Optimization of Biodiesel Production from Used Cooking Oil (mixed) & Performance Analysis of CI Engine fueled with Biodiesel-Diesel Blend

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by

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CERTIFICATE OF RECOMMENDATION

This is to certify that the thesis entitled "**Optimization of Biodiesel Production from Used Cooking Oil (mixed) & Performance Analysis of CI Engine fueled with Biodiesel-Diesel Blend.**" is a bona fide work carried out by **SUBRATA BAGDI**, Roll No- **M4ENR19013** under our supervision and guidance for partial fulfilment of the requirement for Post Graduate Degree of Master of Technology in Energy Science & Technology, during the academic session 2017-2019.

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The foregoing thesis is hereby approved as a credible study of an engineering subject carried out and presented in a manner of satisfactory to warranty its acceptance as a prerequisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not endorse or approve any statement made or opinion expressed or conclusion drawn there in but approve the thesis only for the purpose for which it has been submitted.

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DECLARATION OF ORIGINALITY AND COMPLIANCE OF ACADEMIC ETHICS

I, hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his Master of Technology Energy science & Technology studies during academic session 2017-2019. All information in this document has been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited and referred all material and results that are not original to this work.

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Dedicated

to

My Father

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ABBREVIATIONS

SFC = Specific Fuel Consumption

BTE = Brake Thermal Efficiency

CI = Compression Ignition

EGT = Exhaust Gas Temperature

ml/kwh = milliliters per Kilowatt-hour

cSt = Centistoke

rpm = Revolution per minute

ml/hr =milliliters per hour

B10 = 10% Biodiesel and 90% Petro-diesel

B20 = 20% Biodiesel and 80% Petro-diesel

B30 = 30% biodiesel and 70% Petro-diesel

B40 = 40% biodiesel and 60% Petro-diesel

B50 = 50% biodiesel and 50% Petro-diesel

WCO = waste cooking oil or used cooking oil mixed

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CHAPTER 1: INTRODUCTION

The rapidly increasing energy demand all over the world due to the growth of the world population, rising living standards and increased economic activities also caused enormous amount of greenhouse gas (GHG) emission. According to the organization of the petroleum Exporting countries, OPEC [10], by 2040 world fuel oil demand will reach up to 109.4 million barrel per day. However, this higher oil fuel demand is facing two major challenges, scarcity of the resource and negative environmental impact due to its use. It is well known that the petrol consumption has the biggest share of all energy resources because it has used for transportation (land, air, and sea), power plants, construction, and industrial activities. Use of diesel fuel is higher than other petrol products due to high efficiency of diesel engines over other internal combustion engines (ICE) [11]. Therefore, many studies aimed to substitute fossil diesel fuel with renewable fuels. In 1900, Dr. Rudolf Diesel exhibited a diesel engine operating with 100% peanut oil at the World Exhibition [12].

In 2005, India consumed 30 million tons of oil in the transport sector, of which 29% is gasoline and 71% is diesel [13]. The Indian energy demand is expected to grow at an annual rate of 4.8% over the next couple of decades [14]. Many scenarios projected that India will at least double its oil consumption by 2030 [15], which will make India the third largest oil consumer in the world [16]. Biofuel production could potentially play a major role in the country.

According to the International Energy Agency (IEA) [4], the production of biofuel increased from 50 megaton per year in 2010 to 80 megaton per year in 2018 and it will be targeted to 200 megaton per year in 2023. The global advanced biofuel project development by country shown in Fig.1.1, where India singly contribute 18% of total biofuel production in the world. A number of developmental activities are being taken up in the country for the production of biofuels, which include a 5% compulsory blend of ethanol in gasoline. These trials are ongoing in various states and the Government of India aims to increase the blends of biofuels with gasoline and diesel to 20% by 2020.

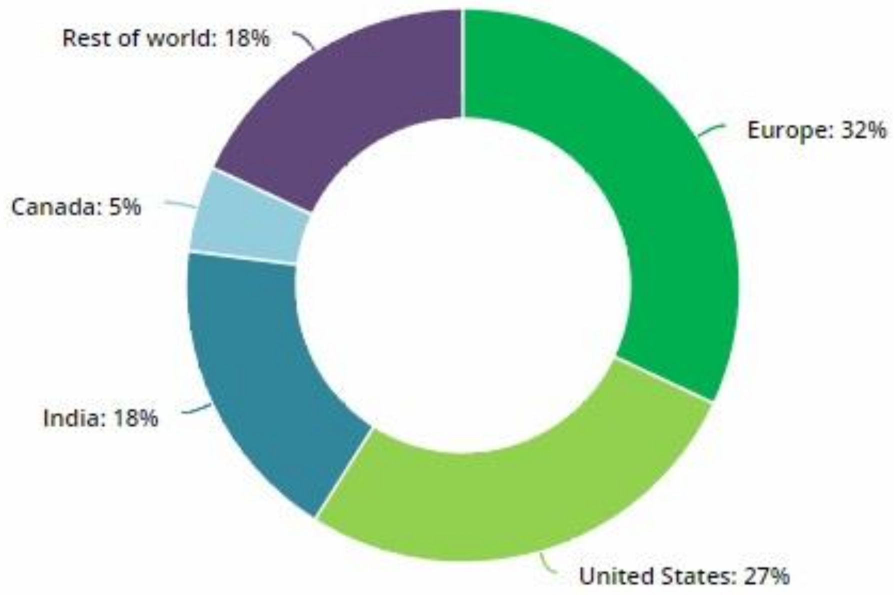


Fig. 1.1- Global advanced biofuel project development report by IEA

According to the Ministry of Railways of Govt. of India, Indian Railways reportedly consume more than two billion liters of diesel per year. The Ministry also reports that a small reduction in its diesel consumption through blending of biodiesel can create substantial saving in its fuel bill with benefits of cleaner environment due to low carbon emissions. National Policy on Bio-Fuels by Ministry of New and Renewable Energy, Govt. of India, proposes an indicative target of 20% biodiesel blending by the year 2017 [10].

Vegetable oils can be used as alternative fuels because they are biodegradable, nontoxic, and clean fuels. Vegetable oils and their derivatives as diesel engine fuels lead to substantial reductions in sulfur, carbon monoxide, polycyclic aromatic hydrocarbons, smoke and particulate emissions.

Biodiesel, a diesel fuel substitute that can be made from a variety of oils, fats, and greases, is of interest to farmers for a number of reasons: It can provide an additional market for vegetable oils and animal fats; it can allow farmers to grow the fuel they need for farm machinery; and it can decrease the dependency on imported oil since fuel feedstocks can be grown domestically.

Biodiesel is a renewable source of energy that can help reduce greenhouse gas emissions and minimize the “carbon footprint” of agriculture. It contributes less to global warming because the carbon in the fuel was removed from the air by the plant feedstock.

The low viscosity and superior fuel properties of biodiesel make it better alternative fuel than raw vegetable oil. On the other hand, studies related to disadvantages of biodiesel such as high fuel consumption, poor cold starting performance, and high NO_x emissions are drawing attention. Biodiesel studies aim to analyze and improve the fuel properties, the engine characteristics, and the exhaust emission of vegetable oil-based biodiesel. Many studies on the use of vegetable oils as fuel in diesel engines can be found.

The studies have investigated different aspects and properties of the biodiesels. It can be seen from these studies that there are significant changes between the measured parameters.

CHAPTER 2: AIM AND OBJECTIVE OF PRESENT STUDY

This study compares engine performances of five different type biodiesel samples by using the same experimental system. Major aim and objective of this study is to

1. Optimization of the biodiesel production from Waste Cooking Oil of Soybean and Sunflower Oil.
2. To produce biodiesel on the laboratory scale from Waste Cooking Oil of Soybean and Sunflower Oil by Transesterification method using optimized parameters.
3. Find out the properties of produced biodiesel and compare it to petroleum-based diesel fuel.
4. To analyze the combustion performance of biodiesel, when blended with Petro Diesel in the ratio of B-10, B-20, B-30, B40 and B50.
5. To measure the Specific Fuel Consumption of the engine by varying the load applied on the engine and record the resultant fuel consumption while comparing the fuel consumption for the same load when only Petro Diesel is applied.
6. To analyze the Exhaust gas Temperature of engine for different load at different biodiesel blend.
7. To check whether engine performance improves or deteriorates with the increasing ratio of biodiesel applied.

CHAPTER 3: LITERATURE REVIEW

3.1 Optimization of Biodiesel Production

There are so many feedstocks from which we can produce biodiesel. We can make biodiesel by various methods and the reagent and catalyst used depending on the characteristics or properties of the feedstock. Hideki F et al. [5] reported that transesterification using alkali catalyst gives the highest level of conversion of triglyceride to their corresponding esters in short reaction times. Therefore, this process has been widely used for biodiesel production.

Banerjee N et al. [1] produce biodiesel from used vegetable oil, a locally available feedstock. The process parameters were optimized and a maximum biodiesel yield achieved was 94% at the catalyst (NaOH) concentration 0.69 wt.%, Methanol to Oil molar ratio 15:1, temperature 55 °C and the time of reaction 90 minute. The biodiesel properties are density 0.87 g/cm^3, kinematic viscosity 5.9 centistokes, calorific value 7816 kcal/kg and flash point 179°C.

The free fatty acid (FFA) contain in the feedstock, vegetable oil is a significant parameter. If the free fatty acid (FFA level of oil is greater than 2%, it has to be reduced by esterification to avoid soap formation in transesterification. The flow diagram of biodiesel production [6] given in Fig. 3.1.1.

