used alkali catalysts are sodium hydroxide (NaOH), sodium methoxide (NaOCH3), potassium hydroxide (KOH), and potassium methoxide (KOCH3).

In general, increasing catalyst concentration (in range 0.5 to 1.5% wt/wt) had curvilinear effect on the conversion obtained, with yield inhibited at high catalyst concentration. The yield best was obtained at around 1% (wt/wt) catalyst concentration and a reduction in yield observed as catalyst concentration is increasing. 100-200% excess alcohol is used, which drives the reaction in the forward direction and favours bio-diesel production. Methanol and ethanol are commonly used, especially methanol because of its low cost. But, a very high molar ratio of alcohol to vegetable oil is avoided due to it might interfere with the separation of bio-diesel and glycerol post transesterification reaction which is caused reduction of yield.

While bio-diesel has many advantages compared with petroleum diesel, its high production cost has become the primary barrier to its commercialization. Currently, bio-diesel unit price is 1.5-3.0 times higher than that of petroleum derived diesel fuel depending on feedstock. However, waste vegetable oils are generally low cost and usually can be collected from restraints.

The other low cost feedstocks for bio-diesel production are from waste grease, from soapstock, and from jatropha oil. However, since all these feedstocks contain high FFA, it will cause soap and water formation when using an alkaline catalyst, which could decrease the ester yield and make the separation of ester, and glycerol more difficult. Acid catalysts can convert FFAs into esters, but the reaction rate is too slow. Moreover, this process requires more alcohol and large reactors and is corrosive.

The next chapter presents the experimental techniques and “Fuelpod” machine at University of Huddersfield used in the bio-diesel production from pure and waste vegetable oils by using trasesterification process.

CHAPTER – 3

BIO-DIESEL PRODUCTION PROCESS

3.1 Introduction

Bio-diesel is a mixture of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conforms to the requirements of ASTM D6751 [205,206]. Table 3.1 lists comparable properties of Bio-diesel and conventional diesel. It can be seen that bio-diesel can be used either as a substitute for conventional diesel fuel or, more commonly, in fuel blends. Bio-diesel has advantages over petroleum-based diesel including higher lubricity which prolongs engine life and reduces the frequency of engine component replacement, a higher cetane number and a higher flash point, meaning better and safer performance, and the presence of oxygen (~10%) which improves combustion and reduces CO and hydrocarbon emissions.

The ASTM standards ensure both safety in the production of bio-diesel and quality of the end product. The following generalization which can be defined as follows:

- Complete reaction to establish an equilibrium
- Removal of all free fatty acids
- Removal of all traces of glycerol, base catalyst and excess alcohol.

Following ASTM standards allows production of bio-diesel fuel of repeatable quality sufficient to be used for testing. Bio-diesel produced in our lab from vegetable oils exhibited gave improved engine performance and reduced exhaust emissions. Its stability was acceptable according to the ASTM D6751, which was correlated to the content of pigments, such as gossypol [207,208].

Table 3.1: American Society for Testing and Materials (ASTM) Standards of maximum allowed quantities in diesel and bio-diesel [205,206].

Property	Diesel	Bio-diesel
Standard	ASTM D975	ASTM D6751
Composition	HC[a] (C10-C21)	FAME[b] (C12-C22)
Kinematic viscosity (mm^2/s) at 40 °C	1.9-4.1	1.9-6.0
Boiling point (°C)	188-343	182-338
Flash point (°C)	60-80	100-170
Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 16
Water (vol %)	0.05	0.05
Carbon (wt %)	87	77
Hydrogen (wt %)	13	12
Oxygen (wt %)	0	11
Sulphur (wt %)	0.05	0.05
Cetane number (ignition quality)	40-55	48-60
Stoichiometric air/fuel ratio (AFR)	15	13.8
HFRR[c] (µm)	685	314
BOCLE[d] scuff (g)	3600	>7000

[a] Hydrocarbons. [b] Fatty Acid Methyl Esters. [c] High Frequency Reciprocating Rig. [d] Ball-on-Cylinder Lubricity Evaluator.

3.2 Materials and Methods

3.2.1 Materials

Methanol and sodium hydroxide were purchased from Fisher Scientific (Loughborough, Leicestershire, UK). Pure vegetable oils such as sunflower oil, rapeseed oil, corn oil and soybean oil were bought from local shops in Huddersfield, United Kingdom. Waste cooking oil was supplied by Huddersfield University Catering Services. The diesel oil (B0) was obtained for specialist oil suppliers as commercially available diesel is B5.

3.2.2 Fatty Acid Profile

3 mg of oil was weighed and mixed with 50 ml of ethanol. The mixture of oil and alcohol was heated on a hotplate, until almost boiling. At this stage 3 drops of phenolphthalein were added to the mixture as a pH indicator. Then 0.025M ethanolic NaOH was added drop by drop for transesterification, this give the solution a faint permanent pink colour. While titrating the contents of the flask was swirled by magnetic stirrer to thoroughly mix the contents. The end point of the titration was when the pink colour shown in Figure A.1 (the same colour as in the neutralised ethanol) persisted for about 20-30 seconds.

3.3 Experimental Setup Design

A commercial bio-diesel processor "Fuelpod" manufacturer was used for the production of bio-diesel from rapeseed oil, sunflower oil, soybean oil, corn oil and waste vegetable oil, see Figure 3.1. Batches of fifty litres of each type of vegetable oil were used in the transesterification vessel. For the transesterification process shown in Figure 3.2, 50 L of vegetable oil was taken in a single tank section and heated at 65^{o}C for 2-3 hours. The NaOH required for the transesterification was added to the tank as a mix of 200 gm of NaOH dissolved in 8 L of methanol (the amount of NaOH was increased if the oil contained a measurable amount of free fatty acid, since free fatty acid consumes NaOH, converting it to the sodium salt). Oil Methyl Ester forms the upper layer in the separating funnel and glycerol forms the lower layer, see Figure 3.3.

The machine processor which converted vegetable oil to bio-diesel in this study is a complete system used at the University of Huddersfield automotive laboratory for making bio-diesel.

Figure 3.1: Fuelpod for transesterifying oils

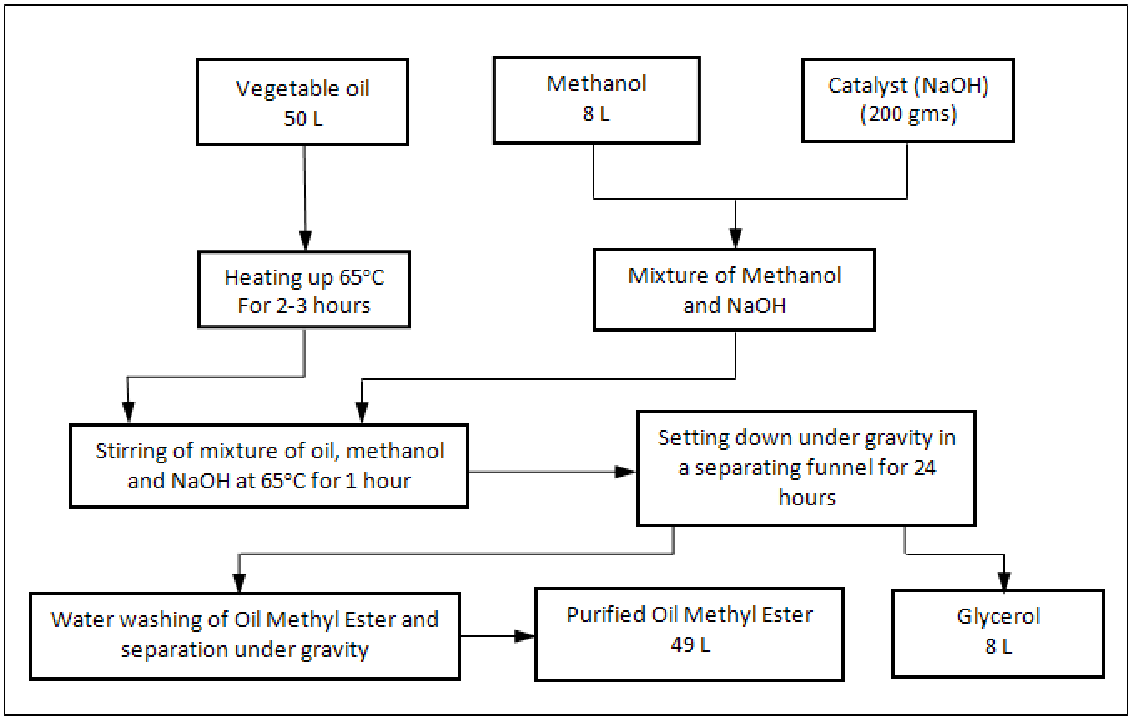


Figure 3.2: Flow chart for transesterification process

After at least 2 hours the amount of glycerol in the bottom of the drain pan was measured. If there is a 10 to 12 % separation the base oil has reacted properly. Glycerol has a dark brown colour, while bio-diesel fuel has a clear yellow appearance somewhat like apple juice, see Figure 3.3 below.

Figure 3.3: Bio-diesel and glycerol separation

3.3.1 Titration Process

Titration was used to determine the acidic level of the base oil and calculate the amount of base catalyst required for reaction. This step was necessary to determine the correct amount of catalyst to use, to avoid undesired results and unusable fuel. The equipments and materials were used for the experimental of titration process is shown in Figure A.2.

3.3.2 Oil Titration Test Procedure (see Figure A.3)

Placed a clean glass beaker in each circle on the laminated card, squirt methanol into the left hand beaker about $5mm$ deep, squirt titrant solution into the right hand beaker about $5mm$ deep, use a clean eyedropper to place $10ml$ of methanol into the centre beaker, added 3 drops of pH indicator to the centre beaker (should appear yellow), used a clean eyedropper to place 1ml of oil into the centre beaker, mix thoroughly used a squirting action with the eyedropper (should appear yellow/ orange), use the wheel on the pipette handle to draw titrant into the pipette up to exactly the zero mark, Slowly drip titrant until a stable blue/green is seen (as in Figure A.3). This was achieved after 15-20 seconds, and read the pipette to determine how much titrant was added. The instruction manual for the "Fuelpod" specified how much catalyst was needed (as seen in Figure A.4 manufacture laminated card).

3.3.3 Methanol and Sodium Hydroxide Mixture Prepare

The first step after titration result was to prepare the mixture of methanol and sodium hydroxide, see Figure A.5. For this a plastic container was used to avoid the risk of the alcohol corroding the container over time. 8 litres of methanol was added to the container along with either 200 grams or 400 grams of sodium hydroxide for pure oils and waste oil (high FFA content about 4.4%) respectively. This process can be seen in Figure A.5. After that the container was connected with the system as shown in Figure A.6.

3.3.4 Kinematic Viscosity Measurement

The greatest difference between vegetable and diesel oils is their viscosities. The high viscosity of crude oil may contribute to the formation of carbon deposits in engines, incomplete fuel combustion and reduced life of an engine. Thus it is important to know the viscosity of vegetable oil before it is use it as fuel. Figure A.7 shows the equipment used to measure kinematic viscosity. According to ASTM Bio-diesel standard D6751 test method D445, the kinematic viscosity for bio-diesel will be between 1.9 and 6.0 mm^2/s at 40^oC. For this range of viscosities, a B size U-tube viscometer is suitable as it has range of between 2 to 10 mm^2/s [222].

Also used was U-tube viscometer size D, which is suitable for vegetable oils, and has a kinematic viscosity range 20-100 mm^2/s [222]. The results obtained are as a results section. The U-tube viscometers were kept in a water bath which provided stable temperatures of 20^oC, 40^oC and 70^oC.

3.3.5 Iodine Number

Iodine numbers were subsequently measured using the Wijs titration method. Samples were dissolved in 1.0 ml cyclohexane and mixed with iodine monochloride (the Wijs solution), after which a cork was inserted and the solution was allowed to stand for 30 minutes. Subsequently, 2 ml potassium iodide and 10 ml distilled water were added, and the prepared sample solutions were titrated using 0.1 mol/litre thiosulphate. The experiment apparatus is shown in Figure A.8.

3.3.6 Calorific Value Measurement

During this study, the energy content of bio-diesel fuels and vegetable oils was determined by practical experiment using the bomb calorimeter shown in Figure A.9. The test process required the following supplies:

- Parr Bomb calorimeter and power supply,
- Pellet press,
- One 18-30°C thermometer graduated to 0.01°C,
- Timer,
- Oxygen tank,
- Towel,
- 4-litre beaker,
- 2000 ml graduated cylinder,
- Fuse, and
- Bomb Calorimeter Manual.

The amount of sample was exactly 1 g and the oxygen pressure was exactly 30 atm. The ignition leads were connected, and the bomb immersed in 2 litres of water. The final steady temperature of the can is then determined by extrapolation and recorded. The water heat equivalent of the calorimeter was found using heat benzoic acid and then determines the heat of combustion of naphthalene and the unknown.

The standard enthalpy of combustion for a substance is defined as the enthalpy change (ΔH_T^o) which accompanies a process in which the given substance undergoes reaction with oxygen gas to form specified combustion products such as CO_2(g), H_2O(l), N_2(g), SO_2(g), all reactants and products being in their respective standard states at the given temperature T.

Thus the standard enthalpy of combustion of benzoic acid at 298.15°K is $\Delta H^o{}_{298.\ 15}$ for the process:

$$C_6H_5CO_2H(S) + \frac{15}{2O_2(g)} = 7CO_2(g) + 3H_20(l) \qquad (3.1)$$

The enthalpy of combustion can be calculated from the temperature rise, which results when the combustion reaction takes place under adiabatic conditions in a calorimeter. It is important that the reaction in the calorimeter take place rapidly and completely. To this end, the material is burned in a steel bomb with oxygen under a pressure of about 30 atm. A special acid-resistant alloy is used for the construction of the bomb because water and acids are produced in the reaction.

The first law of thermodynamics, $\Delta U = q - w$ (3.2)

Where: ΔU = internal energy change for system,
$q =$ energy transfer into system by heat flow, and
$-w$ = work done by system may be applied to the actual calorimeter process, for adiabatic conditions, $q = 0$.

In the present experiment, w, which consists mainly of the work of stirring, can be neglected and Eq. (3.2) then becomes:

$$\Delta U_c = 0 \tag{3.3}$$

Where: $\Delta U_c =$ energy change for the actual calorimeter process.

Since the energy change is independent of path by which the change occurs:

$$\Delta U_c = \Delta U_{T1} + \int_{T_1}^{T_2} C dT \tag{3.4}$$

Where: $\Delta U_{T1} =$ internal energy change for system,
$T_1 =$ initial temperatures in the calorimeter process,
$T_2 =$ final temperatures in the calorimeter process, and
$C =$ heat capacity of can and contents under the conditions of the experiment.

Since the temperature change is small, it is usually valid to consider C to be constant, so that the integral becomes equal to $C(T_2 - T_1)$. One then obtains:

$$\Delta U_{T1} = -C(T_2 - T_1) \tag{3.5}$$

It may be observed that a temperature rise corresponds to a negative ΔU_{T1}, that is, to a decrease in energy for the imagined isothermal process.

The next step is to calculate $\Delta U_T o$ from ΔU_{T1}. Although the energy is not sensitive to changes in pressure, the correction to standard states, called the Washburn correction, may amount to several tenths of one percent and is important in work of high accuracy. The principal Washburn correction terms allow for the changes in U associated with (1) changes in pressure, (2) mixing of reactant gases and separating product gases, and (3) dissolving reactant gases in, and extracting product gases from, the water in the bomb.

The standard enthalpy change $\Delta H_{T1}o$ may then be calculated. The definition of H leads directly to:

$$\Delta H_{T1}o = \Delta U_{T1}o + \Delta(PV) \qquad (3.6)$$

Since the standard enthalpy and energy for a real gas are so defined as to be the same, respectively, as the enthalpy and energy of the gas in the zero-pressure limit, the ideal-gas equation may be used to evaluate the contribution of gases to $\Delta(PV)$ in Eq. (3.6). The result is:

$$\Delta(PV) = (n_2 - n_1)RT \qquad (3.7)$$

Where: $n_2 =$ number of moles of gaseous products and $n_1 =$ number of moles of gaseous reactants.

3.3.7 Test Procedure

1 g of the sample is formed into a pellet by means of a pellet press; this is done to prevent an incomplete reaction due to scattering of material during combustion. The pellet is weighed and placed in the sample pan. The fuse wire, of measured length about 10 cm and known heat of combustion per unit length, is attached to the two terminals and adjusted to give firm contact with the pellet. It is important to avoid getting kinks in the fuse wire since fusion may occur at such points before the portion of wire in contact with the pellet becomes hot enough to initiate combustion. The surfaces at which closure of the bomb is to be effected must be kept scrupulously clean and every precaution taken to avoid marking them. The parts of the dismantled bomb should be placed on a clean, folded towel.

The cover is carefully assembled with the bomb and tightened. The bomb is then connected to the oxygen tank, and oxygen is admitted slowly until the pressure is 30 atm. The valves are then closed, the pressure in the line is released, and the bomb is removed. 2000 ml of water is then placed in the calorimeter can, within the adiabatic jacket. The temperature of this water was adjusted so as to be at least several degrees below the upper limit of the thermometer range and preferably close to room temperature. The ignition leads were connected and the bomb is immersed in the water. The water in the can must cover the bomb. If gas bubbles escape, the assembly ring may require tightening, or the gaskets may need to be replaced.

The cover of the adiabatic jacket is set in place and the thermometer lowered into position. The thermometer in the can is read for a few minutes to be sure that equilibrium has been attained. This temperature is recorded as the initial temperature T_1. The ignition switch is then closed until fusion of the wire is indicated by extinction of the lamp. However, the switch should not be held closed for more than about 5 sec because damage to the ignition unit or undue heating by passage of current through the water may result. If combustion has occurred, the temperature of the water in the can will be seen to rise within a few seconds. Otherwise the leads should be examined, the voltage output of the ignition circuit checked, or the bomb opened and examined for possible problems. After a successful ignition, the temperature of the calorimeter rises quickly. After several minutes the rate of change of the temperature becomes small. The final steady temperature of the can is then determined by extrapolation and recorded as T_2.

3.3.8 Calculations

Two runs were made with benzoic acid for determination of the heat capacity of the calorimeter, and two with oil sample for determination of the enthalpy of combustion. Calculations for the heat capacity (C) may be written as:

$$C = mC_{H2O} + C_o \tag{3.8}$$

Where:

m = mass of water in can, and

C_{H2O} = heat capacity of water per gram = 0.999 cal deg^{-1} g^{-1} at room temperature.

C_o = represents the heat capacity of the calorimeter (bomb and contents, can, immersed portion of thermometer, etc.). The value of C_o is assumed to be the same for all runs.

For the tests using benzoic acid, internal energy change for the system (ΔU_{T1}) is known, and C_o may be calculated from the measured temperature rise. The value of ΔU_{T1} is calculated from 6318 cal per gram of benzoic acid burned and the value specified by the manufacturer for the wire burned (2.3 cal cm^{-1} for Parr 45C10 No. 34 B & S gauge Chromel C), see Figure 3.4.

The data for the naphthalene runs were used to calculate the standard enthalpy change (ΔU_{T1}^{o}) and the standard heat of combustion (ΔH°_{T1}); for student work, the difference between ΔU_{T1} and ΔU^{o}_{T1} may be considered negligible. The values of ΔU°_{T1}, and ΔH_{T1} should be reported for 1 mole of sample. The standard enthalpy of formation of naphthalene is then calculated from the values -94.05 and -68.32 kcal $mole^{-1}$ for the standard enthalpies of formation of CO_2(g) and H_2O(I), respectively, at 25°. If the experimental values of T_1 are within a few degrees of 25°, the correction of the enthalpy of combustion from T_1 to 25° may be omitted.

Figure 3.4: Benzoic acid and fuse wire for bomb calorimeter

ΔT is determined for each run as follows: the temperature is plotted as a function of time using a spread sheet program. A linear least square fit is performed over the pre- and post-ignition periods and the results extrapolated over the entire time period as shown in Figure 3.5.

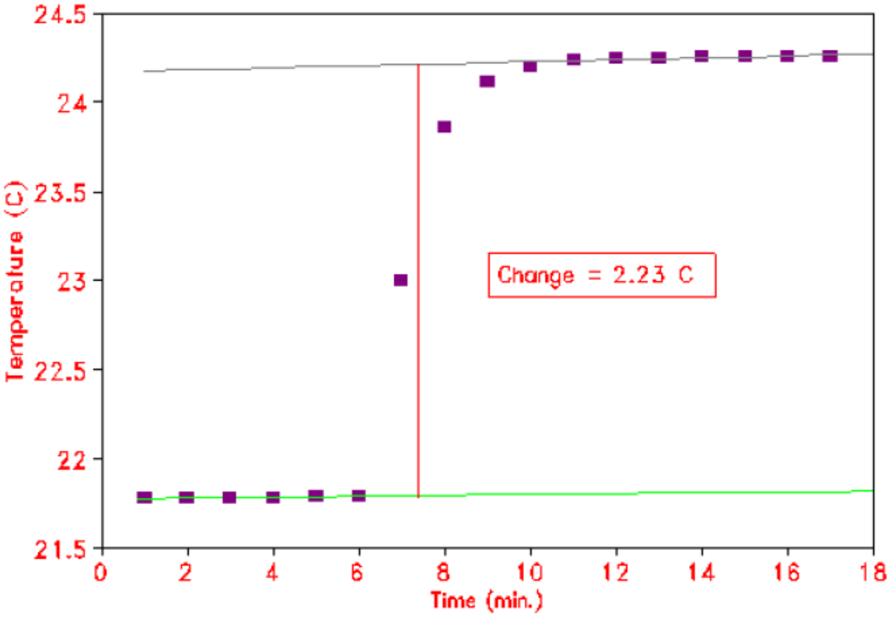


Figure 3.5: Temperature versus time for sample combustion of benzoic acid

Draw a vertical line such that areas A and B shown in Figure 3.6 are equal. The top and bottom of the line correspond to temperatures T_2 and T_1, respectively, and the length of the line is (T_2 - T_1), is taken as ΔT for the combustion reaction.

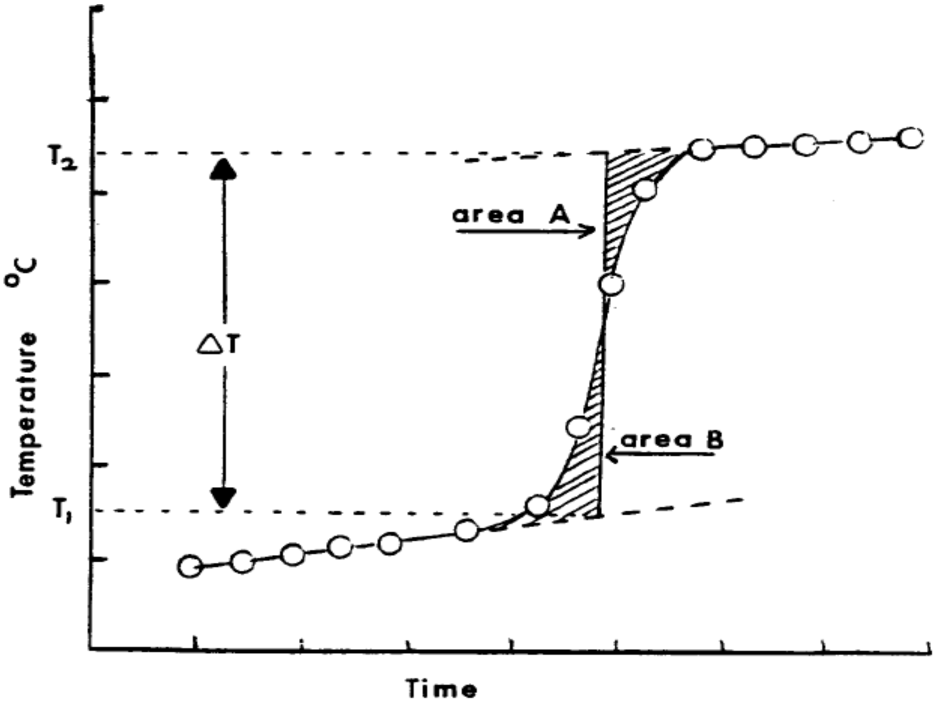


Figure 3.6: Calculation of the change in temperature due to the combustion process

3.4 Results and Discussion

3.4.1 Glycerol Separation and Bio-diesel Washing

Washing of final ester products is a very important activity during bio-diesel processing. The ester was washed several times through the distilled water creating fine mist from the top through a spray. Kemp [209] reported that fine mist washing produces less agitation with less soap formation. Washing can be improved by using hot wash water of 50-60°C [210].

3.4.2 Conversion Efficiency and Effect of Catalyst Content

The experimental ester production was repeated for each batch of pure and waste cooking oils to determine the yield of ester and glycerol. The ester conversion was obtained from the Fuelpod system. The average yield of ester was found to be 49 litres and 35 litres from pure and waste cooking oil respectively. Thus, the average yield of ester obtained after transesterification process was about 98 % by volume from the pure oils and 70 % from the waste oil. On the other hand, the average amount of glycerol obtained as a by-product from 50 litres of oil was 8 litres, as shown in Figures 3.2 and 3.3.

Issariyakul et al. [125] obtained an ethyl ester conversion of waste cooking oil contained approximately 5-6% by weight of free fatty acid of up to 97%. The authors used a two stage acid and alkali catalyzed transesterification. Leung et al. [114] reported that the conversion of waste cooking oil using sodium hydroxide catalysts was approximately 86%. Zheng et al. [95] showed that methyl ester conversion of waste cooking oil in acid catalyzed transesterification can reach up to 99% using a very high methanol to oil ratio (250:1). Transesterification for waste cooking oil was carried out using 0.4%, 0.6%, 0.8%, 1.0% and 1.2% catalyst concentration. With 0.4 % of catalyst concentration, no reaction was observed as there was no separated layer of ester and glycerol. With the catalyst concentration of 0.6%, 0.8% and 1.0%, ester yield were approximately 50%, 91% and 40%, respectively (see Figure 3.7).

