Experimental investigations on the utilization of waste cooking oil based biodiesel & n-butanol in CI Engine

A Dissertation

Submitted in partial fulfilment of the requirement

For the award of degree of

Masters in Technology

In

Environmental Science and Technology

Submitted

By

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July 2014

DECLARATION

I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled "**Experimental investigations on the utilization of waste cooking oil based biodiesel & n-butanol in CI Engine**" has been carried out by me under the supervision and guidance of ***Dr S. K. Mahla, School of Energy and Environment, Thapar University, Patiala.***

Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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CERTIFICATE

This is to certify that thesis entitled, "**Experimental investigations on the utilization of waste cooking oil based biodiesel & n-butanol in CI Engine**" submitted by **Ms. Manu Jindal** in partial fulfilment of the requirements for the award of **Masters in Technology** Degree in **Environmental Science & Technology** at **Thapar University, Patiala** is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any Degree or Diploma.

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ABSTRACT

In recent years, two problems roused people's concern. One is energy crisis caused by the depleting of petroleum fuel. The other one is environmental issues such as greenhouse effect, global warming, etc. Therefore, renewable energy sources utilization technology and bio-energy production technology developed fast for solving such two problems. Biodiesel is receiving increased attention as an alternative, non-toxic, biodegradable, and renewable diesel fuel. The production of biodiesel from waste vegetable oil offers a triple-facet solution: economic, environmental and waste management.

Butanol is a potential alternative to ethanol and offers many benefits including a much higher heating value and lower latent heat of vaporization. It also has a higher cetane number than ethanol and improved miscibility in diesel fuel. Additionally, butanol is less corrosive and less prone to water absorption than ethanol, which allows it to be transported using the existing fuel supply pipelines.

Experimental work was conducted to evaluate the effect of using n-butanol-biodiesel-diesel blends on the engine performance parameter of a single cylinder direct injection compression ignition engine with the engine working at different loads. Blends of biodiesel-diesel fuel (B20, B40 and B60) and biodiesel-diesel-n butanol (nB10 and nB20) were prepared and engine performance parameters and emissions were checked. The performance parameters evaluated include brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), brake specific energy consumption (BSEC), brake power (BHP). Emission parameters included HC, CO_2, CO, NOx, and smoke. Results were compared with the neat diesel. Emissions were reduced by 25-50% and efficiency increased by 13% with B20 blend. The experiment shows that 20% biodiesel blended with diesel and 10% n butanol blend gave best results and can be used without any modification in the diesel engine with point of view of decreased bsfc, increased efficiency and reduction in emissions.

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NOTATIONS AND ABBREVIATIONS

ASTM	American Society for Testing Materials
BSFC	Brake specific fuel consumption
BTE	Brake Thermal Efficieny
BSEC	Brake Specific Energy Consumption
BHP	Brake Horse Power
BSN	Bosch Smoke Number
^oC	Degree Celsius
cc	Centimeter cube
CI	Compression ignition
CO	Carbon monoxide
CO_2	Carbon dioxide
NOx	Nitric Oxides
cS	Centistokes
FFA	Free Fatty Acid
g	Gram
hr	Hour
HC	Hydrocarbon
IC	Internal combustion
IS	Indian Standards
kg	Kilogram
kW	Kilowatt
KOH	Potassium hydroxide
L	Litre
ml	Mililitre
mg	Miligram

CHAPTER 1
INTRODUCTION

1.1ENERGY AND ENVIRONMENT

With the exception of the hydroelectricity and nuclear energy, the majority of the world energy needs are supplied through petrochemical sources, coal and natural gas. All of these sources are finite and at current usage rates will be consumed in the future **[25].** The depletion of world petroleum reserves and increased environmental concerns has stimulated recent interest in alternative sources for petroleum based fuels **[12].**

1.1.1 Indian Power Sector

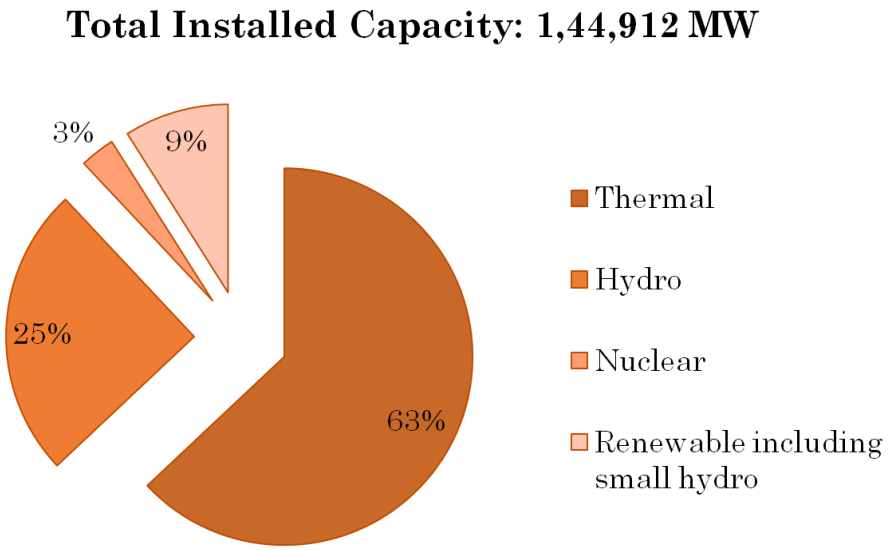


Figure 1.1: Energy division in India [49]

With the decrement in conventional energy and the increasingly stringent emission standards, it is important to develop new internal combustion engines with low emissions, high fuel efficiency and high specific power **[19].**

1.1.2 Energy Consumption Trend

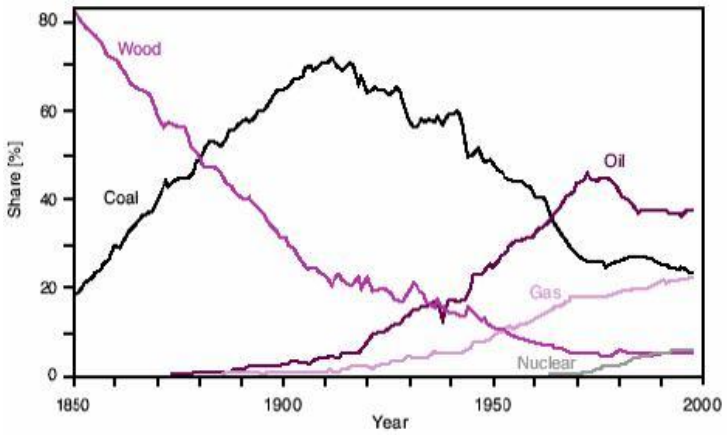


Figure1.2: Energy Use Trends [49]

1.1.3 Energy bills

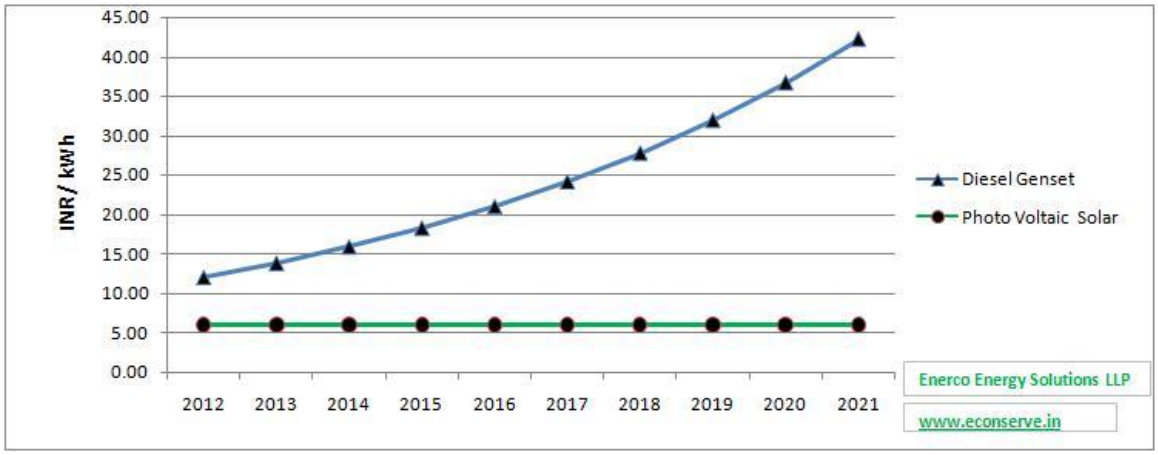


Figure1.3: Energy Bills [49]

In this perspective, considerable attention has been given towards the production of biodiesel as a diesel substitute. Moreover, biodiesel fuel has become more attractive because of its environmental benefits, due to the fact that plants and vegetable oils and animal fats are renewable biomass sources **[31].**

1.2 ALTERNATIVE FUELS

The growing interest in alternative fuels for IC engines is motivated by three important considerations:

1. Alternative fuels generally produce fewer vehicle emissions that contribute to smog, air pollution and global warming;
2. Most alternative fuels are not derived from finite fossil-fuel resources; and
3. Alternative fuels can help any nation become more energy independent.

Alternative fuels, known as non-conventional or advanced fuels, are any materials or substances that can be used as fuels, other than conventional fuels. Conventional fuels include: fossil fuels (petroleum (oil), coal, and natural gas), as well as nuclear materials such as uranium and thorium, as well as artificial radioisotope fuels that are made in nuclear reactors.

Some well-known alternative fuels include

- Biodiesel
- Bio-alcohol (methanol, ethanol, butanol)
- Chemically stored electricity(batteries and fuel cells)
- Hydrogen
- Non-fossil methane, propane and natural gas
- Other biomass sources (Biogas, Producer gas)

Biodiesel: Biodiesel is derived from vegetable oils and animal fats. It usually produces less air pollutants than petroleum-based diesel.

Alcohol fuels: Methanol and ethanol fuel are primary sources of energy; they are convenient fuels for storing and transporting energy. These alcohols can be used in internal combustion engines as alternative fuels. **Butanol** has another advantage: it is the only alcohol-based motor fuel that can be transported readily by existing petroleum-product pipeline networks, instead of only by tanker trucks and railroad cars. **Ethanol** is produced domestically from corn and other crops and produces less greenhouse gas emissions than conventional fuels. **Methanol** could

become an important alternative fuel in the future, however, as a source of the hydrogen needed to power fuel-cell vehicles.

Hydrogen: Hydrogen can be mixed with natural gas to create an alternative fuel for vehicles that use certain types of internal combustion engines. Hydrogen is also used in fuel-cell vehicles that run on electricity produced by the petrochemical reaction that occurs when hydrogen and oxygen are combined in the fuel "stack."

Propane: Propane, also called liquefied petroleum gas or LPG, is a byproduct of natural gas processing and crude oil refining. Already widely used as a fuel for cooking and heating, propane is also a popular alternative fuel for vehicles. Propane produces fewer emissions than gasoline, and there is also a highly developed infrastructure for propane transport, storage and distribution.

Natural Gas: Natural gas is an alternative fuel that burns clean and is already widely available to people in many countries through utilities that provide natural gas to homes and businesses. When used in natural gas vehicles—cars and trucks with specially designed engines—natural gas produces far fewer harmful emissions than gasoline or diesel.

Stored Electricity: Electricity can be used as a transportation alternative fuel for battery-powered electric and fuel-cell vehicles. Battery powered electric vehicles store power in batteries that are recharged by plugging the vehicle into a standard electrical source. Fuel-cell vehicles run on electricity that is produced through an electrochemical reaction that occurs when hydrogen and oxygen are combined. Fuel cells produce electricity without combustion or pollution.

Biomass based fuel: Biogas is usually 50% to 80% methane and 20% to 50% carbon dioxide, with traces of gases such as hydrogen, carbon monoxide, and nitrogen. In contrast, natural gas is usually more than 70% methane, with most of the rest being other hydrocarbons (such as propane and butane) and traces of carbon dioxide and other contaminants.

1.3 BIODIESEL

Technical Definition for Biodiesel (ASTM D 6751) and Biodiesel Blend: *Biodiesel, n* - a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751.

Biodiesel Blend, n - a blend of biodiesel fuel meeting ASTM D 6751 with petroleum-based diesel fuel, designated BXX, where XX represents the volume percentage of biodiesel fuel in the blend.

1.3.1 Biodiesel and raw vegetable oil

Fuel-grade biodiesel must be produced to strict industry specifications (ASTM D6751) in order to insure proper performance. Biodiesel that meets ASTM D6751 and is legally registered with the Environmental Protection Agency is a legal motor fuel for sale and distribution. Raw vegetable oil cannot meet biodiesel fuel specifications, it is not registered with the EPA, and it is not a legal motor fuel.

1.3.2 Biodiesel Scenario in India

As India is deficient in edible oils, non-edible oil is the main choice for producing biodiesel. According to Indian government policy and Indian technology effects, some development works have been carried out with regards to the production of transesterified non edible oil and its use in biodiesel Indian Institute of Science, Bangalore, Tamilnadu Agriculture University Coimbatore, PAU Ludhiana, IIT Delhi, MERADO etc. Generally a blend of 5% to 20% is used in India (B5 to B20). Research is carried out in Kumaraguru College of Technology for marginally altering the engine parameters to suit the Indian Jatropha seeds and to minimize the cost of transesterification.

1.3.3 Environmental Considerations

Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the Clean Air Act. Emissions from the use of biodiesel in combustion engines are greatly reduced compared to conventional petroleum diesel fuels by up to 100% sulfur dioxide, 48% carbon monoxide, 47% particulate matter, 67% total unburned hydrocarbons and up to 90% reduction in mutagenicity **[22].** Perhaps the most significant reductions based on life cycle analysis is the 78% reduction in carbon dioxide which is considered the most important green house gas in climatic models. It was showed that biodiesel has much higher biodegradability than low sulfur diesel fuel and the addition of biodiesel to diesel fuels actually promotes the biodegradability of diesel fuel, making the blends more environmentally attractive **[48].** Based on engine testing, using the hot stringent emissions testing protocols required by

EPA for certification of fuels or fuel additives in the US, the overall ozone forming potential of the speciated hydrocarbon emissions from biodiesel was nearly 50% less than that measured for diesel fuel.