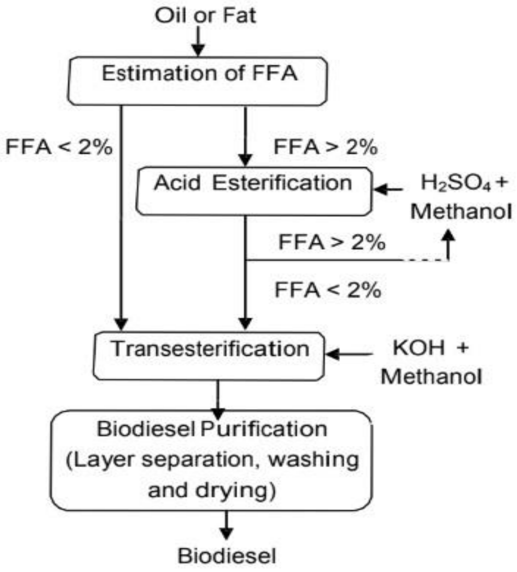


Fig. 3.1.- Flow diagram of biodiesel production

Paul S et al. [2] optimize the biodiesel production from Indian sesame oil and achieved the yield of 95.5%, use NaOH as catalyst 0.5% (wt./wt.), methanol to oil molar ratio 6:1, a reaction time of 1.5 hr. and reaction temperature 55 °C, at reaction stirring rate of 1000 rpm. Find the biodiesel properties within the range of Indian standard properties of biodiesel specified in IS 15607:2005. The brake thermal efficiency (BTE) of lower blends of sesame biodiesel (B5 and B10) were very close to diesel fuel.

Karim A. Younis et al. [7] find the optimum parameters for production of biodiesel from sesame seed oil and used cooking oil. By finding the optimum parameter one by one i.e. first finding the optimum temperature, then optimum methanol to oil molar ratio, then the catalyst amount and then time and finally get the optimum parameters for maximum yield. Yuan-Chung Lin et al. [8] give a comparison report on biodiesel production by using conventional heating system compared to the microwave system. Optimization had been done in both the system by optimizing the parameters one by one. Conclude that microwave heating system is better than the conventional heating system because microwave system takes only 7 minutes to produce the maximum yield of 96.2%, while conventional heating system required 90 minutes and produce 95.6% yield. Also, the total amount of energy required in microwave heating system is 10 times less than that of the conventional heating system.

Bisheswar Karmakar [9] done an experimental investigation to synthesize biodiesel from inedible commercial grade castor at optimum parameters by finding them using Taguchi method for optimization. The feedstock was subjected to esterification under the experimental conditions suggested by L16 Taguchi orthogonal approach. optimized conditions: reaction temperature of 50 °C, reaction duration of 1 h, catalyst concentration of 1% w/w, methanol to oil ratio of 20:1 and agitation speed of 700 rpm. Identification of noteworthy parameters were carried out employing Taguchi approach and emerged significant parameters were: molar ratio of oil to methanol, agitation speed, reaction temperature and catalyst concentration with contributing factors of 59.6%, 16.95%, 12.59%

and 10.82% respectively.

3.2 Performance and emission characteristics of various biodiesel and its blend in C.I engine

Biodiesel-Diesel Blend

Muralidharan et al. [18] evaluated the performance and emission characteristics with various blends of waste cooking oil biodiesel. Biodiesel was used with different blend ratios, 20%, 40%, 60%, and 80% with diesel. A constant speed engine with 1500 rpm was used for test purpose, and the results were compared with standard diesel operation.

For all the fuels with increase in load, the Break thermal efficiency (BTE) increased. With the increase in the percentage of biodiesel, the BTE decreased because of the higher fuel consumption and lower calorific value of biodiesel. B40 had the maximum BTE of 38.46%, i.e., 4.1% higher than diesel. With the increase in load, the exhaust gas temperature (EGT) decreased. Due to the lesser calorific value of the biodiesel with the increase in the percentage of biodiesel in the blend, the EGT decreased. For all the blends of the waste cooking oil 13 biodiesel used in this experiment, the mechanical efficiency increased with the increase in load. The blends had higher mechanical efficiency because of the high reaction activity of the fuel. The fuel with blend of biodiesel had higher NOx than diesel because the plant oil naturally had the nitrogen content along with it, and this would get involved in the production of NOx. The peak temperature produced during the combustion of the biodiesel was higher than diesel, so the NOx produced during the combustion of biodiesel was higher than diesel. The higher viscosity of the biodiesel blends led to poor atomization character and these resulted in an increase in HC compared with diesel. The ignition delay of biodiesel was higher than diesel, so more fuel was accumulated in the cylinder. This led to the production of more unburned hydrocarbons in the case of biodiesel. With the increase in load, the CO increased because more amount of fuel was injected during high load, and so CO emission increased.

Biodiesel-Alcohol Blend

Huseyin Aydin et al. [19] discussed the Effect of ethanol blending with biodiesel on engine performance and exhaust emissions in a CI engine. For that Commercial diesel fuel, 20% biodiesel and 80% diesel fuel, called here as B20, and 80% biodiesel and 20% ethanol, called here as BE20, were used in a single cylinder, four strokes direct injection diesel engine. Here biodiesel is produced from sunflower oil. The fuel properties of BE20 were quite similar to conventional diesel fuel in its main characteristics. The addition of Biodiesel and Ethanol to diesel fuel changes the physicochemical properties of the blends. By using ethanol, density, kinematic viscosity, low calorific value and aromatics fractions of the blends decrease. Simultaneously, H/C ratio and oxygen content of the blends are enhanced, which has some favorable effects on the ignition and combustion of the blends the effect of test fuels on engine 9 torque, power, brake specific fuel consumption, brake thermal efficiency, exhaust gas temperature, and CO, CO2, NOx and SO2 emissions was investigated.

The torque of engine obtained for BE20 was higher than both those obtained for diesel and B20 fuels. The power of BE20 was very close to that of DF while that of B20 was slightly lower. The average brake specific fuel consumption for BE20 fuel was lower than that of B20 and was almost the same as that of standard diesel fuel. The highest percent of exhaust temperature during the exhaust were obtained with blend of BE20. The NOx emissions were slightly increased with the use of both biodiesel–ethanol blend and standard diesel fuel with respect to those of the biodiesel–diesel blend. But as for CO2 emissions, that have a vital effect on global warming, a drastic decrease was obtained for B20 fuel when compared with those of both diesel and BE20 fuels. For B20 the average CO2 decrease was about 67% and 67.5% when compared to diesel and BE20 fuels, respectively. The CO and SO2 emissions were reduced with the use of both biodiesel–ethanol and biodiesel-diesel blends with respect to those of the neat diesel fuel.

Performance and emission characteristics of an engine was tested by Chang et al. [20] using different blends and different ratios: WCO biodiesel–diesel–water containing acetone–butanol–ethanol (ABE).

Water containing ABE solution blended with diesel–biodiesel produced 7.88% BTE higher than diesel and diesel– WCO biodiesel blends. At high load conditions, B50 and B75 produced almost equal BTE as that of diesel. Because of the lesser heating value of the biodiesel, with the increase in the percentage of biodiesel in the blend, the brake specific fuel consumption increased. At higher loads, the BTEs of fuel with the blends of bio-diesel with different proportions such as B25, B50, and B75 were almost equal, but at lower load, the BTE of B50, B75 had lesser efficiency than diesel. At higher loads, the lubricity of biodiesel led to produce efficiency equal to that of diesel, but at lower load conditions, the viscous factor of biodiesel led to poor atomization and eventually to lesser efficiency of biodiesel.

The blend containing biodiesel-50%, ABE-25%, and diesel-25% had the higher efficiency than diesel and blends with other combinations. This was because of the lower cetane number that helped to create more time for pre combustion zone and the lower viscosity led to higher atomization and more oxygen content facilitated better combustion. NOx for all the biodiesel blends were higher than for diesel. With the increase in the percentage of biodiesel in the blend, NOx increased. The inbuilt oxygen in the biodiesel was the reason for higher NOx with the biodiesel blends. The NOx for water containing ABE–biodiesel-diesel blends was reduced up 10 to 63.1% than diesel. With the addition of water containing ABE with biodiesel, the NOx production was reduced more when compared to biodiesel–diesel blends. With the addition of 25% of ABE with biodiesel–diesel blend, the NOx reduced up to 22.7% than WCO biodiesel–diesel blend. The water containing ABE had a similar character of biodiesel such as lower cetane number and higher oxygen content, but NOx was reduced due to the lower heating value and higher latent heat of vaporization of water that led to lower cylinder temperature eventually resulting in lower NOx. The cetane number for water containing ABE had lower value, so it led to higher ignition lag and increased the duration of higher temperature which is one of the main key factors in the NOx production, but the higher latent heat of vaporization of water containing ABE led to decrease in cylinder temperature and NOx production was decreased. The higher oxygen content in the water containing ABE was the reason for the reduced particulate matter. The PM for water containing ABE–biodiesel-diesel blends was reduced up to 30.7% than for diesel.

CHAPTER 4: BIODIESEL PRODUCTION

4.1 Feedstocks used for biodiesel production

The raw material used for biodiesel production is called feedstock. There are so many feedstocks from which biodiesel can be produced, the feedstocks are categorized below.

Biodiesel is derived from biological sources, such as vegetable oils or fats, and alcohol. Commonly used feedstocks are shown in Table 4.1.