It was observed that the ester yield decreased with the increase in sodium hydroxide concentration. With 1.2% catalyst concentration, a complete soap formation was observed. This is because the higher amount of catalyst caused soap formation [110]. The rise in soap formation made the ester dissolve into the glycerol layer (see Figure 3.7).

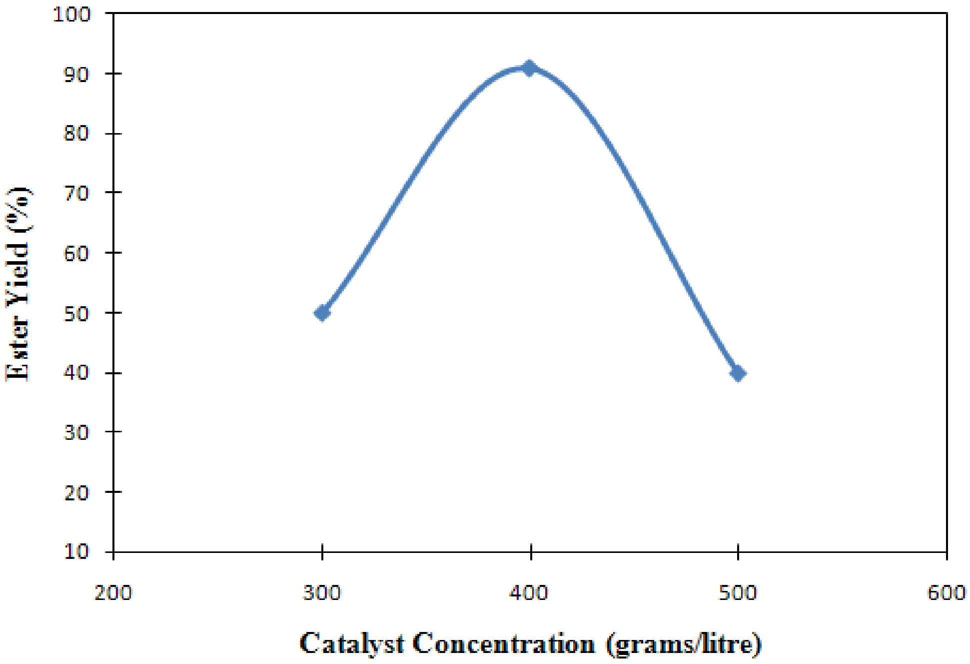


Figure 3.7: Effect of catalyst concentration on ester yield conversion

3.4.3 Fatty Acid Content Analysis

Fatty acid contents are the major indicators of the properties of bio-diesel since the amount and type of fatty acid content in the bio-diesel largely determine its viscosity. Duplicate samples were used to determine the fatty acid content of the bio-diesel product. Table 3.2 shows the Free Fatty Acid (FFA) content (calculated as oleic acid) of each type of oil used in this experiment. Bio-diesel from the waste cooking oil contained the highest amount of FFA content, an average 4.4%. The pure vegetable oils contained only about 0.15%, which are within permitted levels for being used directly for reaction with an alkaline catalyst to produce bio-diesel. The qualitative and quantitative analyses of fatty acid content are comparable with the study reported by Issariyakul et al. [125].

As mentioned earlier when FFAs react with an alkaline catalyst they cause soap and water formation which decrease the ester yield and prevent the separation of ester, glycerol, and wash water. Moreover, soap formation raises the viscosity and causes gel formation [90, 101,113,135]. If FFA concentration of the vegetable oil is higher than 0.5%, alkaline catalysts should not be used in the transesterification due to soap formation [90,98,218-220]. Nevertheless, some authors state that an alkaline catalyst can be used in transesterification up to an FFA level of 5% [216].

Table 3.2: Percentage of FFA Content

Type of oil	FFA Content (%) (calculated as oleic acid)
Sunflower	0.13
Rapeseed	0.12
Soybean	0.16
Corn	0.17
Waste Vegetable	4.4

3.4.4 Viscosity and Density of Vegetable Oils and Methyl Ester

High viscosity is the major problem preventing the use of vegetable oils and animal fats directly in diesel engines. The high viscosity of these oils is due to their large molecular mass (in the range of 600-900) which is about 20 times higher than that of diesel fuel [55]. The reduction in viscosity during the transesterification process reduces the problems associated with using vegetable oil in the engine. The viscosity of the pure and waste cooking oil was determined by using U-tube viscometer. Three samples of each type were used for the experiments. The average viscosity of pure and waste cooking oil sample was measured to be 52 mm^2/sec and 70 mm^2/sec at 20°C respectively. The measured viscosity of bio-diesel methyl ester at 40°C was 4.92 mm^2/sec, which is in the range recommended by ASTM (1.9-6.0 mm^2/sec at 40°C, see Table 3.1).

The density of pure and waste cooking oil measured at 15°C was 915 kg/m^3. The density of bio-diesel at 15°C was found to be 883 kg/m^3. Tate et al. [211] reported that density is a function of temperature and decreased linearly for canola methyl esters, soy methyl esters, and fish oil ethyl esters by 1.23 kg/m^3 for temperatures between 20–300°C.

3.4.5 Separations of Bio-diesel and Glycerol

Figure 3.8 shows the vessel in which the reaction mixtures were allowed to cool after completion of transesterification. After the mixture had cooled, crude bio-diesel and glycerol phases could be seen clearly. This phase separation occurred within a few minutes. However, the crude bio-diesel was cloudy and opaque. Clear separation was observed after 12-24 hours of settling.

Bio-diesel

Glycerol

Figure 3.8: Separation of bio-diesel and glycerol

3.4.6 Cloud point, Pour point and Flash point

The samples were tested to determine the fuel characteristics according to ASTM Bio-diesel Fuel Quality Assurance Standard Test (ASTM shown in Table 3.1). Tables 3.3 and 3.4 show the summary of the test results.

The cloud and pour point are also the important properties of bio-diesel fuel. Cloud point is the temperature at which a cloud of wax crystals first appears in the oil when it is cooled. The pour point is the lowest temperature at which the oil sample can still be poured as a liquid. These properties are related to the use of bio-diesel in cold temperatures. Table 3.3 shows a number of these properties for vegetable oils commonly used in bio-diesel production.

Table 3.3: Properties of vegetable oils commonly used in bio-diesel production

Type of vegetable oil	Density (kg/m^3 at 15^{o}C)	Kinematic viscosity (mm^2/s at 40^{o}C)	Calorific value (MJ/kg)	Cloud point (^{o}C)	Pour point (^{o}C)	Flash point (^{o}C)	Iodine number
Rapeseed	910	37.98	37.37	-3.9	-6.7	246	103.8
Corn	920	39.3	37.37	-1.1	-40.0	277	94.4
Soybean	915	35.28	36.75	-3.9	-12.2	254	102.8
Sunflower	920	33.72	37.26	7.2	-15.0	274	96.8
Waste oils	910	41.7	37.16	0	-39.7	279	81.57

Table 3.4: Properties of diesel fuel and bio-diesel fuels produced from different vegetable oils

Fuel type	Density (kg/m^3 at 15^{o}C)	Kinematic viscosity (mm^2/s at 40^{o}C)	Calorific value (MJ/kg)	Cloud point (^{o}C)	Pour point (^{o}C)	Flash point (^{o}C)	Cetane number
Rapeseed oil methyl ester	880	4.47	37.70	-1	-11	163	57
Corn oil methyl ester	880	4.78	37.45	0	-10	167	59
Soybean oil methyl ester	885	5.23	37.34	1	-7	178	55
Sunflower oil methyl ester	885	4.53	37.50	1	-6	173	60
Waste oil methyl ester	885	5.58	37.90	2	-7	179	62
Diesel	845	2.4	42.54	-5	-17	67	50

Table 3.4 shows the same properties for the methyl ester produced from rapeseed oil, corn oil, soybean oil, sunflower oil and waste cooking oil. The cloud point ranged between -1°C and 2°C. Lang et al. [212] reported the cloud point of ethyl esters of linseed oil, canola, sunflower and rapeseed oil were -2°C, -1°C, -1°C and -2°C, respectively whereas the corresponding methyl esters had cloud point of 0°C, 1°C, 1°C and 0°C. The cloud point of ethyl esters were approximately 2°C lower than those of the corresponding methyl esters. This indicates that the ethyl esters perform marginally better in cold temperatures than the corresponding methyl esters. For diesel the cloud temperature is -5°C, which means it will perform better at low temperatures than any of the bio-diesel fuels.

The pour points from rapeseed, corn, soybean, waste and sunflower oils ranged between -11°C and -6°C. Lang et al. [212] reported the pour point of ethyl esters of linseed oil, canola, sunflower and rapeseed oil were -6°C, -6°C, -5°C and -15°C respectively whereas the methyl esters of corresponding oils were reported to be -9°C, -9°C, -8°C and -15°C respectively. Lee et al. [213] argued that the cloud points were affected by the presence of mono-glycerides, however, the pour points were not affected. Moreover, the *cis* double bond present in the erucic acid of rapeseed oil hampered the lowering of the pour point for esters. The type of fatty acid branched chain available in the original oil has an impact on the pour point.

The flash point is the temperature at which the fuel will start to burn when it comes to contact with a flame or hot surface [215]. It is an important temperature from the safety point of view during storage and transportation. This temperature is correlated with its volatility, which is an important fuel feature for engine starting. The combination of high viscosity and low volatility of a fuel causes bad cold engine start up, misfire and ignition delay [217]. A fuel with high flash point may cause carbon deposits in the combustion chamber.

As shown in Table 3.4, the flash point of all bio-diesel fuels are far above that of diesel fuel, reflecting the non-volatile nature of these fuels. In spite of the fact that the flash points of vegetable oils were reduced through transesterification, they were still higher than those of diesel fuel, regardless of whether the bio-diesel was from pure vegetable oils or from waste cooking oil. However, if they are compared with each other, it was seen that the flash points of bio-diesels from waste oils was higher than those from pure vegetable oils since they have relatively more saturated fatty acids in their composition. The higher the cetane number and lower the volatility, smaller the amount of fuel that burns in the premixed combustion because the ignition delay ends sooner and less fuel evaporates. Therefore, NOx emission decreases due to lower combustion pressure and temperature [216].

3.4.7 Cetane, Iodine Number and Calorific Value

Cetane numbers are the indicators of ignition properties of the fuel. The higher the cetane number, the more efficient the ignition is. Because of its higher oxygen content, bio-diesel has a higher cetane number compared to petroleum diesel. The cetane number of rapeseed, corn, soybean, sunflower and waste cooking oil from experiment were found to be 59, 57, 59, 55, 60 and 62, respectively. Hilber et al. [214] reported the cetane number of methyl esters of rapeseed oil, soybean oil, palm oil, lard and beef tallow to be 58, 53, 65, 65 and 75 respectively. Among these bio-diesel feedstocks, beef tallow has the highest cetane number. The higher cetane number indicates the higher engine performance of beef tallow compared to other fuels, resulting in lower emission of all pollutants other than oxides of nitrogen (NOx). As beef tallow has the higher amount of saturated fatty acids, the increase in the saturated fatty acids content positively enhanced the cetane number of the bio-diesel. The oxidative stability of bio-diesel fuels also increases due to the presence of higher amount of saturated fatty acids. However, the drawback of higher amount of saturated fatty acid content in bio-diesel fuel is that the cold filter plugging point occurs at a higher temperature.

The traditional measure of the degree of bonds was given by the iodine number and can be determined by adding iodine to the vegetable oil. The amount of iodine in grams absorbed per 100 ml of vegetable oil was then the iodine number. The higher the iodine number, the more unsaturated (the greater the number of double bonds) the vegetable oil and the higher is the potential for the vegetable oil to polymerise. The iodine number of rapeseed, corn, soybean, sunflower and waste cooking oil from experiment were found to be 104, 94, 103, 97 and 82, respectively. The iodine number can be easily reduced by transesterification of vegetable oil with methanol using sodium hydroxide as catalyst. The methanol breaks the double bond and converts the vegetable oil into more saturated oil which reduces the tendency to polymerise.

On the other hand, the calorific values of methyl esters of vegetable oils were found to be about 37 MJ/ kg, while the calorific value of diesel fuel was 42.5 MJ/kg. The presence of chemically bound oxygen in vegetable oils lowers their calorific values by about 12 % as shown in the Tables 3.3 and 3.4.

3.4.8 Economic Assessment for Bio-diesel Based on the Vegetable Oil

Bio-diesel is currently produced from high quality food-grade vegetable oils (rapeseed oil in Europe and soybean oil in the USA) using methanol and an alkaline catalyst. The end cost of the bio-diesel mainly depends on the price of feedstock. The high cost of the food-grade oils increases the cost of bio-diesel and prevents its usage. Unfortunately, bio-diesel's economic viability has gone from bad to worse because of the recent increases in the vegetable oil prices. In the middle of 1990s, the cost of feedstock accounted for 60–75% of the total cost of bio-diesel fuel [27], but today about more than 85% of the costs of production are tied up in feedstock costs [79, 116]. Haas et al. [116] investigated the dependence of bio-diesel production costs on the cost of the feedstock and found a linear relationship between the two, with a change of US $0.020/l in the product cost per US $0.022/kg change in oil cost. This means that the relationship between the feedstock mass input and bio-diesel mass output is about 1:1.

To become an economically viable alternative fuel and to survive in the market, bio-diesel must compete economically with diesel fuel. However, the raw material cost of bio-diesel is already higher than the final cost of diesel fuel. Nowadays, bio-diesel unit price is 1.5–3.0 times higher than that of petroleum derived diesel fuel depending on feedstock [78,79,124].

In order to make bio-diesel an economically suitable fuel and increase its marketability, its high cost must be lowered. Low cost and profitable bio-diesel can be produced from low cost feedstocks such as used waste vegetable oils, animal fats, soapstocks, and greases [78,90]. Using such resources will affirmatively affect the bio-diesel break-even price and the difference between the prices of bio-diesel and diesel fuel could be lowered to an acceptable value. In the literature, there are several studies about cost accounting of bio-diesel from various feedstocks [88, 95, 101, 125-131], (see literature survey in chapter 2).

3.5 Conclusions

In summary, the Fuelpod machine was use for bio-diesel production from pure and waste vegetable oil without any optimization process. The experiments results were shown that the maximum yield was 98% and 75% for pure vegetable oil and waste vegetable oil respectively. These results were obtained by using methanol: oil molar ration of 4.5:1 and catalyst concentration of 0.4% (wt/wt) at a reaction temperature of 65^{o} and time of 180 min.

On the other hand, the experimental oils prosperities were shown, that the greatest difference between vegetable and diesel oil was their viscosity. It was between 34-40 mm^2/s for vegetable oil and 2.4 mm^2/s for diesel oil. After esterification of vegetable oil, there was significant reduction of viscosity and it was only about 5 mm^2/s. The next chapter will be presenting the experimental technique for optimization of bio-diesel production process by using response surface methodology (RSM). The results of yield from optimization condition will be comparing with yield from non-optimization condition.

CHAPTER – 4

OPTIMISATION OF FUEL MANUFACTURE PROCESS

4.1 Introduction

As explained previously, bio-diesel is derived from vegetable oils or animal fats through transesterification (also called alcoholysis) [85,109,208,212,232-234,244] which uses alcohols in the presence of a catalyst (e.g., base, acid or enzyme depending on the free fatty acid (FFA) content of the raw material) that chemically breaks the molecules of triglycerides into alkyl esters as bio-diesel fuels with glycerol as a by-product. The commonly used alcohols for the transesterification include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are adopted most frequently, particularly methanol due to its low cost.

Commonly used feedstocks (vegetable oil) for transesterification include soybean oil, rapeseed oil, etc. Recently there has been substantial research on bio-diesel production from sunflower oil [109,124,207,208,232,235,243,244], and a conversion rate of between 72% and 94% was obtained by enzyme catalyzed transesterification when the refined sunflower oil reacted with short-chain primary and secondary alcohols. The application of solid acid catalysts to sunflower oil transesterification was investigated by Demirbas [243] who showed that the yield of methyl ester was above 90% after 1200 second of reaction at a molar ratio of methanol to sunflower oil of 41:1, a temperature of reaction 525 K and different percentages of catalyst concentration.

In contrast, transesterification of sunflower oil by different basic catalysts (sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide) produced a bio-diesel yield in the range 86.5-99.7% under the same reaction conditions [109]. All these studies had the one aim of producing a high yield of bio-diesel by optimized reaction conditions based on optimized parameters in terms of alcohol/oil molar ratio, catalyst concentration, reaction temperature, and time. However, in nearly in all the studies there existed complex interactions among the variables that substantially affected the bio-diesel yield.

Response Surface Methodology (RSM), is an experimental strategy first described by Box and Wilson in 1951 for determining optimal conditions for multivariable systems, and is considered an efficient technique for process optimization [236]. RSM is useful in the solution of many types of industrial problems. Generally, one of these problems is optimization of the response in chemical process. In the industrial world, a very important problem is determining the conditions that optimize the process.

In the chemical process of Figure 4.1b, this implies determining the levels of time and temperature that result in maximum yield. An RSM study that began near point A in the Figure 4.1b would eventually lead the experimenter to the region near point B. A second-order model could then be used to approximate the yield response in a narrow region around B, and from examination of this approximating response surface the optimum levels or condition for time and temperature could be chosen [242].

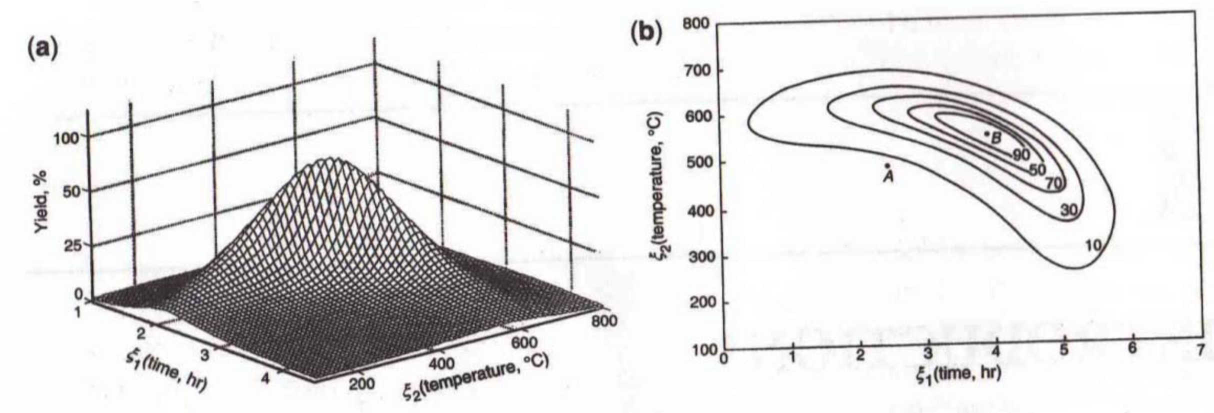


Figure 4.1: (a) A theoretical response surface showing the relationship between yield of a chemical process and the process variable reaction time (ξ_1) and reaction temperature (ξ_2). (b) A contour plot of the theoretical response surface [242].

In this study, RSM was applied to optimize the chemical reactions of transesterification of sunflower oil with methanol in the presence of sodium hydroxide to produce the highest yield of bio-diesel.

RSM addresses optimisation by:

1) Providing an understanding of how the test variables affect the selected process response;
2) Determining the interrelationships between the test variables;
3) And characterises the combined effect that all the influential test variables may have on process response.

Because of these qualities, RSM has been increasingly used in bio-diesel production. For example, Ghadge and Raheman [237] used this method to optimize the pre-treatment process for reducing the FFA content of mahua oil to below 1% for maximum bio-diesel production. In their study, it was found that the three variables, methanol quantity, acid catalyst concentration, and reaction time could significantly affect the acid value of the product. Similarly, Tiwari et al. [117] deduced a quadratic polynomial model using RSM to optimize these same three parameters to reduce acid value of the jatropha oil (Jatropha curcas) before its conversion to bio-diesel.

Li et al. [238] applied RSM to develop a polynomial model which was used to predict the yield of bio-diesel when using whole cell biocatalyst. The authors adopted central composite design to study the effect of tert-butanol quantity, methanol quantity, water content and dry biomass of the immobilized cell on bio-diesel (methyl ester) yield. Most recently, RSM has been used for optimizing bio-diesel production from waste rapeseed oil with high FFA [239].

4.2 Materials and Methods

4.2.1 Materials used and Fatty Acid Profile of Vegetable Oils

The materials used and their acquisition is described in Section 3.2.1. The process of titration is described in Section 3.2.2 and the equipment shown in Figure 1.4.

In accord with the approved method of the American Oil Chemists Society (AOCS) [240], the following equation was used to calculate the percentage FFA content of vegetable oils:

$$\%Free\ Fatty\ Acid\ (as\ olieic\ acid) = \frac{T \times M \times 28.2}{W} \qquad (4.1)$$

Where:

T = Titration value (ml of NaOH),

M = Molarity of NaOH (0.025M or 0.025 mol/ml)

W = Mass of oil sample (g), and

28.2 = Molar mass of sample (g/mol)

4.2.2 Experimental Design

To optimize the reaction condition to produce a high yield of bio-diesel with high purity, the response surface regression (RSREG) method was adopted in the design of the experiment. This methodology is a sequential process that usually starts at one reasonable operating condition, and then requires three stages to achieve a set of "better" conditions as rapidly and efficiently as possible.

The sunflower oil reacted with methanol in the presence of NaOH to produce methyl esters of fatty acids (bio-diesel) and glycerol as shown in Figure 4.2. In this study, the reaction temperature was kept constant, at 60°C or 35°C.The amount of methanol needed was determined by the methanol/oil molar ratio as following:

$[32(g) \times \frac{Oli(g)}{900(g)} \times M{:}O\ molar\ ratio]$, where 1mol of methanol equal to 32(g) and 1mol of vegetable oil equal to 900(g). An appropriate amount of catalyst dissolved in the methanol was added to the precisely prepared sunflower oil. The percentage of the bio-diesel yield was determined by comparing the weight of up layer bio-diesel with the weight of sunflower oil added.

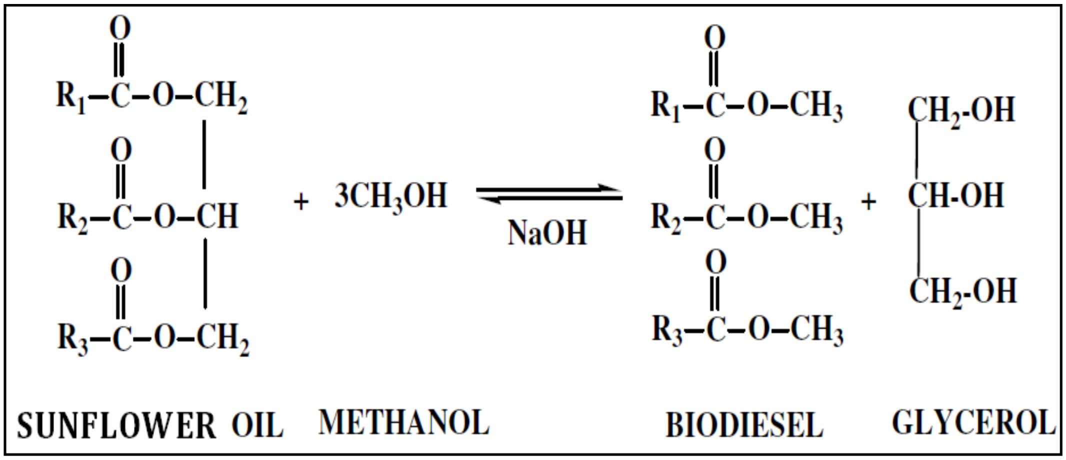


Figure 4.2: Chemical reaction for sunflower bio-diesel production

Experiments were conducted in a laboratory-scale setup. A 500 ml, three-necked flask equipped with a condenser, a magnetic stirrer and a thermometer was used for the reaction. The flask was kept in the 60°C or 35°C water bath and stirring speed was maintained at 350 rpm. The reaction production was allowed to settle before removing the glycerol layer from the bottom, and using a separating funnel to obtain the ester layer on the top, separated as bio-diesel, (Figure 4.2).

Optimization of the transesterification process was conducted via a 3-factor experiment to examine effects of methanol/oil molar ratio (M), reaction time (T), and catalyst concentration (C) on yield of methyl ester using a central composite rotatable design (CCRD). The CCRD consisted of 20 experimental runs ($2^k + 2k + m$, where k is the number of factors and m the number of replicated centre points), eight factorial points (2^k), six axial points ($2 \times k$), and six replicated centre points ($m = 6$). Here k is the number of independent variables, and k=3 should provide sufficient information to allow a full second-order polynomial model [15]. The axial point would have $a = 8^{1/4} = 1.6818$. Results from previous research [239] were used to establish a centre point of the CCRD for each factor. The centre point is the median of the range of values used: 6/1 for methanol/oil molar ratio, 1% catalyst concentration and 70 min reaction time. Table 4.1 shows the levels used for each factor, and to avoid bias, the 20 experimental runs were performed in random order as shown in Table 4.2. Design-Expert 8.0 software was used for regression and graphical analyses of the data obtained.