AVERAGE BIODIESEL EMISSIONS COMPARED TO CONVENTIONAL DIESEL, ACCORDING TO EPA

Emission Type	B100	B20
Regulated		
Total Unburned Hydrocarbons	-67%	-20%
Carbon Monoxide	-48%	-12%
Particulate Matter	-47%	-12%
Nox	+10%	+2% to -2%
Non-Regulated		
Sulfates	-100%	-20%*
PAH (Polycyclic Aromatic Hydrocarbons)**	-80%	-13%
nPAH (nitrated PAH's)**	-90%	-50%***
Ozone potential of speciated HC	-50%	-10%

Figure1.4: Biodiesel Emissions acc to EPA [50]

- Estimated from B100 result
- ** Average reduction across all compounds measured
- *** 2-nitroflourine results were within test method variability

1.3.4 Waste vegetable oils

Every year many millions of tonnes of waste cooking oils are collected and used in a variety of ways throughout the world. This is a virtually inexhaustible source of energy, which might also prove an additional source of power. These oils contain some degradation products of vegetable oils and foreign material. However, analyses of used vegetable oils indicate that the differences between used and unused fats are not very great and in most cases simple heating and removal by filtration of solid particles suffices for subsequent transesterification. The cetane number of a used frying oil methyl ester was given as 49, thus comparing well with other materials. Cooking oils contain many types of vegetable based oils as well as rendered animal oils. There are enough used cooking oils and fats generated all over the world annually, including 18 billion pounds of soybean oil and 11 billion pounds of animal fat, to produce an

estimated 5 billion gallon of biodiesel. Fats, moisture, proteins and animal fragments extracted from meats during the frying process could become an important component of waste cooking oils particularly when they affect the biodiesel production process in terms of filtration requirements, potential poisoning of the catalyst and altered fatty acid ester composition in the final product. Waste cooking oils having less than 15 percent free fatty acids (FFA) as a by product of oxidation are considered yellow grease and when oils exceed 15 percent FFA, as might occur particularly in the summer months during storage of waste grease, they are considered a lower value brown grea **[6].** According to them, Yellow grease maybe combined with lower FFA yellow grease to be sold at a higher price. It was proposed an acid-catalyzed esterification process for waste cooking oil conversion to biodiesel **[48].**

1.3.5 Advantages of Biodiesel

The advantages of biodiesel are as follows

- It is a renewable substitute for petroleum and diesel fuels.
- Only alternative fuel to fully complete health effects testing requirements of the Clean Air Act.
- It reduces compounds linked to cancer by 80-90%.
- It cuts emissions like PM, CO and unburned hydrocarbons.
- It has low sulfur and aromatic content.
- It is readily available and biodegradable fuel.
- It has higher flash point than diesel.
- Its combustion efficiency is high.
- It has better lubricity properties than diesel.
- It has lower HC, CO_2, CO emissions as compared to petroleum and diesel fuels.
- It has less particulate emissions than petroleum and diesel fuels.
- It contributes to domestic energy security.
- It provides highest energy content of any alternative fuel.
- It works in any diesel engine with few or no modifications.
- Biodiesel is the safest fuel to use, store and handle.
- It demonstrates similar fuel economy, horsepower and torque as petroleum diesel.
- Seamlessly transitions a diesel fleet to a cleaner burning program.

1.3.6 Limitations of biodiesel

- Biofuels have a lower energy output than traditional fuels and therefore require greater quantities to be consumed in order to produce the same energy level.
- Biodiesel may start to solidify between 4-5ºC (40ºF) depending on the oil used leading to cold weather starting problems. During the winter, a 50/50 mix of regular diesel/biodiesel blend should be used.
- To refine biofuels to more efficient energy outputs, and to build the necessary manufacturing plants to increase biofuel quantities, a high initial investment is often required.
- There is concern that using valuable cropland to grow fuel crops could have an impact on the cost of food and could possibly lead to food shortages.

1.4 n- Butanol

n- Butanol has many advantages over ethanol, including a higher energy density due to two extra carbons, and can be used in gasoline engines without modification. *n*- Butanol is less hygroscopic and evaporative than ethanol and has been recently regarded as a more viable transportation biofuel than ethanol **[10].** Also fuel testing demonstrates that high octane biobuatnol can deliver the exceptional performance characteristics as compared to 10% ethanol blend, which has further resulted in improved energy density/fuel economy as compared to current biofuel blends for use in existing fuels infrastructure **[7].** Butanol has a lower autoignition temperature than methanol and ethanol. Therefore, butanol can be ignited easier when burned in diesel engines. Butanol appeared the good properties compared with its homologues such as 2-butanol, iso-butanol and tert-butanol and other fuels such as Gasoline and ethanol.

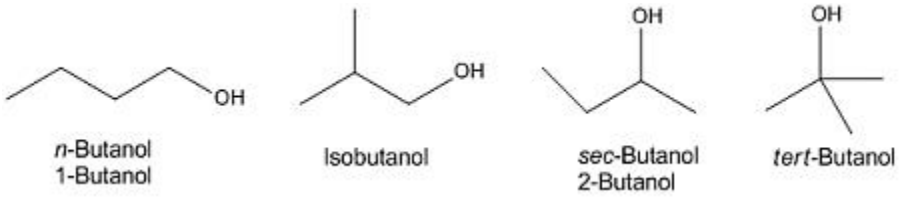


Figure1.5: Various forms of Butanol [51]

1.4.1 Production of butanol

Butanol can be obtained using chemical technologies, such as Oxo-synthesis and aldol condensation. It is also possible to produce butanol in the process of fermentation by bacteria and butanol as one of the products called biobutanol. The most popular bacteria species used for fermentation is Clostridium acetobutylicum. Because the main products of this process containing acetone, butanol and ethanol, the fermentation is called ABE fermentation **[35].**

1.4.2 Applications

It has been demonstrated that n-butanol can be used either 100% in unmodified 4-cycle ignition engines or blended up with diesel to at least 30% in a diesel compression engine or blended up with kerosene to 20% in a jet turbine engine in 2006 **[38].** Utilizing the waste materials improve the economy of butanol production that makes bio-butanol great potential to be the next new type of biofuel in spite of the existing drawbacks.

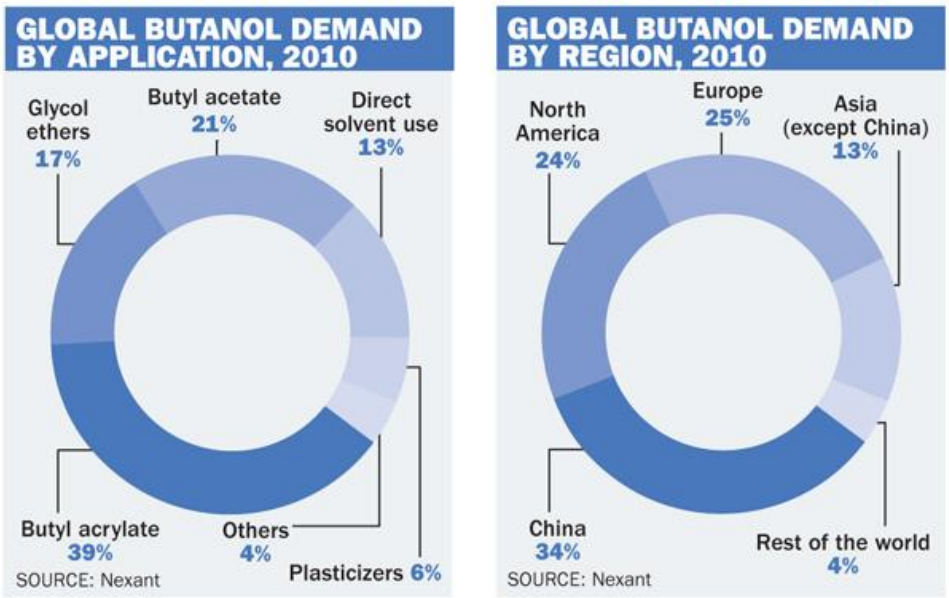


Figure1.6: Butanol Demand [51]

1.5 CI ENGINE (DIESEL ENGINE)

The diesel engine is an internal combustion engine that uses the heat of compression to initiate ignition and burn the fuel that has been injected into the combustion chamber. The diesel engine has the highest thermal efficiency of any standard internal or external combustion engine due to its very high compression ratio. Low-speed diesel engines (as used in ships and other applications where overall engine weight is relatively unimportant) can have a thermal efficiency that exceeds 50%.

The concept behind compression ignition involves using the latent heat built up by highly compressing air inside a combustion chamber as the means for igniting fuel. The process involves compressing a charge of air inside the combustion chamber to a ratio of approximately 21:1 (compared to about 9:1 for a spark ignition system). This high level of compression builds tremendous heat and pressure inside the combustion chamber just as fuel is primed for delivery. An injection nozzle plumbed into the combustion chamber sprays a mist of precisely metered fuel into the hot compressed air where upon it bursts into a controlled explosion that turns the rotating mass inside the engine.

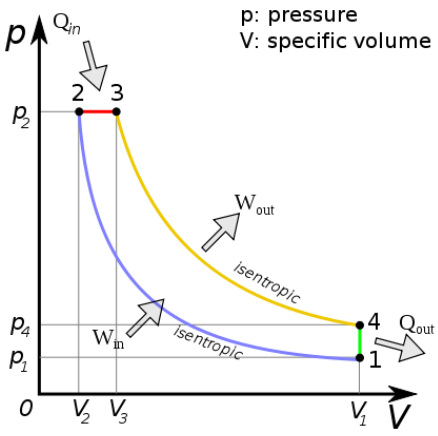


Figure1.7: CI engine [52]

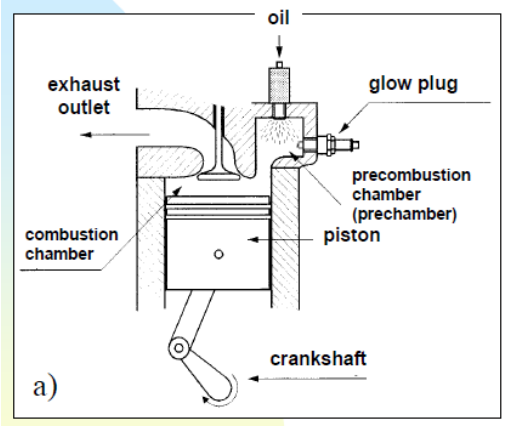


Figure 1.8: Scheme of CI Engine

In operating principle of combustion

1. Oil is injected into the combustion chamber
2. The oil jet is atomized to droplets
3. Droplets undergo evaporation.
4. Vapors are mixed with hot air and combustible mixture is formed.

Rudolf Diesel patented the first diesel engine in 1892 in Berlin, Germany, working for Linde Enterprises after moving from Paris. In 1894, He demonstrated a production scale engine nearly 3 m high, which exploded as he narrowly escaped his life. In 1900, he demonstrated a working diesel engine using peanut oil as fuel at the World Exhibition in Paris. Prior to his mysterious death in 1913, he stated that *"the use of vegetable oils as engine fuels may seem insignificant today but such oils may become, in the course of time, as important as petroleum and the coal tar products of the present time."*

Conventional diesel engines may operate on biodiesel (B100) or blends such as B20 (20% biodiesel and 80% diesel) without major modifications and improve overall performance. The increasing solvent effect and lubrication properties with B20, B100 and E-biodiesel provide increased engine performance and life expectancy. Injection timing may be adjusted to accommodate even better thermal efficiency when conventional diesel engines are operated using biodiesel. This results in significantly lower particulate emissions and carbon deposits in the engine and at the injector nozzles.

1.6 ASTM Specifications for Diesel Fuel Oils (D975-97)

Diesel fuel is characterized in the United States by the ASTM standard D 975. This standard identifies five grades of diesel fuel described below.

Grade No.1-D and Low Sulfur 1-D: A light distillate fuel for applications requiring a higher volatility fuel for rapidly fluctuating loads and speeds as in light trucks and buses. The specification for this grade of diesel fuel overlaps with kerosene and jet fuel and all three are commonly produced from the same base stock. One major use for No. 1-D diesel fuel is to blend with No. 2-D during winter to provide improved cold flow properties. Low sulfur fuel is required for on-highway use with sulfur level < 0.05%.

Grade No. 2-D and Low Sulfur 2-D: A middle distillate fuel for applications that do not require a high volatility fuel. Typical applications are high-speed engines that operate for sustained periods at high load. Low sulfur fuel is required for on-highway use with sulfur level < 0.05%.

Grade No. 4-D: A heavy distillate fuel that is viscous and may require fuel heating for proper atomization of the fuel. It is used primarily in low and medium speed engines.

ASTM D975 specifies the property values shown in following Table for these grades of diesel fuel. The surprising aspect about ASTM D 975 is how few requirements are actually included. The standard says nothing about the composition of the fuel or its source. It only defines some of the property values needed to provide acceptable engine operation and safe storage and transportation.

Table 1.1: Requirements for Diesel Fuel Oils (ASTM D 975-97)

	Grade	Grade	Grade	Grade	Grade
Property	LS #1	LS #2	No. 1-D	No. 2-D	No. 4-D
Flash point °C, min	38	52	38	52	55
Water and sediment, % vol, max.	0.05	0.05	0.05	0.05	0.50
Distillation temp., °C, 90%					
Min.	--	282	--	282	--
Max.	288	338	288	338	--
Kinematic Viscosity,					
mm^2/s at 40°C					
Min.	1.3	1.9	1.3	1.9	5.5
Max.	2.4	4.1	2.4	4.1	24.0
Ramsbottom carbon residue,					
on 10%, %mass, max.	0.15	0.35	0.15	0.35	--
Ash, % mass, max.	0.01	0.01	0.01	0.01 0.10	
Sulfur, % mass, max	0.05	0.05	0.50	0.50 2.00	
Copper strip corrosion,					
Max 3 hours at 50°C	No. 3	No. 3	No. 3	No. 3	--
Cetane Number, min.	40	40	40	40	30
One of the following					
Properties must be met:					
(1) cetane index	40	40	--	--	--
(2) Aromaticity,					
% vol, max	35	35	--	--	--

1.7 Objectives of this project

The aim of this experimental endeavor was to produce, characterize and analyze the engine performance and emission characteristics of biodiesel pressed from low quality WCO. n-butanol was used as additive to reduce the viscosity and cold flow properties of biodiesel. The main objectives of the project were as following:

- Standardization of transesterification process for biodiesel production.
- Determination of the properties of biodiesel produced from waste cooking oil as per ASTM standards.
- Study of performance characteristics with various blends of n butanol and WCO blends including BHP, BSFC, BTE, BSEC.
- Study of emission characteristics with various blends of n butanol and WCO blends including HC, CO, CO_2, Nox, Smoke.
- Comparative performance and emission analysis of WCO and n-butanol blends with fossil fuel diesel.

CHAPTER 2

REVIEW OF LITERATURE

2.1 INTRODUCTION

The alternatives to diesel fuel must be technically feasible, techno-economically competitive, environmentally acceptable, and readily available **[39].** Many of these requisites are satisfied by vegetable oils or, in general, by triglycerides. Vegetable oils became one of the most popular feedstocks for renewable fuel and are widely available from a variety of sources. In previous years, vegetable oil was not a preferred choice for alternative diesel fuels due to its high cost when compared to conventional diesel. There are also many problems associated with vegetable oil being used directly in a diesel engine, i.e. higher viscosity, incomplete combustion, higher flash point, lube oil dilution, high carbon deposits, ring sticking, scuffing of the engineliner, injection nozzle failure and both higher cloud and pour points **[26].** According to **[21],** the viscosity of vegetable oils is 10-20 times higher than the petroleum fuel, therefore directly using vegetable oils as a fuel can cause engine problems like injector fouling and particle agglomeration.