Table 4.1: feedstock used for biodiesel Production

Vegetable Oils	Animal fat	Others
Jatropha oil, Soybeans, Sunflower, Rapeseed, Canola, Mustard	Lard, Tallow, poultry fat	Recycled Restaurant Cooking Oil (a.k.a. Yellow Grease)

Natural vegetable oils and animal fats are extracted or pressed to obtain crude oil or fat. This extracted liquid contains free fatty acids, phospholipids sterols, water, odorant and other impurities. Refined oil and animal fats also have free fatty acid content and water. Residual water and free fatty acid have significant effect on the reaction [30].

4.2. Biodiesel production method

There are so many investigations on biodiesel production of the nonconventional feedstock of oils and have reached a faster pace in the last few years. Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of hydrocarbon-based diesel fuels. An adaptation of the vegetable oil as a CI engine fuel can be done by the following methods.

(1) Dilution, (2) Transesterification, (3) Pyrolysis, (4) Micro-emulsification.

4.2.1 Dilution:

The dilution of vegetable oils can be accomplished with such material as diesel fuels, solvent or ethanol. Dilution results in the reduction of viscosity and density of vegetable oils. The addition of 4% ethanol to diesel 67 fuel increases the brake thermal efficiency, brake torque and brake power while decreasing the brake specific fuel consumption. Since the boiling point of ethanol is less than that of diesel fuel, it could assist the development of the combustion process through an unburned blend spray [30].

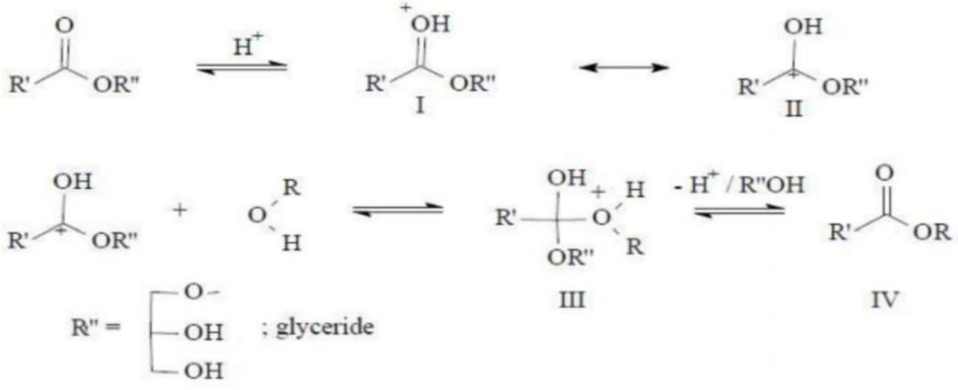
4.2.2 Transesterification:

Three basic types of transesterification processes depending upon the catalyst used are

1. Acid-catalyzed transesterification.
2. Base-catalyzed transesterification.
3. Lipase catalyzed transesterification.

4.2.2.1 Acid-Catalyzed Transesterification.

The transesterification process is catalyzed by Bronsted acids, preferably by sulfonic and sulphuric acids these catalysts give very high yields in alkyl testers, but the reactions are slow, requiring typically temperatures above 100°C and more than 3 h to reach complete conversion [12].



R' = carbon chain of the fatty acid
R = alkyl group of the alcohol

Fig.4.1- Acid-Catalyzed Transesterification

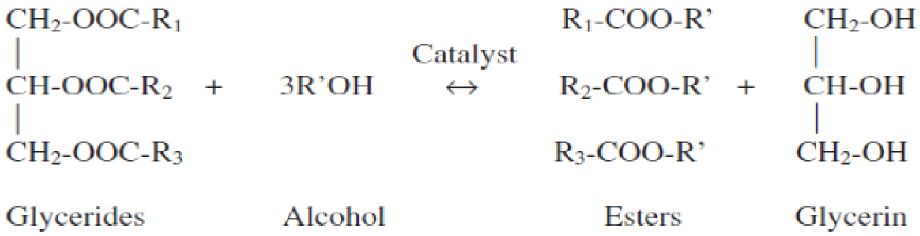
The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 4.1. for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the tester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new tester IV, and to regenerate the catalyst H+ [23].

4.2.2.2 Base-Catalyzed Transesterification

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. [26] The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure 3.

The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate, from which the alkyl tester and the corresponding anion of the diglyceride are formed [28]. The latter deprotonates the catalyst, thus regenerating the active species, which is now Table to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl testers and glycerol [23].

Alkaline metal alkoxides (as CH_3ONa for the metanalysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes [22].



$$\begin{array}{ccccccc} CH_2\text{-}OOC\text{-}R_1 & & & & R_1\text{-}COO\text{-}R' & & CH_2\text{-}OH \\ | & & & \text{Catalyst} & & & | \\ CH\text{-}OOC\text{-}R_2 & + & 3R'OH & \leftrightarrow & R_2\text{-}COO\text{-}R' & + & CH\text{-}OH \\ | & & & & & & | \\ CH_2\text{-}OOC\text{-}R_3 & & & & R_3\text{-}COO\text{-}R' & & CH_2\text{-}OH \\ \text{Glycerides} & & \text{Alcohol} & & \text{Esters} & & \text{Glycerin} \end{array}$$

Fig. 4.2 Base-Catalyzed Transesterification Reaction

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, from triglycerides diglyceride is obtained, from diglyceride monoglyceride is produced and in the last step, from monoglycerides glycerin is obtained. In all these reactions esters are produced. [21].

$$\text{Triglycerides (TG)} + \text{R}'\text{OH} \underset{k_2}{\overset{k_1}{\leftrightarrow}} \text{Diglycerides (DG)} + \text{R}'\text{COOR}_1,$$

$$\text{Diglycerides (DG)} + \text{R}'\text{OH} \underset{k_4}{\overset{k_3}{\leftrightarrow}} \text{Monoglycerides (MG)} + \text{R}'\text{COOR}_2,$$

$$\text{Monoglycerides (MG)} + \text{R}'\text{OH} \underset{k_6}{\overset{k_5}{\leftrightarrow}} \text{Glycerin (GL)} + \text{R}'\text{COOR}_3.$$

Fig.4.3- Sequence Reaction of Transesterification Process

Process variables

The most relevant variables in the process of Transesterification are as follows:

- Reaction temperature - Ratio of alcohol to vegetable oil
- Amount of catalyst
- Mixing intensity (RPM)
- Raw oils used
- Effect of free fatty acid and moisture content.[29]

Reaction temperature:

The reaction is conducted close to the boiling point of respective alcohol (60–70ºC) at atmospheric pressure for a given time.

The maximum yield of esters occurs at temperatures ranging from 60 to 80ºC at a molar ratio of (alcohol to oil) 6:1.[29]

The ratio of alcohol to vegetable oil:

The stoichiometry of transesterification reaction requires 3 mol of alcohol per mol of triglyceride to yield three mol of fatty ester and 1 mol of glycerol.

The molar ratio has no effect on acid or saponification.

Excess of alcohol is required to drive the reaction to the right. A molar ratio of 6:1 is used in industries. The best is between 9:1 and 12:1.

High molar ratio effects the separation of glycerin due to increase in solubility driving equilibrium to left lowering the yield of esters.[29]

Amount of catalyst:

The catalyst used for the transesterification of triglycerides is as alkali, acid, enzyme or heterogeneous catalysts.

If the oil has high free acid content and more water, acid catalyst H2SO4, H3PO4, HCl is suitable.

Alkali catalyst is more suitable as the reaction occurs 4000 times faster than in acidic catalyst.

Alkali catalyst is less corrosive to industrial equipment's.

The concentration in the range 0.5–1.0% (w/w) has found to yield 94–99% conversion of vegetable oils into ester. [24]

Mixing intensity (RPM):

Mixing is very important as oils or fats are immiscible with NaOH–MeOH or any other catalyst –alcohol solution.

Once mixed and the reaction is started stirring is not required. For e.g.-The yield of methyl esters at 360 rpm and 600 rpm are same after 3 hours of reaction. [29]

Raw oils used*:*

Since different types of vegetable oil and animal fats may contain different types of fatty acids, the fuel related biodiesel properties are generally affected by the choice of raw materials.

The length and the degree of saturation of the fatty acid alkaline chain affects properties such as cetane number, oxidation and cloud point.

The final physical properties of the biodiesel will depend on the properties of the component free fatty acids present and this allows biodiesel to be formulated and selected to have a specific property. It also determines the yield product derived from the respective raw material.[29]

4.2.3 Lipase catalyzed transesterification

Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any coenzymes, are reasonably stable, and often tolerate organic solvents. Their potential for regioselective and especially for enantioselective synthesis makes them valuable tools [24].

4.2.3 Pyrolysis

The pyrolysis refers to a chemical change caused by the application of thermal energy in the absence of air or nitrogen. The liquid fractions of the thermally decomposed vegetable oils are likely to approach diesel fuels. The pyrolyzate has a lower viscosity, flash point, and pour point than diesel fuel and equivalent calorific values. The cetane number of the pyrolyzate is lower. The pyrolyzate vegetable oils contain acceptable amounts of sulfur, water and sediments and give acceptable copper corrosion values but unacceptable ash, carbon residual and pour point. Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis and flash pyrolysis.

4.3 Purification of Biodiesel

Biodiesel produced by transesterification process need to wash to get pure bio diesel. There are two processes by which this could be done.

4.3.1 Wet washing

Wet washing of biodiesel involves washing with distilled water, acidic water and water with organic solvent. Wet washing removes soluble impurities as residual catalyst, methanol, soap and glycerol.