Table 4.1: Independent variable and levels used for CCRD in methyl ester production

Independent Variable	Symbol	Codes and Levels				
		-1.6818	-1	0	1	1.6818
Reaction Time (min)	(X1)T	53	60	70	80	86.8
Methanol/oil Molar Ratio (mol/mol)	(X2)M	0.95	3	6	9	11
Catalyst Concentration (wt.%)	(X3)C	0.16	0.5	1	1.5	1.8

Table 4.2: CCRD arrangement and responses for methyl ester production

Run			Level of Variables			Yield (%) (response)	
Treatment	Random	CCRD component	(X_1)T (min)	(X_2)M (mol/mol)	(X_3)C (wt.%)	Experi-mental	Predicted
1	6	Factorial	(-1)60	(-1)3	(-1)0.5	22.9	24.6
2	14	Factorial	(1)80	(-1)3	(-1)0.5	23.9	15.56
3	5	Factorial	(-1)60	(1)9	(-1)0.5	76.8	70.39
4	10	Factorial	(1)80	(1)9	(-1)0.5	86.8	88.34
5	7	Factorial	(-1)60	(-1)3	(1)1.5	63.6	66.61
6	17	Factorial	(1)80	(-1)3	(1)1.5	41.7	52.65
7	20	Factorial	(-1)60	(1)9	(1)1.5	73.3	86.19
8	12	Factorial	(1)80	(1)9	(1)1.5	95.5	98.79
9	2	Axial	(-1.68)53	(0)6	(0)1	97.0	92.80
10	4	Axial	(1.68)86.8	(0)6	(0)1	98.4	96.17
11	3	Axial	(0)70	(-1.68)0.95	(0)1	10.0	8.10
12	11	Axial	(0)70	(1.68)11	(0)1	90.3	85.77
13	18	Axial	(0)70	(0)6	(-1.68)0.16	21.5	30.80
14	8	Axial	(0)70	(0)6	(1.68)1.8	91.0	75.27
15	1	Center	(0)70	(0)6	(0)1	96.0	97.52
16	15	Center	(0)70	(0)6	(0)1	98.0	97.52
17	13	Center	(0)70	(0)6	(0)1	98.0	97.52
18	19	Center	(0)70	(0)6	(0)1	97.0	97.52
19	9	Center	(0)70	(0)6	(0)1	97.0	97.52
20	16	Center	(0)70	(0)6	(0)1	98.0	97.52

4.2.3 Statistical Analysis

The experimental data presented in Table 4.2 was analyzed using RSREG procedure in the statistic analysis system (SAS) that fits a full second-order polynomial model [15,16],

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=1}^{2} \beta_{ij} x_i x_j \qquad (4.2)$$

Where y is % methyl ester yield, x_i and x_j are the independent study factors, and β_0 , β_i, β_{ii}, and β_{ij} are intercept, linear, quadratic, and interaction constant coefficients, respectively. A confidence level of α = 5% was used to examine the statistical significance of the fitted polynomial model. The RSREG procedure uses canonical analysis to estimate stationary values for each factor. Using the fitted model, response surface contour plots were constructed for each pair of factors being studied while holding the third factor constant at its estimated stationary point. Confirmatory experiments were carried out to validate the model using combinations of independent variables that were not a part of the original experimental design but within the experimental region.

4.3 Results and Discussion

Since higher amounts of FFA (>1% w/w) in the feedstock can directly react with the alkaline catalyst to form soaps, which can then form stable emulsions and prevent separation of the bio-diesel from the glycerol fraction and decrease the yield [245], it is better to select reactant oils with low FFA content or to reduce FFA in the oil to an acceptable level before the reaction. Nevertheless, the FFA (calculated as oleic acid) content of the sunflower oil used in this experiment was, on average, only 0.13% which was within acceptable levels to be directly used for reaction with the alkaline catalyst to produce bio-diesel [221].

The remaining main factors affecting the transesterification include reaction time, temperature, alcohol/oil molar ratio, rate of mixing, and catalyst concentration. In order to optimize the reaction condition to produce a high yield of biodiesel with high purity, response surface method was adopted to design the experiment. This methodology is a sequential process that usually starts at one reasonable operating condition, and then requires three stages to achieve a set of "better" conditions as rapidly and efficiently as possible. The first stage is to conduct experiments to determine the direction so as to take the next move towards the optimal value. The second stage is to perform several runs along the direction as indicated by the first stage until an optimal value was approached. The last step is to deduce a mathematical model (equation) and profile the response surface to determine the optimal condition, which should be validated by the actual process.

4.3.1 Fractional Factorial Design

Based on experience and previous work [245] and since high catalyst concentration can facilitate soap formation, an upper level of the catalyst/oil concentration of 1.8 wt.% was chosen. Table 4.2 shows the experimental matrix for the 2^k factorial design, of which k was the number of factors. Here, k equals 3: T, M and C, which correspond to the uncoded values of the time (min), methanol/oil molar ratio and catalyst concentration (%), respectively. X_1, X_2, and X_3 are coded values corresponding to the uncoded values of T, M and C, respectively. The data in the next to last column of Table 4.2 indicates the response Y (%) (yield of bio-diesel) obtained from each experimental run.

4.3.2 Response Surface Mothodology Analysis of Transesterification

Table 6.3 lists the regression coefficients and the corresponding p-values for the second-order polynomial model. It can be that the regression coefficients of the linear terms for methanol/oil molar ratio and catalyst concentration (M and C, respectively), the quadratic terms in M^2 and C^2, and the interaction terms in *TC* and *TM* had significant effects on the yield (p-value <0.05). Among these, M, C, C^2 and *MC* were significant at the 1% significance level, while M^2 and *TM* were significant at the 5% level.

Using the coefficients determined from Design-Expert 8.0 software program (Table 4.3), the predicted model in terms of uncoded factors for methyl ester yield is:

$$Y_{yield} = -121.52 - 1.29T + 32.05M + 183.66C + 0.49TM - 0.59TC - 4.44MC - 0.05T^2 - 1.99M^2 - 62.91C^2 \quad (4.3)$$

Where Y_{yield} is the methyl ester yield, and T, M and C are the actual values of the test variables.

The results presented in Table 4.3 suggest that linear effects of changes in molar ratio (M) and catalyst concentration (C) and the quadratic effect C^2 were primary determining factors on the methyl ester yield as these had the largest coefficients. That the quadratic effect, M^2 and the interaction effect *MC* were secondary determining factors and that other terms of the model showed no significant effect on Y_{yield}. Positive coefficients, as with M and C, enhance the yield. However, all the other terms had negative coefficients.

Table 4.3: Regression coefficients of predicted quadratic polynomial model for methyl ester production

Terms	Regression Coefficients*	p-value
Intercept		
β_0	-121.52	0.0001
Linear		
β_1 (time)	-1.2865	0.6891
β_2 (molar ratio)	+32.050	0.0001
β_3 (cat. conc.)	+183.66	0.0003
Quadratic		
β_{11} (time)	-0.05293	0.6598
β_{22} (molar ratio)	-1.9870	0.0001
β_{33} (cat. conc.)	-62.906	0.0001
Interaction		
β_{12}(time and molar ratio)	+0.49167	0.0628
$\beta_{13}(\text{timeand cat. conc.})$	-0.59444	0.6821
β_{23}(molar ratio and cat. conc.)	-4.4417	0.0001

*** Because these are calculated values any number of significant figures could be given. However, in the real world an accuracy of 0.01% would be very good so the coefficients are cited to only five significant figures.**

The 3D response surface profile and its contour of the optimal production of bio-diesel based on the equation above is shown in Figure 4.3. This is for the central coded level, Time=70 min. The values in the picture have been transformed back to the uncoded (real) values. Figure 6.3 clearly shows that the catalyst concentration around 1.0% (or within the range of 0.9~1.2%) would most likely yield maximal production of bio-diesel. The yield decreased when the catalyst concentration was outside this range. Since the methanol and triglyceride in the sunflower oil are immiscible, addition of catalyst can facilitate the transesterification reaction, and rapidly increase the yield. However, when the catalyst concentration was too high, soap could be quickly formed which made the separation of glycerol from bio-diesel more difficult, this reduced the yield. In contrast, inadequate usage of catalyst could result in an incomplete reaction and a lower yield.

The RSM shown in Figure 4.3 shows the optimal value of the methanol/oil molar ratio for the yield, and that too high or too low values of the methanol/oil ratio have negative effects. This can be explained by the fact that the transesterification is an equilibrium reaction in which excess alcohol will, on the one hand, drive the reaction to the right, increasing yield; but on the other hand will help increase the solubility of glycerol resulting in the reaction driven to the left, thus decreasing the yield. Too low a methanol/oil molar ratio also led to an incomplete reaction. Therefore, both catalyst concentration and methanol/oil molar ratio exhibited optimal values. The RSM demonstrated that the optimal conditions for catalyst concentration and methanol/oil molar ratio were about 1% and 6:1, respectively, very close to the SAS ridge max analysis results that will be discussed in the following section.

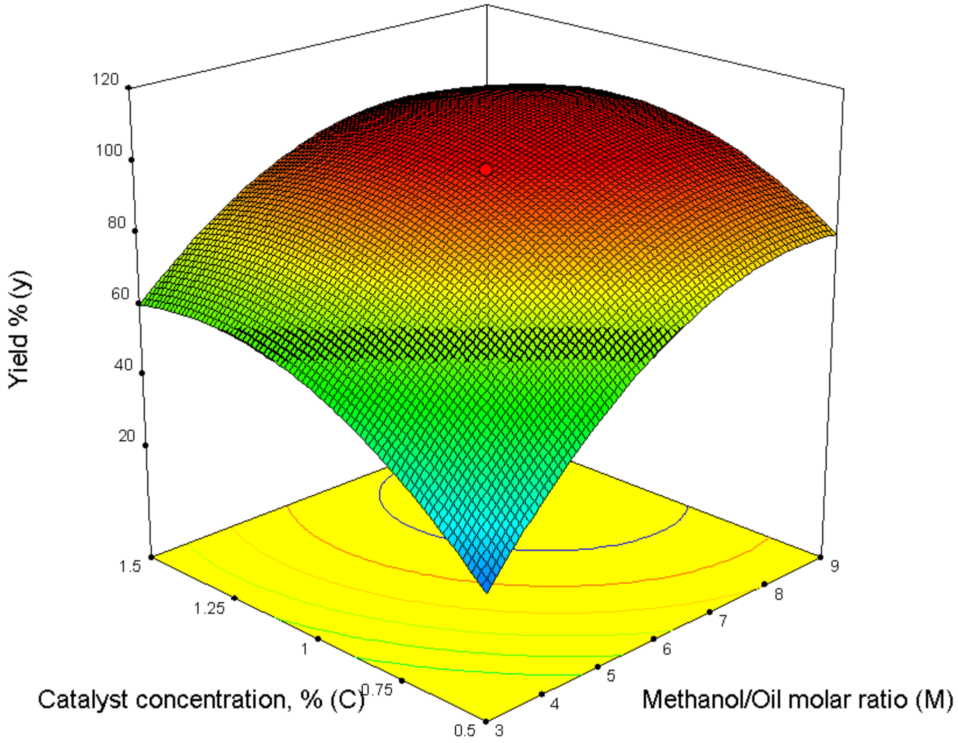


Figure 4.3: Response surface and contour plot of the effects of methanol/oil molar ratio and catalyst on the yield of bio-diesel

The ridge max method computes an estimate of the ridge of optimum response with increasing radii from the original centre, to give an optimal condition or set of conditions for maximum bio-diesel production. The ridge max analysis showed that theoretically the maximum yield could approach 100% at a methanol/oil molar ratio of 7.9 and catalyst concentration of 1.0%. Using these suggested optimal conditions bio-diesel yield was 97% - very close to the theoretical value. When the methanol/oil ratio was decreased to 6.0 while keeping all other parameters the same as those mentioned above, we found that the bio-diesel yield reached 95%. Although the yield decreased from 97% to 95%, on the basis of cost-efficiency and processing safety considerations we suggest using a molar ratio of methanol to oil at 6.0:1 for bio-diesel production.

Table 4.4 shows the analysis of variance (F-test) and the p-value for this model. The F-value is 24.73 and the p-value is smaller than 0.0001, demonstrating the suitability of the deduced model. The R^2 value (=0.9570) indicates that the quadratic model was able to predict 95.7% of the total variance and only 4.3% of the total variance was not explained by the model.

Table 4.4: Analysis of variance (ANOVA) for the quadratic model

Variance Source	Sum of Squares*	Degrees of Freedom	Mean Square*	F-value	P-value
Regression	17903	9	1989.3	24.73	< 0.0001
Linear	7281.6	1	7281.6	90.51	< 0.0001
Quadratic	4608.9	1	4608.9	57.29	< 0.0001
Interaction	355.11	1	355.11	4.38	0.0620
Residual error	804.53	10	80.450		
Total error	18708	19			
$R^2 = 0.9570$					

***Quoted to five significant figures.**

4.3.3 Effect of Parameters

Figures 4.4-4.6 present contour plots of methyl ester yield (wt.%) in terms of coded factors to show the relationships between the dependent and independent variables of the developed model. Each contour curve presents the effect of two variables on the methyl ester yield, holding the third variable at constant level. Remarkable interaction between the independent variables can be observed if the contour plots have an elliptical profile.

Figure 4.4 shows the strong interaction between methanol/oil molar ratio (*M*) and catalyst concentration (*C*). This can also be confirmed by the small p-value (0.0001) for *MC* term. It can also be seen from the figure that starting from low catalyst concentrations, the methyl ester yield increased with increasing catalyst concentration.

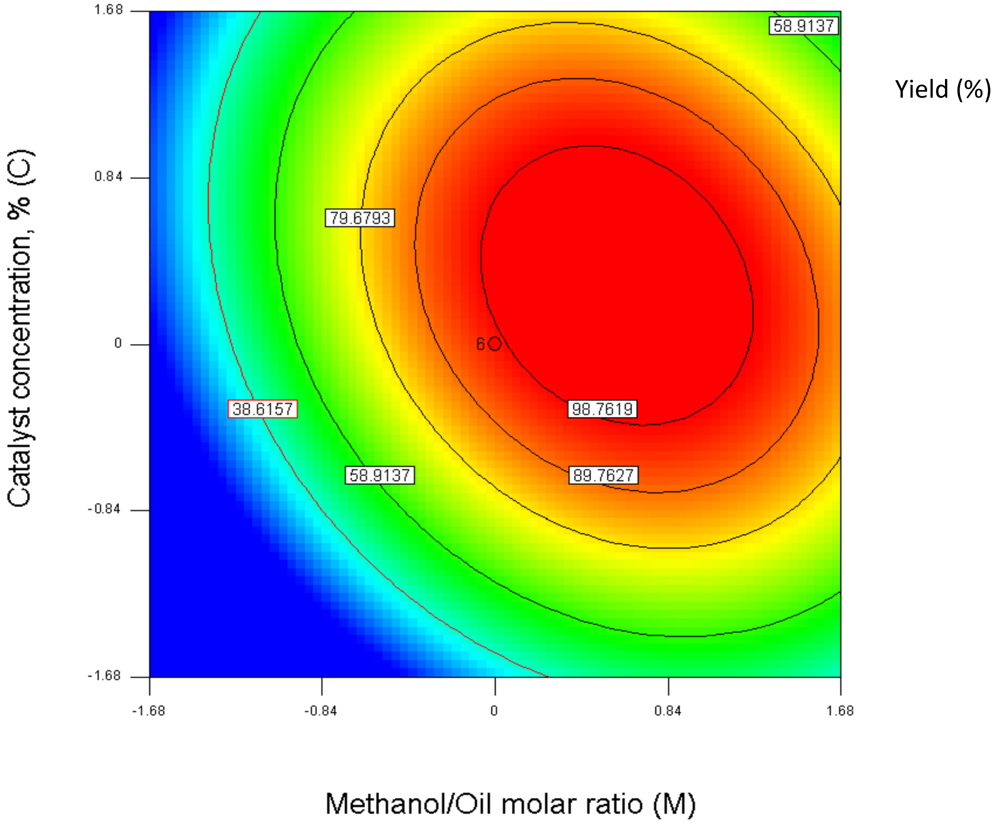


Figure 4.4: Effect of methanol/oil molar ratio and catalyst concentration on methyl ester production with temperature 65°C and reaction time 70 min

However, once the catalyst concentration was greater than its centre point value, the reverse trend was observed. A similar pattern was observed when increasing the methanol/oil molar ratio. This could be due to the fact that the positive coefficient for C and M played a major role when the catalyst concentration and methanol/oil molar ratio were at lower levels, while at higher levels, the interaction term MC and quadratic terms M^2 and C^2 had a more significant negative effect, leading to a decrease of yield. This was consistent with physical considerations; that since the methanol and triglyceride in the sunflower oil are immiscible, addition of catalyst can facilitate the transesterification reaction, and rapidly increase the yield. However, when the catalyst concentration became too high, soap could be quickly formed which made the separation of glycerol from bio-diesel more difficult, thus reducing the yield. Similarly, the increase of the amount of methanol will, on one hand, drive the reaction to the right since the transesterification reaction is an equilibrium process; but on the other hand excess methanol will help increase the solubility of glycerol resulting in the reaction being driven to the left, decreasing the yield.

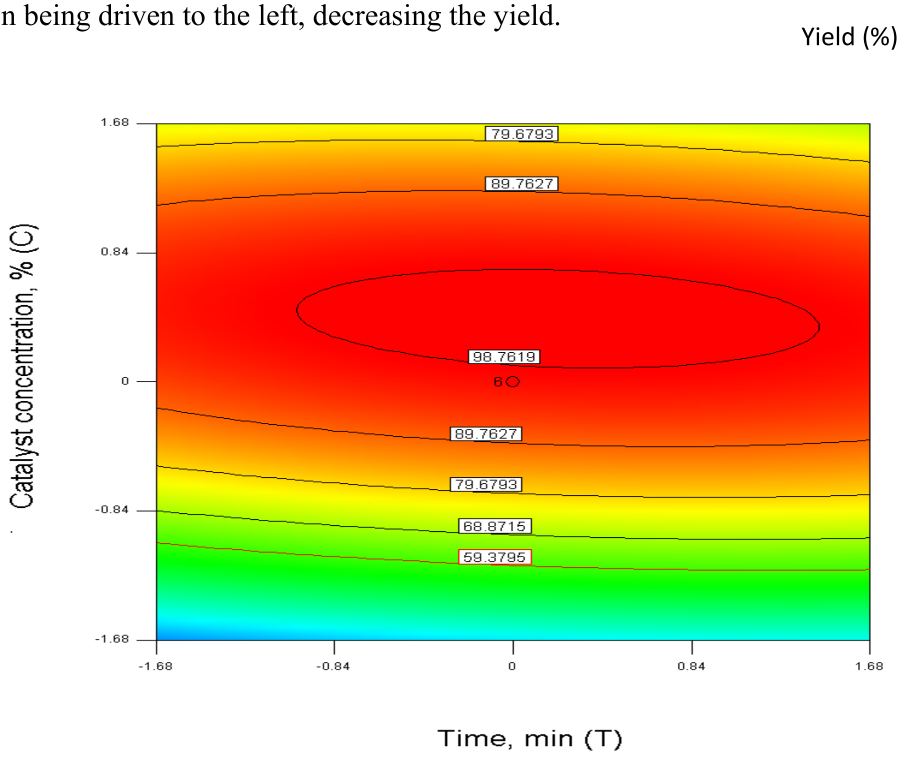


Figure 4.5: Effect of reaction time and catalyst concentration on methyl ester production with temperature 65°C and methanol/oil molar ratio 6.0:1

Figure 4.5 shows the effect of changes in the reaction time and catalyst concentration on the methyl ester yield. At a fixed level of catalyst concentration, there appears to be no significant change in methyl ester yield with increasing reaction time, within the limits set. Similar results are observed in the Figure 4.6 when the catalyst concentration is fixed. This could explain the high p-value (0.6891) for the T term in the model, indicating the non-significance of this parameter.

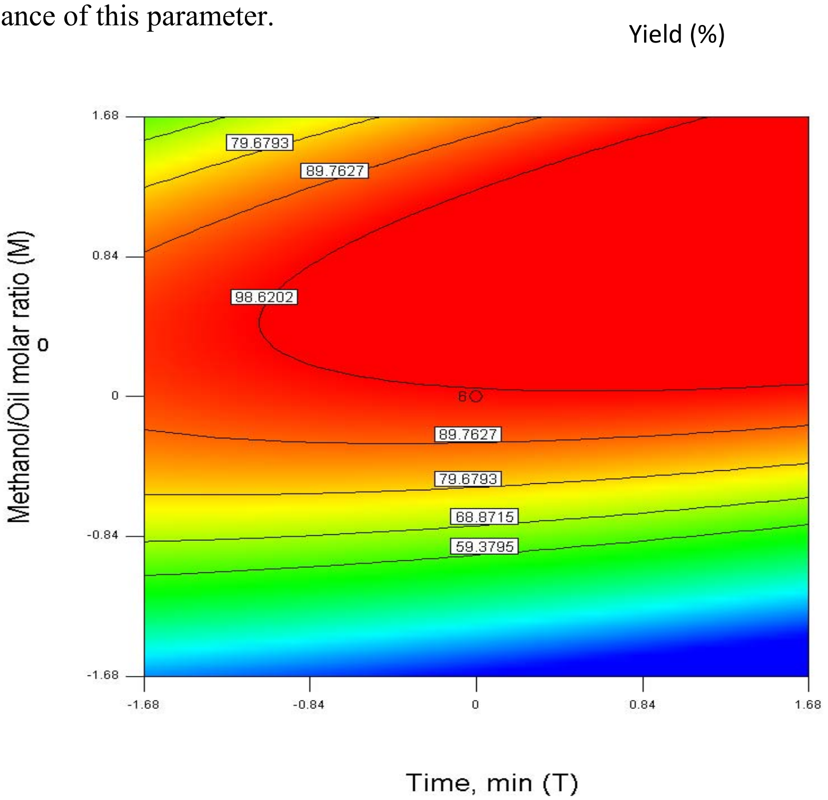


Figure 4.6: Effect of methanol/oil molar ratio and reaction time on methyl ester production with temperature 65^{o}C and catalyst concentration 1%

4.3.4 The Response Surface and Ridge Max Analysis

Twenty additional centre-point runs were performed to check the curvature of the response surface. The additional experiments (Table 4.5) were carried out with a coded distances of -1.68 , -1.0 , 0.0 , 1.0 and 1.68 when the reaction temperature and stirring speed were fixed at 35^{o}C and 200 rpm respectively. Then eight factorial points, six axial points and six centre points were found. The matrix corresponding to the central composite design is shown in Table 4.5. Using the Design-Expert program, a second-order polynomial equation (4.4) was deduced for the experimental data:

$$Y_{yield} = -259.30 - 1.18T + 90.98M + 136.78C - 0.02TM + 0.06TC + 5.99MC + 0.01T^2 - 7.05M^2 - 83.34C^2 \quad (4.4)$$

The analysis of variance revealed that this model was adequate to express the actual relationship between the response and significant variables, with a satisfactory coefficient of determination (R^2=0.81), which indicated 81% of the variability in the response could be explained by the 2nd-order polynomial predictive equation (4.4).

Table 4.5: Central composite design

Run			**Level of Variables**			
Treatment	**Random**	**CCRD component**	**(X_1)T (min)**	**(X_2)M (mol/mol)**	**(X_3)C (wt.%)**	**Yield (%) (response)**
1	7	Factorial	(-1)50	(-1)5	(-1)0.5	51.09
2	12	Factorial	(1)70	(-1)5	(-1)0.5	56.60
3	8	Factorial	(-1)50	(1)7	(-1)0.5	67.94
4	2	Factorial	(1)70	(1)7	(-1)0.5	72.71
5	16	Factorial	(-1)50	(-1)5	(1)1.5	54.08
6	6	Factorial	(1)70	(-1)5	(1)1.5	60.75
7	5	Factorial	(-1)50	(1)7	(1)1.5	82.93
8	9	Factorial	(1)70	(1)7	(1)1.5	88.87
9	15	Axial	(-1.68)43.2	(0)6	(0)1	92.27
10	4	Axial	(1.68)76.8	(0)6	(0)1	93.17
11	18	Axial	(0)60	(-1.68)4.32	(0)1	54.63
12	20	Axial	(0)60	(1.68)7.68	(0)1	94.45
13	10	Axial	(0)60	(0)6	(-1.68)0.16	26.51
14	19	Axial	(0)60	(0)6	(1.68)1.8	42.60
15	17	Center	(0)60	(0)6	(0)1	93.49
16	13	Center	(0)60	(0)6	(0)1	93.49
17	14	Center	(0)60	(0)6	(0)1	93.49
18	3	Center	(0)60	(0)6	(0)1	93.49
19	1	Center	(0)60	(0)6	(0)1	93.49
20	11	Center	(0)60	(0)6	(0)1	93.49

The response surface profile and its contour of the optimal production of yield based on equation 4.4 is shown in Figures 4.7, 4.8, 4.9 and 4.10, for which the temperature set 35°C, and the rate of mixing was 200 rpm. The RSM demonstrated that the optimal conditions for catalyst concentration and methanol/oil molar ratio were about 1% and 7.5, respectively, very close to the SAS ridge max analysis results discussed early.