2.2 ABOUT BIODIESEL

Codd et al. (1975) reported that vegetable oils are natural products, therefore, subjected to some variation in composition and content of fatty acids. The most common fatty acids present in vegetable oils are reported. It is clear that unlike diesel fuel, vegetable oils contain significant amount of oxygen in addition to carbon and hydrogen. The presence of different fatty acids is also dependent to a number of factors such as botanical variety, climatic conditions, soil composition, rainfall and temperature.

Goering et al. (1981) studied the content of different fatty acids in various vegetable oils. Since, fatty acid contents of vegetable oils have been found to be a significant factor in reducing carbon builds up in the engine, therefore, the oils with lower level of saturation are more desirable for fuels.

Pryde (1982) defined vegetable oils as fatty esters of glycerol known as triglycerides that comprise one molecule of glycerol and three molecules of fatty acids, generally, with non branched chains of different length and degrees of saturation. The chemical structure of vegetable oil is shown in Fig 2.1 where R1, R2 and R3 represent the hydrocarbon chain of fatty acids. This chain for vegetable oils may be same or different in length, number and position of double bonds. Except crambe and some varieties of rapeseed, all other vegetable oils possess maximum 18 carbon atoms with 2 to 3 double bonds whereas diesel fuel has 12 to 18 carbon atoms. Thus, unlike diesel fuel, vegetable oils contain sufficient amount of oxygen in addition to hydrogen which may facilitate burning in combustion chamber of the engine.

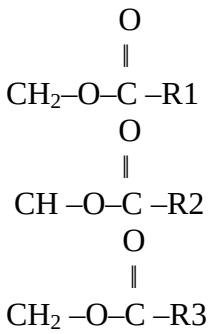


Figure 2.1: Chemical Structure of Vegetable Oils

Peterson (1986) reported that the molecular weight of the glycerol portion (C3H5) in a triglyceride molecule is 41whereas the combined molecular weight of the fatty acid radicals (RCOO) comprising the remainder of the molecule varies with different fats from about 650 to 970 in molecular weight. Thus the fatty acids contribute 94 to 96 percent of the total weight of the molecule. This composition of fatty acid is crucial and it affects very much the chemical and physical properties such as viscosity, density, heat value of a fuel oil.

Scholl and Sorenson (1993) reported that emissions and unburnt particles were reduced by utilizing a soyabean methyl ester in a CI engine, while a 15.1% increase in energy efficiency, 3.55% reduction in PM10, 7.49% reduction in PM2.5, 43-90.2% reduction in total PAH and 63.1-89.6% decrease in total BaP equivalent was noted down. But land competition with food crops, pre treatment cost, secondary pollutants with trans-esterification have limited the use of crop based bio-fuels. Waste cooking oil or non-edible oil can be good alternatives. Butanol was also found suitable additive.

Alfuso et al. (1993) carried emission tests of a direct injection, compression ignition diesel engine on rapeseed methyl ester. It was reported that rapeseed methyl ester promoted a rise in NOX, decrease in HC and CO and reduction in smoke. Particulate matter produced by rapeseed methyl ester in transient cycles was higher than that obtained with diesel fuel. The contribution of soluble organic fractions was reported to be higher at low loads. The rapeseed methyl ester produced more soluble organic fractions and particulate matter than the diesel fuel at lighter loads while as in proximity of full load the trend was the opposite. The emission of hydrocarbon from diesel was higher at lighter loads and lower at higher loads. Carbon monoxide emission was about the same at different loads on diesel but it reduced with rapeseed methyl ester and nitrogen oxide production was generally higher on bio-fuel.

Fangrui Maa et al. (1995) described the four primary ways to make biodiesel, direct use and blending, micro-emulsions, thermal cracking (pyrolysis) and trans-esterification. Of the several methods available for producing biodiesel, trans-esterification of natural oils and fats was the method of choice. The purpose of the process is to lower the viscosity of the oil or fat. Although blending of oils and other solvents and micro-emulsions of vegetable oils lowers the viscosity, engine performance problems, such as carbon deposit and lubricating oil contamination, still exist. Pyrolysis produces more bio-gasoline than biodiesel fuel. Trans-esterification is basically a sequential reaction. The commonly accepted molar ratio of alcohol to glycerides is 6:1. Base catalysts are more effective than acid catalysts and enzymes. The recommended amount of base used to use is between 0.1 and 1% w/w of oils and fats. Higher reaction temperatures speed up the reaction and shorten the reaction time. The reaction was slow at the beginning for a short time and proceeds quickly and then slowed down again. Base catalyzed trans-esterifications were basically finished within one hour.

Ulf Schuchardta et al. (1998) reviewed the trans-esterification of vegetable oils with methanol as well as the main uses of the fatty acid methyl esters. The general aspects of this process and the applicability of different types of catalysts (acids, alkaline metal hydroxides, alkoxides and carbonates, enzymes and non-ionic bases, such as amines, amidines, guanidines and triamino (imino) phosphoranes) were described. Special attention was given to guanidines, which can be easily heterogenized on organic polymers. However, the anchored catalysts show leaching problems. New strategies to obtain non-leaching guanidine-containing catalysts are proposed. Finally, obtained by transesterification of vegetable oils, are described.

Tickell (1999) stated that Biodiesel can be used alone or mixed in any amount with regular diesel. Because of this biodiesel can be used in any diesel engine or infrastructure without the need for modification. Engines run normally on biodiesel because the fuel has similar properties to regular diesel. Biodiesel has a high cetane rating which improves engine performance. Biodiesel is more lubricating than regular diesel fuel and it can be used to replace sulfur compound lubricating agents which when burned produce sulfur dioxide which is the main cause of acid rain, whereas biodiesel contains no sulfur. **Graboski and McCormick (1998)** and **Lapuerta et al. *(*2008), EPA (2002)** also had same results.

Peterson et al. (2000) used a pickup truck with a 5.9 l turbocharged and intercooled direct injection diesel engine to study effect on regulated emissions from coconut ethyl ester, hydrogenated soybean oil methyl ester, rapeseed ethyl ester, mustard ethyl ester, safflower ethyl ester and a commercial methyl ester of soybean oil having iodine number ranging from 7.88 to 133. These vegetable oil esters were tested neat as well as their 20 percent blend with diesel. It was found that lower iodine number correlated with reduced nitrogen oxides. As iodine number increased from 7.88 to 129.5, the NOX increased by 29.3 percent. Fatty acid with two double bonds appeared to have more effect on increasing NOX than did fatty acids with one double bond. Changes in carbon monoxides (CO), hydrocarbons (HC) and particulate matter (PM) were not linearly correlated with iodine number.

Mustafa Balat et al. (2001) described that the problems with substituting triglycerides for diesel fuels were mostly associated with their high viscosities, low volatilities and polyunsaturated character. The viscosity of vegetable oils, when used as diesel fuel, can be reduced in at least four different ways: (1) dilution with hydrocarbons (blending), (2) emulsification, (3) pyrolysis (thermal cracking), and (4) trans-esterification (alcoholysis). Trans-esterification was the most common method and leads to monoalkyl esters of vegetable oils and fats, now called bio-diesel when used for fuel purposes. The main factors affecting trans-esterification were molar ratio of glycerides to alcohol, catalyst, reaction temperature and pressure, reaction time and the contents of free fatty acids and water in oils. The commonly accepted molar ratios of alcohol to glycerides are 6:1–30:1. Bio-diesel is a cleaner-burning diesel replacement fuel made from natural, renewable sources such as new and used vegetable oils and animal fats. Just like petroleum diesel, bio-diesel operates in compression-ignition engines or Diesel engines. The bio-diesel was characterized by determining its density, viscosity, high

heating value, cetane index, cloud and pour points, characteristics of distillation, and flash and combustion points according to ISO norms. Viscosity is the most important property of biodiesel since it affects the operation of the fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel.

Gerhard Knothe et al. (2005) in their book described the technical concept of using vegetable oils or animal fats or even used oils as a renewable diesel fuel. Biodiesel is the form in which these oils and fats are being used as neat diesel fuel or in blends with petroleum-based diesel fuels. The concept itself may appear simple, but that appearance is deceiving since the use of biodiesel is fraught with numerous technical issues. Accordingly, many researchers around the world have dealt with these issues and in many cases devised unique solutions. This book was an attempt to summarize these issues, to explain how they have been dealt with, and to present data and technical information. Countless legislative and regulatory efforts around the world have helped pave the way toward the widespread application of the concept. This book addressed these issues also. To complete the picture, chapters on the history of vegetable oil-based diesel fuels, the basic concept of the diesel engine, and glycerol, a valuable byproduct of biodiesel production, were included.

Gerhard Knothe (2005) discussed that the fuel properties of biodiesel are strongly influenced by the properties of the individual fatty esters in biodiesel. Both moieties, the fatty acid and alcohol, can have considerable influence on fuel properties such as cetane number with relation to combustion and exhaust emissions, cold flow, oxidative stability, viscosity, and lubricity. Generally, cetane number, heat of combustion, melting point, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing un-saturation. It therefore appeared reasonable to enrich (a) certain fatty ester(s) with desirable properties in the fuel in order to improve the properties of the whole fuel. For example, from the available data it appeared that iso- propyl esters had better fuel properties than methyl esters. The major disadvantage was the higher price of iso-propanol in comparison to methanol, besides modifications needed for the trans-esterification reaction. Similar observations likely hold for the fatty acid moiety.

X. Shi et al. (2005) reported that oxygenated fuels reduce particulate matter emissions for vehicles and recognized as potential sources of renewable fuels. According to him, most

widely form of biodiesel is made from methanol and oils as methyl ester. **Graboski and co workers** tested primary methyl esters in B100 and blended form and found biodiesel more lubricating than conventional diesel. Also, PM emissions were reduced greatly but NOX slightly increased. PM emissions are largely dependent upon Oxygen content. Catalytic treatment is effective to control NOX emissions.

Prommes et al. (2006) stated that many efforts have been made to reduce use of petroleum fuels for power, transport and another purposes. Biodiesel is much better than regular diesel as it is renewable, domestically produced and environment friendly. It reduces CO, PM, unburnt HC emissions. Biodiesel is not only used as alternative to diesel but also as additive for diesohol- a blending of ethanol with regular diesel.

Deepak Aggarwal et al. (2006) did research on biodiesel-fueled engines. It produced less CO, unburnt HC, reduced PM emissions compared to mineral diesel fuel but higher NO_X emissions. He checked that exhaust gas recirculation (EGR) is effective to reduce NO_X emissions from diesel engines because it lowers the flame temperature and oxygen content in combustion chamber. However it resulted in higher PM emissions. Thus, the drawback of higher NO_X emissions while using biodiesel may be overcome by employing EGR. His objective was to investigate the usage of biodiesel and EGR simultaneously in order to reduce the emissions of all regulated pollutants from diesel engines. He used a 2-cylinder, air cooled, constant speed DI diesel engine and measured various emissions. He calculated engine performance parameters and checked that application of EGR with biodiesel blends resulted in reduction in NO_X emissions without any significant penalty in PM emissions or BSEC.

Hu Chen et al. (2008) added vegetable methyl ester in ethanol-diesel fuel to prevent separation of ethanol from diesel. He investigated engine performance and emission characteristics of fuel blends on a diesel engine and compared these with traditional diesel fuel. Results showed that torque of the engine decreased by 6-7% for every 10% (by volume) ethanol added to the diesel fuel without modification on the engine. BSFC increased with addition of oxygen from ethanol but EBSFC of oxygenated fuels was at same level to that of diesel. Smoke and PM emissions reduced significantly although smoke reduction was more considerable than PM reduction. PM components were affected by oxygenated fuels. When blended fuels were used, NOX emissions were almost the same or slightly higher than NOX emissions when diesel

fuel was used. Fuelling the engine with oxygenated diesel fuel showed increased CO emissions at low and medium loads but reduced CO at high and full loads when compared to pure diesel fuel.

Purnanand Vishwanathrao Bhale et al. (2008) worked on the low temperature properties of biodiesel. The biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds will display higher cloud points and pour points. The cold flow properties of biodiesel were evaluated with and without pour point depressants towards the objectives of identifying the pumping and injecting of these biodiesel in CI engines under cold climates. Effect of ethanol, kerosene and commercial additive on cold flow behavior of this biodiesel was studied. A considerable reduction in pour point had been noticed by using these cold flow improvers. A considerable reduction in emission was obtained.

Chotuichien A. et al. (2009) checked that methyl esters were better than ethyl esters in improving blend stability. So, methanol was preferred as a solvent. 5% butanol provides stable mixture and acceptable fuel properties. So it is considered as more suitable additive.

P. Pramanik et al. (2011) observed that vegetable oils having higher FFA content are difficult to process directly through alkali catalysis. First acid catalyzed (methanolic sulfuric acid) for 4 hours to convert FFA into methyl esters and then trans-esterification with methanolic KOH was done. They prepared bio-fuel additive from harmful toxic argemone oil. Also they compared engine efficiency and pollution parameters with those of traditional diesel fuel and other biodiesels.

M. Mathiyazhagan et al. (2011) researched on the non-edible oils as feed stocks for biodiesel production to reduce the cost of biodiesel. Normally alkali catalyzed method was followed for biodiesel production process. However the non-edible oils having high FFA content which is not suitable for normal trans-esterification process. Hence a two-step catalyzed method was used to prepare the biodiesel. High FFA content of non-edible oils were efficiently converted into biodiesel fuel. Figure 2.1 shows the flow diagram of biodiesel production from non-edible oils.

S.K. Mahla et al. (2012) worked on linseed methyl esters and checked performance and emission characteristics of different blends in diesel engine. They examined the properties,

performance and emission of B15, B20 and B30 and compared it to diesel. Results indicated that B20 is an optimum fuel blend in terms of better performance and reduced emission than diesel fuel. However, B15 and B30 blend showed reasonable efficiencies, lower smoke, CO and HC emission. BTE of B20 was superior to diesel at all load conditions. Smoke, HC and CO emission for diesel at different loads was found to be higher as compared to biodiesel blends of B15, B20 and B30

Jilin Lei et al. (2012) stated that need of new internal combustion engine is increasing as conventional energy decreases and stringent emissions are increasing. The engines should have low emissions, increased efficiency and fuel specific power. He proved that ethanol can be used as a solvent but its solubility in diesel and therefore blend stability is a problem.

Abdullah Abuhabaya et al. (2013) used response surface methodology (RSM) technique to optimize methyl ester production at a fixed temperature. He developed a second order model successfully 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. He found optimized conditions at 7.7:1 methanol/oil molar ratio, 1% NaOH concentration by weight, 200 rpm mixing rate and 60 minutes reaction time and resulted in actual biodiesel yield of 95%. He varied these ratios but that did not prove to be cost effective. Taking his results into fact, a blend of 20% methyl ester could be used effectively as an alternative suitable fuel in compression ignition engines.