Wet washing with distilled water:

Chongkhong et al. [25] conducted an experimental neutralization technique instead of distillation to purify the transtesterified product. The process was carried out using 3M of sodium hydroxide in water. Then 2%wt. of sodium chloride was dissolved in the solution to remove the soap formation. Water at 60-80°C was used to wash the tester phase which was allowed to settle and then heated to evaporate residual water.

Wet washing with acidic water and water with organic solvent:

To get purified biodiesel, Siler-Marinkovic and Tomasevic treated a reaction mixture mainly consisted of methyl esters and glycerol obtained by acid-catalyzed transesterification of sunflower oil catalyzed by sulfuric acid. This mixture was filtered, washed first with petroleum ether and then four times with water until the wastewater was neutral [27].

4.3.2 Dry Washing

Dry washing removes contaminants from crude biodiesel by adsorption or passing crude biodiesel through a bed of ion-exchange resin. Most operating procedure of dry washing of biodiesel has been developed by trial and error [28].

Different adsorbent materials are used for treating crude biodiesel, such as magnesium silicate (Magnesol), calcium magnesium silicate, and cheap bio-sorbents.

Also, different types of ion-exchange resins are applied for waterless refining of crude biodiesel. Usually, small styrene beads coated with polar functional groups are employed.

CHAPTER 5: EXPERIMENTAL STUDY ON BIODIESEL PRODUCTION

Biodiesel production is the process of producing the biofuel, biodiesel, through the chemical reactions transesterification and esterification This involves vegetable or animal fats and oils being reacted with short-chain alcohols (typically methanol or ethanol).
the experimental study has been carried out inthree sequential stages (1) collection of WCO feedstock and testing of properties (2) Optimization and production of biodiesel samples, (3) determination of their physical and chemical properties, and (4) engine tests.

In this study, transesterification method is preferred for biodiesel production. Two different types of used vegetable oils (soybean, sunflower) were collected and 1:1 mixture of used soybean oil and used sunflower oil is used as feedstock in this study.
The oils were collected from university canteen. The density of the feedstock (mixture of oil) was measured by the use of beam balance and specific gravity bottle. The kinematic viscosity was measured with the help of Ostwald Viscometer at 40 °C with water as a reference liquid. The free fatty acid (FFA) contain of the feedstock was also measured because if FFA is more than 2%, the FFA level of the oil has to be reduced by esterification to avoid soap formation in transesterification [6A].

5.1 Pre-Processing of WCO Feedstock

Feedstock like used vegetable oil or say waste cooking oil (WCO) requires the removal of impurities before it is used for Transesterification. Waste cooking oil was collected from college canteen, KOH pellets and CH3OH are both available in the laboratory.
The waste cooking oil collected from the canteen was dirty, solid particles and dust contaminated in it. The main drawback of using WCO as a feedstock in biodiesel production is the presence of unwanted contents, such as FFA, water and other solid impurities.

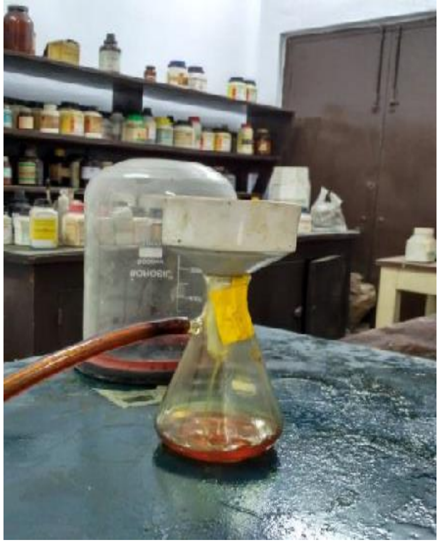


Fig 5.1: Vacuum filtration

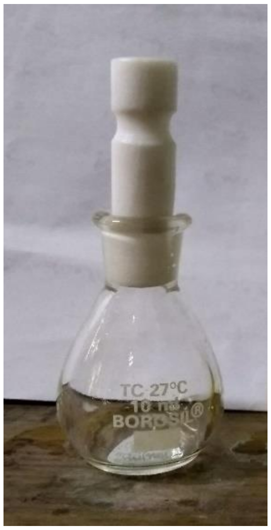


Fig.5.2- Specific gravity bottle

Steps to remove unwanted particles and water are mentioned below.

- WCO sample is heated to above 100°c in air oven for 30 minutes to eliminate water content.
- Then WCO is passed through waste cotton to filter (Fig 3.1) the larger food particles.
- After this process, only the black carbon particles are left. This was removed through vacuum filtration technique.

5.2 Density measurement of WCO:

The density of WCO sample is measured by specific gravity bottle of 10 ml shown in Fig.4.2.

Weight of empty beaker = 18.970 gm Volume of oil taken = 10 ml

Weight of the filled bottle = 28.234 gm

Wight of 10 ml Oil = 28.234-18.970 = 9.264 gm

Hence density = 9.264/10 = 0.9264 gm/ml

5.3 Measurement of free fatty acid (FFA%):

The average molecular weight of soybean oil = 920 g/mol

The average molecular weight of sunflower oil = 876 g/mol

The average molecular weight of 1:1 mixture of sunflower oil and soybean oil

$$= \frac{920+876}{2} = 898 \text{ g/mol}$$

Density of the oil = 0.9264 g/ml

Molecular weight of potassium hydroxide = 56.1 g/mol

Acid value = $\frac{56.1 \times V \times N}{W}$

Where, V = Volume in mL of standard potassium hydroxide solution.

N = Normality of the potassium hydroxide solution

W = Weight in gm of the sample

Prepare 1-gram KOH dissolved in one liter distilled water. So, the normality of the KOH solution = (1/56.1) N. take 1ml of WCO sample (W=1×0.9264 g). Mix the oil with 10 ml isopropyl alcohol properly, add four drops of phenolphthalein used as colour indicator. Now add the KOH solution drop by drop by the use of a burette. Note down the amount of KOH volume (V) required to neutralize the oil sample by observing the change in colour. Volume of KOH solution required in the experiment (i) V= 0.8 ml

(ii) V= 0.9 ml

Average volume required = 0.85 ml

So, Acid value = $\frac{56.1 \times 0.85 \times (\frac{1}{56.1})}{0.9264}$ = 0.9175 mg KOH / gm

Acid value = FFA%×1.99

FFA% = $\frac{\text{Acid value}}{1.99} = \frac{0.9175}{1.99}$ = 0.461%

As the FFA% is less than 2%, acid esterification is not needed, direct transesterification reaction can be done for biodiesel production by the use of alkaline catalyst [6].

Methyl alcohol (CH_3OH) as alcohol and potassium hydroxide (KOH) as a catalyst were used in the production of biodiesel samples. The parameters like amount of methanol, amount of KOH, reaction time and temperature were optimized so that the production of the biodiesel yield can be maximized.

Calculation of raw materials:

Calculation of raw materials used for biodiesel production. A sample calculation is given here.

Volume of WCO sample = 100 ml.

Density of WCO sample = 0.9264 g/ml.

Weight of 100 ml WCO = 100×0.9264 = 92.64 gm.

Molecular weight of WCO sample = 898 g/mol.

Molar ratio, methanol: oil = 9:1

It implies that 1 mol of oil requires 9 mol of alcohol.

Molecular weight of methanol = 32 g/mol.

898 gm of oil requires 9×32 gm of methanol

92.64 gm of oil requires 9×32×92.64/898= 29.698 g of Methanol

Density of methanol= 0.7918 g/ml

Volume of methanol required= 29.698/0.7918= 37.5 ml

KOH is taken 1% w/w of oil

This implies, 100gm of oil requires 1gm of KOH

So, 92.64 gm of oil will require 92.64/100= 0.9264 gm of KOH

Hence, for the reaction- Amount of oil= 100ml

Amount of methanol = 38 ml (for molar ratio 6:1)

Reaction temperature = 55°C Amount of KOH= 0.9264 g (for 1%w/w)

Reaction time = 120 minute

Results

From the above experiment, the product obtained from 100ml WCO.

Amount of glycerin from sunflower biodiesel = 23 ml.

Amount of crude biodiesel obtained = 110 ml.

Amount of Biodiesel yield after purification = 94 ml.

5.4 Procedure for biodiesel production:

Step 1:

After calculation, measured 0.9264 gm of KOH pallet in digital weighing machine and put that in a laboratory flask.

Step 2:

Measured 38 ml methanol in a graduated cylinder and pour that to the same laboratory flask by the help of a funnel.

Step3:

Laboratory flask contained methanol and KOH. A magnetic stirrer put into the flask. Then the flask put on the plate of the magnetic stirrer machine. KOH and Methanol solution mixed for 15 minutes at magnetic stirrer machine.

Fig 5.5: Methanol and KOH Mixing

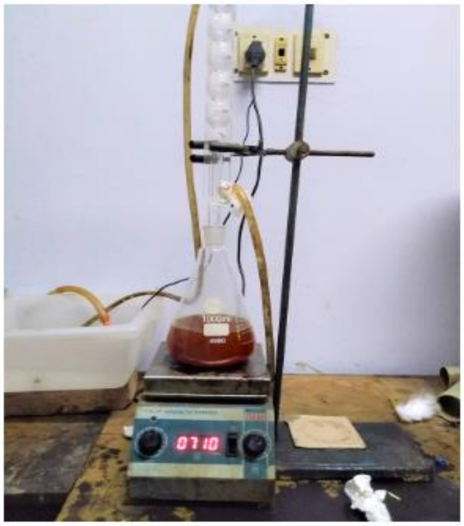


Fig 5.6: Transesterification with heating and stirring

Step 4:

After 15 minutes 100 ml waste cooking oil has been poured to the laboratory flask and maintained the required temperature, wait till the reaction time for completion of the reaction.