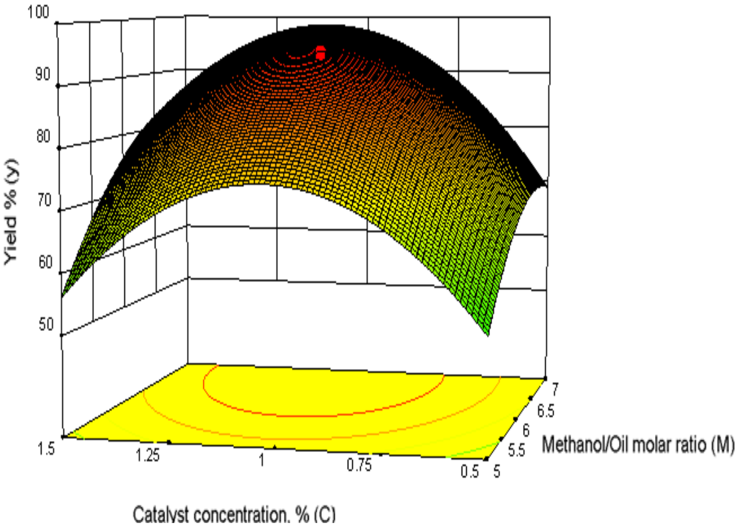


Figure 4.7: Response surface and contour plot of the effects of methanol/oil molar ratio and catalyst concentration on the yield of bio-diesel with temperature 35°C and reaction time 60 min

RSM analysis of the second experimental results suggested optimal conditions as: methanol/oil molar ratio, 6.8; temperature, 35°C; time, 66 min; catalyst concentration, 1.1 %; and rate of mixing, 200 rpm. This optimized condition was validated with actual bio-diesel yield of 95%. The decrease of the methanol/oil molar ratio from 6.8/1 to 6.0/1 while keeping the other variable parameters at their respective optimal values produced bio-diesel with a yield of 94%. Thus bio-diesel yield increased by 1% but at the cost of significantly increasing the molar ratio of methanol versus oil from 6.0 to 6.8, which does not appear to be cost-effective. We suggest using a methanol/oil molar ratio at 6.0 for the optimal production of bio-diesel from sunflower oil.

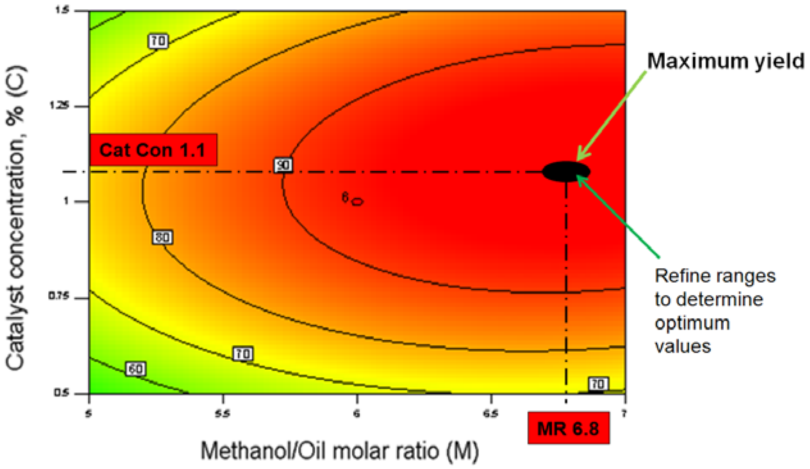


Figure 4.8: Effect of methanol/oil molar ratio and catalyst concentration on methyl ester production with temperature 35°C and reaction time 60 min

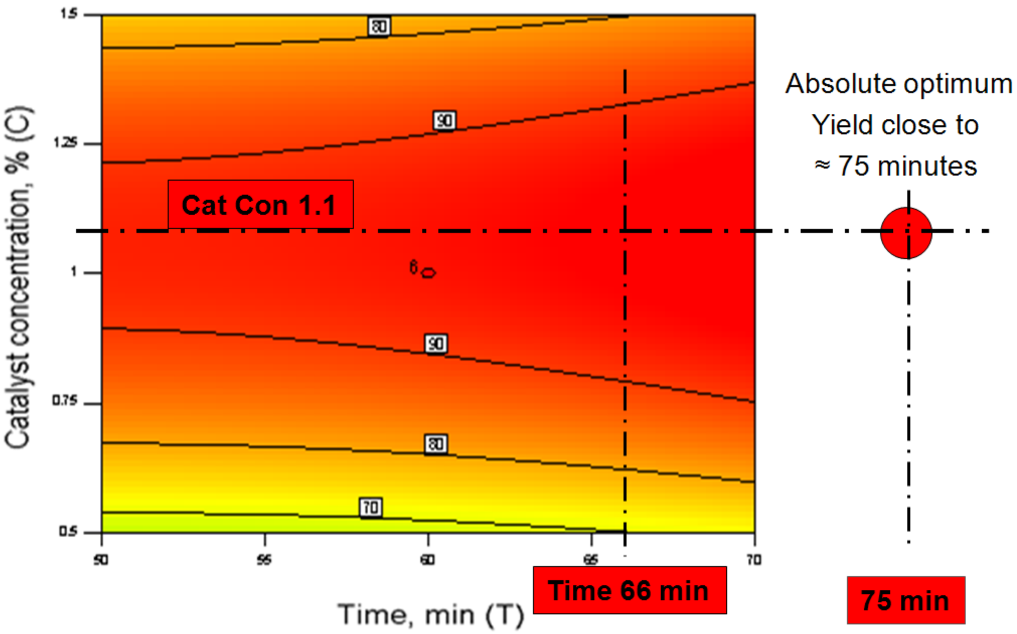


Figure 4.9: Effect of reaction time and catalyst concentration on methyl ester production with temperature 35°C and methanol/oil molar ratio 7.7:1

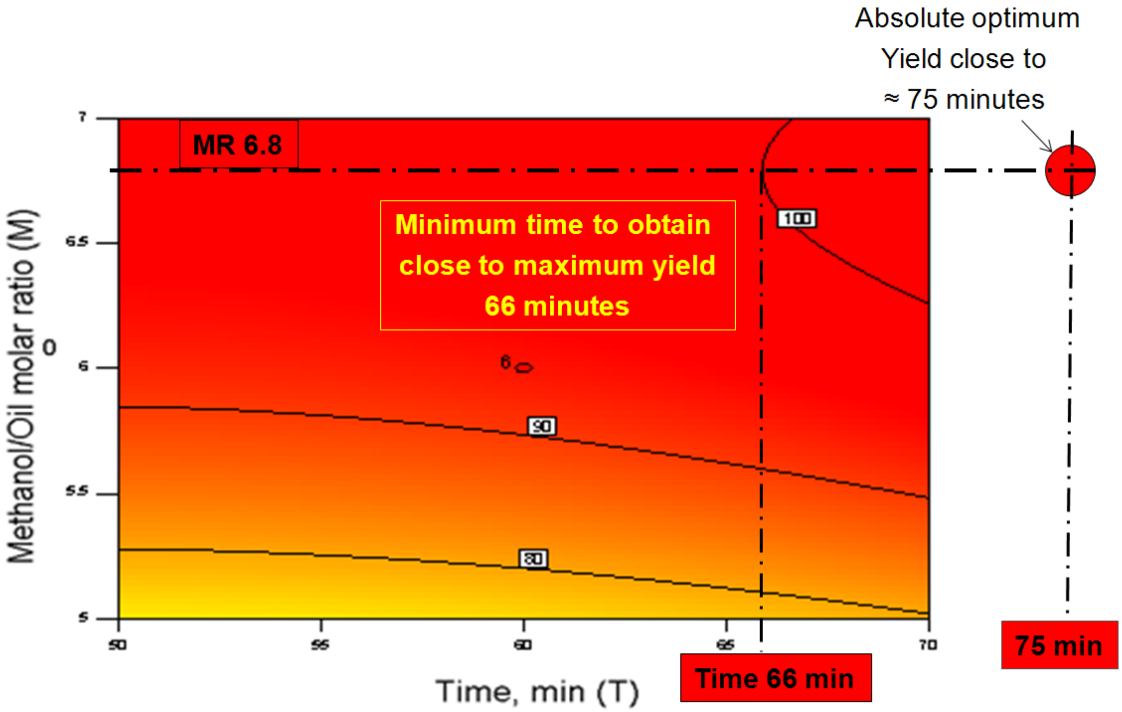


Figure 4.10: Effect of methanol/oil molar ratio and reaction time on methyl ester production with temperature 35°C and catalyst concentration 1.0%

4.4 Conclusions

In summary, RSM is useful in the solution of many types of industrial problems. Generally, one of these problems is optimization of the response in chemical process. In this study, RSM was used to optimization of transesterification process. The study intended to make use of the RSM process to maximize the production of bio-diesel (methyl ester in this experiment) from sunflower oil using the conventional transesterification method. In addition to using the RSM for optimizing the methanolysis of sunflower oil it was a desire to develop a mathematical model which would describe the relationships between the variables and so allow yield to be predicted before the production process was finalised.

A 20 experimental runs were conducted via a 3-factor experiment to examine effects of methanol: oil molar ratio, reaction time, and catalyst concentration on yield of methyl ester. The experimental results were showed that the optimal condition as methanol: oil molar ratio, 6.8:1, and catalyst concentration, 1.1%, at reaction time 66 min, and temperature 35^{o}C. This optimized condition was validated with actual bio-diesel yield of 95%. The decreased of methanol: oil molar ratio from 6.8:1 to 6.0:1 while keeping the other variable parameters at their respective optimal values produced bio-diesel with a yield of 94%. By comparison the results of yield from optimization conduction and non-optimization conduction, it was conclude as shown in the Table 4.6 below.

Table 4.6: Overall results & recommended production values

	Before	**After**
Yield	98%	100%
Time (min)	180	68
M:O molar ratio	4.5:1	6.8:1
Catalyst Concentration	1.0%	1.1%
Temperature	65ºC	35ºC

The next chapter will be presenting the experimental set up for testing an engine performance and exhaust gas emissions by using bio-diesel from non-optimized condition in compression ignition engine. The results of engine performance such as engine brake power, torque, brake specific consumption and thermal efficiency and exhaust gas emissions such as CO, THC, CO_2, and NOx by using pure bio-diesel and bio-diesel blends will be comparing with standard diesel.

CHAPTER – 5

ENGINE PERFORMANCE AND EMISSIONS USING METHYL ESTER FROM VEGETABLE OILS AND STANDARD DIESEL

5.1 Introduction

Increased environmental awareness has helped prompt the development of bio-diesels in an effort to reduce environmental pollution. As described earlier in chapter three of this thesis, generally bio-diesels contain 10% to 11% oxygen by weight, have a higher cetane number than petroleum diesel, have no aromatics, and have attractive environmental benefits, such as lower emissions of CO, CO_2 and unburned hydrocarbons (HC) [223, 224].

Engine performance testing of bio-diesels and their blends is indispensible for evaluating their relevant properties. Several research groups [223, 226] have investigated the properties of a bio-diesel blend with soybean oil methyl esters in diesel engines and found that particulate matter (PM), CO, and soot mass emissions decreased, while NO_x increased. Labeckas et al. [224], examined the performance and exhaust emissions of rapeseed oil methyl esters in direct injection diesel engines, and found that there were lower emissions of CO, CO_2 and HC. Similar results were reported by Kalligeros et al. [227], for methyl esters of sunflower oil and olive oil when they were blended with marine diesel and tested in a stationary diesel engine.

Raheman et al. [228], studied the fuel properties of karanja methyl esters blended with diesel from 20% to 80% by volume. It was found that B20 (a blend of 20% bio-diesel and 80% petroleum diesel) and B40 (a blend of 40% bio-diesel and 60% petroleum diesel) could be used as an appropriate alternative fuel to petroleum diesels because they apparently produced less CO, NO_x emissions, and smoke density. Lin et al. [229], confirmed that emission of polycyclic aromatic hydrocarbons (PAH) decreased when the ratio of palm bio-diesel increased in a blend with petroleum diesel. In general, bio-diesel demonstrated improved emissions by reducing CO, CO_2, HC, PM, and PAH emissions though, in some cases, NO_x increased. In the literature survey, there are several studies of compression ignition engines running on diesel fuel and bio-diesel from various feedstocks [190-138,208].

In this study, five bio-diesel products produced from corn oil, rapeseed oil, soybean oil, sunflower oil and waste vegetable oil (WVO) were tested on a diesel engine located in the Engine Testing Automotive Laboratory at the University of Huddersfield in Huddersfield, UK. The engine performance and emissions were evaluated and compared with that obtained using standard diesel fuel.

5.2 Material and Methods

Sunflower oil methyl esters SOME A and SOME B were produced from the same crude sunflower oil through two different reaction conditions to prepare the SOME with the highest conversion. Based on response surface methodology an optimized transesterification reaction (i.e., temperature 60^{o}C, catalyst of NaOH 1.0% based on weight of crude sunflower oil, methanol/oil molar ratio at 6:1, and reaction time of 70 min) with conversion rate of 97% was used to prepare SOME A, while SOME B was obtained from non-optimized conditions (i.e., temperature 65^{o}C, catalyst of NaOH 0.4% based on weight of crude sunflower oil, methanol/oil molar ratio at 4.5:1 and reaction time of 60 min) with percentage yield of 90% SOME B of crude sunflower oil. Briefly, a certain amount of crude sunflower oil was weighed and added to a fixed Erlenmeyer, then a calculated amount of catalyst (NaOH) dissolved in the required amount of methanol was added. The reaction flask was immersed in a water bath to keep the temperature constant throughout the reaction with defined agitation.

The bio-diesels, sunflower oil bio-diesel (B.Sun.oil) from non-optimized condition, rapeseed oil bio-diesel (B.Rap.oil), soybean oil bio-diesel (B.Soy.oil), corn oil bio-diesel (B.Cor.oil), fresh waste vegetable oil (B.WVOF) and old waste vegetable oil bio-diesel (B.WVOO) were evaluated for engine performance and exhaust gas emissions compared to standard diesel (St.Diesel). On the other hand waste vegetable oil (WVO) was blended at B5 (5% of bio-diesel to 95% of standard diesel by volume), B10, B15 and B20 and evaluated for engine performance and emissions compared to standard diesel as well.

5.3 Engine Experiments

The steady state engine test runs were carried out on an engine test bed using a 2009 2.2L Ford Puma engine from the Ford Transit van. The test engine and dynamometer were controlled by a microprocessor system equipped with data acquisition and logging. Sensors were fitted to the engine and the dynamometer, to measure relevant parameters and send the data to the control system. The sensors measured engine load, engine speed, inlet air temperature, exhaust gas temperature, lubrication oil temperature, fuel consumption and the cooling water temperature. The system allows for highly accurate measurement of the main exhaust emission components. The test bed instrumentation is described in the Appendix B.

The specifications of the four-stroke, Ford Puma 2.2 V348 140 PS direct injection diesel engine, turbocharged diesel test engine were: bore = 89.9 mm, stroke = 94.6 mm, engine capacity = 2402 cc, compression ratio = 17.5:1, fuel injection release pressure = 135 bar, max power = 130 kW @ 3500 rpm, max torque = 375.0 Nm @ 2000-2250 rpm. See also Figures B.1 and B.2.

The engine was tested in a series of steady state operating conditions at engine speeds of 1500, 2200, 2600, 3000 and 3300 rev/min and engine loads of 25%, 50%, 75% and 100% open throttle valve. It should be noted that 100% throttle valve conduction of operation means full load operation of the engine. This gave a total of 20 stage readings. At each of these conditions the engine was allowed to settle and warm up for about 15 minutes and then the results acquired at a rate of 15 per second with the values averaged over the last 10 minutes of operation. During the experiments, the cooling water and engine oil temperatures were constant at about 80°C, and the laboratory temperature was within 20-25°C. The gas analysers and the measuring equipment were calibrated before each experiment.

The operating conditions were automatically programmed into a test cycle using the CP Engineering Cadet V12 software. This test cycle was used for each of the different fuels tested. During the test cycles the data for the parameters discussed in the next sections and the Introduction above were logged constantly, see Figure B.3.

The performance parameters measured included brake torque (Nm) and fuel consumption (kg/s). Brake power (kW), specific fuel consumption and fuel thermal efficiency where evaluated by using Equations (B.1), (B.2) and (B.3), respectively.

5.3.1 Gas Analysis System

During these experiments emission concentrations of carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), hydrocarbons (HCs) and the oxides of nitrogen (NO_x) were measured (Table 5.1). CO_2 and O_2 were measured in percentage of total volume (%), while CO, HC and NOx, were measured in parts per million (ppm). The emissions were measured using a Horiba exhaust gas analyser EXSA 1500 system (Figure B.4). The system claims highly accurate measurement of the main exhaust emission components.

As shown in Table 5.1 the concentrations of the carbon monoxide CO in the exhaust samples were measured by a Horiba Exsa-1500 non-dissipative infrared (NDIR) analyser, with measurements range of 0 – 5,000 ppm. The concentrations of the total hydrocarbons THC in the exhaust samples were measured by a Horiba heated flame ionisation detector (FID) analyser, with measurements range of 0 – 50,000 ppm. The FID analyser needs to be configured to be used with samples containing oxygen, as in the case of engines fuelled with bio-diesel. The reason is that the presence of oxygen reduces analyser response by slowing down ion production.

The concentrations of oxides of nitrogen in the exhaust samples were measured by a Horiba chemiluminescent (CLA) analyser, with measurement range of 0 – 5,000 ppm. Based on the specifications given by the manufacturers, the span repeatability of the three analysers is less than ±1% of the relative scale, and the span drift is less than ±1% of the full scale over a 24 hour period.

Table 5.1: Horiba Exsa 1500 and BG3 micro dilution tunnel for transient diesel particulate

Constituent	Symbol	Analyser Method	Analyser Range
Carbon monoxide	CO	NDIR	0 - 5000ppm, 0 – 10 vol%
Carbon dioxide	CO_2	NDIR	0 - 10, 20 vol%
Nitrogen/ oxides of nitrogen	N/NO_x	CLD (dry)	0 - 100, 500, 1000, 5000 ppm
Oxygen	O_2	MPA	0 - 10, 25 vol%
Total hydrocarbons	THC	Heated FID (wet)	0 - 100, 500, 1000, 5000, 10,000, 50,000 ppmC

5.4 Results and Discussion

The experimental results obtained from the tests carried out on engine performance and exhaust emissions are presented in this section. These include results at different speeds and loads for the different fuels i.e. standard diesel fuel and the five bio-diesel products. The results are discussed from the viewpoint of using bio-diesel as an alternative fuel for compression ignition engines.

5.4.1 Petroleum Diesel Benchmark

As the purpose of these tests was to compare bio-diesel and bio-diesel blend fuels with their petroleum diesel counterpart the engine was first tested using petroleum diesel as the fuel to establish a base line for comparison. Petroleum diesel is a fossil fuel and is notorious for appearing to be a dirty fuel, but has a high energy content of about 44 MJ/kg. With diesel engines the air and fuel is not premixed, instead they mix as they enter the combustion chamber and combustion is initiated by the temperature rise due to compression alone.

Diesel engine combustion is never perfect and dissociation occurs. This causes the engine to produce and emit pure carbon particles, which can cause the exhaust to appear black in colour. This in itself proved a problem for the sensor, as the carbon particles clogged the filters of the Horiba exhaust analyser faster than expected, and they (and the hoses connected to the exhaust) needed cleaning prior to any run.

Tables 5.2 and 5.3 show the results for the petroleum diesel for 4 runs at engine speeds 1500, 2200, 2600, 3000 and 3300 rpm. From this data only a min, mean, and max values was found for each engine speed, and these formed the benchmark results.

Table 5.2: Petroleum Diesel Benchmark (1)

	RPM		
CO_2 %	1500	min	7.2501
		Mean	7.4056
		max	7.6611
	2200	min	6.4164
		Mean	6.4329
		max	6.4494
	2600	min	5.4407
		Mean	6.0958
		max	6.7509
	3000	min	6.5903
		Mean	7.0706
		max	8.5508
	3300	min	5.0373
		Mean	5.3705
		max	5.7038

	RPM		
CO ppm	1500	min	43.5310
		Mean	45.4941
		max	47.4572
	2200	min	19.1934
		Mean	20.1533
		max	21.1133
	2600	min	27.7987
		Mean	27.8411
		max	27.8836
	3000	min	20.0524
		Mean	24.7022
		max	29.3519
	3300	min	26.1330
		Mean	26.9771
		max	27.8211

	RPM		
THC ppm	1500	min	35.4325
		Mean	39.4293
		max	43.4261
	2200	min	30.9360
		Mean	33.0090
		max	37.0820
	2600	min	31.1878
		Mean	33.4268
		max	41.6658
	3000	min	31.3537
		Mean	32.8494
		max	38.3451
	3300	min	33.0904
		Mean	33.3163
		max	40.5423

	RPM		
NOx ppm	1500	min	555.6114
		Mean	560.6207
		max	565.6300
	2200	min	422.3955
		Mean	439.0035
		max	455.6114
	2600	min	306.7931
		Mean	337.6360
		max	368.4790
	3000	min	620.2169
		Mean	661.1953
		max	672.1738
	3300	min	804.4765
		Mean	805.1109
		max	805.7453

Table 5.3: Petroleum Diesel Benchmark (2)

	RPM		
O_2 %	1500	min	11.1912
		Mean	13.4051
		max	13.4190
	2200	min	12.4190
		Mean	14.6318
		max	14.8446
	2600	min	13.9510
		Mean	15.0117
		max	15.0723
	3000	min	13.9748
		Mean	14.9685
		max	15.9622
	3300	min	14.3614
		Mean	16.8174
		max	17.2734

	RPM		
Power kW	1500	min	20.1206
		Mean	22.0933
		max	24.0659
	2200	min	28.0008
		Mean	28.3628
		max	28.7248
	2600	min	20.1206
		Mean	25.4864
		max	30.8522
	3000	min	18.6850
		Mean	19.3277
		max	19.9703
	3300	min	17.3181
		Mean	17.4904
		max	17.6628

	RPM		
Torque Nm	1500	min	128.0958
		Mean	140.6042
		max	153.1126
	2200	min	121.5369
		Mean	123.1069
		max	124.6770
	2600	min	107.8078
		Mean	110.5596
		max	113.3115
	3000	min	59.4899
		Mean	61.5274
		max	63.5650
	3300	min	50.1144
		Mean	50.6116
		max	51.1087

	RPM		
SFC g/kWh	1500	min	175.0043
		Mean	217.6848
		max	260.3653
	2200	min	207.3771
		Mean	234.7209
		max	262.0646
	2600	min	237.1376
		Mean	261.4010
		max	285.6644
	3000	min	310.6533
		Mean	341.4114
		max	372.1696
	3300	min	321.6966
		Mean	360.6600
		max	399.6234

5.4.2 Methyl Ester from Waste Vegetable Oil

The first fuel tested was the bio-diesel from WVO, B5, B10, B15, and B20 blends of this were tested. The oil in these tests had been mainly used for deep fries for only about three weeks and was provided free. Most fast food restaurants use their oil for longer, because with time the heated oil becomes more acidic which has too beneficial consequences the time taken to reach frying temperature is reduced and, as it begins to contain more hydro carbons, the fried food takes on a more golden look. It is common practice for restaurants of this nature to leave some used oil when adding new oil, this allows the old oil to be contaminated and speeds the process of making the new oil more acidic.

Each of the four blends was run twice on the engine at 1500, 2200, 2600, 3000 and 3300 rpm. The dynamometer load setting was fixed for all runs. Tables 5.4 to 5.7 show the combined results of running the bio-diesel WVO. Over 300 data points were taken for each rpm and blend. The data was cleaned of any noise and only three values were taken into analysis. The minimum, mean, and maximum values were taken from the average of the two runs, to provide a more baseline result.