2.3 About n-butanol

Rice et al. (1991) measured emissions levels for CO, NOx, and unburned fuel (UBF) for 20% by volume blends of methanol ethanol and butanol in gasoline in a four-cylinder spark-ignition engine under a variety of operating conditions. It was found that the alcohol blended fuels exhibited lower CO emissions than pure gasoline mainly due to a “leaning” effect caused by the lower stoichiometric air-fuel ratios of the fuels due to their partially oxidized nature. It was also found that butanol and gasoline had similar UBF emissions whereas ethanol and methanol had higher values, especially in the lean region. Lastly, it was found that NOx levels were modestly lower for the alcohol fuels due to their lower energy densities resulting in lower peak flame temperatures.

Alasfour (1997) conducted several studies on iso-butanol-gasoline blends which focused on engine performance characteristics (brake specific fuel consumption, exhaust gas temperature, and thermal efficiency) and the effects on the first- and second-law efficiency of an SI engine. The influence of preheating the inlet air and ignition timing on NOx emissions and the effects of equivalence ratio, ignition timing, and engine speed on unburned hydrocarbon emissions were examined.

Yacoub et al. (1998) examined blends of alcohols and gasoline with carbon numbers C1 to C5 (methanol to n-pentanol) on the basis of the oxygen content of the fuel. The results indicated that fuels blended with higher alcohols (butanol and n-pentanol) had lower knock resistance than neat gasoline. In addition, all alcohol blends had lower CO and UHC emissions and the blends with oxygen contents of 5% had higher NOx emissions due to the lower enthalpies of vaporization and higher flame temperatures of the fuels.

Gautam et al. (2000) investigated the combustion and emissions characteristics of higher alcohol-gasoline blends using a CFR engine. It was found that the brake-specific emissions were lower for all of the blends due the greater knock resistance of the fuels allowing higher compression ratios to be used and that knock resistance was mainly a function of the oxygen content of the blend. Ignition delay and in-cylinder pressure data showed that the higher-alcohol/gasoline blends had higher flame speeds which were also attributed to the higher oxygen content of the fuel. Lastly, it was found that the brake specific fuel consumption was 15-19% lower for the alcohol-gasoline blends.

Wang Y N et al. (2008) worked on butanol and stated that butanol blends have higher BTE (Brake Thermal Efficiency) than diesel due to O_2 content in blend fuels. B10 had highest BTE which means that BTE improvement will not occur with increasing addition of alcohol. There is an optimum ratio of reactants. At higher loads, CO emissions increased and vice versa. NOX emissions decreased slightly. Smoke reduction at heavier loads was noted down significantly.

Szwaja S et al. (2009) indicated that n-butanol has similar thermo-physical properties to those of conventional gasoline. It can directly alternate the gasoline as neat fuel or in blended form from a combustion and energy density perspective for SI engine. It has higher O_2 content

which shortens ignition delay. Soot, NO_X, CO decreased and ISFC, HC increased slightly. Byproduct glycerol yields significant amount of butanol.

Dernotte et al. (2010) examined the emissions characteristics of several butanol-gasoline blends on a volume basis using a port fuel-injection spark-ignition engine and found that B60 and B80 produced 18% and 47% more UHC emissions than neat gasoline, respectively. B80 also displayed a noticeable decrease in NOx emissions at all equivalence ratios tested as a result of the combustion deterioration evidenced by increased UHC emissions; peak NOx emissions decreased by 10%. It was also found that B80 was the only butanol-blended fuel which did not produce lower CO emissions than gasoline.

Szwaja and Naber (2010) tested n-butanol over a range of spark timings, compression ratios, and loads to examine its combustion characteristics through analysis of in-cylinder pressure measurements and mass fraction burned profiles. It was found that the bulk burn duration for n-butanol was similar to that of gasoline and that the spark timing should be retarded with respect to the maximum brake torque (MBT) timing for gasoline. Additionally, it was found that n-butanol and gasoline behaved similarly in terms of combustion knock due to compression ratio and spark timing. It was concluded that n-butanol is suitable for use in spark-ignition engines in either blended form or as a neat fuel from a combustion and energy density perspective.

Zhang and Boehman (2010) investigated the oxidation of neat n-butanol and a mixture of n-heptane and 1-butanol in a motored engine at an equivalence ratio of 0.25. Heat release analyses showed that the oxidation of 1-butanol produced no noticeable low temperature heat release behavior, whereas an n-heptane/1-butanol mixture exhibited pronounced cool flame behavior.

Oßwald et al. (2010) examined the flame chemistry of the isomers of butanol and found that the four isomers exhibited similar macroscopic characteristics, including temperature, major species profiles, and equilibrium mole fractions although the intermediate species pool was highly dependent on the specific fuel. It was also found that 2-butanol offered the greatest benefits regarding potential emissions from butanol combustion since it exhibited low hydrocarbon mole fractions and relatively low amounts of toxic oxygenated pollutants although

it was noted that its use as a future biofuel is uncertain since a promising approach for its production has yet to be established.

Egolfopoulos et al. (2010-11) performed a comparative experimental and computational study on premixed flames of butanol, ethanol, and methanol and the four isomers of butanol. It was found that n-butanol/air flames propagated faster than both sec-butanol/air and iso-butanol/air flames, while tert-butanol/air flames propagated the slowest of the four isomers, 8 confirmed by **Gu et al. (2010)** who examined the laminar burning velocities and flame instabilities of the four butanol isomers.

Agathou et al. (2011) studied non-premixed flames of butanol, ethanol, and methane using a counter-flow burner and measured major combustion species, temperature profiles, and extinction strain rates in addition to examining ignition delays of butanol, ethanol, and n-heptane in a zero-dimensional piston-cylinder assembly using the kinetics model of Dagaut.

Wigg et al. (2012) examined the emissions of neat n-butanol, ethanol, and gasoline, and showed that gasoline and butanol was closest in engine performance and that the UHC emissions of neat n-butanol were between two and three times those of gasoline with a maximum reduction in NOx emissions of 17% at stoichiometry. CO emissions were similar for butanol and ethanol and were lower than those of gasoline.

2.4 Summary from Literature

It appears from the past research that the approaches of using vegetable oils as diesel engine fuel include use of neat vegetable oil, esterified vegetable oil and blends of vegetable oils or vegetable oil esters with diesel fuel. Over a short period of time, an unmodified engine can perform satisfactorily on neat vegetable oils or their blends with diesel but there is a decrease in maximum power and about 10 percent increase in fuel consumption relative to diesel. However, use of vegetable oils or their blends with diesel is associated with both short term and long term problems. The short term problems include difficult cold starting, plugging and degumming of filters, line and injectors and engine knocking. Though these problems are not universal but have been noted in different places. The potential long term problems include coking of injector nozzles, carbon deposits on the piston and cylinder head, dilution of the crankcase lubricating

oil, excess wear on the rings, pistons and cylinders and failure of the engine lubricating oil due to oxidation and polymerization. These problems are correlated to basic properties of vegetable oils such as naturally occurring gums, high viscosity, acid composition, free fatty acids content and low cetane ratings.

The gumming materials present in oils can collect and clog the filter, lines and injectors. Viscous oils when injected to the cylinder do not atomize properly and may result in incomplete combustion of fuel, build- up of carbon deposits on injectors, cylinder head and piston. Some of this unburnt fuel blew by the piston rings in to crankcase causing dilution of lubricating oil. The accumulation of these oils in the crankcase combined with the heat and pressure of operation may cause lubricating oil to solidify due to oxidation and polymerization of vegetable oils which may result in complete failure of the lubricating oil and may ruin the engine. Based on the above, esters of vegetable oil have been recommended in the place of neat vegetable oils. Since the esters are less viscous than neat vegetable oils and, therefore, improved engine performance through better atomization and combustion in the cylinder was observed when either neat esterified oils or their blends with diesel were used. The esterification reduces the viscosity and removes glycerol from the oil. Hence the problems of cold start, plugging of filters, fuel lines, injectors' carbon deposition, oxidation and polymerization of lubricating oil are least associated particularly when blends of esterified fuel were used as engine fuel. The use of oxygenated fuels has led to solution of some of these problems.

It was recommended that to obtain maximum ester formation by transesterification the neat vegetable oils or refined oils with a free fatty acids content less than 0.5 percent (acid value less than 1 percent) be used. Both ethyl and methyl alcohols could be used and a molar ratio of alcohol to oil of 6:1 gives optimum conversion to the ester. The transesterification process is rapid with an alkali based catalyst. These catalysts should be stored under anhydrous conditions free from air.

Further, emission characteristics of ethyl and methyl esters of vegetable oils have been found essentially similar to diesel fuel. The studies indicate reduction in emission of HC and CO on esterified vegetable oils compared to diesel. The NO_X and particulate matter are related and tend to change inversely with each other, differing from diesel by almost 10 to 15 percent. In

view of the above, use of either esterified vegetable oils alone or their blends with diesels appear to be promising alternative fuels of the future.

2.5 GAP IN LITERATURE

A lot of work has been done on trans-esterification of edible oils. Limited amount of work is done for the extraction of the biodiesel through trans-esterification from non-edible oils. In India, the high cost of edible oils prevents their use in biodiesel preparation. But non-edible oils are affordable for biodiesel production. Cost associated with biodiesel is reduced due to the low cost of the non edible oils. Tonnes of used cooking oil are wasted every year. It could be used for some useful purpose which can solve the problem of disposal of oil as well as increasing energy demand up to some extent. The awareness of biodiesel is less in India which is required to raise at large scale. The addition of oxygenated fuel increases the stability of blends. More research is needed on this aspect also. Thus due to the unawareness of the benefits of this unutilized oil to extract biodiesel limited amount of research work has been done on its use in diesel engines. The complex regulation mechanism of butanol synthesis is still need to be further study. For the strain improvement, for example, constructing better butanol tolerance strains, more suitable hosts and genetic methods are required to be set up. Furthermore, more efficient techniques for removing the inhibitors in the lignocellulosic hydrolysate need to be developed. In addition, from the economic point of view, the integrated system of hydrolysis, fermentation, and recovery process also are important to be further developed to reduce the operation cost of butanol synthesis.

CHAPTER 3

MATERIALS AND METHODS

3.1 Biodiesel production

Four methods to reduce the high viscosity of vegetable oils to enable their use in common diesel engines without operational problems such as engine deposits have been investigated **[18]:**

- blending with petrodiesel (Dilution)
- pyrolysis
- microemulsification (cosolvent blending)
- transesterification

Pyrolysis

Pyrolysis is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules The liquid fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. The pyrolyzates have lower viscosity, flash point, and pour point than diesel fuel and equivalent calorific values. The cetane number of the pyrolyzate is lower. The pyrolysed vegetable oils contain acceptable amounts of sulphur, water and sediment and give acceptable copper corrosion values but unacceptable ash, carbon residue and pour point.

Micro-emulsification

The formation of micro-emulsions (co-solvency) is one of the potential solutions for solving the problem of vegetable oil viscosity. A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1±150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or nonionic amphiphiles. A micro-emulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, an alcohol and a surfactant and a cetane improver, with or without diesel fuels. Water (from aqueous ethanol) may also be present in order to use lower proof ethanol, thus increasing water tolerance of the micro-emulsions.

Dilution

Dilution of vegetable oils can be accomplished with materials as diesel fuels, solvent or ethanol.

Trans-esterification

Only the transesterification reaction leads to the products commonly known as biodiesel, i.e., alkyl esters of oils and fats. Di- and monoacylglycerols are formed as intermediates in the transesterification reaction.

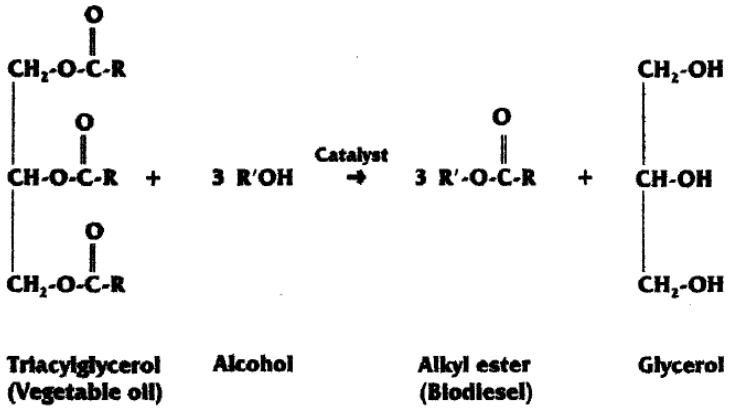


Figure3.1: The transesterification reaction. R is a mixture of various fatty acid chains. The alcohol used for producing biodiesel is usually methanol (R′= CH3).

Generally, transesterification can proceed by base or acid catalysis.However, in homogeneous catalysis, alkali catalysis (NaOH/KOH or the corresponding alkoxides) is a much more rapid process than acid catalysis. In addition to the type of catalyst (alkaline vs. acidic), reaction parameters of base-catalyzed transesterification include the molar ratio of alcohol to vegetable oil, temperature, reaction time, degree of refinement of the vegetable oil, and effect of the presence of moisture and FFA. For the transesterification to give maximum yield, the alcohol should be free of moisture and the FFA content of the oil should be <0.5%. The absence of moisture in the transesterification reaction is important because according to the transesterification equation, hydrolysis of the formed alkyl esters to FFA can occur. Similarly, because triacylglycerols are also esters, the reaction of the triacylglycerols with water can form FFA. At 32°C, transesterification was 99% complete in 4 h when using an alkaline catalyst (NaOH or NaOMe).

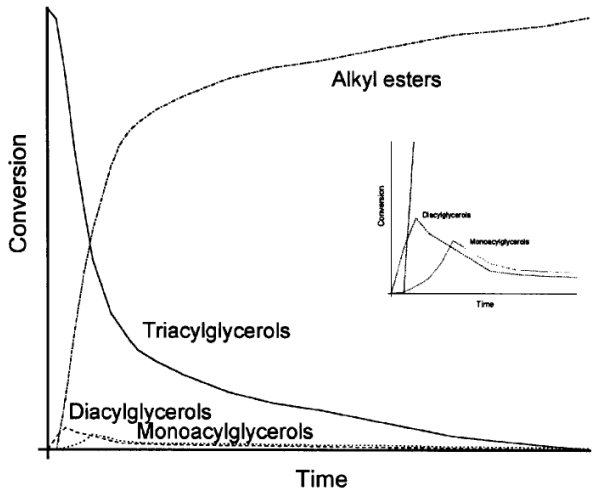


Figure3.2: Qualitatively depicts conversion vs. reaction time for a transesterification reaction taking into account the intermediary di- and monoacylglycerols.

3.1.1 Free Fatty Acid analysis

Titration is necessary to first determine the best route for biodiesel production whether using the conventional alkali-catalyzed approach, acid-catalyzed approach or acid pretreatment followed by the alkali approach.

1. If the titration shows an excess of 15 percent or greater free fatty acid concentration, acid catalyzed approach is followed. e.g brown greases.
2. If it is between 5 and 15 %, then acid treatment followed by alkali approach is chosen. e.g yellow greases.
3. If it is below 5%, alkali treatment is followed. e.g vegetable oils. It is cost effective approach as cost of acid treatment is prohibited.