Transesterification has been done by the help of a magnetic stirrer machine. This machine has been used to rotate the mixture above 700 rpm and helped to mix the sunflower oil and methanol. In magnetic stirrer machine there is a hot plate on which the laboratory flash has been fixed. Hot plate temperature in this case has been maintained to 55 degree centigrade.

Separation in separating funnel

The product mixture obtained from the laboratory flask is kept for settling in a separating flask for 10-12 hours i.e. overnight to separate glycerin from accurately. As the glycerin is denser than biodiesel, it settles at the bottom creating a perfect separating layer. The glycerin is then separated carefully by a controlling knob and the glycerin is taken out carefully and is measured by a measuring cylinder. The glycerin is obtained is brownish in color.

After the glycerin separation the crude biodiesel is taken out from the same outlet for further purification.

Fig 5.7: Separation of biodiesel and glycerin

Purification of Biodiesel

Transesterification reaction is a reaction that is widely considered and mostly adopted to produce commercial biodiesel. The trans esterified products undergo different purification techniques in order to purify biodiesel from glycerol and other by-products. The main objective of biodiesel washing is to remove free glycerol, soap, excess alcohol, and residual catalyst. Water washing is generally carried out to remove soap, catalyst, methanol and other contaminants from biodiesel, using deionized water.

Distilled water at 60 °C was used for biodiesel washing. Biodiesel after separation has been collected in a beaker along with the heated water and air is passed by means of the aquarium air pump that creates bubbles inside the water with the help of aquarium stone. Thus, the impurities, catalyst and methanol are dissolve into the water. After that it is put into the separating funnel for separation and collection of pure biodiesel.

3 sets of washing are done for one batch of crude biodiesel. This amount of washing is sufficient for the removal of excess catalyst, free fatty acids and glycerol molecules inside biodiesel. Acidity of the waste water is tested by litmus paper and the purification done till the pH of the waste water is around 7.

The biodiesel thus produced is free from catalyst, free fatty acid, and excess methanol and glycerol particles. But the biodiesel may contain moisture as it was subjected to water previously, so a heating or any other form of de-moisturization facility is needed in this regard.

Remove moisture from biodiesel

After washing, the moisture present in the biodiesel has to be removed as presence of moisture decreases the flash point and calorific value of the fuel. It also increases the viscosity of the fuel.

So, the biodiesel has been poured in to beaker and placed that inside an air oven. The biodiesel is heated at 100°C in an air oven for 10hours to remove any kind of moister. The biodiesel becomes transparent after heating.

Chapter 6: Optimization of biodiesel production from waste cooking oil

In this study, the feedstock used is a mixture of used soybean oil and used sunflower oil 1:1 ratio. The aim of this study is to optimize the process parameters of the alkali catalyzed transesterification reaction for obtaining maximum FFA conversion. Parameters such as reaction temperature, duration of reaction, concentration of acid catalyst, molar ratio of oil to methanol and agitation speed were considered for their impacts on the process and affects the yield. The method used for optimization is well known as 'One Factor at a Time' (OFAT). Taking one factor, varying this while the other factors are constant. Take the best result of that factor for maximum yield. Now this best result will be constant, take another factor and do the same. By doing this one by one we get the optimized results of all the factors. We get the maximum yield at optimum condition.

Different values or levels for each parameter of factor were examined by optimizing one factor at a time. The different levels for each factor given below.

Parameter/Factor	Levels
Reaction temperature (°C)	45, 50, 55, 60
Methanol to oil molar ratio	6:1, 9:1, 12:1
Reaction time (minute)	60, 90, 120
Amount of KOH (%wt./wt.)	0.5, 0.75, 1, 1.25

6.1 Effects of reaction temperature on the yield

Transesterification can occur at different temperatures, depending on the properties of oils. Transesterification of WCO oil was carried out using methanol as alcohol and KOH as alkaline catalyst at different reaction temperatures ranged between 45 °C to 60 °C. It was observed that at 55 °C the yield of produced biodiesel was the highest value. Experiments were performed using various reaction temperatures to investigate the influence of these temperatures on the yield. As displayed in Fig. 5a, catalyst concentration of 1 wt.%, a methanol-to-oil molar ratio of 6:1, reaction time of 120 min, and reaction temperatures of

45, 50, 55 and 60 °C. the yields produced were 91%, 92%, 93% and 89% respectively. As displayed in Fig. 5a, catalyst concentration of 1 wt.%, a methanol-to-oil molar ratio of 9:1, reaction time of 120 min, and reaction temperatures of 45, 50, 55 and 60 °C. the yields produced were 88%, 91%, 94% and 90% respectively. An increase in the temperature from 45 to 55 °C caused a substantial increase in yield and then decrease when the temperature was further increased to 60 °C.

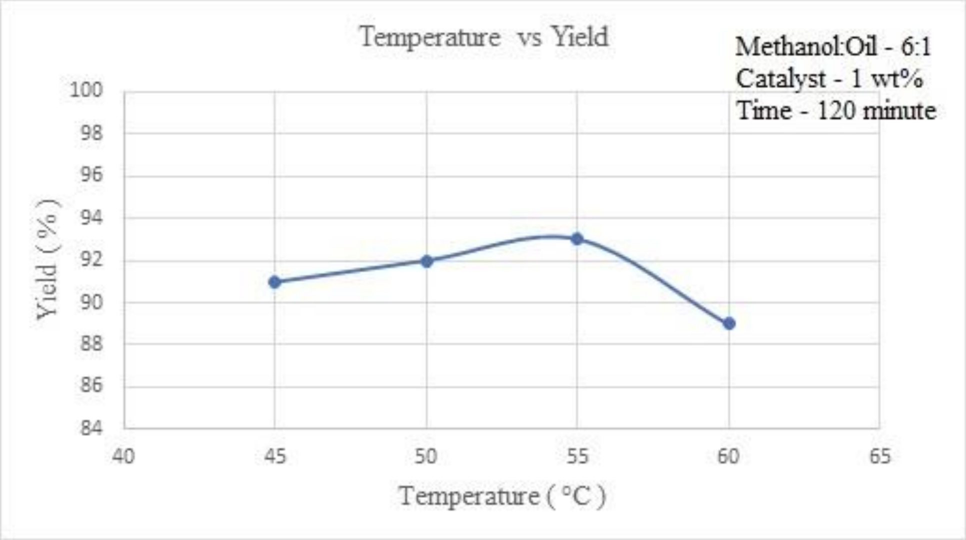


Fig.6.1.1: Temperature vs Yield graph

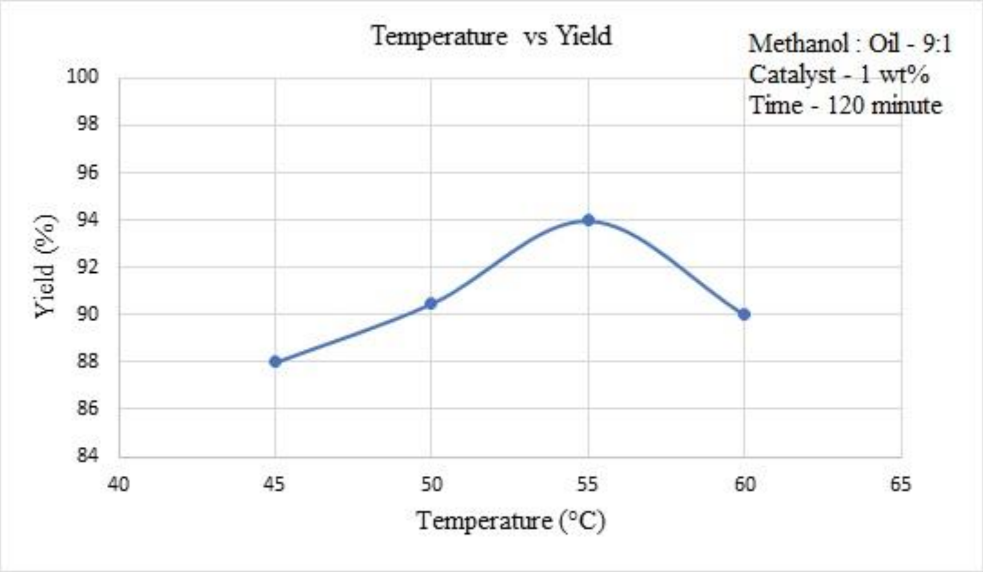


Fig.6.1.2: Temperature vs Yield graph

6.2 Effects of molar ratio of methanol/oil on the yield

Experiments were performed using various methanol-to-oil molar ratios to investigate the influence of these ratios on the yield. catalyst concentration of 1 wt.%, a reaction temperature of 55 °C, a reaction time of 120 min, and methanol-to-oil molar ratios 6:1, 9:1 and 12:1. As displayed in Fig. 4a, an increase in the molar ratio from 6 to 9 caused a substantial increase in yield from 93% to 94% and then the yield decreased from 94% to 92%. Same experiments were done at different temperature 60 °C and the results as illustrated in Fig. 4b, an increase in molar ratio from 6 to 9 caused a substantial increase in yield from 89% to 91% and then the yield decreased from 91% to 90% when the molar ratio increased from 9 to 12. The molar ratio 9 is the most suitable, the better yields were achieved at 9:1 mole ratio (methanol: oil) and there was no increasing in production yield when higher mole ratios were used. This means that 9:1 mole ratio provides sufficient excess of methanol to shift transesterification equilibrium toward biodiesel product.