Table 5.4: Waste Vegetable Oil Blends Compiled Data (1)

	RPM		**B5**	**B10**	**B15**	**B20**
CO_2 %	1500	min	7.3985	7.6427	7.7065	6.6347
		Mean	7.8618	7.7965	7.8329	6.6969
		max	7.9251	7.8503	7.8592	6.7591
	2200	min	6.6389	7.288	7.2793	5.6879
		Mean	6.7983	7.6017	7.4309	6.2569
		max	6.9576	7.9153	7.5826	6.8259
	2600	min	6.3732	6.2678	6.2553	5.3433
		Mean	6.5612	6.536	7.0101	5.4841
		max	6.7492	6.8042	7.6925	5.6249
	3000	min	8.4393	8.3203	8.119	5.5642
		Mean	8.5221	8.4798	8.4253	5.7642
		max	8.6049	8.6394	8.7316	5.9642
	3300	min	6.3306	6.1959	6.1693	4.2767
		Mean	6.7385	6.416	6.1878	4.6009
		max	7.1463	6.6362	6.2063	4.9251

	RPM		**B5**	**B10**	**B15**	**B20**
CO ppm	1500	min	41.531	41.145	40.677	40.038
		Mean	43.494	42.615	40.865	40.8
		max	45.457	43.385	41.053	41.562
	2200	min	19.093	19.273	19.008	17.851
		Mean	19.153	19.697	19.417	19.066
		max	24.113	23.82	22.527	20.281
	2600	min	25.799	23.912	19.158	18.775
		Mean	26.841	26.134	24.311	24.18
		max	27.884	26.356	24.463	24.586
	3000	min	21.052	19.161	18.843	17.947
		Mean	23.702	23.276	22.246	21.684
		max	27.352	25.392	23.648	20.421
	3300	min	24.133	21.235	17.805	17.077
		Mean	25.077	24.544	23.915	23.33
		max	28.821	25.853	22.025	17.582

Table 5.5: Waste Vegetable Oil Blends Compiled Data (2)

	RPM		**B5**	**B10**	**B15**	**B20**
THC ppm	1500	min	35.78	35.494	31.368	29.466
		Mean	38.066	36.624	33.43	31.408
		max	38.951	38.753	35.493	30.351
	2200	min	25.807	23.038	23.089	19.18
		Mean	31.379	30.336	27.649	24.359
		max	33.951	30.635	29.209	26.537
	2600	min	27.07	25.438	20.702	20.185
		Mean	31.411	29.015	28.892	27.279
		max	31.752	30.592	30.082	28.374
	3000	min	30.107	28.804	26.193	18.857
		Mean	31.706	31.055	30.459	25.241
		max	40.305	39.306	34.725	29.625
	3300	min	30.503	26.804	23.415	17.188
		Mean	31.439	27.815	25.686	25.253
		max	33.375	32.826	30.957	23.318

	RPM		**B5**	**B10**	**B15**	**B20**
NOx ppm	1500	min	560.8456	563.8930	566.0218	569.1154
		Mean	563.2078	565.7700	570.9784	572.0343
		max	571.5700	570.6470	573.9351	583.9532
	2200	min	440.2031	444.9288	446.6325	450.1110
		Mean	441.1200	446.1520	446.7898	451.5786
		max	443.0369	454.4921	446.9472	465.0462
	2600	min	330.7853	328.4038	332.9416	337.5019
		Mean	338.4238	339.7305	341.2159	343.5423
		max	342.0624	341.0572	345.4901	345.5826
	3000	min	660.7023	668.2092	669.7857	668.8105
		Mean	663.3685	668.4008	670.8460	671.9464
		max	667.0348	671.5924	673.9062	673.0823
	3300	min	818.7010	820.3886	827.6678	829.3783
		Mean	820.0553	823.7204	830.5262	830.9918
		max	826.4095	830.0522	833.3846	836.6053

Table 5.6: Waste Vegetable Oil Blends Compiled Data (3)

	RPM		**B5**	**B10**	**B15**	**B20**
O_2 %	1500	min	10.8650	11.3796	11.7187	13.1057
		Mean	10.9788	11.7356	12.0524	13.3547
		max	11.0927	12.0916	12.3860	13.6038
	2200	min	12.4181	12.5871	12.6762	14.4121
		Mean	12.4626	12.8075	13.3702	14.6023
		max	12.5072	13.0279	14.0641	14.7925
	2600	min	13.5880	13.8544	13.9540	12.1896
		Mean	14.2570	14.0148	14.6645	12.7739
		max	14.9261	14.1753	15.3750	13.3581
	3000	min	11.1874	11.3711	11.7049	14.4860
		Mean	12.4131	11.8730	12.8290	14.5065
		max	13.6387	12.3750	13.9530	14.5270
	3300	min	13.5134	13.8694	13.9725	16.0909
		Mean	13.7192	14.1222	14.8432	16.2594
		max	13.9250	14.3749	15.7139	16.4280

	RPM		**B5**	**B10**	**B15**	**B20**
Power kW	1500	min	20.4430	20.1462	18.8092	17.2489
		Mean	21.9734	21.7496	21.5587	21.5149
		max	26.5039	24.7529	24.9081	23.5810
	2200	min	27.4873	27.2985	23.9765	20.7634
		Mean	28.1796	27.8999	27.2337	27.1937
		max	30.8719	28.9013	28.4910	28.6240
	2600	min	24.2632	23.1437	21.8553	20.7692
		Mean	25.3839	25.0677	24.8850	24.6776
		max	31.7046	30.5917	30.1147	30.5861
	3000	min	18.9797	17.5500	15.2516	15.0338
		Mean	19.2465	18.9574	18.7293	18.5509
		max	20.5133	20.1649	19.4069	19.2681
	3300	min	16.0829	15.6063	14.7186	13.6518
		Mean	17.3899	17.2982	17.1861	17.1335
		max	18.4970	17.9901	17.0537	17.0152

Table 5.7: Waste Vegetable Oil Blends Compiled Data (4)

	RPM		**B5**	**B10**	**B15**	**B20**
Torque Nm	1500	min	139.3160	136.6673	133.5394	130.9702
		Mean	139.4772	137.4757	135.6322	133.6227
		max	141.6384	139.2840	136.7250	134.2752
	2200	min	121.9931	120.8288	120.4308	118.5112
		Mean	122.5086	121.2385	120.4635	119.7753
		max	127.0241	125.6482	122.4962	120.0395
	2600	min	109.8284	107.7109	105.6521	103.3388
		Mean	110.0284	109.5309	107.2442	105.3709
		max	115.2285	112.3510	110.8364	109.4029
	3000	min	59.6004	56.2316	52.2793	50.5813
		Mean	61.4455	60.5378	60.4597	60.0269
		max	65.2907	62.8440	61.6401	61.4725
	3300	min	44.3246	41.9452	40.3780	40.1862
		Mean	50.4644	50.2868	49.4815	49.4504
		max	52.6042	51.6284	48.5850	48.9146

	RPM		**B5**	**B10**	**B15**	**B20**
SFC g/kWh	1500	min	236.7470	240.7708	242.1002	242.4072
		Mean	238.5646	241.1980	243.0680	244.5997
		max	240.3822	241.6253	244.0357	244.7921
	2200	min	256.2700	259.1789	260.0473	260.4020
		Mean	256.6119	259.8715	260.2087	260.6743
		max	256.9537	260.5642	260.3700	261.9466
	2600	min	279.6171	288.0495	289.3730	290.0286
		Mean	279.9062	289.1014	289.9560	292.1929
		max	280.1953	290.1532	290.5391	292.3571
	3000	min	374.2292	375.7091	375.5214	376.0627
		Mean	374.5271	376.8853	376.3592	376.3964
		max	374.8250	378.0615	377.1970	378.7300
	3300	min	396.7245	398.1989	409.7252	410.1843
		Mean	397.4386	399.7837	410.0502	411.5685
		max	398.1527	401.3685	410.3752	413.9528

When comparing the means of sets of data it is necessary to know the standard deviations of the data Equation 5.4 shows the formula for standard deviation:

$$\sigma = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \overline{x})^2} \qquad (5.1)$$

Where: $\overline{x}$ = the mean of the values x_i

The mean is defined by equation 5.5:

$$\overline{x} = \frac{1}{N}\sum_{i=1}^{N} x_i = \frac{x_1 + x_2 + \cdots + x_N}{N} \qquad (5.2)$$

Where: N is the number of data points

The results of these calculations can be seen in Table 5.8.

From the Table 5.8 the values yielded for the standard deviation, it is apparent that the data taken from the runs is accurate enough and has a high level of repeatability that it can be used in a direct comparison with the petroleum diesel benchmark.

The first step into comparing these data versus the benchmark is to establish a percentage difference in the means of the data sets taken for the benchmark. Table 5.9 shows us the results in percentage difference for all values, which include, 1500, 2200, 2600, 3000 and 3300 for the rpm ranges for all four bio-diesel blends.

Table 5.8: Standard Deviation for Blends of Bio-diesel Waste Vegetable Oil

#	RPM	**B5**	**B10**	**B15**	**B20**
CO_2	1500	0.23	0.09	0.07	0.05
	2200	0.13	0.26	0.12	0.46
	2600	0.22	0.22	0.59	0.11
	3000	0.07	0.13	0.25	0.16
	3300	0.33	0.18	0.02	0.26
CO	1500	1.60	0.93	0.15	0.62
	2200	2.35	2.05	1.57	0.99
	2600	0.85	1.10	2.47	2.65
	3000	2.58	2.59	2.02	1.55
	3300	2.02	1.94	2.55	2.84
O_2	1500	0.09	0.29	0.27	0.20
	2200	0.04	0.18	0.57	0.16
	2600	0.55	0.13	0.58	0.48
	3000	1.00	0.41	0.92	0.02
	3300	0.17	0.21	0.71	0.14
THC	1500	1.34	1.35	1.68	0.79
	2200	3.40	3.51	2.60	3.09
	2600	2.13	2.16	4.17	3.63
	3000	4.48	4.51	3.48	4.42
	3300	1.20	2.63	3.16	3.44
NOx	1500	4.60	2.85	3.26	6.42
	2200	1.18	4.25	0.13	6.72
	2600	4.70	5.68	5.21	3.43
	3000	2.60	1.55	1.75	1.81
	3300	3.36	4.01	2.33	3.10
Power	1500	2.57	1.91	4.99	2.64
	2200	1.46	0.66	1.90	3.42
	2600	3.28	3.16	3.41	4.04
	3000	0.67	1.07	1.82	1.85
	3300	0.99	1.00	1.13	1.61
Torque	1500	1.06	1.09	1.32	1.43
	2200	2.26	2.18	0.97	0.67
	2600	2.50	1.91	2.17	2.52
	3000	2.37	2.74	4.16	4.83
	3300	3.51	4.28	4.10	4.25
SFC	1500	1.48	0.35	0.79	1.08
	2200	0.28	0.57	0.13	0.67
	2600	0.24	0.86	0.48	1.06
	3000	2.60	0.96	0.68	1.81
	3300	0.58	1.29	0.27	1.56

Table 5.9: Percentage difference of WVO with respect to petroleum diesel

#	RPM	**B5**	**B10**	**B15**	**B20**
CO_2	1500	0.76	1.23	0.37	-1.47
	2200	1.02	2.62	1.52	-2.74
	2600	1.07	0.66	1.88	-2.82
	3000	0.73	1.54	2.19	-1.50
	3300	1.27	0.85	0.32	-1.48
CO	1500	-4.40	-6.33	-10.17	-10.32
	2200	-4.96	-2.27	-3.65	-5.40
	2600	-3.59	-6.13	-12.68	-13.15
	3000	-4.05	-5.77	-9.94	-12.22
	3300	-7.04	-9.02	-11.35	-13.52
O_2	1500	-18.10	-12.45	-10.09	-0.38
	2200	-14.83	-12.47	-8.62	-0.20
	2600	-5.03	-6.64	-2.31	-14.91
	3000	-17.07	-20.68	-14.29	-3.09
	3300	-18.42	-16.03	-11.74	-3.32
THC	1500	-3.46	-7.12	-15.22	-20.34
	2200	-4.94	-8.10	-16.24	-26.21
	2600	-6.03	-13.20	-13.57	-18.39
	3000	-3.48	-5.46	-7.28	-23.16
	3300	-5.64	-16.51	-22.90	-24.20
NOx	1500	0.46	0.92	1.85	2.04
	2200	0.48	1.63	1.77	2.86
	2600	0.23	0.62	1.06	1.75
	3000	0.33	1.09	1.46	1.63
	3300	1.86	2.31	3.16	3.21
Power	1500	-0.54	-1.56	-2.42	-2.62
	2200	-0.65	-1.63	-3.98	-4.12
	2600	-0.40	-1.64	-2.36	-3.17
	3000	-0.42	-1.92	-3.10	-4.02
	3300	-0.57	-1.10	-1.74	-2.04
Torque	1500	-0.80	-2.23	-3.54	-4.97
	2200	-0.49	-1.52	-2.15	-2.71
	2600	-0.48	-0.93	-3.00	-4.69
	3000	-0.13	-1.61	-1.74	-2.44
	3300	-0.29	-0.64	-2.23	-2.29
SFC	1500	9.59	10.80	11.66	12.36
	2200	9.33	10.72	10.86	11.06
	2600	7.08	10.60	10.92	11.78
	3000	9.70	10.39	10.24	10.25
	3300	10.20	10.85	13.69	14.12

Further simplifying the information, an average of the values was taken to provide an overall aspect of the difference between the WVO and the petroleum benchmark. This can be seen on Table 5.10.

Table 5.10: Overall Percentage Difference

	B5	**B10**	**B15**	**B20**
CO_2	0.97	1.38	1.26	-2.00
CO	-4.81	-5.90	-9.56	-10.92
O_2	-14.69	-13.65	-9.41	-4.38
THC	-4.71	-10.08	-15.04	-22.46
NOx	0.67	1.31	1.86	2.30
Power	-0.52	-1.57	-2.72	-3.19
Torque	-0.44	-1.38	-2.53	-3.42
SFC	9.18	10.67	11.47	11.91

5.4.3 Carbon Dioxide (CO_2) Emissions of Waste Vegetable Oil Bio-diesel Blends

As was stated previously the results of bio-diesel blend fuels over the petroleum diesel should show decrease in the emissions of CO, HC, with a slight increase in NOx, and overall similar values for CO_2. This trend can be seen in Figure 5.1.

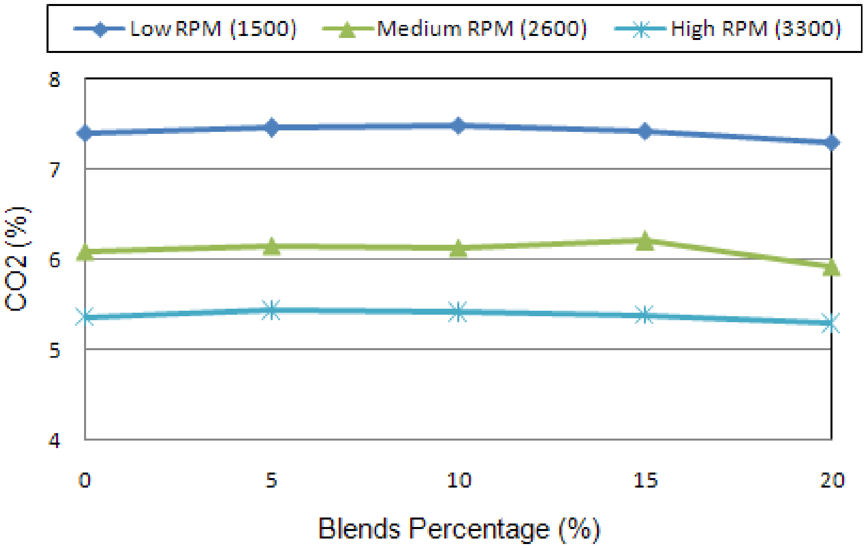


Figure 5.1: Carbon dioxide emissions for different bio-diesel blends

Focusing on only one speed (3300 rpm) allows for a clearer picture of what is happening during the change from B5 to B20 bio-diesel blends. To have a clearer picture the values are normalized to those for petroleum diesel. In this case as seen in Figure 5.2 as well, petroleum diesel is denoted by B0, meaning there is zero % bio-diesel present in the blend. Normalizing the graph will show more clearly how the effects of running bio-diesel fuel blends have on the emissions of a diesel engine. To normalize the values the following relation was used equation (5.2):

$$[(WVO\ value - \ Petroleum\ diesel\ value)/\ Petroleum\ diesel\ value]\ x\ 100\%. \qquad (5.3)$$

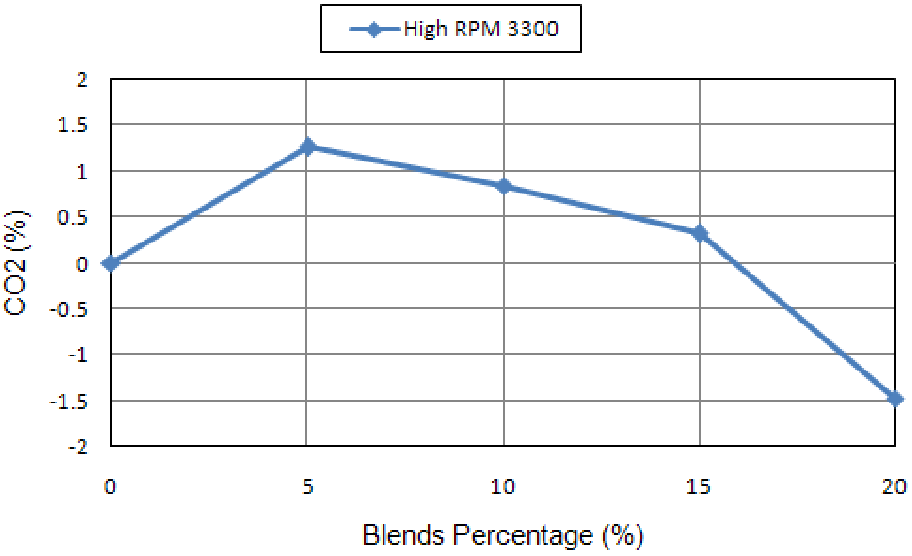


Figure 5.2: Normalized carbon dioxide emission against bio-diesel blend for engine speed 3300 rpm

To understand why this initial increase in CO_2 occurs it is important to understand the chemical reaction of combustion and how the products are formed - in this case the emissions. Petroleum diesel fuel consists of 86.5% Carbon (C), 13.2% Hydrogen (H) and 0.3% Sulphur (S) and air consists of 78.08% Nitrogen (N), 20.95% Oxygen (O2) and 0.93% Argon (Ar). The molecular weight of carbon is rounded to 12 and hydrogen to 1. So the number of moles of carbon and hydrogen in the fuel are respectively:

- $86.5/12 = 7.21$
- $13.2/1 = 13.2$

The sulphur will be neglected from this analysis as it composes a very small proportion, and is not present in bio-diesel. Equation 5.6 shows the chemical reaction that occurs in the combustion chamber. This chemical equation is equilibrated with respect to the stoichiometric balance.

$$C_X H_Y + \left(O_2 + \frac{0.79}{0.22} N_2\right) \Rightarrow xCO_2 + \frac{y}{2} H_2O + a\left(\frac{0.79}{0.22} N_2\right) \tag{5.4}$$

Where:

$$a = \frac{x+y}{4}$$

In the case of petroleum diesel these values:

$$a = \frac{7.21 + 13.2}{4} = 5.10$$

For diesel fuel $C12H23,\ X = 12\ and\ Y = 23$

Bio-diesel has a chemical equation $CH_3OOCR_{1,2,3}$, and provides a new combustion equation:

$$(C_X H_Y) \cdot Z\% + (CH_3OOCR) \times (1 - Z\%) + a\left(O_2 + \frac{0.79}{0.22} N_2\right)$$
$$\Rightarrow xCO_2 + \frac{y}{2} H_2O + a\left(\frac{0.79}{0.22} N_2\right)$$

When bio-diesel is present there is additional carbon, hydrogen and oxygen to be added to the reaction. The resulting problem is seen at B5, this additional carbon caused the emitted CO_2% to increase. This then falls as the proportion of bio-diesel is increased and a state similar to that for petroleum diesel is reached at about B20. Following this trend it is estimated that at higher concentrations of bio-diesel blends (> B20) the CO_2% emitted would actually be lower than for petroleum diesel.

5.4.4 Carbon Monoxide (CO) Emissions of Waste Vegetable Oil Bio-diesel Blends

The second emission to be analyzed is CO. Carbon Monoxide is present when dissociation is present in the combustion due to incomplete combustion. Figure 5.3 shows the CO emission for the bio-diesel obtained from WVO. From the data it was clear that the CO emission decreased as the bio-diesel blend increased.

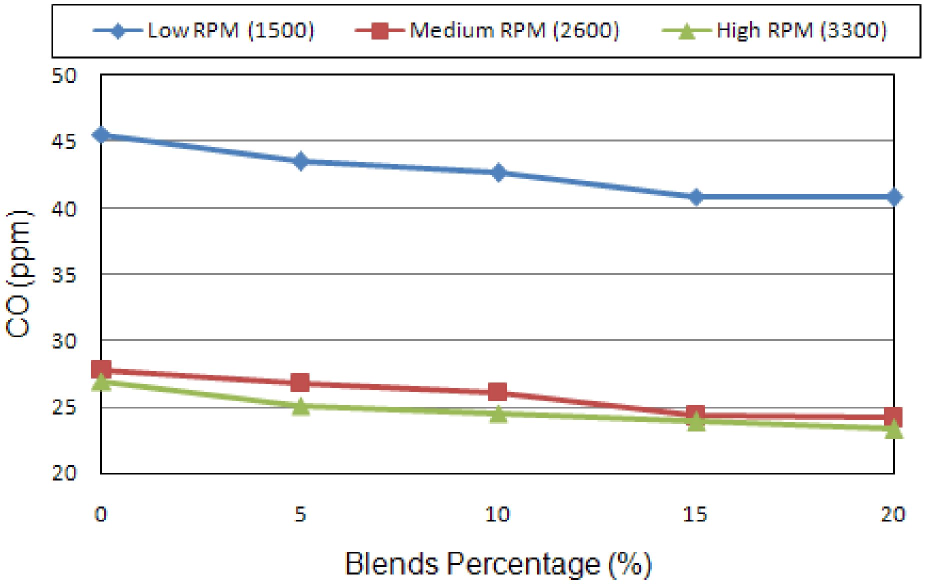


Figure 5.3: Average carbon monoxide emission for different bio-diesel blends

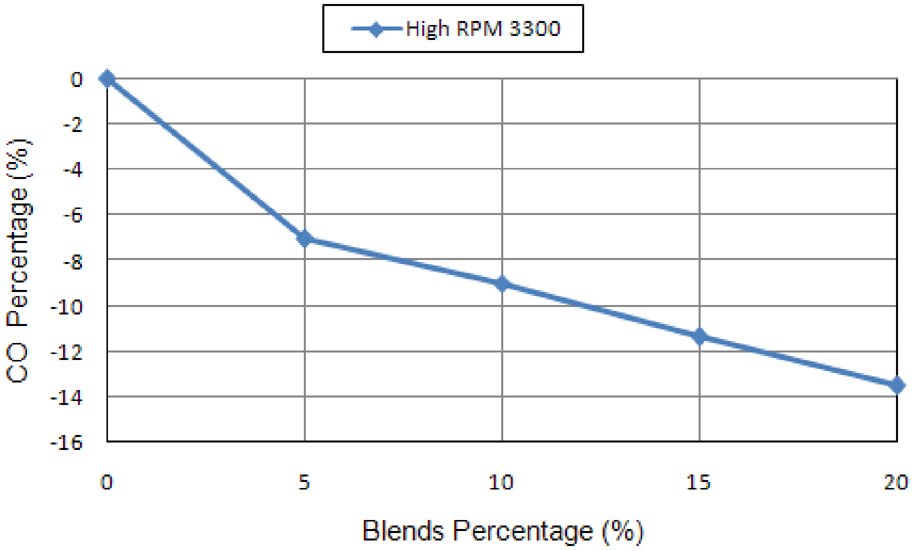


Figure 5.4: Normalized carbon monoxide emissions for different bio-diesel blends

From Figure 5.4 it was clear that as the bio-diesel blend increase the normalised CO emission decreases almost linearly. From the previous chemical reaction equations of combustion, it was clear to see that the addition of bio-diesel fuel to the petroleum diesel provides more oxygen which allows for a more complete reaction and combustion, with less dissociation. Since CO was a main by-product of dissociation more complete combustion causes this to decrease as was seen in the data. Bio-diesel has both a higher cetane number (ignition quality) and a higher oxygen content which contribute to a shorter ignition delay period which is important in reducing CO emission.

5.4.5 Hydrocarbon (THC) Emissions of Waste Vegetable Oil Bio-diesel

Total hydro-carbon emission should be reduced by the use of bio-diesel fuel blends. From the data in Table 5.6 was significant and substantial decrease in THC emissions with respect to the benchmark, see Figure 5.5.

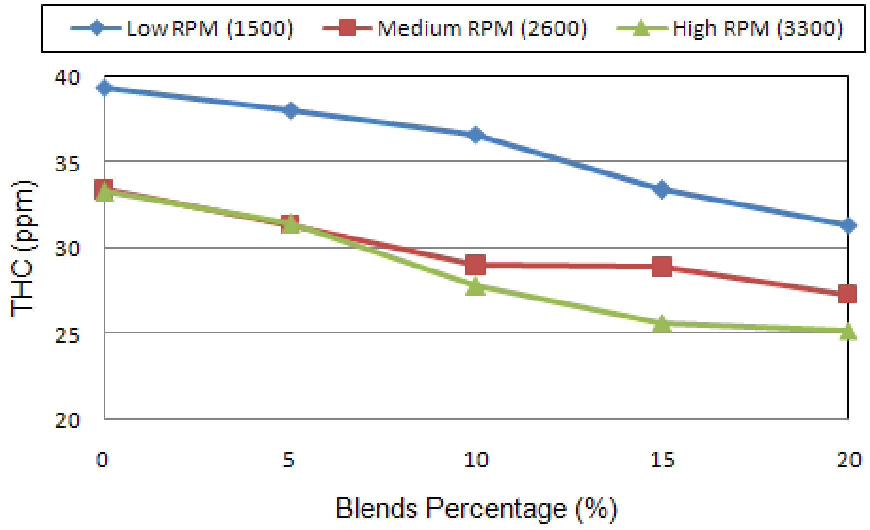


Figure 5.5: Average total hydrocarbon emissions for different bio-diesel blends

As was explained earlier, these WVOs were used for cooking and the hydrocarbons contained in them were slowly eaten away by the high temperatures required to fry food. Thus the proportion of hydrocarbons would naturally be lower than that found in petroleum diesel, i.e. the same reason why CO was decreased. As the combustion becomes more complete less dissociation occurs yielding fewer hydrocarbons in the emissions. The decrease in THCs from over 40 ppm to less than 30 ppm is good for a fuel which is as efficient as petroleum diesel but friendlier to the environment.

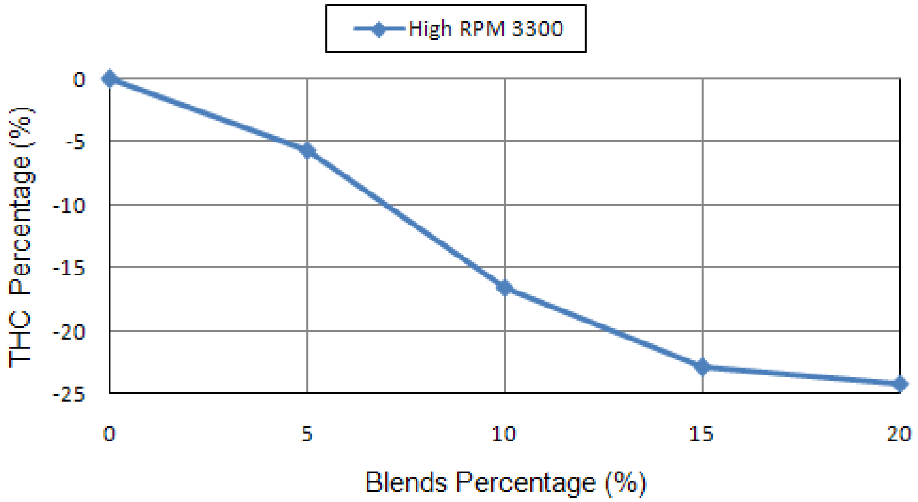


Figure 5.6: Normalized total hydrocarbon emissions for different bio-diesel blends

5.4.6 Oxide of Nitrogen (NOx) Emissions of Waste Vegetable Oil Bio-diesel Blends

An oxide of nitrogen (NOx) was the only emission which did not seem to show a decrease relative to petroleum diesel. In fact it increasing steadily as the percentage of bio-diesel blend increased, see Figure 5.7. From the data it was apparent that the change is only being incremented at B20 by a maximum value of 3.21%, yet with a mean more resembling that of 2.33%.