However, the concentration of FFA greater than 1% will lead to soap formation, making the downstream washing tougher. Soap formation occurs more rapidly than biodiesel formation, thus excess of catalyst is required. The intermittent glycerolysis using glycerol to convert FFA to MAGs typically at high temperatures is often used to remove the free fatty acids prior to trans esterification. Titration determines the amount of excess catalyst needed in reaction. Typical concentration of catalyst to achieve efficient trans-esterification around 1% by weight and any excess catalyst is added beyond 1% based on titration values.

1. Measure 10 ml of ethanol in a test tube.
2. Measure 1 ml of oil and mix with ethanol.
3. Add about .5 ml of phenolphthalein solution.
4. Titrate the oil-ethanol solution with 1 g/l KOH solution in distilled water using a burette until color begins to turn pink after adequate mixing.
5. Estimate amount of KOH needed for trans esterification using formula

$$Y = 9 + x$$

Where y= grams of KOH catalyst (usually 9-15 g) to use in 1 L of oil (900 g)

X= milliliters of KOH used in titration.

Following titration, an approach is followed.

1. 9 to 15 g catalyst required- alkali treatment
2. More than 15 g catalyst- acid treatment.

FFA composition

Table 3.1: Fatty acid composition (wt %)

Myristic (C14:0)	.9
Palmitic (C16:0)	20.4
Palmitoleic (C18:1)	4.6
Stearic (C18:0)	4.8
Oleic (C18:0)	52.9
Linoleic (C18:2)	13.5
Linolenic (C18:3)	.8
Arachidic (C20:0)	.12
Eicosenic (C20:1)	.84
Behenic (C22:0)	.03
Erucic (C22:1)	.07
Tetracosanic (C24:0)	.04
Mean molecular weight (g/mol)	856

This fatty acid composition is used to find out how much alcohol to oil molar ratio is required for neutralization of oil sample.

1. Average molecular weight is found out by adding the product of wt% with respective weights of fatty acids.
2. Then, total molecular weight is calculated by the equation

$$\textbf{Mol wt} = (\textbf{avg mol wt} \times \textbf{3}) + (\textbf{wt of glycerol}) - (\textbf{wt of 3 H2O})$$

3. Total weight is calculated by multiplying density of sample and total volume.
4. Now the equivalent weight to volume can be calculated by unitary method.
5. Also, the alcohol to oil molecular ratio can be found out by using above information.

3.1.2 Trans-esterification reaction

Alkali catalyzed trans-esterification reaction of waste cooking oil was performed. Its details are as given below

Materials Required

Conical flask, measuring cylinder, methanolic KOH, thermometer, waste cooking oil, separating funnel, distilled water, heating plate with stirrer

Procedure

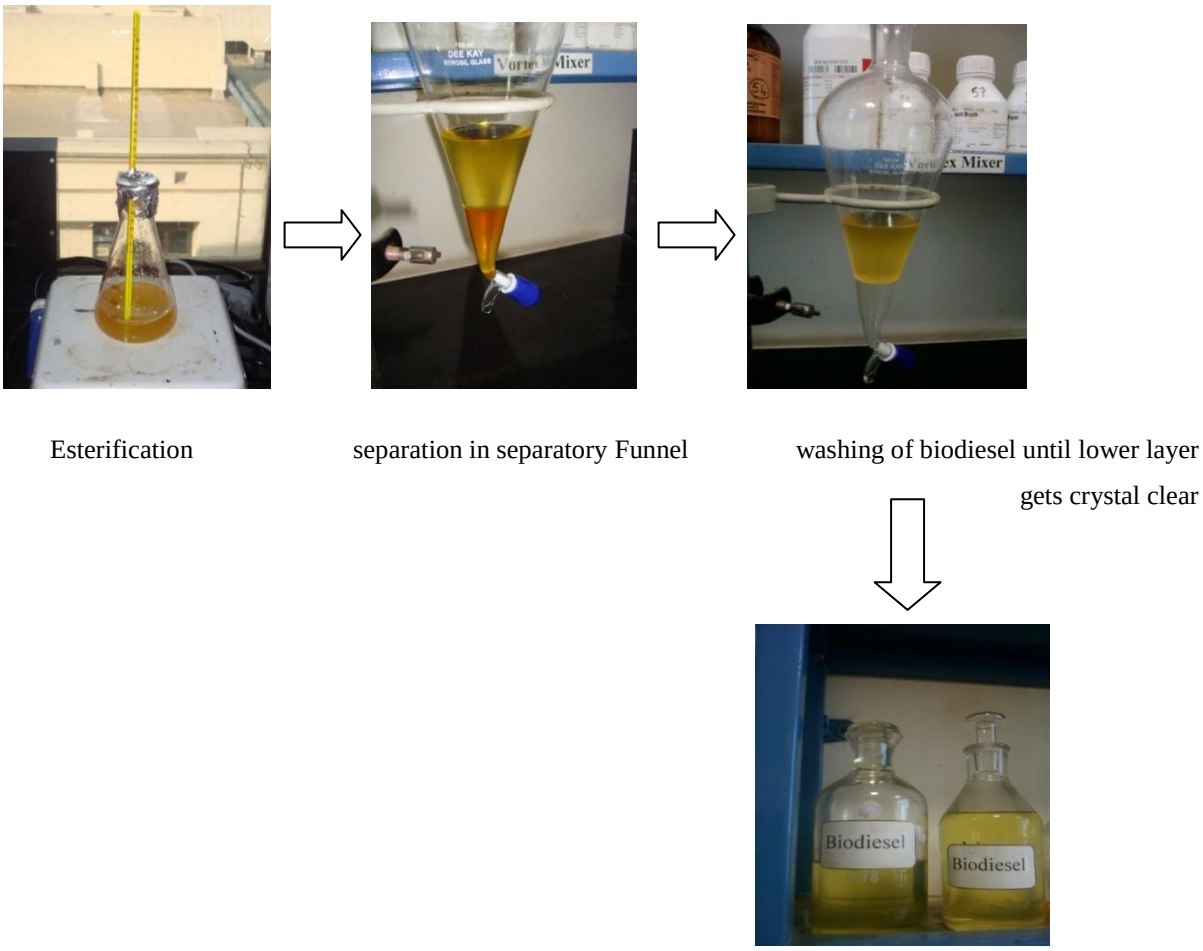
Biodiesel was produced using 6:1 methanol: oil ratio and 1% wt of KOH.

1. 250 ml of oil sample was poured into a 500 ml of conical flask and heated for 15-20 mins to lower its viscosity.
2. Methanol and KOH were mixed in a beaker by heating or stirring using magnetic stirrer for 5 minutes.
3. Methanol and KOH solution was added to pre heated waste cooking oil.
4. Solution was kept on a magnetic stirrer at 55ºC at a set RPM for about 2 hours.
5. After 120 minutes the beaker was removed and poured into a separating funnel. It was kept undisturbed overnight.

6. In the separating funnel the separation of gumming agents and debris took place thus making 2 separate layers.
7. Lower layer had the debris along with gumming agents and upper layer contained biodiesel free from gumming agents.
8. The excess soap was removed by washing 7-8 times with hot water in the separating funnel.
9. The oil was heated again to remove any water present.

During stirring the conical flask was covered with aluminum foil throughout and no water was added to it so that no saponification occurs.

Production of biodiesel:



Esterification separation in separatory Funnel washing of biodiesel until lower layer gets crystal clear

Figure 3.3: Biodiesel production from waste cooking oil

3.1.3 Blend formation

Biodiesel made was mixed with diesel fuel in different proportions and blends were prepared in order for its physical testing and engine testing.

Biodiesel-diesel blending

Three blends were made of biodiesel from waste cooking oil and diesel.

i. B20 i.e. 20% biodiesel was mixed with 80% of diesel.
ii. B40 i.e. 40% biodiesel was mixed with 60% of diesel.
iii. B60 i.e. 60% biodiesel was mixed with 40% of diesel.

Biodiesel-diesel-n butanol blending

Two blends were made by mixing biodiesel from waste cooking oil and diesel and n-butanol.

i. nB10 i.e. 10% biodiesel, 10% n butanol and 80% diesel.
ii. nB20 i.e. 20% biodiesel, 20% n butanol and 60% diesel.

The above blends were then tested for physical properties and for engine performance.

3.2 Properties of Biodiesel

Several physical properties of biodiesel were checked and some were tested in the lab of MERADO Institute (CSIR Lab), Ludhiana.

- Density
- Viscosity
- Calorific value
- Flash point
- Fire point
- Cloud point
- Pour point

3.2.1 Density

Density can be defined as the mass of an object divided by its volume. Density was checked in Thapar environment lab itself.

Procedure

1. Weigh the empty 50 ml beaker.
2. Now fill it with 50 ml distilled water and weigh again.
3. Make it empty and again fill it with 50 ml biodiesel and then re-weigh.

$$\text{Density} = \frac{\text{Weight of biodiesel} - \text{weight of empty beaker}}{\text{Weight of distilled water} - \text{weight of empty beaker}}$$

The relative density of the selected fuels as mentioned above at 150 deg.C was determined as per **IS: 1448 [P: 32]: 1992**. A mercury thermometer of 0 – 1000 deg. C range was also used to measure the temperature of fuels kept inside the temperature control chamber.

The weights of the empty pyknometers were subtracted from the weights of the filled ones to get the weight of the fuel samples. Three replicates were taken for each sample and their mean was calculated. This value when divided by the volume of the fuel sample gave the density of the fuel sample. The density of distilled water at 150ºC was also determined.

3.2.2 Kinematic viscosity

The viscosity of a liquid is a measure of internal friction of the liquid in motion. It plays an important role in the performance of an engine fuel system operating through a wide range of temperature. Kinematic viscosity affects the injection system. Low viscosity can result in an excessive wear in the injection pumps and power loss due to pump leakage whereas high viscosity may result in excessive pump resistance, filter blockage, high pressure and coarse atomization affecting the atomization and fuel delivery rates.

A Redwood Viscometer No.1 of Widson make was used for measurement of kinematic viscosity of selected fuel samples. The instrument measures the time of gravity flow in seconds of a fixed

volume of the fluid (50ml) through specified orifice made in an agate piece as per **IS: 1448 [P : 25] 1976**. The apparatus could be used for flow time between 30 to 2000 seconds.

Figure 3.4: Viscometer

Procedure

1. Heat the viscometer bath to a few degrees above the desired test temperature. Pour the prepared sample into the oil cup through a filter of metal gauge not courser than BS 100 mesh (152 μ). Adjust the temperature of the bath until the sample in the cup is maintained at the test temperature stirring the contents of bath and cup during this procedure preferably using continuous stirring for the bath. Stir the sample during the preliminary period e.g by means of the ball value, closing the bottoms of the jet by suitable means, but do not stir the sample during the actual determination. When the temperature of the sample has become suite steady at the desired value, adjust the liquid level by allowing the sample to flow out until the surface of the sample touches, the filling point. Place the oil cup and curved slot in the voccr. Place the clean, dry, stand 50 millimeters from the bottoms of the jet. Do not insulate the flask in any way. Life the ball value and simultaneously supporting the oil cup thermometer by means of the sample reaches the graduation mark of the flask and note the final reading of the cup thermometer.
2. Reject any determination of the temperature of the sample in the oil cup varies during the run by more than .1ºC for temperatures of 60ºC or below by more than .3ºC or by more than 8.5ºC at 121ºC.

Kinematic viscosity in centistokes was then calculated from time units by using the relationships given by **Guthrie (1960)**:

$$V = .26t - \frac{179}{t} \qquad \text{when } 34 < t < 100$$

$$V = .24t - \frac{50}{t} \qquad \text{when t} > 100$$

V = kinematic viscosity in centistokes

t = time for flow of 50 ml of sample

3.2.3 Calorific value

The heat of combustion or calorific value of a fuel is an important measure since it is the heat produced by the fuel within the engine that enables the engine to do the useful work. The gross heat of combustion of fuel samples was determined as per IS: 1448 [P:6] : 1984 with the help of a Widson Scientific Works make Isothermal Bomb Calorimeter.

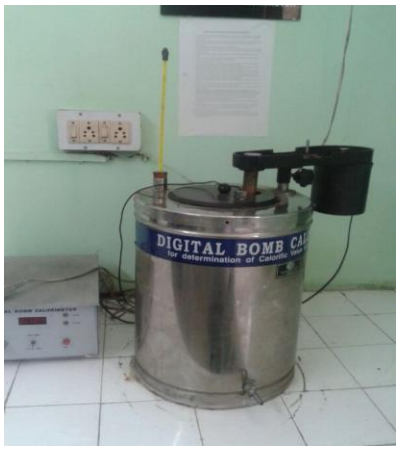


Figure 3.5: Bomb Calorimeter

Procedure

1. Accurately weigh in the crucible of sample about 1 gm of the air dried material ground to pass through IS sieve 20 (2110 microns).
2. Stretch a piece of the firing wire across the electrodes within the Bomb Tie 15 cm, length of the sewing cotton around the wire, place the crucible in position and arrange the loose ends of the thread in each determination.
3. Introduce into the body of bomb two milliliters of distilled water.
4. Reassemble the bomb, screws have the fingers, finally tightening if necessary, avoiding excessive pressure.

5. Charge the bomb as slowly with oxygen from a cylinder to a pressure of 25 atmospheres without displacing its original content.
6. Close the valve effectively, using as little pressure as possible, and detach the bomb from oxygen supply.
7. Weigh into the calorimeter vessel a quantity of water sufficient to submerge the cover of bomb to a depth of at least two centimeters leaving the terminals projecting.
8. Use the same weight of the water in all the tests.
9. Transfer the calorimeter vessel to the water jacket; lower the bomb carefully into the calorimeter vessel and having as circuit through a switch for subsequent firing of the charge.
10. Adjust the stirrer, place the thermometer and covers in position and start the stirring mechanism which must be kept in continuous operation at a constant speed during the experiment.
11. After an interval of not less than ten readings for five minutes at equal intervals of not more than one minute, tapping the thermometer lightly during 10 seconds prior to each reading. If, over a period of 5 minutes, the average deviation of the individual values of the rate of change of temperature is less than .00172ºC per minute, close the circuit momentarily to fire the charge and continue the observation of the temperature at intervals of similar duration to those of preliminary period.
12. If the rate of change of temperature is not constant within this limit, extend the preliminary period until it is constant.
13. In the chief period, which extend from the instant of firing until the time after which the rates of change of temperatures again become constant, take the earlier readings to .001ºC.
14. Determine the rate of change of temperature in the after period (which follows the chief period) by taking reading at 1 minute.
15. Remove the bomb from the calorimeter and after the lapse of half an hour from the time of firing, allow the acid mist to settle, release the pressure by opening the valve. Verify that the combustion has been competed by nothing the absence of any sooty deposit within bomb. The presence of any trace of sooty deposit indicates incomplete combustion and invalidates the test.