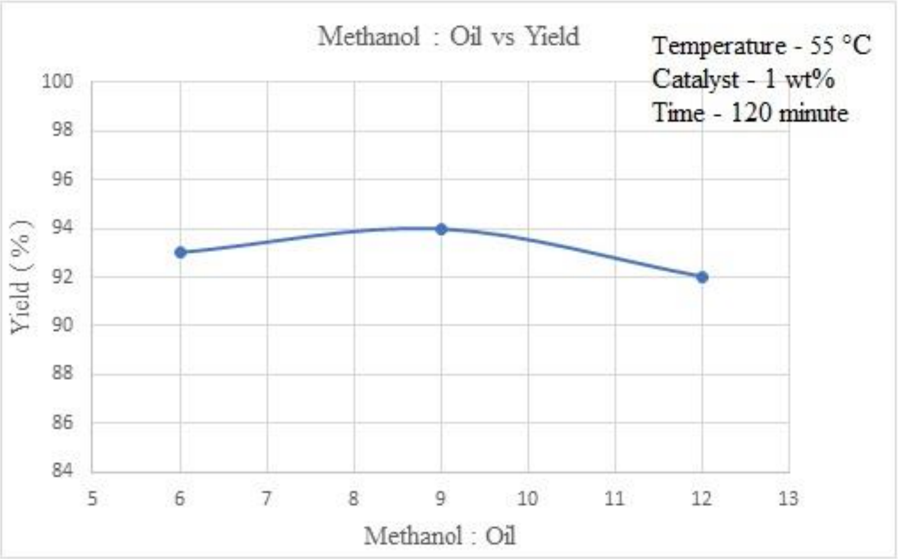


Fig 6.2.1: Molar ratio vs Yield graph

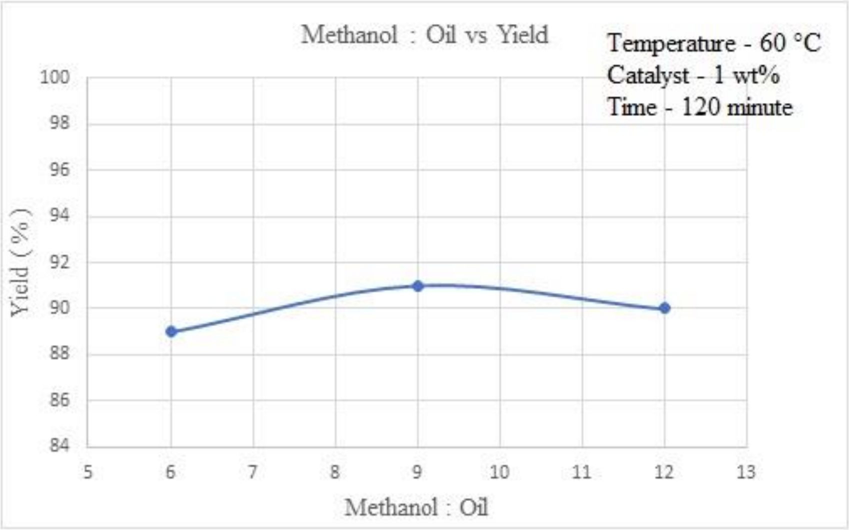


Fig 6.2.2: Molar ratio vs Yield graph

6.3 Effects of reaction time on the yield

Experiments were performed using various reaction times to investigate the influence of these reaction times on the yield. The experiments were carried out by using KOH as catalyst concentration of 1 wt.%, a reaction temperature of 55 °C, a methanol-to-oil molar ratio of 9:1, and reaction times of 60, 90 and 120 minutes. As displayed in Fig. 3a, the yields produced were 92%, 95% and 95% respectively. An increase in reaction time from 60 to 90 min caused a substantial increase in the yield and then a decrease in yield from 90 to 120 minute.

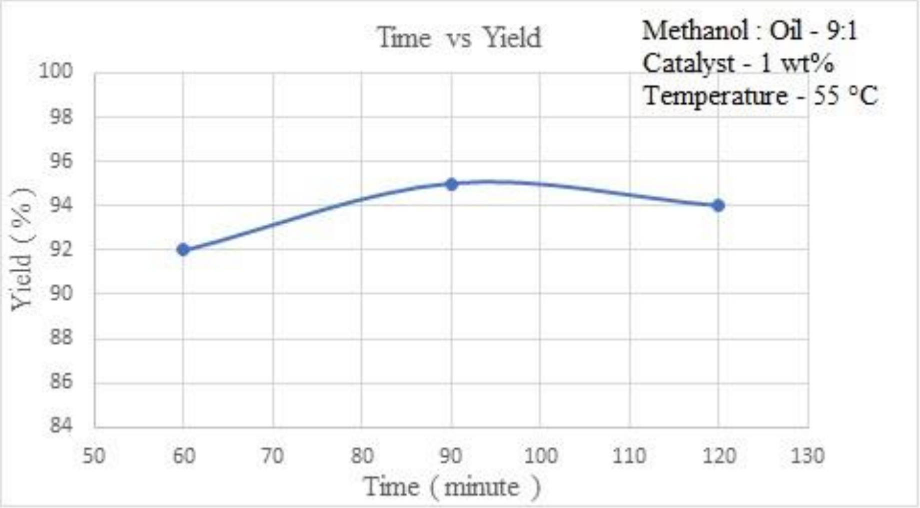


Fig 6.3: Time vs Yield graph

6.4 Effect of (KOH) Catalyst Amount on the yield

Experiments were performed using various catalyst amounts to investigate the influence of these catalyst amounts on the yield. Under the optimum values of temperature 55°C, methanol: oil mole ratio 9:1 and the reaction time 90 minutes, production yield of WCO biodiesel was examined by using different amounts of KOH. The fractions of the catalyst were 0.5 wt.%, 0.75 wt.%, 1 wt.% and 1.25 wt.%. As displayed in Fig. 2a, the yields produced were 93%, 92%, 95% and 90% respectively. It was observed that 1 wt.% KOH to WCO oil was enough to catalyze the transesterification process and gave desired alkaline medium. The yield decreased by 1 % from 93% to 92% as the catalyst amount increased from 0.5 wt.% to 0.75 wt.% respectively. Then the yield increased as the catalyst amount increased from 0.75 wt.% to 1.0 wt.%, and then decreased as the catalyst amount further increased from 1.0 wt.% to 1.25 wt.%. Therefore, the highest production yield was obtained at 1 wt.% KOH and the yield amount is 95% as shown in figure (3).

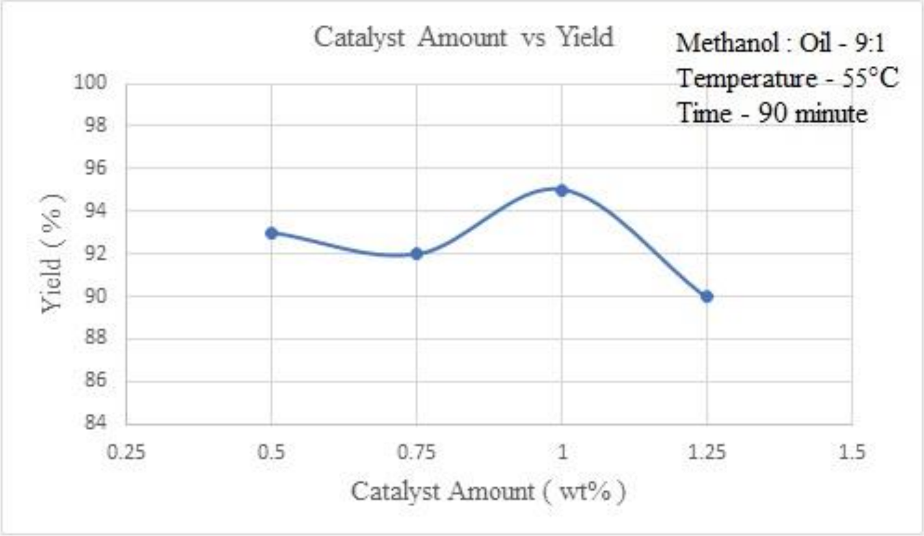


Fig 6.4: Catalyst amount vs Yield graph

Chapter 7: Property testing of the biodiesel

To ensure quality biodiesel, there are standards for testing the fuel properly to see that it meets specifications for use. ASTM (an international standards and testing group) has a method to legally define biodiesel for use in diesel engines, labeled ASTM D751.

Density, Kinematic viscosity at 40°C, Flash point, Fire point, Calorific value, Cetane number, Acid value, Cloud point, Pour point.

7.1 Density of Biodiesel

The fuel density affects engine calibration and power as the fuel mass injected/stroke varies with fuel density. High-density fuels also have a higher viscosity thus, influence injection characteristics. Increase in the fuel density advances the dynamic injection timing by up to 1°CA. Thus, the fuel density affects engine combustion and emissions. PM (particulate matter) emissions generally increase with increase in fuel density.