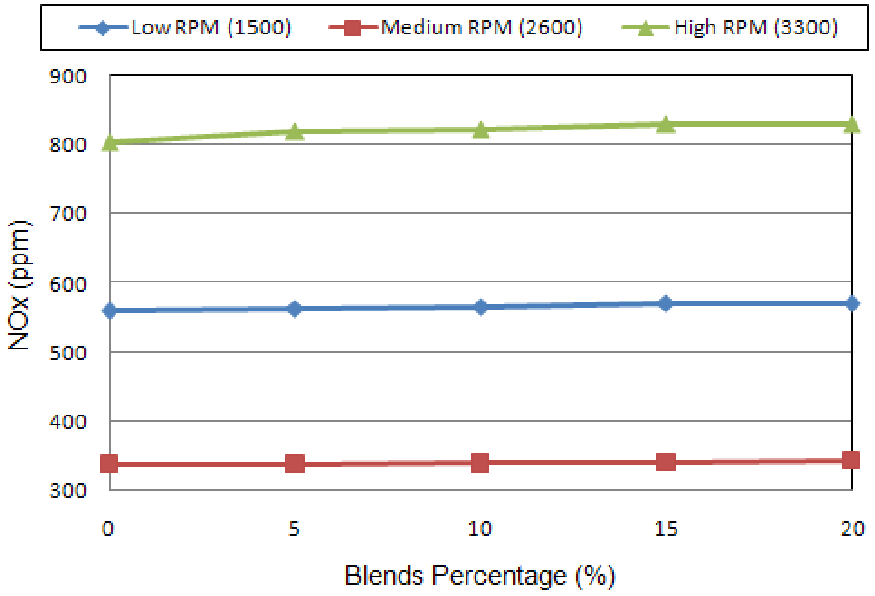


Figure 5.7: Average emissions of oxides of nitrogen for different bio-diesel blends

Normalizing the NOx allows for a clearer picture of what is going on, Figures 5.8 – 5.10 show the NOx trend for each of the three RPM ranges, low, medium, and high.

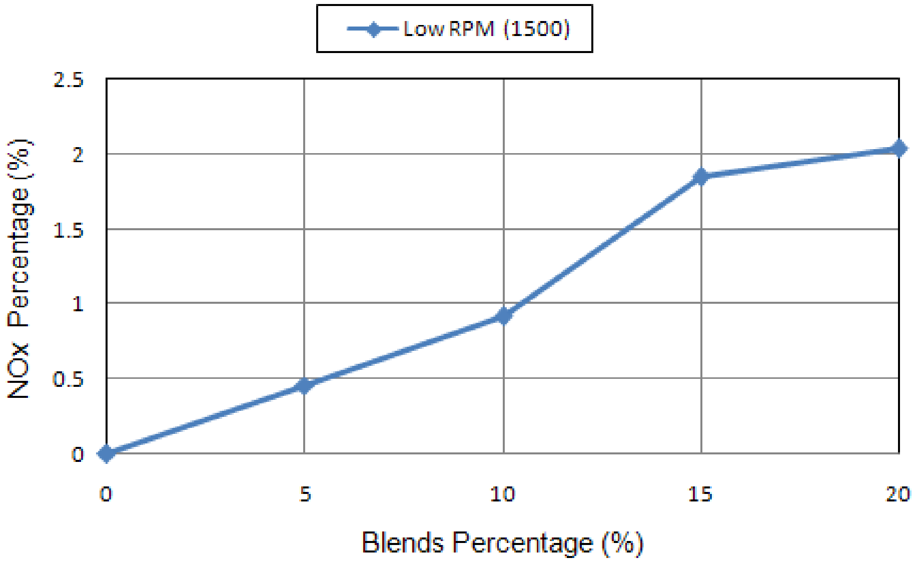


Figure 5.8: Normalized Oxide of Nitrogen for different bio-diesel blends (Low RPM)

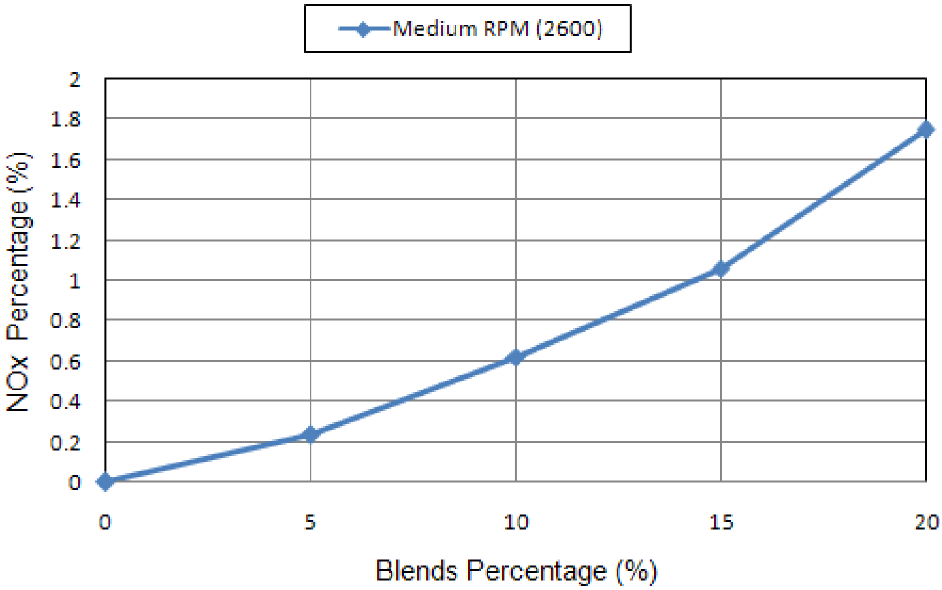


Figure 5.9: Normalized NOx for different bio-diesel blends (Medium RPM)

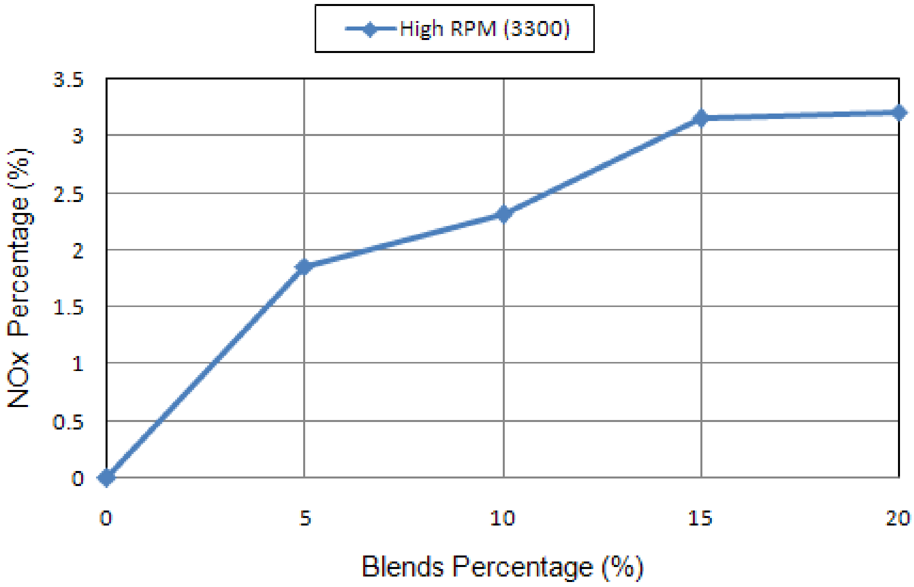


Figure 5.10: Normalized Oxide of Nitrogen for different bio-diesel blends (High RPM)

At low and middle speeds there is clear increase in NOx emissions as the blend goes from B10 to B20. For these speeds it was estimated that as the increase in proportion of WVO increases the NOx emission will be increase at a similar rate. However at high engine speeds there appears to be a limit to the NOx emissions, and if this trend continues there would be little further increase in NOx emissions as the proportion of WVO in the blend increased.

Increase in NOx could be due to an increase temperature due to high oxygen content of the combustion with increase in proportion of bio-diesel. This may be due to experimental design. Since the engine was not being running, there is no airflow over it to cool it and there is a consequent temperature rise. This increase in temperature may be the cause of the slight increase in NOx emissions. The toxicity level of this green house gas makes any increase in its emission a concern.

However, bio-diesel blend contains no sulphur, and technologies exist to control NOx emissions where sulphur is not present. Furthermore, newer electronically controlled diesel engines manage to decrease NOx emissions by 80-90%.

5.4.7 Torque and Power for Waste Vegetable Oil Bio-diesel Blends

Sunflower oil itself has a relatively low energy content, but the bio-diesel fuel produced from it has a value (about 37.5 MJ/kg, see Table 4.1) close to that of petroleum diesel; this means that efficiency and output is lower but only by a small percentage. Figure 5.11 and 5.16 show the curves for power and torque respectively.

By simple proportions it the energy content of the blend can be calculated. Energy content of blend = (%diesel x 42.5 + %bio-diesel x 37.5). It can be seen from Figure 5.11 that the loss in power is close to the value predicted. At 20% bio-diesel the calculated power is 41.5 MJ/kg, a decrease of 2.35% compared to petroleum diesel, the measured decrease was about 1.72%.

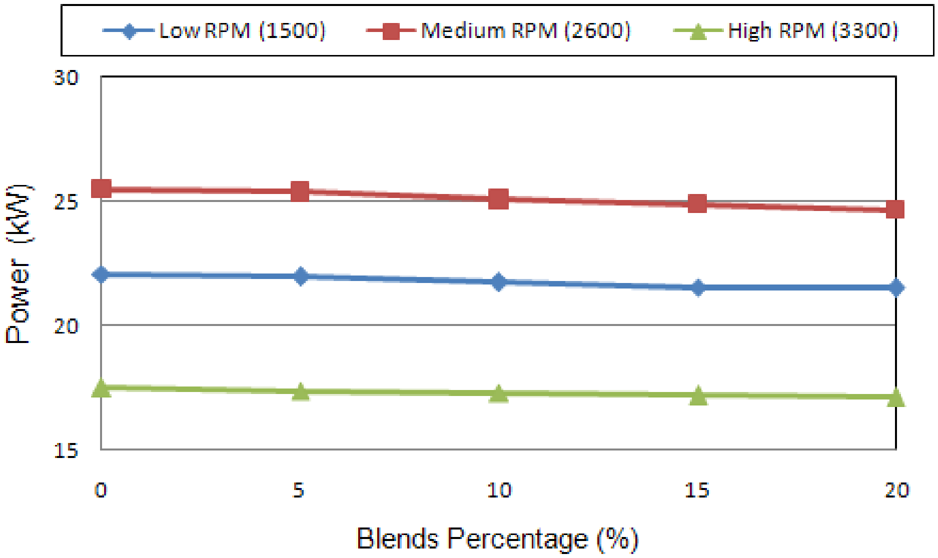


Figure 5.11: Average power output for different bio-diesel blends

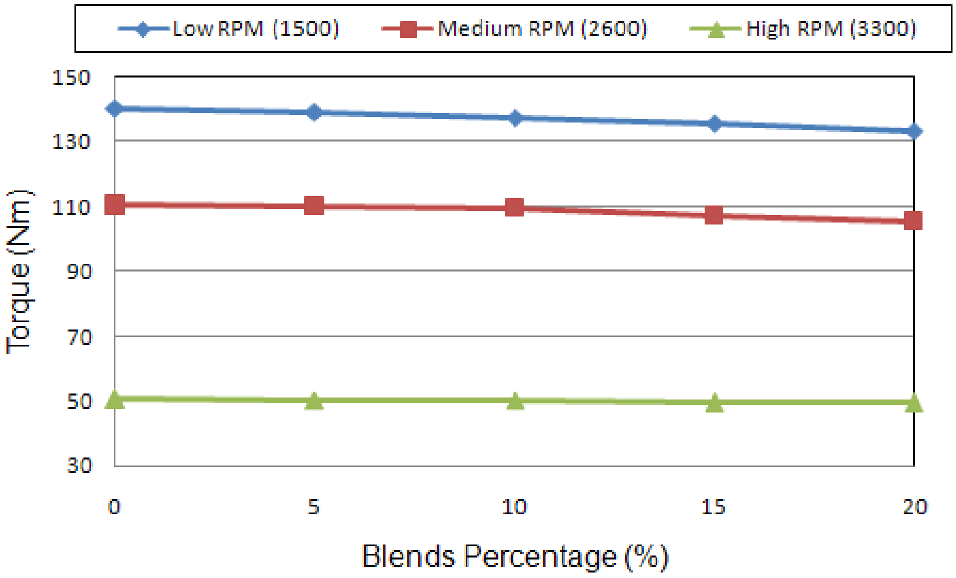


Figure 5.12: Torque output for different bio-diesel blends

The same trend in the results was seen for torque, there was a progressive decrease in torque as the proportion of bio-diesel in the blend increased, see Figures 5.12 and 5.13. The decrease in torque was more apparent than that of the power, because diesel engines are more focused on torque curves than power curves.

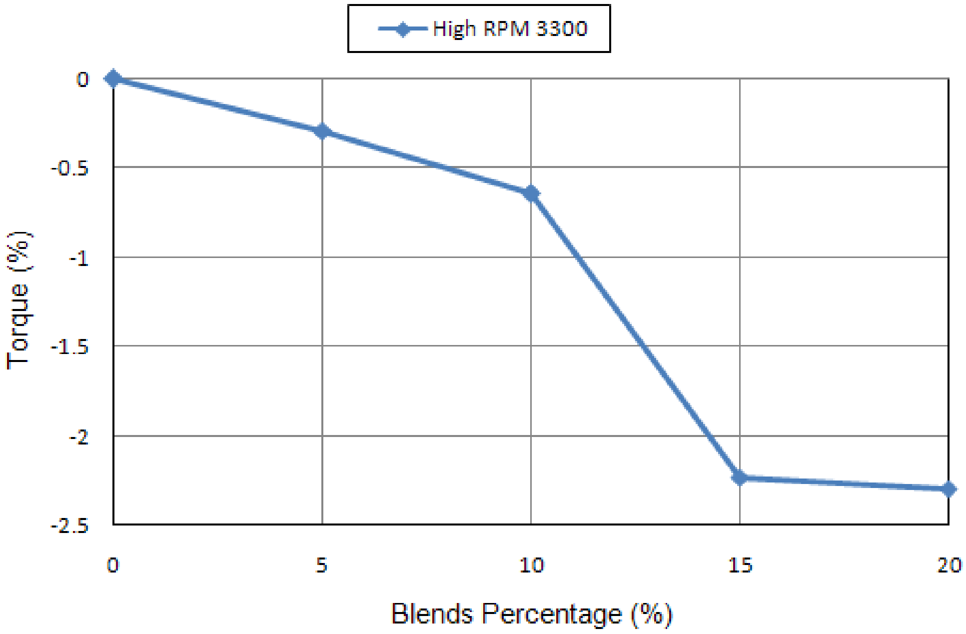


Figure 5.13: Normalised decrease in Torque output for different bio-diesel blends at 3300 rpm

5.4.8 Engine Performance for a Range of B100 Bio-diesels

Figure 5.14 shows the variation in the brake power with the engine speed of the test engine operated at full load with standard petroleum diesel and five bio-diesels produced from corn oil, rapeseed oil, soybean oil, sunflower oil and WVO. The brake power reached its peak value at the speed of about 2600 rpm for all fuels. The brake power of the engine with standard diesel was higher than for any bio-diesel. Standard petroleum diesel produced 8.4% and 5.6% more power than rapeseed bio-diesel at engine speed 2600 and 3300 rpm, respectively. Because the bio-diesels have lower calorific values than that of standard diesel, both torque and brake power is reduced. However, difference in brake power between standard diesel and the bio-diesels were very small in most cases.

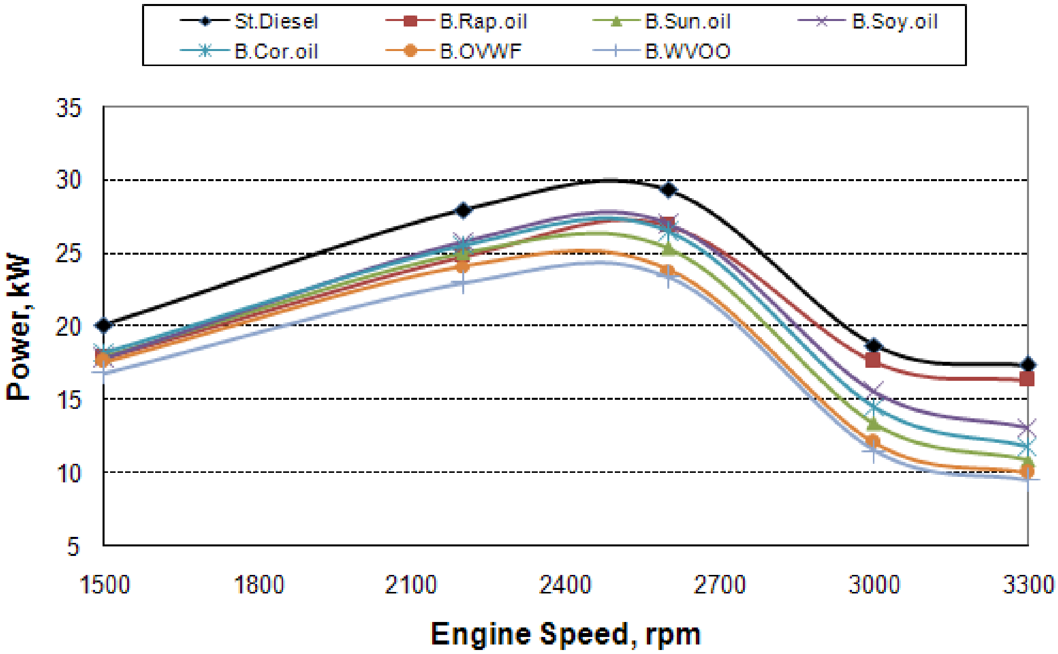


Figure 5.14: Average power output against engine speed at full load with petroleum diesel and bio-diesels as fuel

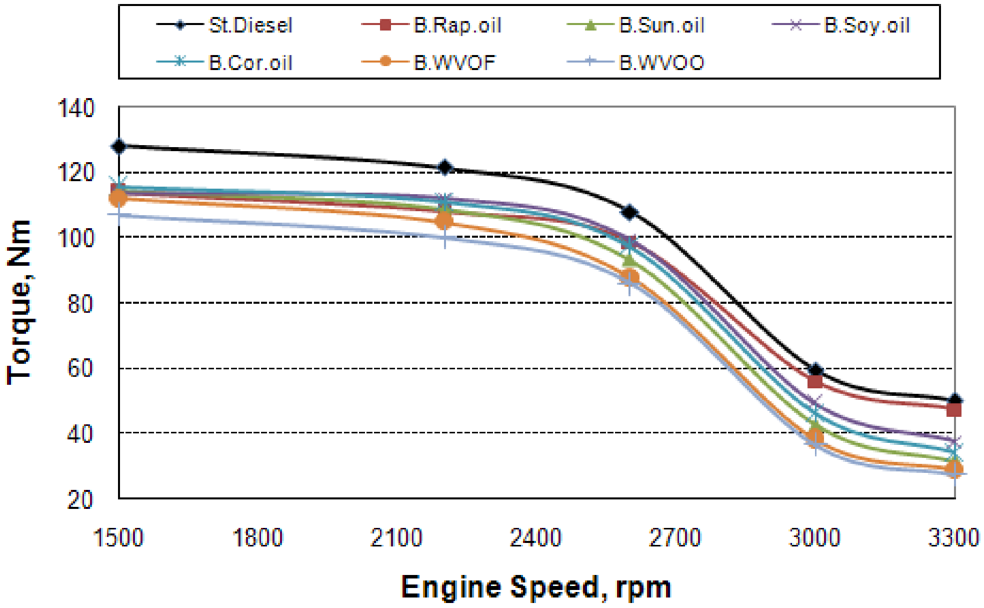


Figure 5.15: Average torque output against engine speed at full load with petroleum diesel and bio-diesels as fuel

Figure 5.15 shows the variation in the torque of the engine fuelled with standard diesel and different type of bio-diesel versus engine speed. It was observed that the engine yields the maximum torque for all fuels in the speed range of 1500 to 2000 rpm, while the minimum torque was obtained in the range of 3000 to 3300 rpm. The torque of the engine fuelled with standard diesel was higher than for bio-diesel. The reason for the reduction of torque with bio-diesel can also be attributed to the lower calorific value of the bio-diesel. The mean increase in the torque between standard diesel and bio-diesel was determined as 8.2%.

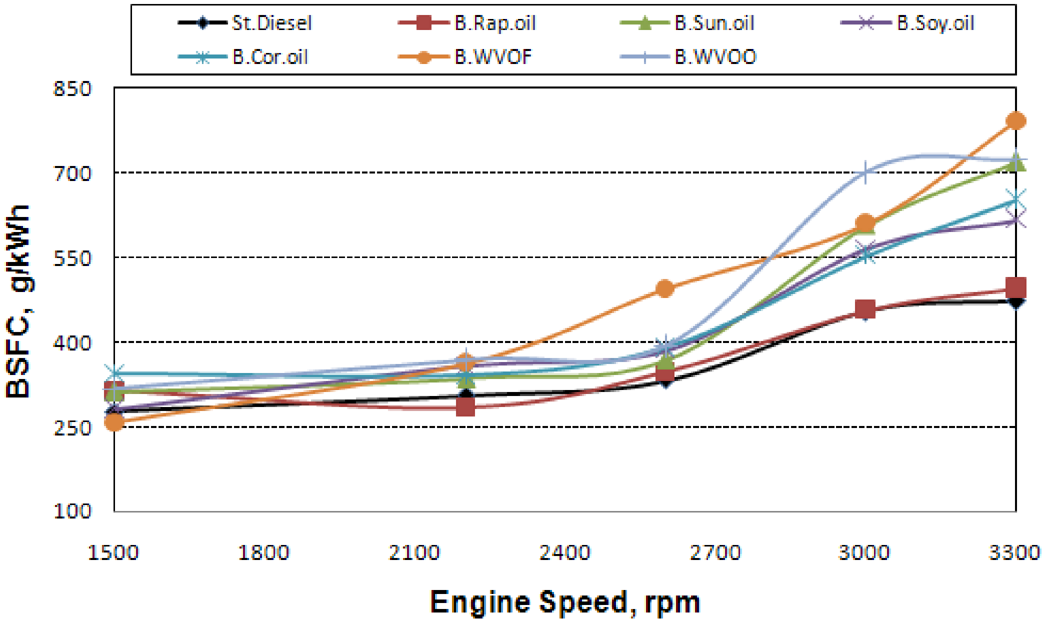


Figure 5.16: Average brake specific fuel consumption with engine speed at full load with petroleum diesel and bio-diesels as fuel

Figure 5.16 shows the variations in the BSFC in g/kWh for both standard diesel and bio-diesels with respect to the engine speed. The BSFC is the ratio of the fuel consumed in g/sec to the engine brake power. The BSFC for bio-diesel operation was on an average 11.6% higher than that for standard diesel operation. This increase may be attributed to the collective outcomes of the higher fuel density, higher fuel consumption and lower brake power due to lower calorific value of the bio-diesel. The highest BSFC was obtained using bio-diesel from WVO. Compared to bio-diesel from WVO, the BSFC was, on average, 13.2% and 12.8% lower for standard diesel and rapeseed bio-diesel, respectively.

Brake thermal efficiency for standard diesel and bio-diesel as a function of engine speed are shown in Figure 5.17. The maximum thermal efficiency for standard diesel and bio-diesels (with the exception of B.Rap.oil) was observed to occur close to 1500 rpm. It was seen that bio-diesel has higher thermal efficiency than standard diesel and the mean difference in thermal efficiency between them was about 1.5%. The improvement of thermal efficiency with bio-diesel can be attributed to the oxygen content and higher cetane number of bio-diesel. These properties lead to favourable effects on the combustion process and a slight improvement thermal efficiency for bio-diesel operation in spite of the lower calorific value of bio-diesel.