16. Wash out the contents of the bomb with hot distilled water into a hard glass beaker washing the bomb cap the crucible.
17. Add a measured excess, say 25 ml, of .1 N sodium carbonate solution and boil down to 10 ml to convert any metallic sulfates or nitrates to the less soluble carbonate or hydroxide the consumption of alkali carbonate is equivalent to the sulfates or nitrates together with the free sulfuric or nitric acids.
18. Filter, wash and make up to 100 ml.
19. To determine the sulfur content take 50 ml portion of this solution and follow the method.
20. Determine the total acidity by titrating a 50 ml portion with .1N HCl using methyl orange as indicator, the titer representing the excess alkali in one half of the quantity of sodium carbonate solution added to the washings.

The heat of combustion of the fuel samples was calculated using the equation given below:

$$Hc = \frac{Wc \times \Delta T}{Ms}$$

Where,

Hc = Heat of combustion of the fuel sample, Cal / g

Wc = Water equivalent of the calorimeter, Cal / ºC

Δ T = Rise in temperature, ºC

Ms = Mass of sample burnt, g

3.2.4 Flash and fire point

Flash Point measures the tendency of a fuel to form a flammability mixture with air under controlled laboratory conditions. This is the property that must be considered in assessing the overall flammability and hazard of material. Flash Point can indicate the possible presence of highly volatile and flammable material in relatively non volatile material. It is defined as the lowest temperature at which the fuel gives off enough vapors and ignites for a moment. The Fire Point is an extension of Flash Point in a way that it reflects the condition at which vapor burns continuously for five seconds. The Fire Point is always higher than flash point by 5 to 8ºC.

Procedure

1. Fill the fuel sample in the test cup up to the specified level and heat by heating the air with the help of a heater.
2. Stir the fuel sample at a slow constant rate.
3. Heat the sample in such a way that the rate of temperature is approximately 5ºC per minute.
4. Measure the temperature with the help of a mercury thermometer having range of -10 to 4000ºC.
5. At every 1ºC temperature, introduce the flame for a moment with the help of a shutter.
6. Record the temperature at which a flash will be appeared in the form of sound and light as the flash point.
7. Record the temperature at which fuel vapor catches fire and stays for minimum of 5 seconds as fire point.

3.2.5 Cloud and pour point

The Cloud and Pour point are the measure which indicates that the fuel is sufficiently fluid to be pumped or transferred. Hence, it holds significance to engines operating in cold climate. The Cloud Point is defined as the temperature at which a cloud or haze of wax crystal appears at the bottom of a test jar when chilled under prescribed conditions. The Pour Point is defined as the temperature at which the fuel ceases to flow. Both properties may indicate the tendency towards filter plugging and flow problems in the fuel line.

Procedure

1. Fill the 12 cm high and 3 cm in diameter glass tube of the apparatus enclosed in an air jacket with a freezing mixture of crushed ice and NaCl crystals.
2. Take out the glass tube containing fuel sample from the jacket at every 1ºC interval as the temperature falls.
3. Inspect the cloud formation.
4. Consider the point at which haze will be first seen as cloud point.
5. Follow the same procedure for determination of pour point.
6. Pre heat the sample to 48ºC and then cool to 35ºC in air.
7. Fill the sample in the glass tube.

8. Place the cooled sample in the apparatus and withdraw from the cooling bath at 1ºC interval for checking its flow ability.
9. Consider the temperature 1ºC above the temperature at which no motion of fuel was observed for five seconds on tilting the tube to a horizontal position.
10. Make three replications.

3.2.7 TLC

TLC is a very common method for trying to determine how many different compounds are present in a sample. This test provides qualitative information about how many different compounds are present in a mixture. For this analysis technique, very small quantities of the samples are placed on the special TLC plates. The plate is put in a container with a solvent or solvent mixture. The solvent runs up the plate and will separate the different kinds of molecules based on polarity differences and size differences.

Procedure

1. Dissolve silica and hexane so that they are in liquid state. Put glass slide in mixture immediately and let the slide dry.
2. Now, take a drop of sample on lower end of glass slide.
3. Prepare a solvent of hexane and methyl acetate in the ratio of 9:1.
4. Put the slide in solvent carefully that solvent should not touch the point initially. Now let the slide soak the solvent.
5. Keep the slide in iodine chamber for few minutes and let it dry.
6. Check for fatty acids, oil or ester points after some time. The presence of spots indicates the presence of respective constituent.

3.3 Experimental Test Rig set up

3.3.1 Engine Specification

Details of the engine and other components of the test set up used along with general procedure are described. The performance evaluation of a 3.73 kW engine on selected fuels was carried out. The engine specification is shown in Table 3.2.

Table 3.2: Engine Specifications

Parameters	**Details**
Manufacturer	Kirloskar Oil Engines Limited India
Engine Type	Vertical, 4-stroke
Dynamometer	Eddy Current
Rated Engine Brake Power, kW	3.73
Rated Engine Speed, rpm	1500
Number of Cylinder	1
Bore, mm	80
Stroke, mm	110
Displacement Volume, cc	252.9
Compression Ratio	16.5:1
Cooling System	Air Cooled
Horse Power	6.5
Injection Pressure, kg/cm^2	200
Voltage, V	240
Current, Ampere	17.5

Figure 3.6: Engine set up

Experimental set-up

The engine test set-up available in the Pollution Control Centre, Kurali was used. The set-up includes the following facilities:

- EC–15 eddy current dynamometer with electronic controller.
- Kirloskar make, 3.73 kW, constant speed engine, variable compression ratio

3.3.2 Exhaust Emissions Measurement

The emissions of carbon monoxide, unburnt hydrocarbons, nitric oxide and nitrogen dioxide by Different fuels at various loads were measured.

The exhaust emission parameters were analyzed by the HG-540 automotive emission gas analyzer. The exhaust emissions parameters with their respected test methods are given in Table 3.3:

Table 3.3: Emission parameter test method

S.NO.	Parameters	Test methods
1.	HC, CO, CO_2	NDIR (Non dispersive Infra red method)
2.	O_2 , Smoke	Electronic Chemical Method

Figure 3.7: Neptune HG-540 automotive emission analyzer

Experimental procedure

1. At particular load condition insert the sensors into the provided outlet for exhaust gases to escape into the environment.
2. Exhaust gases passes through these sensors to the respective analyzer attached with it.
3. After entering into the analyzer the readings are displayed on the digital screen.
4. After 2-3 minutes when the values are stabilized 3 readings are noted down.
5. Mean value of the three readings is evaluated.
6. Sensors are removed for the values on the analyzers to settle down again to zero value.
7. Repeat the above procedure for different fuel and load condition respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Sampling

The sample of waste cooking oil (WCO) was taken from the mess of I Hostel, Thapar University, Patiala. Trans-esterification, blending and analysis of test fuels were carried out at the Environment lab of School of Energy and Environment (SEE) in Thapar University, Patiala. Characterization of fuel properties was carried out at Merado Institute, Ludhiana.

4.2 Charcaterization of properties of diesel, WCO biodiesel and n-butanol according to ASTM standards.

Table 4.1: Properties

Property	ASTM std	Diesel	Biodiesel (B100)	n-Butanol
Density (kg/m^3)	900	835	868	810
Kinematic Viscosity (cSt)	1.9-6	2.72	4.38	3.64
Flash Point (ºC)	>130	78	155	29
Fire Point (ºC)	>53	83	160	
Cloud Point (ºC)	-3 to 12	c<10	1	
Pour Point (ºC)	-15 to 10	-6	-2	-45
Calorific value (kJ/kg)	>33000	43400	39488.592	33000
FFA %	<2.5	---	.12	---

4.3 Qualitative analysis (TLC)

Biodiesel was checked for qualitative conversion if it was converted or not. TLC (Thin Layer Chromatography) was done for this purpose. In it, 3 samples were run on the slide simultaneously.

Sample 1 was of crude oil. Sample 2 was of Biodiesel from waste cooking oil and 3rd was from oil mixed with alcohol.

Figure 4.1: TLC Analysis

Results:

- Sample 1 showed fatty acids spots and oil spots. There was no ester noted which means no conversion to biodiesel.
- Sample 2 was of biodiesel which showed only esters spots. Neither fatty acids nor oil spots were noted. It means 100% conversion to biodiesel has occurred.
- Sample 3 showed fatty acids and ester spots which indicates some oil has converted into biodiesel but no complete conversion has occurred.

4.4 Performance Characteristics

Effect on Brake Power

Brake Power is the power output produced by diesel engine. It is taken in kW

$$\text{Brake Power} = \frac{\text{V X I}}{\eta g \times 1000}\text{kW}$$

Figure 4.2 shows the variation of brake power with engine loads. It is observed from figure 4.2 that with the increase in engine load, the brake power increases. This trend is similar for all the tested fuels. However, biodiesel blend B60 showed higher brake power as compared to other blends. The reduction in BP may be due to lower calorific value of the tested fuels.

At full load, the maximum brake power output of B60, B40 and B20 blends is 3.78 kW, 3.6 kW and 3.5 kW respectively. n-butanol blends produces maximum brake power of 3.5 and 3.47 kW respectively. Brake power prodoced by diesel at full load was 3.68 kW.

B20 showed less percentage increse in BHP as compared to diesel. At lower loads it was just 1-2% and higher loads it increased upto 5%. n- Butanol blends had almost same variation as B20 or less than B20. B60 showed higher increase in BHP of about 15-20%. B40 had average increase range of up to 8%.

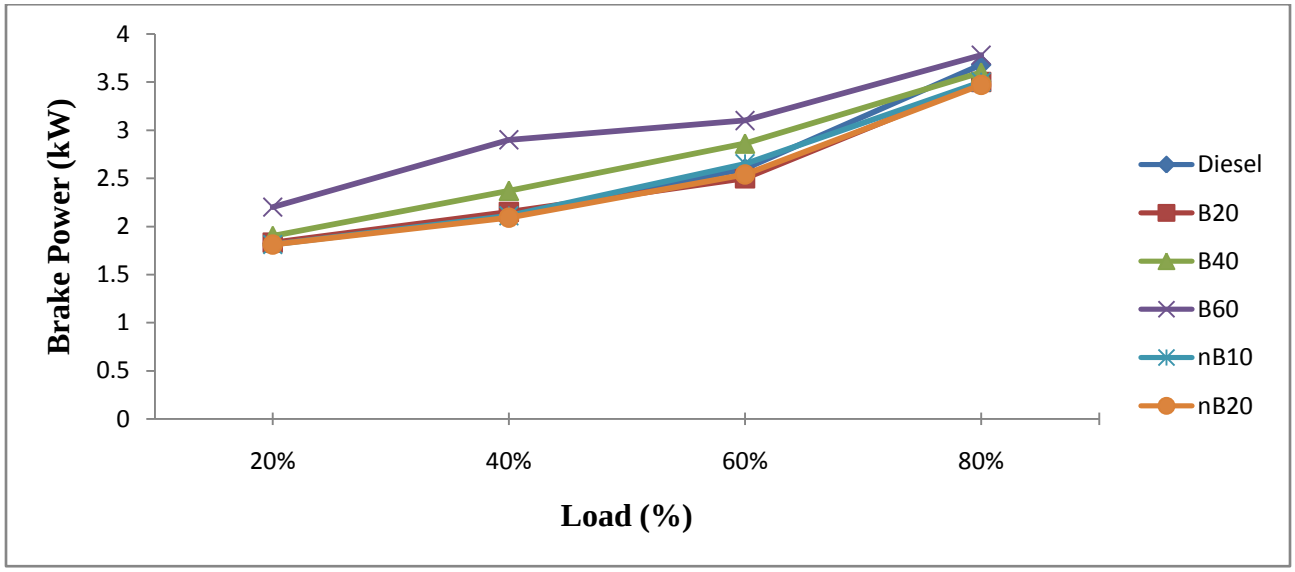


Figure 4.2: Variation of brake power with engine load

Effect on Brake specific fuel consumption

The Brake Specific Fuel Consumption is estimated from the brake power output of the engine and the equivalent mass flow rate of fuels. It is governed by the quality of combustion of fuel.

$$\text{BSFC} = \frac{\text{Mf}}{\text{BHP}}$$

It can be observed from figure 4.3 that a higher BSFC is noticed in B60 blend. This may be due to the lower calorific value of the fuel blend. The difference in BSFC of various blends is not significantly different at higher engine loads because less energy from fuel is required at higher loads as compared to lower loads. At full load, the bsfc value of B60, B40 and B20 are 287, 265 and 230 g/kW-hr respectively where as that of nB10 and nB20 are 280 and 290 g/kW-hr.

Even the fuel of higher calorific value gives lesser or equivalent work output compared to fuel of comparatively lower calorific value**.** It is due to higher hydrocarbons emissions or partial burning of fuel during combustion. Figure 4.3 shows the variations of Brake Specific Fuel Consumption for Diesel, Diesel-Biodiesel blends and Diesel-Biodiesel-n Butanol blends at various loads.

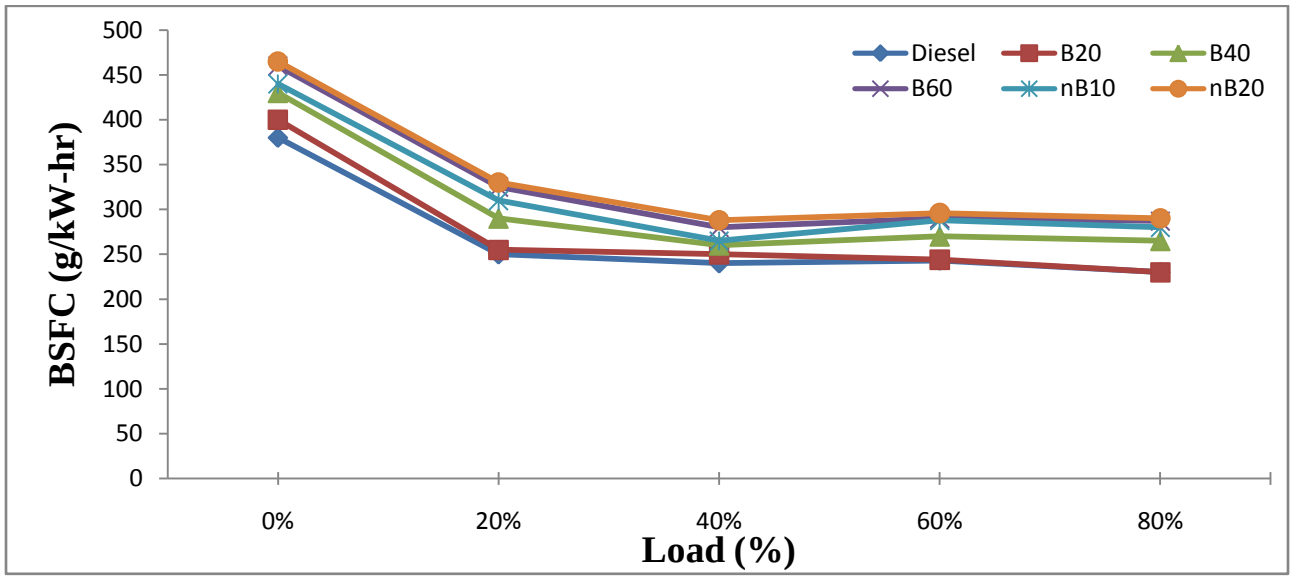


Figure 4.3: Variation of BSFC with engine loads

Effect on Brake thermal Efficiency

Brake Thermal Efficiency is directly related to Brake Power Output from Diesel engine and it varies inversely with Calorific value and Equivalent mass flow.

$$\text{BTE} = \left[\frac{\text{BP } X \text{ 3600}}{\text{Mf } X \text{ CV}}\right] X \text{ 100}$$

It can be observed from Figure 4.4 that brake thermal efficiency increases with increase in engine load. A slight drop in efficiency was found with B40 and B60 blends of WCO methyl ester when compared to diesel. This drop in thermal efficiency must be attributed to low calorific value of methyl ester. It was observed that the brake thermal efficiency of B20 is better than petro–diesel at all load tested. Also, efficiency dropped down with the addition of n-Butanol. At full load, BTE of diesel is 24.3% where as of B20, B40 and B60 is 26.4, 24.1 and 22.4% respectively. Butanol blends showed efficiency of 23.6 and 20.7% for nB10 and nB20 respectively.