Or If density increase, viscosity of fuel also increases so high viscosity fuel resulting in larger fuel droplets. If fuel droplets are large that result in incomplete combustion of fuel, so efficiency definitely decreases.

density measurement of diesel:

Weight of empty beaker = 18.19268 g Volume of oil taken = 10 ml

Weight of the filled beaker = 26.40368 g

Wight of biodiesel = 26.40368 – 18.19268 = 8.211 g

Hence density = $\frac{8.211}{10}$ = 0.8211 gm/ ml ≈ 0.82 g/ml

density measurement of WCO biodiesel:

Weight of empty beaker = 18.19268 g Volume of oil taken = 10 ml

Weight of the filled beaker = 27.81533g

Wight of biodiesel = 27.70533 – 18.96387 = 8.74146 g Hence density = $\frac{8.74146}{10}$ = 0.874146 gm/ ml ≈ 0.8742 g/ml

7.2 Kinematic Viscosity at 40 °C

The viscosity of biodiesel is slightly on the higher side as compared to ULSD. As a result of that higher viscosity creates difficulties in atomization at the injector outlet during combustion process. It varies from 2.7 to 6.0 centistokes as compared to 1.3 to 2.4 of ULSD. So, biodiesel used in Compression Ignition engines in blended form and at slightly elevated temperatures to reduce the viscosity to some extent. Ostwald viscometer (shown in Fig 4.3) has been used to measure the viscosity of the oil. Ostwald viscometer, also known as U-tube viscometer or capillary viscometer is a device used to measure the viscosity of the liquid with a known density. The method of determining viscosity with this instrument consists of measuring the time for a known volume of the liquid (the volume contained between the marks A and B) to flow through the capillary under the influence of gravity. Ostwald viscometers named after the German chemist Wilhelm Ostwald (1853- 1932).

The instrument must first be calibrated with materials of known viscosity such as pure (deionized) water. Knowing the value of viscosity of one liquid, one can calculate the viscosity of other liquid.

$$\eta = \eta_o \left(\frac{t \times \rho}{t_o \times \rho_o} \right)$$

Where,

η and η_0 are the coefficient of viscosity of liquid and water, ρ and ρ_0 are densities of liquid and water, respectively.

t and t_0 are the time require to outflow the liquid and water respectively.

Water is passed through the capillary and three readings are taken of the time water takes to fall from the upper mark to the lower mark.

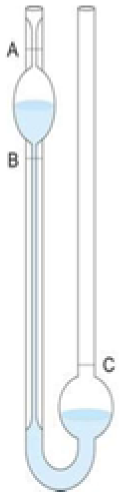


Fig 5.3: Oswald Viscometer

The apparatus has to be dried before pouring biodiesel into it. Then biodiesel produced from used vegetable oil is passed through the viscometer's capillary.

Two or more readings are taken of the time biodiesel takes to fall from the upper mark to the lower mark.

Viscosity of diesel:

Time taken by water to fall from the upper to the lower mark = 43.96 sec

= 44.14 sec

= 43.80 sec

Average time taken = 43.97 sec

Time taken for diesel to fall from upper to lower mark = 241.49 sec

= 240.30 sec

= 242.06 sec

Average time taken = 241.28 sec

Density of diesel = 0.821 gm/cc

Density of water = 1 gm/ cc

Kinematic viscosity of water at 40°C = 0.658 centistokes.

Kinematic viscosity of diesel = $\frac{0.658\times241.28\times0.821}{43.97\times1}$ = 2.964 centistokes.

Dynamic Viscosity of diesel = (2.964×0.821) = 2.434 mPa-sec

Viscosity of WCO biodiesel:

Average time taken by water to fall from the upper to the lower mark = 43.97 sec

Kinematic viscosity of water at 40°C = 0.658 centistokes.

Density of water = 1 gm/ cc

Time taken for biodiesel to fall from upper to lower mark = 368.24 sec

= 369.11 sec

= 368.05 sec

Average time taken = 368.46 sec

Density of biodiesel = 0.8742 gm/cc

Kinematic viscosity of biodiesel = $\frac{0.658\times368.46\times0.8742}{43.97\times1}$ = 4.82 centistokes.

Dynamic viscosity of sunflower biodiesel = (4.82×0.8742) = 4.214 mPa-sec.

7.3 Flash point and fire point

The fire point of a fuel is the lowest temperature at which the vapour of that fuel will continue to burn for at least 5 seconds after ignition by an open flame. At the flash point, a lower temperature, a substance will ignite briefly, but vapor might not be produced at a rate to sustain the fire.

Fig 7.3: Apparatus for Flash and Fire point measurement

Flash point and Fire point were tested in the laboratory by means of a Flash point testing apparatus, shown in the apparatus consists of a motor, a cup to hold biodiesel, an internal heater and a thermometer of range 3000°C to register the temperature rise. The cup is filled with biodiesel up to a certain mark, as the motor is stirred continuously it causes development of heat inside the biodiesel. There is a provision to introduce fire in the biodiesel.

When the thermometer reading crosses 1000°C, fire is introduced at every 50°C of temperature rise and condition of the introduced fire is observed. If the fire gets engulfed in the biodiesel, it denotes the flash point of the biodiesel. The point where the fire continues to burn denotes the fire point of the biodiesel. If the flash point misses out and fire point is reached then the experiment has to be performed again within those degrees of rise in temperature.

diesel:

Flash point: Fire gets engulfed in the diesel = 56 °C

Fire point: Flame continues to burn = 67 °C

WCO biodiesel:

Flash point: Fire gets engulfed in the sunflower biodiesel = 178 °C

Fire point: Flame continues to burn = 196 °C

7.4 Calorific value

The calorific value (heat of combustion) of a sample is defined as the number of heat units liberated by a unit mass of a sample when burned with oxygen in an enclosure of constant volume. Ramirez-Verduzco et al. revealed that the calorific value increased due to the increase in molecular weight decreased due to the number of double bonds increases [26]. In general, a high calorific value is desirable since it is indicative of the energy content of the fuel. Calorific value is tested in the laboratory with the help of a bomb calorimeter. Heats of combustion as determined in an oxygen bomb calorimeter are measured by a substitution procedure in which the heat obtained from the sample is compared with the heat obtained from combustion of a similar amount of benzoic acid or other standardizing material whose calorific value is known. These measurements are obtained by burning a representative sample in a high-pressure oxygen atmosphere within a metal pressure vessel or bomb.

The energy released by this combustion is absorbed within the calorimeter and the resulting temperature change within the absorbing medium is noted. The heat of combustion of the sample is then calculated by multiplying the temperature rise in the calorimeter by a previously determined energy equivalent or heat capacity determined from previous tests with benzoic acid.

Four essential parts are required in any bomb calorimeter:

1. Bomb or vessel in which the combustible charges can be burned.
2. Bucket or container for holding the bomb in a measured quantity of water, together with a stirring mechanism.
3. An insulating jacket to protect the bucket from transient thermal stresses during the combustion process.
4. Thermocouple for measuring temperature changes within the bucket.

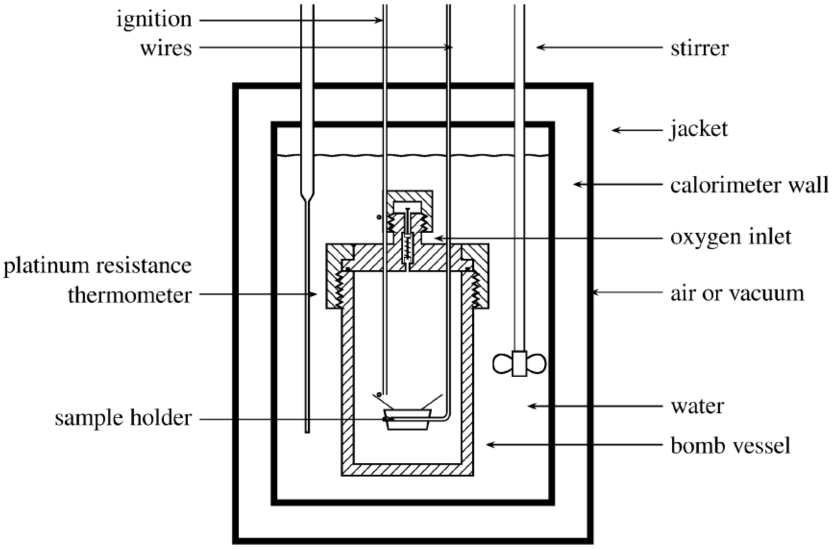


Fig 7.4: Bomb Calorie Meter Schematic Diagram

Fig 7.5: Bomb

Fig 7.6: Bomb Calorimeter

Before a material with an unknown heat of combustion can be tested in a bomb calorimeter, the energy equivalent or heat capacity of the calorimeter must first be determined. This value represents the sum of the heat capacities of the components in the calorimeter, notably the metal bomb, the bucket and the water in the bucket. The amount of heat introduced by the reference sample is determined by multiplying the heat of combustion of the standard material by the weight of the sample burned. Then, by dividing this value by the temperature rise produce in the test, we obtain a resultant energy equivalent for this particular calorimeter.

Mass of benzoic acid = 2.215 gm

Standard heat of combustion of benzoic acid = 26.454 MJ/ kg = 26454 J/g

Temperature rise due to the combustion of benzoic acid = 2.08 °C

Energy equivalent of the calorimeter = $\frac{26454\times 2.215}{6.22}$ = 9420.516 J/°C

As the energy equivalent of the calorimeter is known, now it is easy for us to determine calorific value of any fuel o known mass. The fuel sample taken in a container is burnt inside the bomb and the resultant temperature change is recorded. The calorific value of the sample of unit weight for the particular temperature rise is calculated by multiplying the temperature rise with the energy equivalent of the calorimeter and dividing it by the mass of the sample. A small mass correction is made as some amount of unburnt carbon is left in the container.