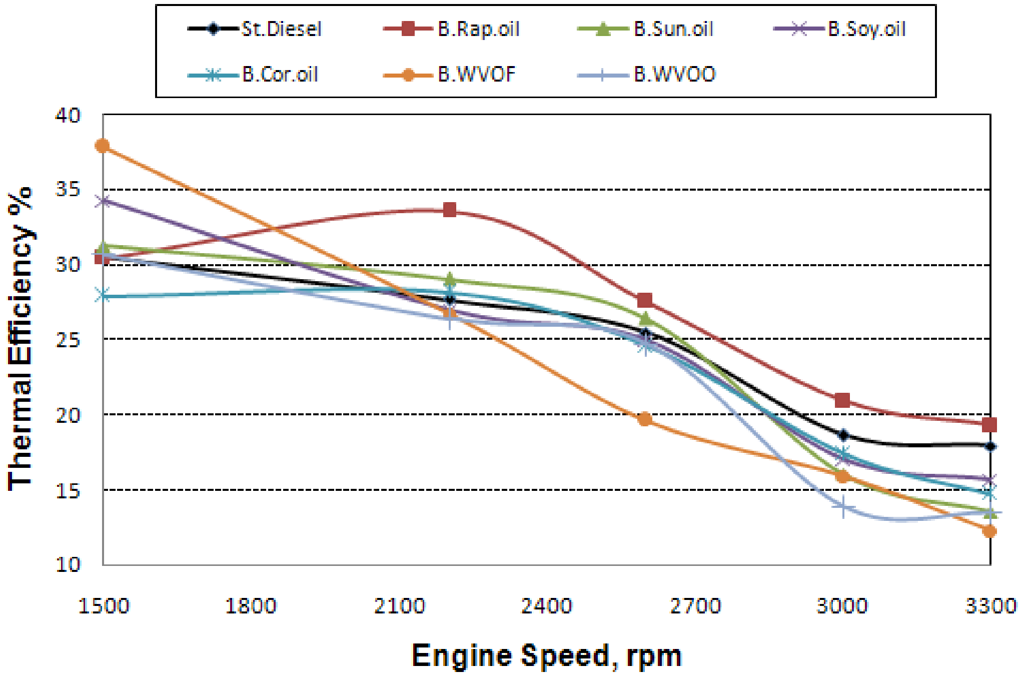


Figure 5.17: Average brake thermal efficiency against engine speed at full load with petroleum diesel and bio-diesels as fuel

Figure 5.18 shows the variation of THC emission with load for standard diesel and six different types of bio-diesel and it can be seen that all the bio-diesels produced relatively lower THC emissions compared to standard diesel. This may be attributed to the availability of oxygen in bio-diesel, which facilitates better combustion. THC emission for bio-diesel was almost identical. On average over the four loads used in the tests, there was a reduction of 33.9% in hydrocarbon emission for WVO bio-diesel, whereas it was 25.9% and 26.4% for sunflower oil bio-diesel and rapeseed oil bio-diesel respectively.

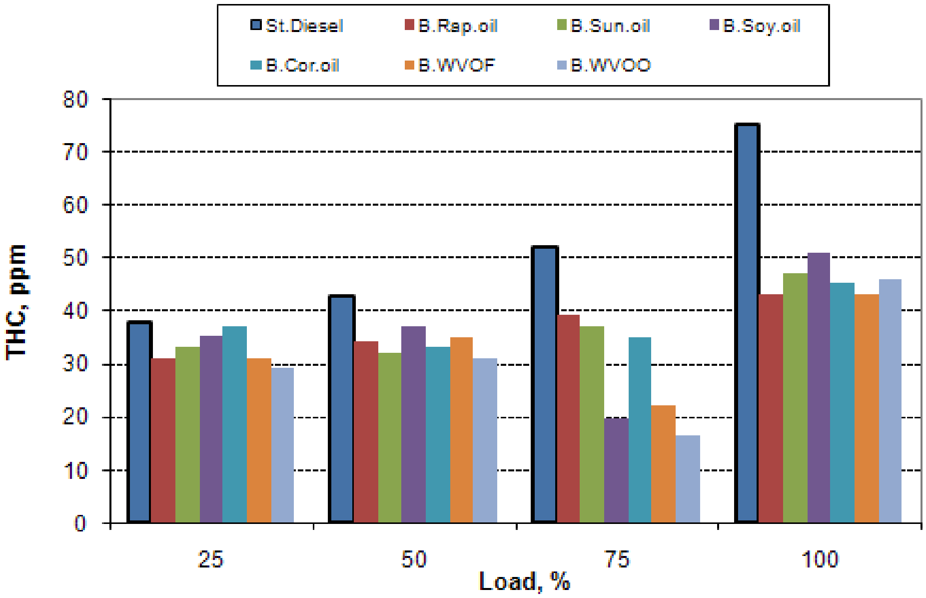


Figure 5.18: Hydrocarbon emissions against engine load at 1500 rpm

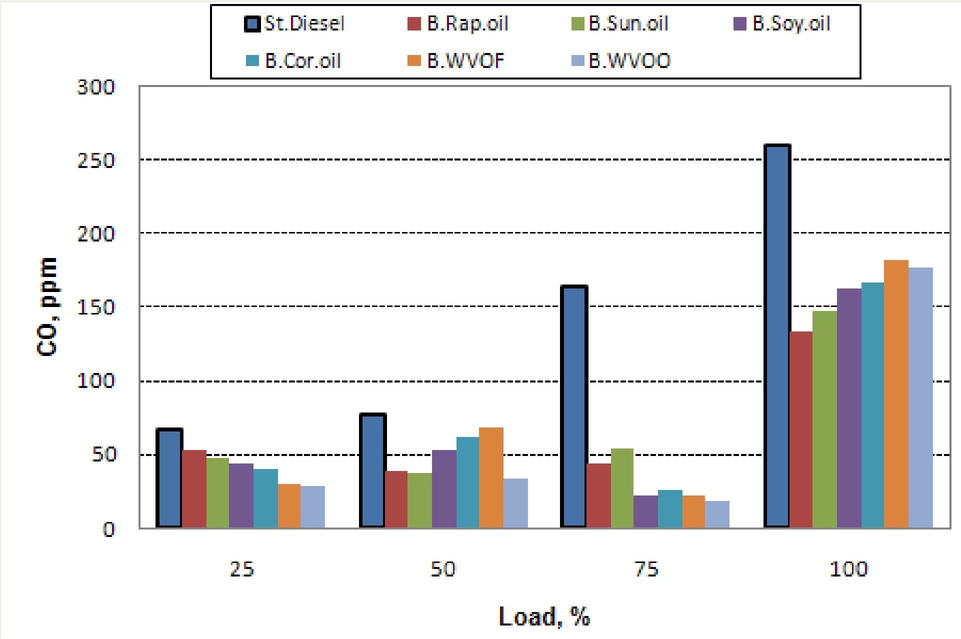


Figure 5.19: Carbon monoxide emissions against engine load at 1500 rpm

The variation of CO emission at different loads for standard diesel and six bio-diesels at 1500 rpm is shown in Figure 5.19. At 25% and 50% loads CO emissions of the petroleum diesel were not too much different from those of bio-diesel. However, at 75% full load CO emissions from standard diesel rose sharply, while the CO emissions from the bio-diesels fell.

At full load the CO emission from standard diesel again rose sharply, but the CO emissions from the bio-diesels rose even more sharply. CO emissions for bio-diesel operation were substantially lower than those for standard diesel operation because bio-diesel has both a higher cetane number and a higher oxygen content which contribute to a shorter ignition delay period which is important in reducing CO emission.

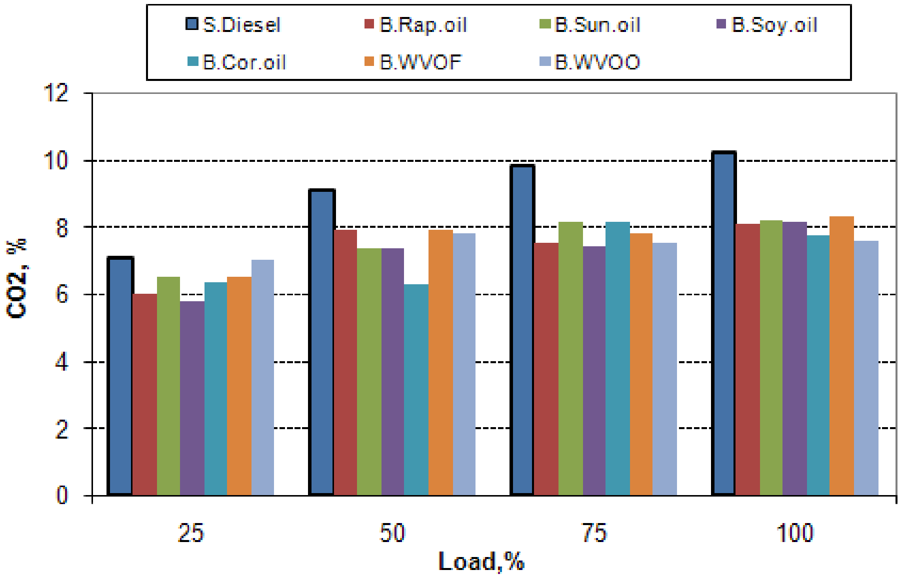


Figure 5.20: Carbon dioxide emissions against engine load at 1500 rpm

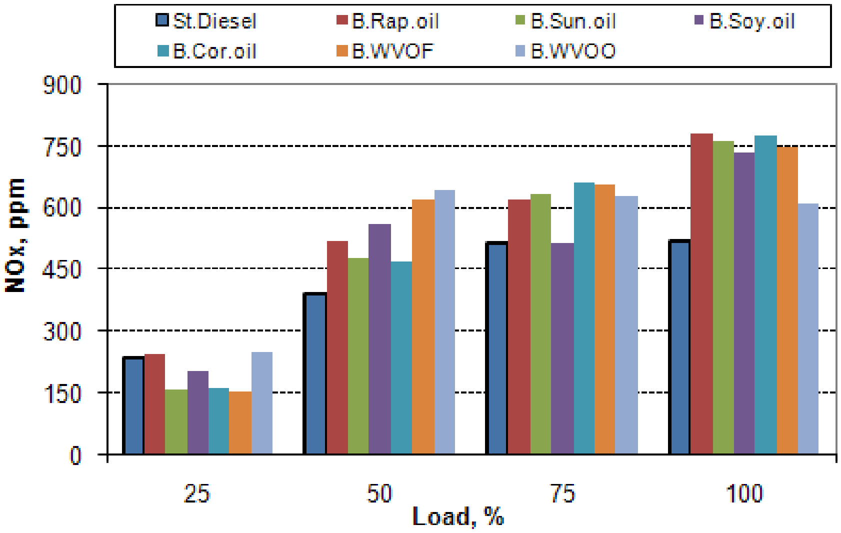


Figure 5.21: Emission of oxides of nitrogen against engine load at 1500 rpm

The variation of CO_2 emission at constant speed 1500 rpm and different loads for standard diesel and bio-diesel is shown in Figure 5.20. The trends are much the same and, in most cases, CO_2 emissions for the petroleum diesel were not much different from those of bio-diesel. Typically, the greater the load the bigger the difference between the CO_2 emitted for standard and the bio-diesels. At full load CO_2 emissions from bio-diesel operations were, on average, 22% lower than those of standard diesel operation. CO_2 emissions are reduced for the same reasons CO emissions are reduced, the bio-diesels have a higher cetane number and higher oxygen content compared to standard diesel.

Figure 5.21 shows variation in the emission of oxides of nitrogen with engine load at 1500 rpm, for standard diesel and six bio-diesels. The NOx emission with bio-diesel was higher than that with standard diesel at most engine loads. It is known that formation of NOx emissions are strongly dependent upon the equivalence ratio, oxygen concentration and burned gas temperature. Many researchers have confirmed that oxygenated bio-diesel causes an increase in NOx emissions. The oxygen content of bio-diesel is the main reason for higher NOx emissions because the oxygen in the bio-diesel can react easily with nitrogen during the of combustion process, thus causing higher emissions of NOx. Normally, complete combustion causes higher combustion temperature, which results in higher NOx formation. In bio-diesel operation, there was an average of 12.5% increase in the NOx emission was measured compared to standard diesel operation.

5.5 Cost Analysis

An alternative fuel despite improvements it may offer in, say reducing greenhouse emissions, enters the world market under the same conditions as established fuels. A product needs to be competitive to be a viable and immediate alternative fuel. Although it might be possible to create a fuel with zero emissions and an output similar to those of 100% petroleum fuels, the cost of such a fuel could over weight its perceived benefits. Any type of alternative fuel needs to be competitive for it to have a real chance of being effective. For this reason, when providing an alternative fuel the cost must be such that the fuel is competitive in the market, while the more important features of the fuel demanded by the customers are optimised. Thus while maintaining costs similar to those of petroleum fuels, reduced emissions is the primary factor demanded by today's world fuel market from any immediate alternative energy solution.

5.5.1 Fundamentals of a cost analysis

Given the similarities of the different bio-diesel blends tested, the question changes into which of these would provide the cheapest solution. Experimental data has shown that six different oils (sunflower oil, corn oil, rapeseed oil, soybean oil, WVOF and WVOO) tend to have similar emission results, with the new and used oils having only a slightly higher margin. Output power and efficiency on average is very similar to that of the petroleum counterpart.

The cost analysis follows a very simple procedure, to determine the unit cost (the price of 1 litre) of the bio-diesel blend. This price must be close to the price of 100% petroleum diesel. In order to obtain this information it is important to first analyze what factors affect the cost of production. Table 5.11 shows the process of the constituents necessary to produce bio-diesel.

Table 5.11: Price of raw materials for bio-diesel production

Material	Batch Capacity	£/Batch	£/Litre
WVOF/WVOO	50 Litres	-	-
Sunflower Oil/Corn Oil	50 Litres	£53.33	£1.07
Rapeseed Oil/Soybean Oil	50 Litres	£40.00	£0.80
Methanol	8.50 Litres	£6.38	£0.75
NaOH	0.200 kg	£1.10	5.50 £/kg
NaOH	0.400 kg	£2.20	

The purpose of this cost analysis is to produce a table of the cost/litre of B5, B10, B15, and B20 for each of the six oils tested. The cost of petroleum diesel, although it changes constantly it can initially be omitted from the analyses. It is assumed that on average for every 50 litres of base oil, 8.5 litres of methanol and 200 grams of catalyst concentration is required for pure vegetable oil and 400 grams of catalyst concentration is required for waste vegetable oil were to be used. These numbers will change depending on the FFA level of the base oil, but the variation will be sufficiently small to allow for the cost of methanol and catalyst to be assumed constant. On the other hand each kilogram of pure vegetable oil and WVO need £0.02 and £0.05 of NaOH respectively. Table 5.12 shows the cost of each of the blends on a per litre bases.

Table 5.12: Cost per litre of bio-diesel blends

Fuel	100%	B5	B10	B15	B20
*Petroleum Diesel	£1.40	-	-	-	-
WVO Bio-diesel	£0.80	£1.37	£1.34	£1.31	£1.28
Sunflower/Corn oil Bio-diesel	£1.84	£1.42	£1.44	£1.47	£1.49
Rapeseed/Soybean oil Bio-diesel	£1.57	£1.41	£1.42	£1.43	£1.44

* Petroleum diesel prices based on average price in UK garages Monday 21st March 2011 [230].

Table 5.12 shows the overall cost of production for one litre of bio-diesel blend. It is clear to see that obtaining free WVO decreases the price of the bio-diesel blend significantly as the proportion of bio-diesel increases. A highest cost of blended diesel was for sunflower oil and Corn oil bio-diesel with a price of £1.49 for B20, making it almost 9 pence per litre more expensive than petroleum diesel and 5 pence per litre more expensive than rapeseed oil and soybean oil bio-diesel. Although the WVO was free, more time is required produce the bio-diesel. Most used oil has to be refined and filtered a number of times. Filtering can take from two hours to five hours before the WVO is ready for bio-diesel production. Although this process can be automated, the time spent during this process can allow for there to be a smaller price difference between the free oil and the purchased refined oil.

5.5.2 Two-Step Optimization Process

Two-step optimization is one of the methods used to obtain a cost effective design for a product. Although there are many processes which can be used to create similar results the two step optimization process using the Tagushi method is one of the most accurate methods. This powerful tool, allows a product to be quickly and accurately optimized providing the best alternative to the market.

The following steps highlight the process conducted to obtain a functional optimization: (1) Obtain four characteristics of the bio-diesel, which have an impact on the use, production, time, and cost. (2) Identify the market requirements. (3) Develop a detailed matrix that matches the customer requirements and characteristics. (4) Set up a transformation process for each characteristic such as identity the output and target and identify the input variables and the levels. (5) Collect the data. (6) Generate response tables for Signal Noise Ratio (S/N) response and average response.

To be able to begin the optimization process for a bio-diesel the production functions must be known. To obtain a competitive bio-diesel blend, the fuel must be shows to decrease emissions, maintain an output of performance similar to that of the petroleum fuels, give similar efficiency to that of the petroleum fuels and, most importantly, be readily available. These features encapsulate the user's perspective of what qualities an alternative fuel for immediate application should possess. Here the bio-diesel decreases emissions, but it also decreases power output and efficiency and has a higher cost/litre. Bio-diesel is regarded as an immediate alternative energy because it can be used in conventional diesel engines to decrease emissions. This is regarded as the strong suit behind bio-diesel.

The six bio-diesel blends in question are going to go through a two step optimization process to obtain the basest oil to use, while maintaining the cost of the fuel within market competition. For this process it is important to be able to analyze the factors involved which are needed by the bio-diesel itself to be successful. The four factors were established to be as follows: A - Base Oil, B - Quality of Oil, C - Acidity and D - Availability. These four factors were chosen because they determine the qualities of the end product. The base oil was important because with this, one can see how much the overall cost will impact the final production, also the selection of base oil defines the other four factors. From this view there are two types of base oils with which to produce bio-diesel, free used WVO and base oil not used before but which needs to be purchased.

The second factor to be taken into consideration is the quality of the base oil. New oil is refined and clean while free used oil needs to be filtered and cleaned. Acidity levels of the base oil impact on production of bio-diesel and time required for production. Base oils which have been used, tend to have higher acidic levels than those which have not been used, yet in some cases the acidity levels vary from new oil to new oil. Higher acidity levels require a higher amount of methanol and catalyst to create a successful reaction. This also creates more glycerine and soap, which requires more time to be able to remove them from the final fuel, which caused decreased bio-diesel yield.

Finally the availability of the base oil is important factor on the production of bio-diesel. Availability controls how much bio-diesel can be created without waiting for delivery.

These four factors have been found to be the most influential with respect to the time required to produce a bio-diesel blend. The four factors (A, B, C and D) were given two levels (1,2) each. As previously discussed for every design there will be compromise between these factors. The two different levels for each factor will allow for the two step optimization to work, and are as shown in Table 5.13. Each one of these levels will be designated by either "1" or "2" to simplify the analysis of the optimization, so there are 2^4 possible combinations.

Table 5.13: 2-Level-4-Factor Experimental Design

#	**Factors**			
Level	**Base Oil (A)**	**Quality (B)**	**Acidity (C)**	**Availability (D)**
1	Free WVO	Used	High	Low
2	Purchased	Refined	Low	High

The properties are all required for the bio-diesel to be competitive in a market dominated by petroleum fuels, while possible "sacrifices" in strength of the factors are available. These "sacrifices" will be seen in the difference between e.g. refined oil which has a cost to the user versus a used WVO which will be free. The higher acidity levels of used oil means a higher ratio of methanol and catalyst concentration for the base oil to successfully produce a usable bio-diesel blend.

On the other hand there's the advantage of having a free base oil as a starting point, as it allows the user to help recycle a waste product, while still maintaining similar results in emission output as its counterpart.

With this information to hand a set of response has to be created for these situations (WVO and pure oils). All the responses (R1, R2 and R3) were based on a similar factor which affects the end product: time in hours. This data can be seen in Table 5.14.

Table 5.14: Responses for methyl ester production in hours

Waste vegetable oil	Sunflower oil/Corn oil	Rapeseed oil/Soybean oil
R1	**R2**	**R3**
12	10	11
10	13	11
8	10	8
8	7	7
9	11	10
9	9	10
11	8	9
5	6	8
9	7	9
7	5	5
7	4	5
2	4	3
8	9	9
6	8	7
7	6	9
3	3	5

Now that data has been tabulated the first step into the two step optimization is to create a detailed matrix of the requirements with the respective characteristics. This matrix allows one to create an easy-to-visualize response table for the four factors and how they are interact with each other. A total of 16 cells will be generated each carrying three responses, which gives the data the simulation of more than one trial run which all different combinations of factors, this simulation represents what will happen during the production and sustainability of a bio-diesel production. Table 5.15 represents the initial matrix outline.

Table 5.15: Taguchi Matrix (Initial Matrix)

				Base Oil			
				Free WVO		Purchased	
				Quality		Quality	
	Level	#	Level	1	2	1	2
Acidity	1	Availability	1	12	10	9	7
				10	13	7	5
				11	11	9	5
		Availability	2	8	8	7	2
				10	7	4	4
				8	7	5	3
Acidity	2	Availability	1	9	9	8	6
				11	9	9	8
				10	10	9	7
		Availability	2	11	5	7	3
				8	6	6	3
				9	8	9	5

From Table 5.16 an expanded table is created which shows the exact combinations, which total 16, and their response of length of production in terms of hours. The table will help obtain the needed information to be able to proceed on the two step optimization process by finding out the Signal Noise Ratio (S/N) and Mean values ($\hat{Y}$). As can be seen by Table 5.16 below, all 16 combinations of factors show their respective responses in hours. This helps the visualization of how these different factors affect the production and eventually the end product of the bio-diesel fuel blend.

Table 5.16: 2-Level 4-Factor Taguchi Matrix L16 (Expanded Matrix)

Run	**A**	**B**	**C**	**D**	**Production time in hours**		
L=16	Base Oil	Quality	Acidity	Availability	R1	R2	R3
1	1	1	1	1	12	10	11
2	1	2	1	1	10	13	11
3	1	1	1	2	8	10	8
4	1	2	1	2	8	7	7
5	1	1	2	1	9	11	10
6	1	2	2	1	9	9	10
7	1	1	2	2	11	8	9
8	1	2	2	2	5	6	8
9	2	1	1	1	9	7	9
10	2	2	1	1	7	5	5
11	2	1	1	2	7	4	5
12	2	2	1	2	2	4	3
13	2	1	2	1	8	9	9
14	2	2	2	1	6	8	7
15	2	1	2	2	7	6	9
16	2	2	2	2	3	3	5

Just by glancing over the responses in Table 5.16 it is clear that the hours required for production range from a minimum of 2 to a maximum of 13 hours. This is a positive statement, as it allows for a clear picture of what types of factor will make a major contribution to the final product. The two step optimization process will now allow this data which is so close in value, to provide the optimal solution of the four factors (A,B,C and D) and their two levels (Level 1 and Level 2).

5.5.3 Considerations for Two-Step Optimization

To be able to continue, the Signal to Noise (S/N) ratio must be calculated. Assume there are n data points, $y_1, y_2, \ldots y_n$. The S/N is given by:

$$S/_N = 10 \log \left[\frac{\frac{1}{n}(S_m - V_e)}{V_e} \right] \qquad (5.5)$$

Where V_e is the variance;

$$V_e = \frac{\sum_{i=1}^{n}(y_i - \bar{y})^2}{n-1} \tag{5.6}$$

$\bar{y}$ is the mean:

$$\bar{y} = \frac{y_1 + y_2 + \cdots + y_n}{n} \tag{5.7}$$

and

$$S_m = \frac{Total^2}{n} \tag{5.8}$$

Taguchi's Signal to Noise ratio, is a log function of the desired output serves as an objective functions for optimization, provides help in data analysis and production of optimum results [231].

Once the S/N ratio is obtained, the optimization process can be completed to provide the factors which would be the best choice. Using the equations above Table 5.17 shows the results of the calculations.

The following step shows how to create the S/N and $\bar{y}$ response tables. The summation of the desired factor and its level must then be divided by its quantity. As shown in Table 5.18 now depicts the final matrix of response values as well as the S/N ratio and the mean, which allows for the two step optimization process to be completed.

Table 5.17: Mean and S/N values

Run	R1	R2	R3	Sm	$\bar{y}$	Ve	S/N
1	12	10	11	363.0	11	1.00	20.8
2	10	13	11	385.3	11	2.33	17.4
3	8	10	8	225.3	9	1.33	17.5
4	8	7	7	161.3	7	0.33	22.1
5	9	11	10	300.0	10	1.00	20.0
6	9	9	10	261.3	9	0.33	24.2
7	11	8	9	261.3	9	2.33	15.7
8	5	6	8	120.3	6	2.33	12.3
9	9	7	9	208.3	8	1.33	17.1
10	7	5	5	96.33	6	1.33	13.8
11	7	4	5	85.33	5	2.33	10.7
12	2	4	3	27.00	3	1.00	9.38
13	8	9	9	225.3	9	0.33	23.5
14	6	8	7	147.0	7	1.00	16.9
15	7	6	9	161.3	7	2.33	13.6
16	3	3	5	40.33	4	1.33	9.89

Table 5.18: 2-Level-4-Factor Taguchi Matrix L16 (Completed Matrix)

Run	**A**	**B**	**C**	**D**	**Production Response in hours**			**Responses**	
L=16	Base Oil	Quality	Acidity	Availability	R1	R2	R3	S/N	$\bar{y}$
1	1	1	1	1	12	10	11	20.8	11
2	1	2	1	1	10	13	11	17.4	11
3	1	1	1	2	8	10	8	17.5	9
4	1	2	1	2	8	7	7	22.1	7
5	1	1	2	1	9	11	10	20.0	10
6	1	2	2	1	9	9	10	24.2	9
7	1	1	2	2	11	8	9	15.7	9
8	1	2	2	2	5	6	8	12.3	6
9	2	1	1	1	9	7	9	17.1	8
10	2	2	1	1	7	5	5	13.8	6
11	2	1	1	2	7	4	5	10.7	5
12	2	2	1	2	2	4	3	9.38	3
13	2	1	2	1	8	9	9	23.5	9
14	2	2	2	1	6	8	7	16.9	7
15	2	1	2	2	7	6	9	13.6	7
16	2	2	2	2	3	3	5	9.89	4

5.5.4 Two-Step Optimization

The values in Table 5.18, are each given a ranking from 1- 4, with 1 being the highest importance based on the highest range produced. This information is used to create the final matrix from which the optimal solution can be established. Tables 5.19 and 5.20 show the S/N and $\bar{y}$ response tables and the respective rankings:

Table 5.19: S/N ratio response

#	**Factor**			
Level	**A**	**B**	**C**	**D**
1	18.73	17.37	16.10	19.20
2	14.36	15.72	16.99	13.88
Range	4.37	1.644	-0.899	5.321
Rank	2	3	4	1

Table 5.20: Mean value response ($\bar{y}$)

#	**Factor**			
Level	**A**	**B**	**C**	**D**
1	9.167	8.583	7.583	8.917
2	6.125	6.708	7.708	6.375
Range	3.042	1.875	-0.125	2.542
Rank	1	3	4	2

Table 5.21 shows how S/N and $\bar{y}$ affect the optimization process, disregarding values which are out of range.