B20 showed higher efficiency as compared to diesel and other blends. B20 proved 13.2% more efficient as compared to diesel at lower loads and 7.3% more at higher loads. Other blends were less efficient though this differnce was very little of about 2-7%. So, B20 blend can be suggested as best blend for biodiesel preparation with WCO.

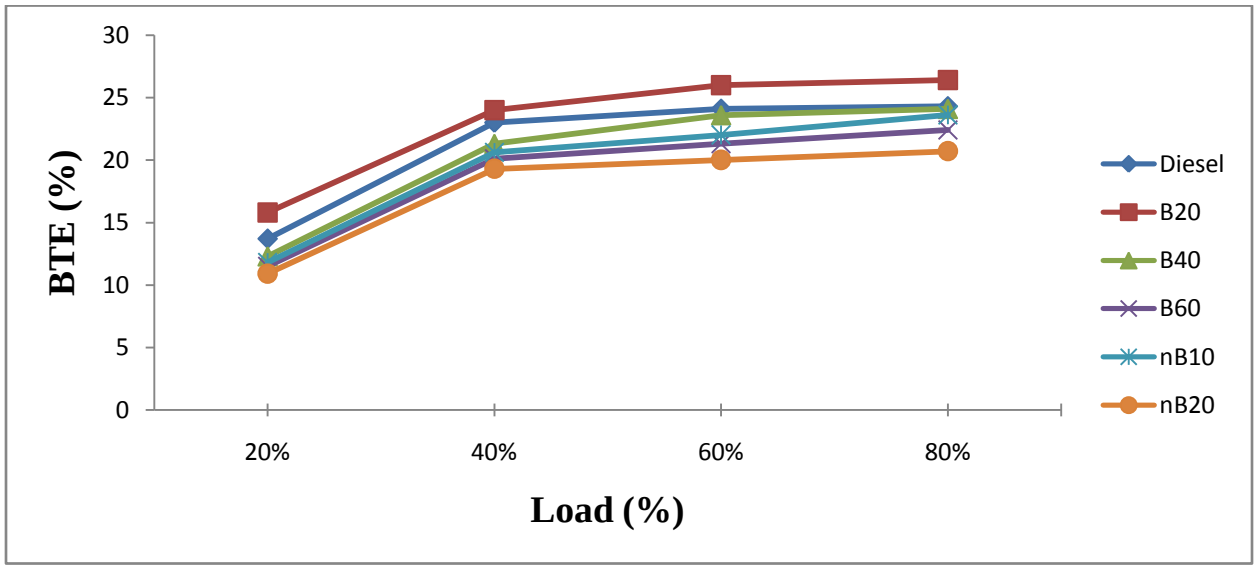


Figure 4.4: Variation of BTE with engine Load

Effect on Brake specific energy consumption

Brake Specific Energy Consumption (BSEC) is a reliable parameter in comparing the fuels of different calorific values. It is the product of calorific value and brake specific fuel consumption and taken as kJ/kW-hr.

$$BSEC = BSFC \text{ X } CV$$

The BSEC decreases with increase in load for all fuel blends. B40 and B60 and nB10 blends showed higher BSEC as compared to diesel at all loads tested. This is mainly due to the slightly lower calorific value as the result consumed more fuel. In Figure4.5, B20 and nB10 blends showed a decrease of about 0.1-9% in BSEC at all load as compared to diesel. B40 and B60 showed increase of about 4-15% in BSEC at all loads. At full load, BSEC of biodiesel blends B20, B40 and B60 is 15000, 21000 and 20000kJ/kW-hr respectively. BSEC of butanol blends nB10 and nB20 is 21700 and 16000 kJ/kW-hr respectively. BSEC of diesel at full load is 17000kJ/kW-hr.

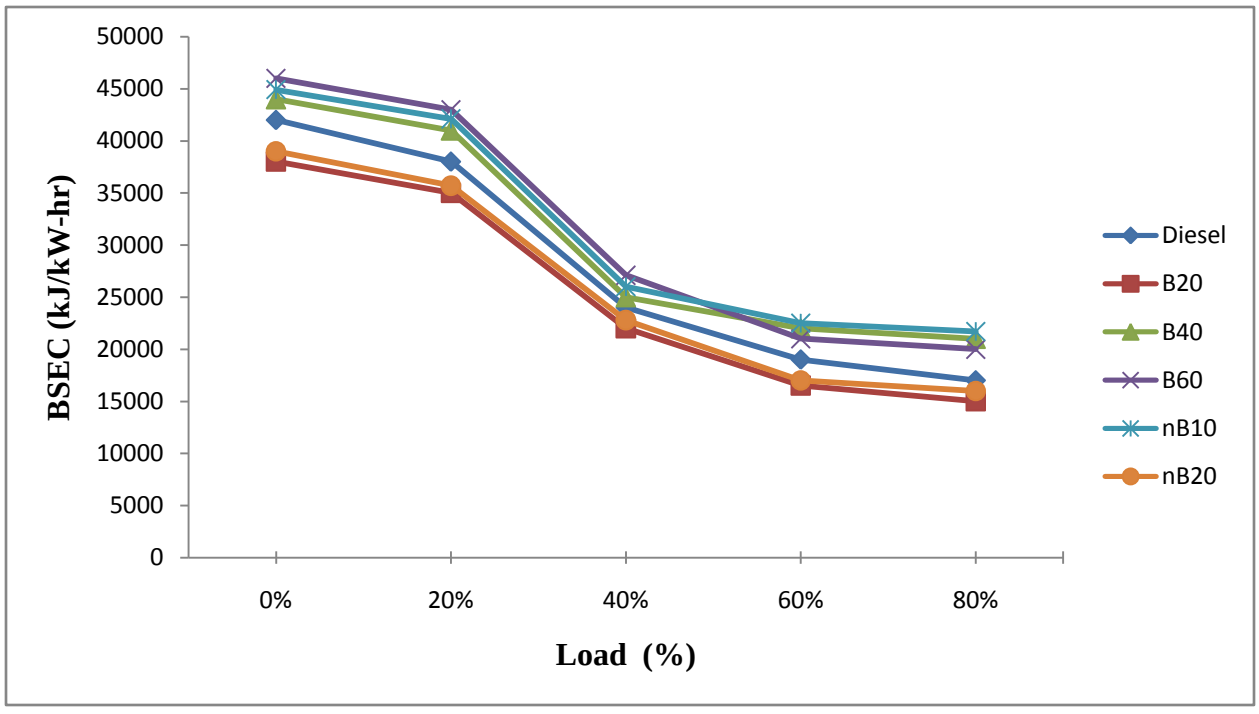


Figure 4.5: Variation of BSEC with engine loads

4.5 Emission Characteristics

Effect on HC emissions

The variation of hydrocarbon emissions with load for diesel, B20, B40, B60 and n-buatnol blends was compared. It was observed that with increase in load, the hydrocarbon emission increases. It is due to entering of rich fuel air mixture in the combustion chamber because of increase in fuel consumption. This leads to improper combustion due to which unburnt hydrocarbon emissions increases. It was also observed that with increase in blend content the HC emission decreases. This is due to the high cetane number of biodiesel blends. Higher cetane number lowers the combustion delay which improves the combustion. Another reason for low hydrocarbon emission with the increase in blend content is due to more oxygen content than diesel fuel. It was observed that HC emissions for diesel fuel were highest and for B60 blend it was lowest.

The decrease in HC emission occurs with increase in biodiesel blend. B60 showed 55-65% at lower loads and 40-50% at higher loads while B20 showed 15-25% decrease in HC emission at all loads. Butanol blends showed 20-45% decrease at all loads. At full load, HC emissions of biodiesel blends B20, B40 and B60 are 43, 35 and 27 ppm respectively. Butanol blends nB10 and nB20 showed 40 and 31 ppm respectively. The HC emission for different fuels with load at single compression ratio and constant speed is illustrated in the following figure.

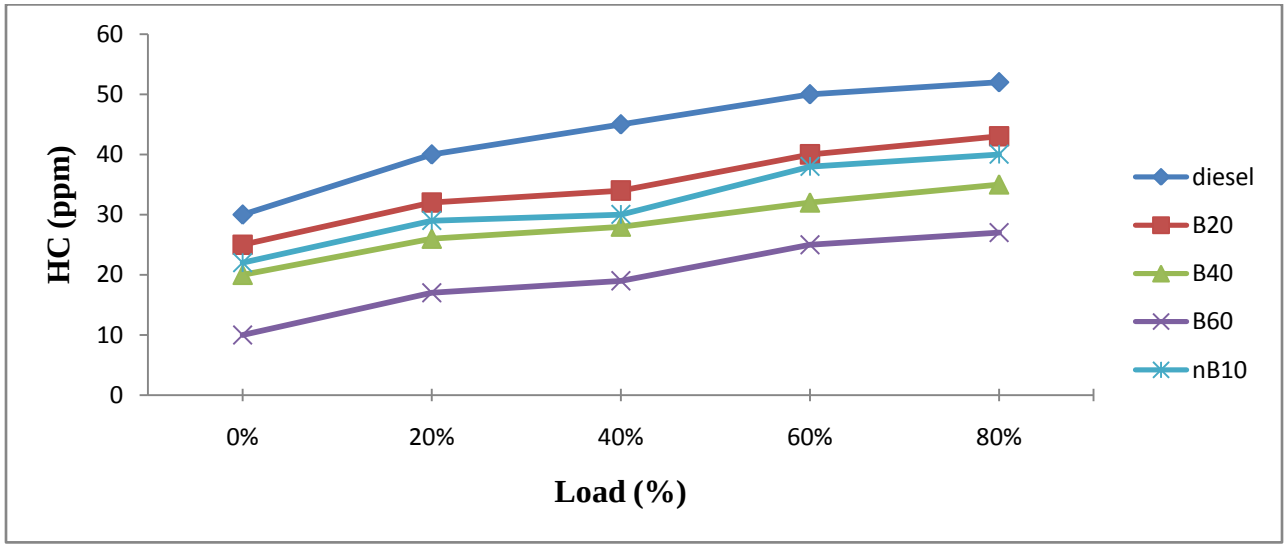


Figure 4.6: Variation of HC Emissions with engine loads

Effect on CO emissions

The carbon monoxide emissions results from incomplete combustion. The CO emissions for diesel fuel, B20, B40, B60 and n-butanol blends with load are compared.

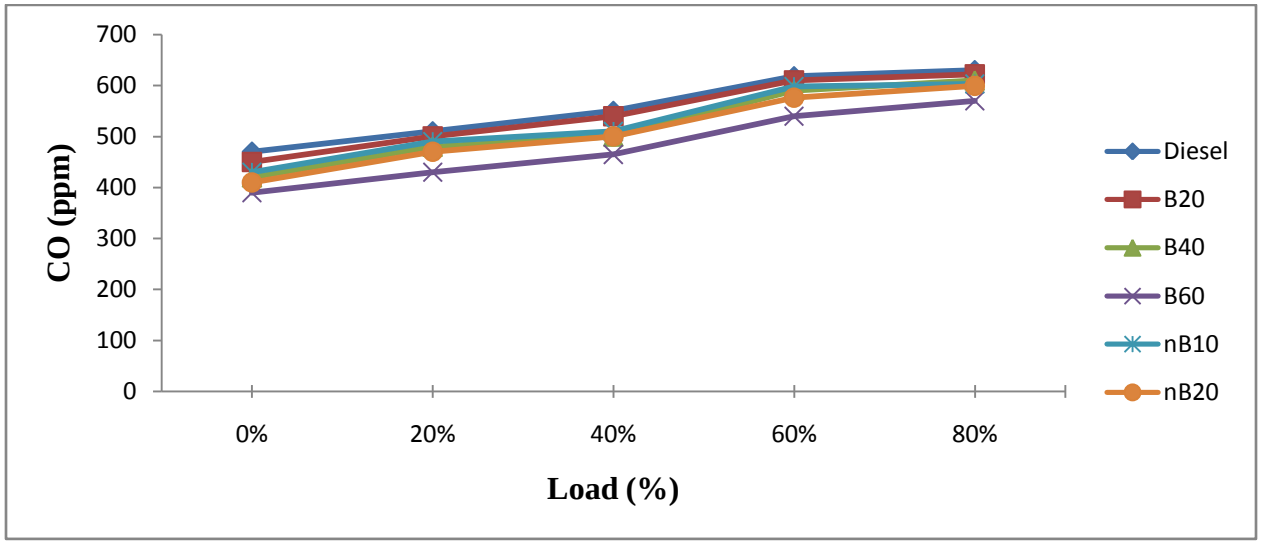


Figure 4.7: Variation of CO Emissions with engine loads

It was observed that with increase in load the CO emissions increased .This is due to the injection of rich air fuel mixture which led to incomplete combustion of fuel. It was observed that CO emissions of B20 blend were nearly same as that of diesel fuel with 1-8% decrease. But with further increase in blend content the emissions were observed to be decreased. This may be due to the higher oxygen content which leads to complete combustion. B40 showed 8-50% decrease and B60 showed 10-25% decrease.

At full load, CO emissions for biodiesel blends B20, B40 and B60 were observed 622, 610 and 570 ppm respectively. Butanol blends nB10 and nB20 showed 603 and 599 ppm respectively. Co emissions of diesel fuel at full load were 630 ppm.

The CO emissions were decreased with increase in n-butanol concentration which lowers the delay period and improves the combustion. Butanol addition lowered the emissions by 3-15%. The CO emissions for the B60 and nB20 blend were found to be the lowest among all fuels. The CO emissions for Diesel, B20, B40, B60 and n-butanol blends with load are illustrated in the above figure.

Effect on NOx emissions

The NOx emissions of diesel, B20, B40, B60 and n-butanol blends with increasing load were compared. The formation of NOx emissions are dependent upon oxygen concentration in fuel, reaction temperature and residence time. It was observed that NOx emissions increase with increase in load. This is because of increase in temperature inside combustion chamber at high loads. NOx emissions were observed to be increased with increase in blend content. This is because of high oxygen content in the biodiesel fuel. Nitrogen from air can easily mix with oxygen and produces the NOx emissions. These emissions were observed to be decreased with content of n-butanol due to lower ignition delay which increases the peak pressure and temperature.

At full load, Nox emissions of biodiesel blends B20, B40 and B60 were observed 390, 420 and 440 ppm respectively. Butanol blends showed 350 and 360 ppm for nB10 and nB20 respectively. Nox emissions of diesel were less 370 ppm.

NOx emissions incresed with WCO methyl ester at the pace of 5-25% where as addition of butanol decreased the Nox emissions by 1-10%. The NOx emissions for diesel, B20, B40, B60 and n-butanol blends with load is illustrated in the following figure.

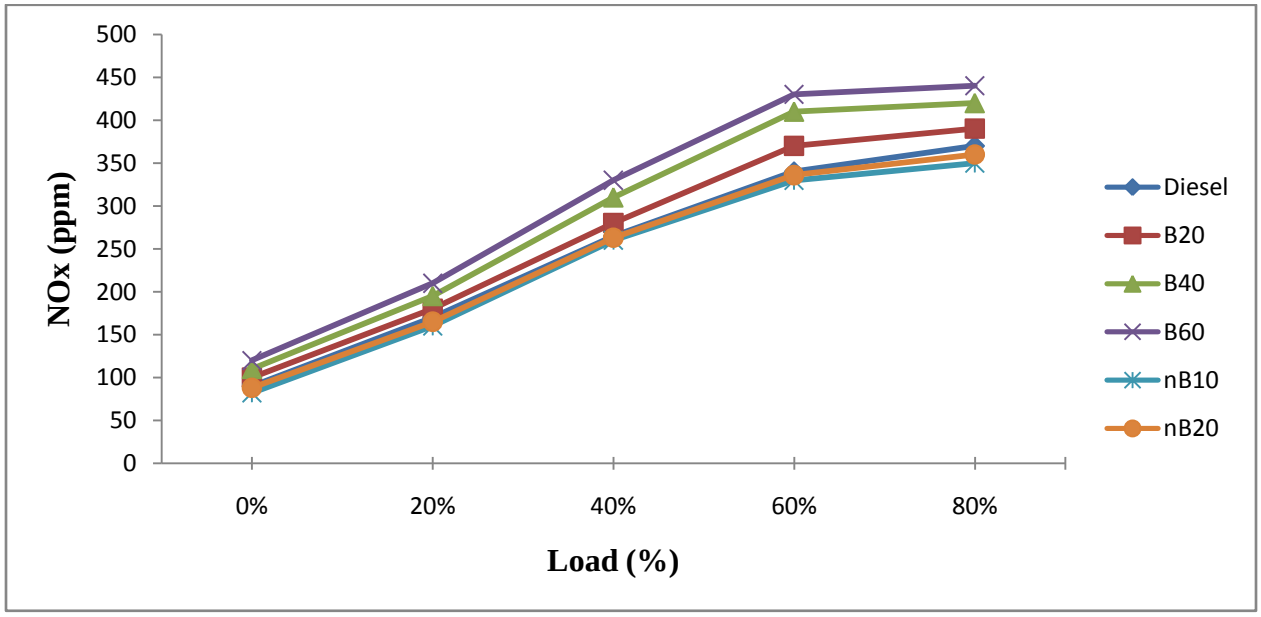


Figure 4.8: Variation of NOx Emissions with engine loads

Effect on CO_2 emissions

CO_2 emission is an indication of complete combustion of fuel in the combustion chamber with the presence of excess O_2. The CO_2 emissions for diesel, B20, B40, B60 and n-butanol blends with load were compared. It was observed that with increase in load the CO_2 emissions increases due to better combustion at high loads. The CO_2 emissions with diesel were highest. As the blend content increased, the CO_2 emissions were decreased. Carbon dioxide is formed on complete combustion of the fuel in oxygen. Here, carbon dioxide formation is less due to the fact that biodiesel in general is a low carbon fuel and has a lower elemental carbon to hydrogen ratio than diesel fuel. The CO_2 emissions were observed to be decreased significantly with the increase in butanol content due to the good oxygen content and lower ignition delay that led to better combustion.

At full load, CO2 emissions for biodiesel blends B20, B40 and B60 were observed 4.6, 4.3 and 3.96% respectively. Butanol blends nB10 and nB20 showed 3.3 and 3% emissions respectively. Diesel showed 4.9% emissions at full load. CO_2 emissions decreased by 4-10% at B20 where as higher blends showed 11-35% decrease. Butanol addition decreased emissions by 30-60% at all loads.

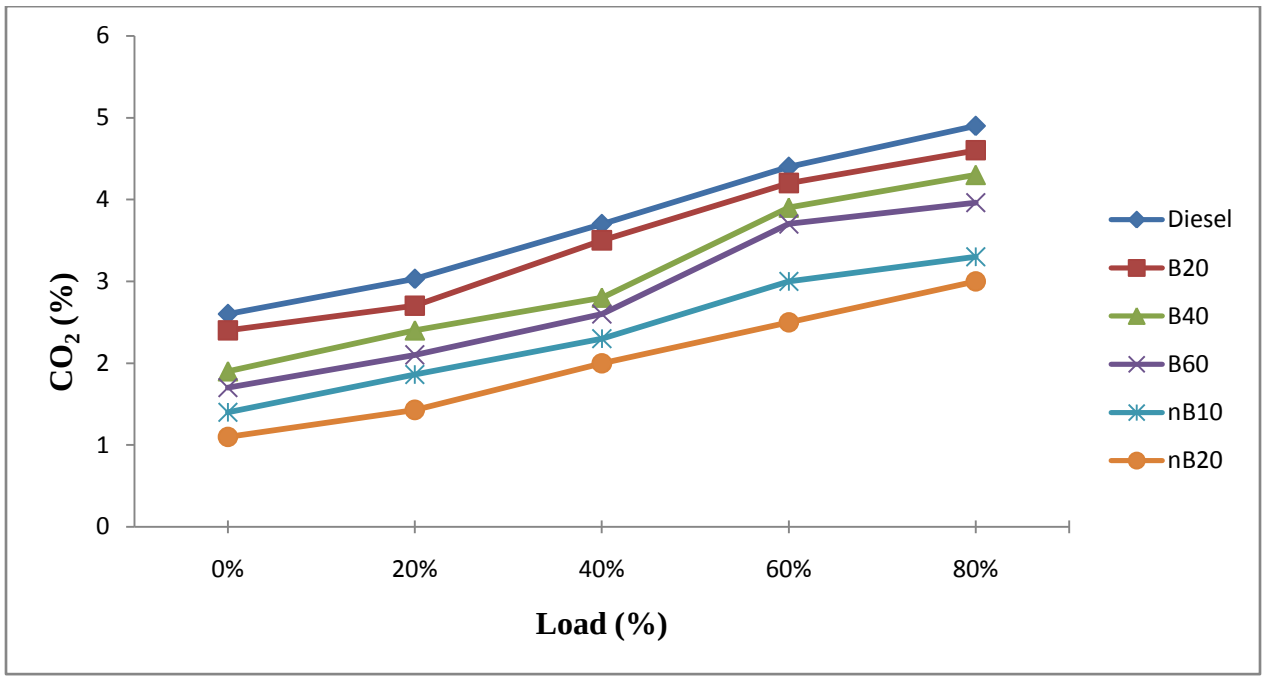


Figure 4.9: Variation of CO_2 Emissions with engine loads

Effect on Smoke emissions

Figure 4.10 represents the smoke opacity variation with biodiesel and n-butanol blends. Smoke opacity was calculated for various blends of biodiesel-diesel and n-butanol-biodiesel-diesel. Biodiesel gives lower smoke emission as compared to petroleum diesel. With increase in biodiesel percentage the smoke opacity increases. Smoke opacity increases with increase in load. B20 blend give higher smoke emission than B40 and B60 blend at all load conditions. This could be due to higher density of fuel which results in slow mixing and insufficient combustion which leads to higher smoke emission. However smoke opacity increased with addition of n-butanol as compared to biodiesel blends but it was lesser than 100% diesel.

At full load, smoke emissions for biodiesel blends B20, B40 and B60 showed 1.96, 1.71 and 1.4 BSN respectivly. Butanol blends showed 2.03 and 2 BSN smoke for nB10 and nB20 respectively. B20 showed 20-28% decrease in smoke where as B40 and B60 showed 34-50% decrease in smoke as compared to diesel. Butanol blends showed 10-25% decrease in smoke as compared to diesel fuel.

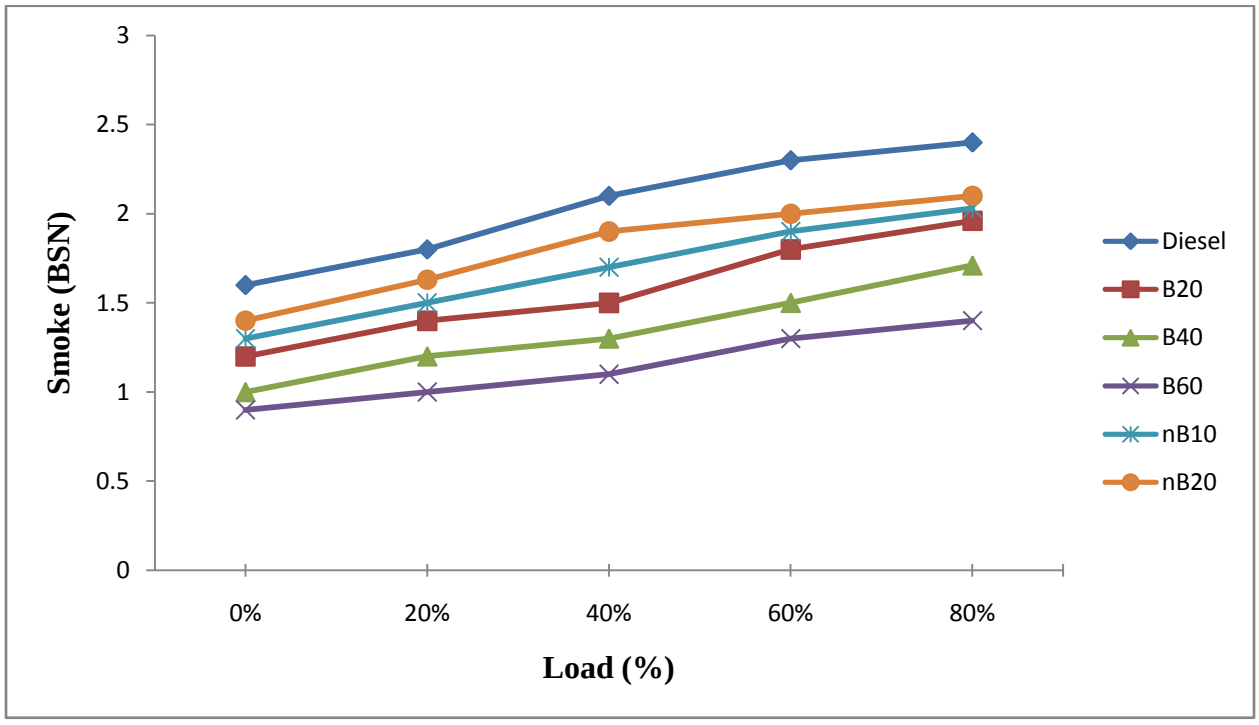


Figure 4.10: Variation of Smoke variations with engine loads

CONCLUSION

Waste cooking oil is promising feestock for biodiesel production. Therefore, this experimental investigation aimed to study the feasibility of biodiesel production from low quality WCO and to characterize the biodiesel and n-butanol blends as well as their performance and emission characteristics.

Following are the conclusions based on the experimental results obtained while operating single cylinder diesel engine fueled with WCO methyl ester and butanol blends in different proportion with diesel fuel.

- Biodiesel was produced from WCO through trans-esterification reaction using oil to alcohol molar ratio 6:1, reaction temprature of 55ºC for 2 hours using alkaline catalyst KOH (1% weight).
- Characterization of B20, B40 and B60 demonstrated that all the important fuel properties of biodiesel are compatible with diesel engine and the engine can satisfactorily perform on these blends without modification.
- The lower blends of WCO methyl ester can be used in diesel engine without any engine modifications. The fuel filter needs to be changed after some interval of time.
- Due to lower calorific value, BTE of biodiesel and n-butanol blends were lower than diesel fuel at all loads. BTE of B20 is superior to diesel at all load conditions.
- B20 gave best results so it could be considered as an optimum fuel blend in terms of performance and reduced emission. The results of nB10 were also considerable. In fact, it gives better results in reducing emissions and in case of BSFC.

Table 5.1: Performance parameters of diesel engine with various fuel blends at full load

Parameter	**Diesel**	**B20**	**B40**	**B60**	**nB10**	**nB20**
BP (kW)	3.68	3.5	3.6	3.78	3.5	3.47
BSFC (g/kW-hr)	230	230	265	287	280	290
BTE (%)	24.3	26.4	24.1	22.4	23.6	20.7
BSEC (kJ/kW-hr)	17000	15000	21000	20000	21700	16000

Table 5.2: Emission parameters of diesel engine with various fuel blends at full load

Parameter	**Diesel**	**B20**	**B40**	**B60**	**nB10**	**nB20**
HC (ppm)	52	43	35	27	40	31
CO (ppm)	630	622	610	570	603	599
NOx (ppm)	370	390	420	440	350	360
CO_2 (%)	4.9	4.6	4.3	3.96	3.3	3
Smoke (BSN)	2.4	1.96	1.71	1.4	2.03	2

The emissions of HC, CO, CO2 and smoke shows decresing trend with increase in biodiesel blend at full load where as NOx increased with increase in Biodiesel blend as compared to diesel.

The addition of butanol can be proved to be useful. 20% blend of biodiesel and 10% blend of butanol along with biodiesel is best alternative to diesel. On the whole, the use of n-butanol and biodiesel blends proves beneficial from the point of view of improvement in engine performance and reduction in emission charcateristics.

Future Prospects

Biodiesel is one of the most viable alternate fuels for the diesel engines. Biodiesel is very easy to replace the petroleum diesel in the modern day engines without carrying out any major changes in it. In the present times when the oil prices are increasing every day and air-pollution has risen to alarming rates, there is more and more awareness for using biodiesel. Further, the future scope of work can be carried in the following areas:

1. To study the oxidation stability of biodiesel.
2. Higher biodiesel and n-butanol blends can be tried for diesel fuel substitution.
3. Performance parameters can be studied at various engine speeds and compression ratio.
4. Fuel additive can be studied to improve the tcold flow properties.
5. Effect of injection pressure and timing on combustion characteristics of various biodiesel blends can be studied.

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