Table 5.21: Importance of the four factors for S/N and $\bar{y}$

S/N		
Factor	**Importance**	**No Variance Disregard**
A	4.3735	
B		1.6435
C		-0.8985
D	5.3209	

$\bar{y}$				
Factor	**High**	**Middle**	**Low**	**Disregard**
A	3.0417			
B			1.8750	
C				-0.1250
D		2.5417		

Tables 5.19 and 5.20 allow the user to see which factors at which level would provide the optimal solution to create a product which can maintain a high standard in fuel, while decreasing the time for production. These variables were used to create Table 5.22 which shows how the values in Table 5.21 interact.

Table 5.22: Response interaction for S/N and $\bar{y}$

Factor	Affect S/N	Affect $\bar{y}$	Affect S/N	Affect S/N + $\bar{y}$	Affect $\bar{y}$	Cost Reduction (Affect neither)
A	X	X	A1		A1	
B						B1,2
C						C1,2
D	X		D1			

Since factors "B and C" does not appear in either table these can be used as either level one or two without any implications for the final product. The final two step optimization design yields the following combination of factors and levels:

- A1 – B1,2 – C1,2 – D1
- Base oil: Free used WVO
- Quality: Refined
- Acidity level: Low
- Availability: High

5.6 Conclusions

In summary, the emissions from the blends and pure bio-diesel, it was found that CO, THC, and CO_2 were reduced significantly, whereas NOx increased slightly, when compared to those of standard diesel. Also, from the combustion analysis it was found the performance of the B20 was as good as that of standard diesel. Taking these facts into account, a blend of 20% methyl ester of WVO and pure vegetable oil can be used as an alternative suitable fuel in compression ignition engines.

On the other hand for the cost analysis, it was the two-step optimization process has shown that to obtain a quality bio-diesel blend while minimizing the time required for production the following factors were preferable: free WVO (which decreases the cost), refined oil (which decreases the time it would take to clean for processing), low acidity level (which means less catalyst and methanol would be used), and finally a high availability.

CHAPTER – 6

CONCLUSIONS AND RECOMMENDATION FOR FUTURE WORK

6.1 Conclusions

6.1.1 Bio-diesel Production and Fuel Properties

The “Fulpod” processor was used for the production of bio-diesel from vegetable oils by using the alkali-catalyzed transesterification process. The maximum ester yield was obtained by using 16% methanol and 0.4% NaOH at a reaction temperature of 65^oC. The fuel properties, such as kinematic viscosity, density, calorific value and cloud, pour and flash point, were measured and listed in Tables 3.3 and 3.4. After esterification of vegetable oils, the kinematic viscosity was reduced from 40 mm^2/s to 5 mm^2/s. For the analyzed samples, the properties were similar in some cases and divergent in others.

Sustainability will always be an issue with replacement fuels as it may affect foodstock supply. There is a need to find alternative fuels but the quantities available from recycled oils will not provide the significant, and increasing, levels needed – 9 trillion litres per year. There is potential with second generation fuels but as this did not form part of the study comment is limited.

6.1.2 Exhaust Gas Emissions and Engine Performances

One of the purposes of this study was to analyze the emissions present by running bio-diesel fuels and its blends on a conventional diesel engine. From the literature review it was apparent that by running a bio-diesel blend fuel there would be a decrease in emissions present while a slight decrease in engine efficiency. The experiential data did confirm these claims showing decreases in almost all the emissions (CO, THC and CO_2) except for NOx.

The study has shown that no matter what type of feedstock is used there will be very similar decreases in emissions and performance of the engine. These performance decreases are neglect able since in real life conditions a decrease of around 2% will not be noticed by the average consumer. Although the purchased refined oils provided better results than those of the waste vegetable oil, the results difference was not of any concern to make decision on which of the fuels would be more useful. On the other hand, from the combustion analysis it was found the performance of the B20 was as good as that of standard diesel. Taking these facts into account, a blend of 20% methyl ester of WVO and pure vegetable oil can be used as an alternative suitable fuel in compression ignition engines.

6.1.3 Cost Analysis

This analysis concluded that the use of bio-diesel lies in a cost analysis rather than a performance aspect. Since the fuels provide similar results a cost analysis was conducted to see what alternative would provides better results. Form the analysis it was clear from the start that obtaining the modified waste vegetable oil not only helped recycle this waste, but was significantly cheaper than running modified pure oils such as sunflower oil, corn oil, rapeseed oil and soybean oil as were used in this study. Furthermore the price difference between a B20 modified waste vegetable oil blends and standard diesel was 12 pence, making it a very cost effective solution.

The biggest problem was seen with the refinement of these oils. Since it takes substantially more time to clean and refine the waste vegetable oil than the straight unused oil. For this a two step optimization process was conducted using the Tagushi method. The function of a two step optimization analysis is to determine if there is a more significant difference between the six different types of feedstock's used accounting for a wider range of parameters. From data analysis, it is still cost effective and time consuming to obtain a free waste vegetable oil. Although the parameters also indicated that the preference of this oil should be abundant, and fairly clean.

Huge quantities of waste cooking oils and animal fats are available throughout the world, especially in the developed countries. Management of such oils and fats pose a significant challenge because of their disposal problems and possible contamination of the water and land resources. Even though some of this waste cooking oil is used for soap production, a major part of it is discharged into the environment. In the EU countries, the total waste cooking oil production was approximately 700,000-1,000,000 tons/yr [29]. The UK produces over 200,000 tons of waste cooking oil per year [252]. The Energy Information Administration in the United States estimated that some 100 million gallons of waste cooking oil is produced per day in USA [42]. As large amounts of waste cooking oils are illegally dumped into rivers and landfills, causing environmental pollution [253], the use of waste cooking oil to produce bio-diesel substitute offers significant advantages because of the reduction in environmental pollution.

6.1.4 Optimisation Process

In summary of this part of study, RSM proved to be a powerful tool for the optimization of methyl ester production at a fixed temperature. A second-order model was successfully developed to describe the relationships between methyl ester yield and test variables, including methanol/oil molar ratio, catalyst concentration, reaction temperature, rate of mixing and reaction time. The optimal conditions for the maximum methyl ester yield were found to be at methanol/oil molar ratio of 6.8:1, NaOH catalyst concentration of 1.1% (by the weight of sunflower oil), reaction temperature 35^{o}C, rate of mixing 200 rpm and a reaction time of 66 min. This optimized condition was validated with actual bio-diesel yield in 95%. Moreover, the decrease of the methanol/oil molar ratio from 6.8/1 to 6.0/1 while keeping the other variable parameters at their respective optimal values produced bio-diesel with a yield of 94%. Thus bio-diesel yield increased by 1% but at the cost of significantly increasing the molar ratio of methanol versus oil from 6.0 to 6.8, which does not appear to be cost-effective. It is suggested that using a methanol/oil molar ratio at 6.0 for the optimal production of bio-diesel from sunflower oil.

6.2 Recommendation for Future Work

This study initiated the work for the optimization and characterization of biodiesel production from refined cooking oils such as sunflower, rapeseed, soybean and corn oil, and waste vegetable oil. The engine performance was to be evaluated along with the emission characteristics for an engine running with bio-diesel and traditional fuels. Following future work is recommended:

- Use RSM in another feedstock to leads at generic effects.
- Optimization and characterization of biodiesel production from sunflower oil with equimolar mixture of ethanol and methanol and assess the effect of temperature on the gossypol concentration in the biodiesel produced.
- Studies to optimize and characterize biodiesel production from canola oil, jatropha oil, and algae oil.
- With the engine test results provided by this study, more steps should be taken to further analyze this immediate alternative fuel. Future work should be conducted on actual road vehicles, to see how the impact of driving a car in varying weather, driver affects the emissions, efficiency and performance of the oil. Along these lines different engines should be used to see if NOx emissions do in fact decrease on some type of engines.
- Busses are a likely candidate for test subjects as they run heavy duty diesel engines, and tend to idle a lot of the time while waiting for researchers. Obtaining a set of 3-4 buses or trucks and equipping each with a bio-diesel blend for 1-2 months will provide results which cannot be duplicated under lab conditions.

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APPENDICES

APPENDIX A

Figure A.1: Free Fatty Acid Content Test

- Titration Process Equipment as Following:

1) Three clean glasses beakers,
2) One clean plastic beaker,
3) Two clean eyedroppers,
4) Pipette handle,
5) Phenolphthalein (pH) indicator solution,
6) Methanol,
7) Titrant solution,
8) Gloves, and
9) Goggles

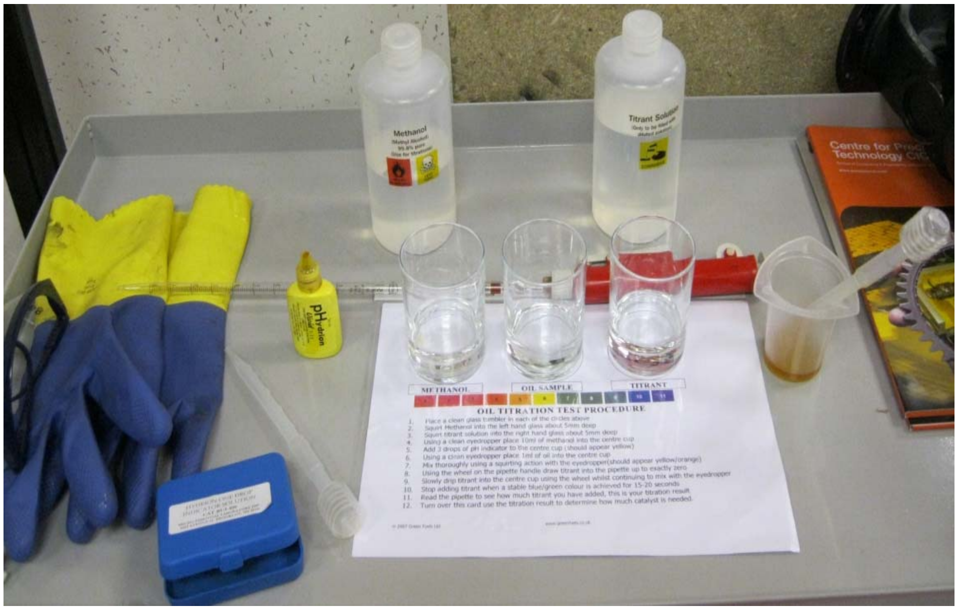
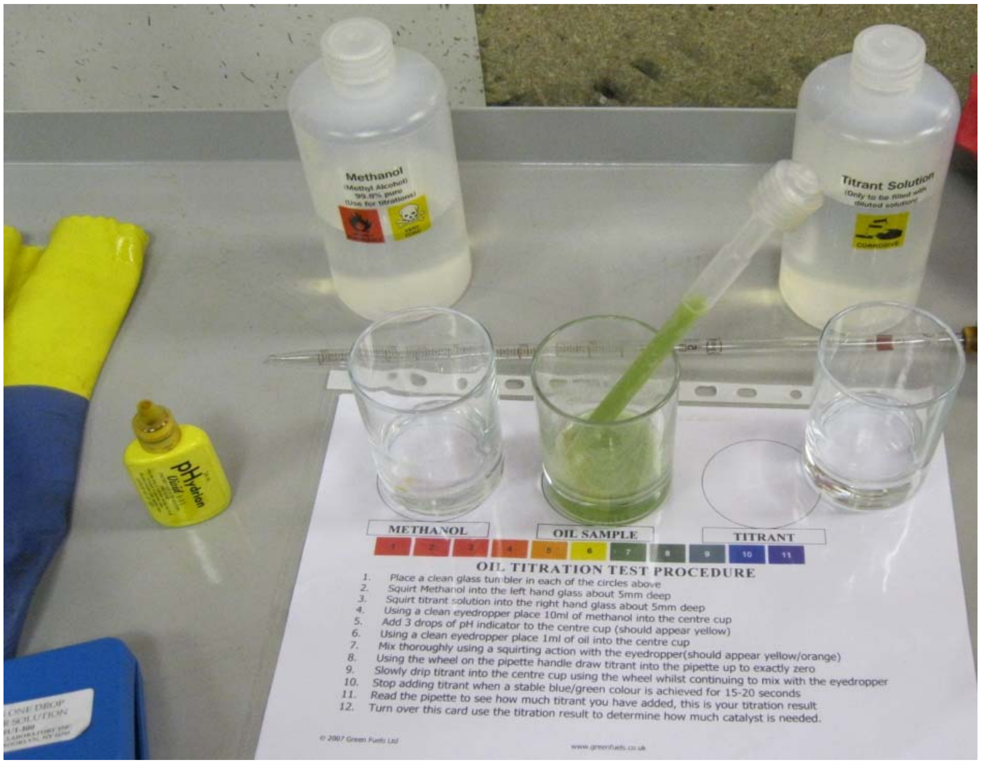


Figure A.2: Supplies used for the titration process

- Equipments of Oil Titration Test:



OIL TITRATION TEST PROCEDURE

1. Place a clean glass tumbler in each of the circles above
2. Squirt Methanol into the left hand glass about 5mm deep
3. Squirt titrant solution into the right hand glass about 5mm deep
4. Using a clean eyedropper place 10ml of methanol into the centre cup
5. Add 3 drops of pH indicator to the centre cup (should appear yellow)
6. Using a clean eyedropper place 1ml of oil into the centre cup
7. Mix thoroughly using a squirting action with the eyedropper(should appear yellow/orange)
8. Using the wheel on the pipette handle draw titrant into the pipette up to exactly zero
9. Slowly drip titrant into the centre cup using the wheel whilst continuing to mix with the eyedropper
10. Stop adding titrant when a stable blue/green colour is achieved for 15-20 seconds
11. Read the pipette to see how much titrant you have added, this is your titration result
12. Turn over this card use the titration result to determine how much catalyst is needed.

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Figure A.3: Oil titration test

Titration Result (mL)	Sodium Hydroxide NaOH (grams) 99.9%pure	Potassium Hydroxide KOH (grams) 90%pure	Methylate (mL)
0.0	175	272	600
0.1	180	280	600
0.2	185	288	600
0.3	190	296	650
0.4	195	303	650
0.5	200	311	650
0.6	205	319	700
0.7	210	327	700
0.8	215	334	700
0.9	220	342	750
1.0	225	350	750
1.1	230	358	750
1.2	235	366	800
1.3	240	373	800
1.4	245	381	800
1.5	250	389	850
1.6	255	397	850
1.7	260	404	850
1.8	265	412	900
1.9	270	420	900
2.0	275	428	900
2.1	280	436	950
2.2	285	443	950
2.3	290	451	950
2.4	295	459	1000
2.5	300	467	1000
2.6	305	474	1000
2.7	310	482	1050
2.8	315	490	1050
2.9	320	498	1050
3.0	325	506	1100
3.1	330	513	1100
3.2	335	521	1100
3.3	340	529	1150
3.4	345	537	1150
3.5	350	544	1150
3.6	355	552	1200
3.7	360	560	1200
3.8	365	568	1200
3.9	370	576	1250
4.0	375	583	1250
4.1	380	591	1250
4.2	385	599	1300
4.3	390	607	1300
4.4	395	614	1300
4.5	400	622	1350
4.6	405	630	1350
4.7	410	638	1350
4.8	415	646	1400
4.9	420	653	1400
5.0	425	661	1400

Figure A.4: Manufacture laminated card (manufacture manual)

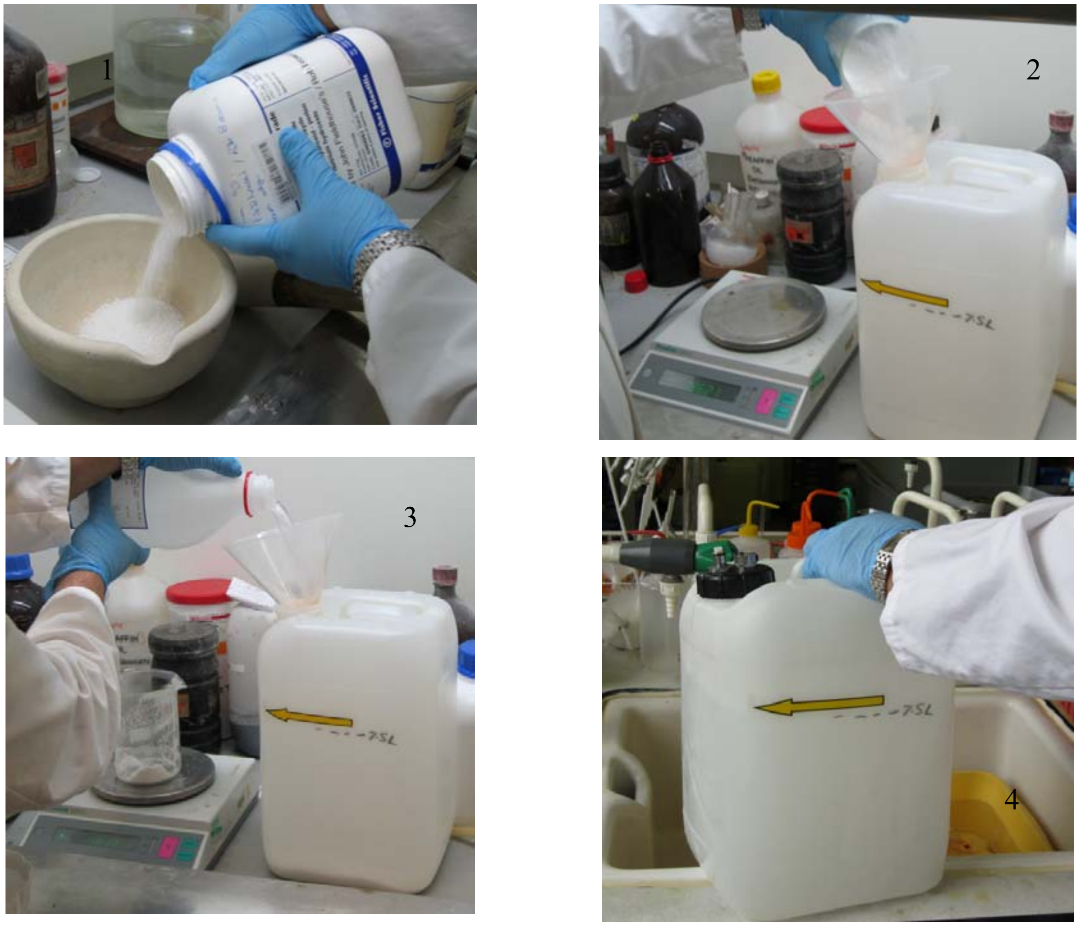

Figure A.5: Bomb calorimeter apparatus

Figure A.6: Container holding mixture of methanol and sodium hydroxide connected with the system

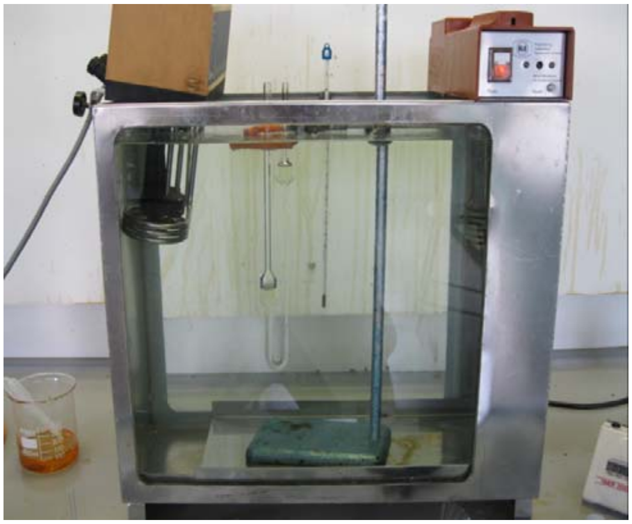

Figure A.7: Equipment for measuring kinematic viscosity

Figure A.8: Iodine number test apparatus

Figure A.9: Bomb calorimeter apparatus

Figure A.10: Experimental equipment for transesterification

APPENDIX B

The test bed instrumentation is described below:

Type: Schenck W230 Eddy Current Dynamometer

- Maximum Speed: 7500 rpm
- Maximum Power: 230 kW from 2200 rpm to 7500 rpm
- Maximum Torque: 750Nm from 600 rpm to 2200 rpm
- Rotor Inertia: 0.53 kgm^2
- Speed Measurement: 60 tooth wheel with inductive pickup
- Torque Measurement Load cell via swing frame torque arm

Control System Description –

- CP Engineering Cadet V12 Control and Data logging System designed specifically for engine testing.
- Potential Capability of 512 Data.
- Logging Channels and 64 PID loops for secondary control hardware.

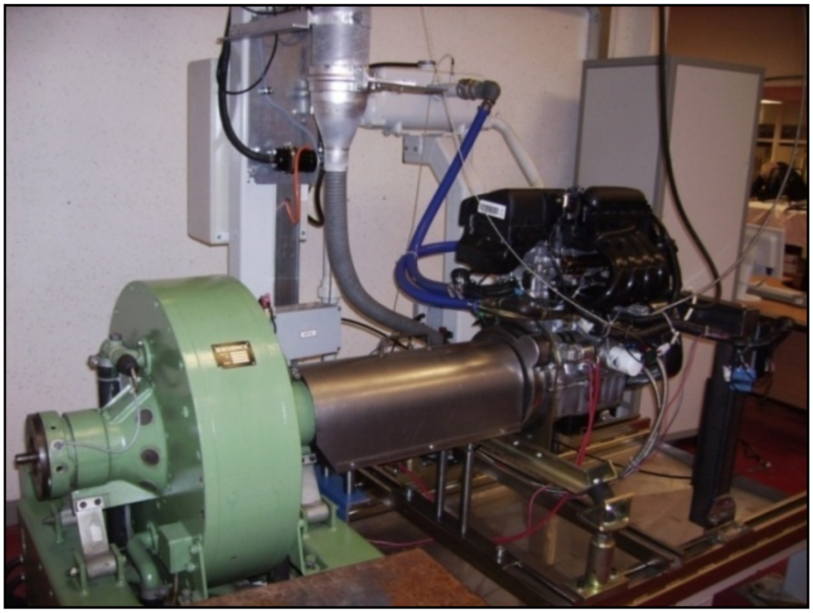

Figure B.1: Photo of test rig, Schenk dynamometer fitted with Ford Puma engine

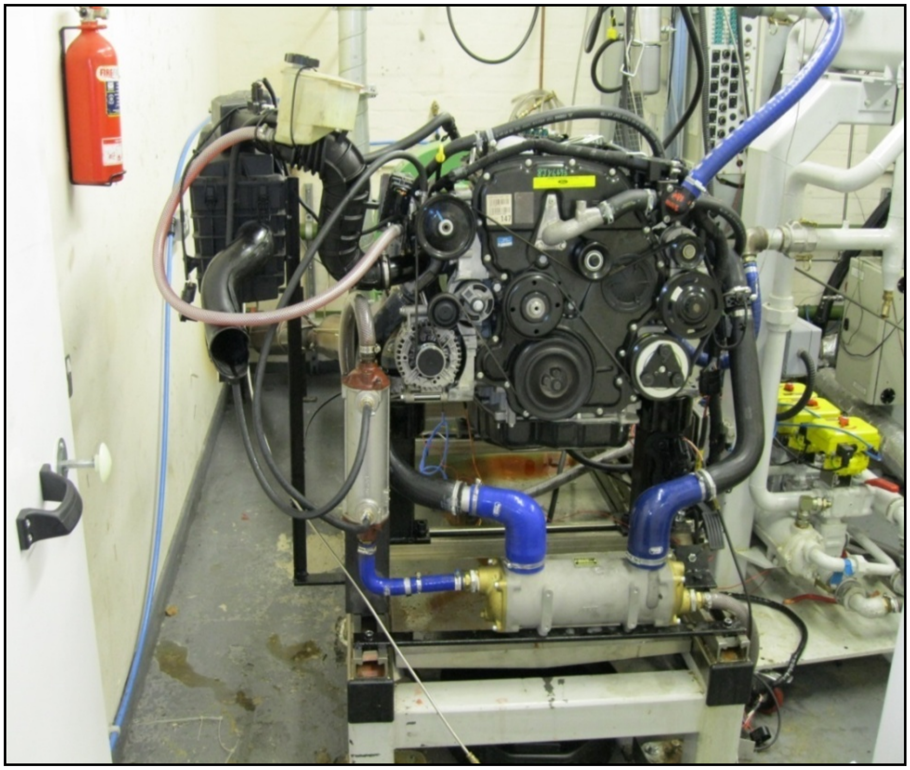

Figure B.2: View of Ford Puma Engine as used in testing

Figure B.3: Data acquisition system visual displays and inputs

The engine brake power (*BP*) in kW was calculated as:

$$BP = \frac{T}{1000} \times \frac{2\pi \times N}{60} \qquad (B.1)$$

Where:

T = Measured brake torque of the engine (Nm),

N = Measured engine speed (rpm).

The brake specific fuel consumption (BSFC) in kgh^{-1}kW^{-1} was calculated as**:**

$$BSFC = \frac{m_f}{BP} \times 3600 \qquad (B.2)$$

Where:

m_f= Measured fuel consumption $\left(\frac{kg}{s}\right)$.

The brake thermal efficiency (Eff, %) was calculated as**:**

$$Eff = \frac{BP \times 1000}{m_f \times C.V.} \times 100 \qquad (B.3)$$

Where:

$C.V$ = Calculated calorific value of the fuel $\left(\frac{J}{kg}\right)$.

Figure B.4: Horiba exhaust gas analyzer EXSA-1500L