WCO biodiesel:

Weight of the empty crucible = 7.842 g

Weight of the crucible with oil = 9.511 g

Weight of the crucible after combustion = 7.927 g

Mass of biodiesel burn = 1.584 gm

Temperature rise due to combustion = 6.45 °C

Energy equivalent of the calorimeter = 9415.035 J/°C

Calorific value of biodiesel from WCO = $\frac{9420.516\times 6.45}{1.584}$ = 38360.055 J/gm

= 38360.055 KJ/ kg

7.5 Cetane number

Cetane number is an important parameter in evaluating the quality of biodiesel fuel. Its determination is usually arduous and expensive. In this study the cetane number has been predicted from the calorific value, flash point, kinematic viscosity and density of biodiesel. The cetane number has been derived from a mathematical relationship between viscosity, density, calorific value and flash point.

$$CN = K5 + K4\,\nu + K3\,HV + K2\,FP + K1\,\rho \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\;(1)$$

Where K1, K2, K3, K4, K5 are constants and ν is kinematic viscosity (mm2 /sec), HV is heating value (MJ/kg), FP is flash point (°C), ρ is density (kg/l).

The constants K1, K2, K3, K4 and K5 are calculated by simple substitution method from Table 2 of data given in the paper written by Sivaramakrishna et. al [17].

Table 8.1: Properties of different biodiesel

Biodiesel	Kinematic Viscosity (mm^2/sec) **ν**	Heating value (MJ/kg) **HV**	Flash point (°C) **FP**	Density (kg/l) **ρ**	cetane number
Babassu	3.6	41.15	127	0.875	63
Rapeseed	4.2	41.55	80	0.882	54
Soybean	4.5	41.28	178	0.885	45
Sunflower	4.6	41.33	96	0.860	49
Peanut	4.9	41.71	176	0.883	54
Palm	5.7	41.24	183	0.880	62

The five equations that were formed from the above Table based on equation (1) are:

63 = K5 + 3.6 K4 + 41.15 K3 + 127 K2 + 0.875 K1 ------------------------- (2)

54 = K5 + 4.2 K4 + 41.55 K3 + 80 K2 + 0.882 K1 ---------------------- (3)

45 = K5 + 4.5 K4 + 41.28 K3 + 178 K2 + 0.885 K1 -------------------- (4)

49 = K5 + 4.6 K4 + 41.33 K3 + 96 K2 + 0.860 K1 -------------------- (5)

54 = K5 + 4.9 K4 + 41.71 K3 + 176 K2 + 0.883 K1 -------------------------- (6)

62 = K5 + 5.7 K4 + 41.24 K3 + 183 K2 + 0.880 K1 -------------------- (7)

When these equations are solved, we get the values of K1, K2, K3, K4 and K5.

From equation (2),

-K5 = 3.6 K4 + 41.15 K3 + 127 K2 + 0.875 K1 -63

or, K5 = 63 -3.6 K4 -41.15 K3 -127 K2 - 0.875 K1 --------------------------(8)

From equations (3) and (8),

54 = 63 -3.6 K4 -41.15 K3 -127 K2 -0.875 K1 + 4.2 K4 + 41.55 K3 + 80 K2 + 0.882 K1

or, -9 = 0.6 K4 + 0.4 K3 -47 K2 + 0.007 K1

or, K4 = (-9 -0.4 K3 + 47 K2 -0.007 K1) / 0.6

or, K4 = -15 -0.66 K3 + 78.33 K2 -0.01166 K1 -------------------------(9)

From equations (4), (8) and (9),

45 = 63 -3.6 (-15 -0.66 K3 + 78.33 K2 -0.01166 K1) -41.15 K3 -127 K2 - 0.875 K1
+ 4.5(-15 - 0.66 K3 + 78.33 K2 -0.01166 K1) + 41.28 K3 + 178 K2 + 0.885 K1

or, K3 = (-4.5 -121.497 K2 -0.000494 K1) / -0.464

or, K3 = 9.698 + 261.846 K2 + 0.001064 K1 -------------------------(10)

From equations (5), (8), (9) and (10),

$$49 = 63 -3.6 \{-15 -0.66 (9.698 + 261.846 K2 + 0.001064 K1) + 78.33 K2 - 0.01166 K1\} - 41.15 (9.698 + 261.846 K2 + 0.001064 K1) -127 K2 -0.875 K1 + 4.6\{-15 -0.66 (9.698 + 261.846 K2 + 0.001064 K1) + 78.33 K2 -0.01166 K1\} + 41.33 (9.698 + 261.846 K2 + 0.001064K1) + 96 K2 + 0.86 K1$$

or, $K2 = -0.07224 -0.000347 K1$ ------------------------ (11)

From equations (6), (8), (9), (10) and (11),

$$54 = 63 -3.6 [-15 -0.66 \{9.698 + 261.846 (-0.07224 -0.000347 K1) +0.001064 K1\} + 78.33 (-0.07224 -0.000347 K1) -0.01166 K1] -41.15 \{9.698 + 261.846 (-0.07224 -0.000347 K1) + 0.001064 K1\} -127 (-0.07224- 0.000347 K1) -0.875 K1 + 4.9 [-15 -0.66 \{9.698 + 261.846 (-0.07224 -0.000347 K1) + 0.001064 K1\} + 78.33 (-0.07224 -0.000347K1) -0.01166 K1] + 41.71 \{9.698 + 261.846 (-0.07224 -0.000347 K1) + 0.001064 K1\} + 176 (-0.07224 -0.000347 K1) + 0.883 K1$$

or, $K1 = (54 -35.34958) /-0.032705$ or, $K1 = -57.0262$

Substituting this value of K1 in equation (10) we get, $K2 = -0.05245$

Substituting the value of K1 and K2 in equation (9) we get, $K3 = -4.0964$

Substituting the value of K1, K2 and K3 in equation (8) we get, $K4 = -16.3382$

Substituting the value of K1, K2, K3 and K4 in equation (7) we get, $K5 = 346.943$

As we have got the values of the constants, we can now find out the derived cetane number of our biodiesel in consideration by from the experimentally found values of density, kinematic viscosity, flash point and heating value. From equation 1, CN of WCO Biodiesel

$$CN = K5 + K4\, \nu + K3\, HV + K2\, FP + K1\, \rho$$

$$CN = 346.943 - 16.3382\times4.82 - 4.0964\times38.36 - 0.05245\times178 - 57.0262\times0.8742$$
$$= 51.866568 = 52$$

Table 7.2: Measured properties of Biodiesel

Density,	0.874 gm/cm^3
Kinematic Viscosity at 40°C	4.82 centistokes
Calorific Value	38.36 MJ/ kg
Flash Point	178 °C
Fire Point	196 °C
Cetane Number	52

CHAPTER 8: ENGINE TESTING

Each biodiesel sample (WCO biodiesel) is blended with diesel fuel at different proportions for using as a fuel in engine tests. These mixtures are described in BX form. The X value indicates the volume percentage of biodiesel in the blend, for example, B20 mixture includes 20% biodiesel and 80% diesel.

Similarly, B100 is 100% biodiesel and 0% diesel. Five different mixtures of fuel for each biodiesel sample (B10 mixture and B20 mixture, B30 mixture, B40 mixture and B50 mixture of pure biodiesel) are used in the engine tests as fuel.

The effective characteristics that are brake power (P_b), specific fuel consumption (SFC), engine exhaust gas temperature have been determined in this experiment for different blend of two different biodiesel and normal diesel fuel.

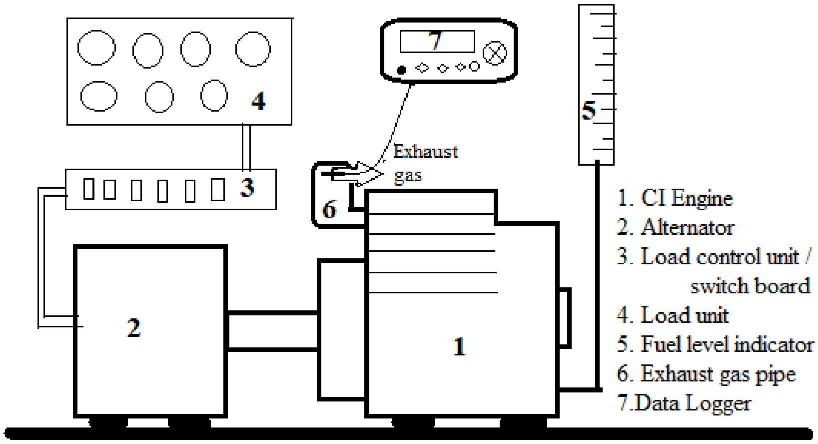


Fig 8.1: Schematic diagram of experimental setup

In the schematic diagram it is clearly shown that a CI engine is coupled with an electric alternator. The engine has been powered by different fuel blend. A fuel level indicator is used to measure the fuel consumption. As the motor is rotated by the CI engine, it is produced electricity. Electricity supplied to the Load unit. In the Load unit, there are few bulb holders which holding bulbs. Bulbs are controlled by the Load control unit. Five 500-watt bulbs, two 200-watt bulbs and one 100-watt bulb are used in this experiment. Fuel consumption has been measured against each Load.

Experimental investigation is carried out on a typical single cylinder, four stroke and constant speed air cooled diesel engine generator. Specifications of the engine are shown below. A Tachometer and a thermometer have been used to measured engine RPM and exhaust temperature.

Table 8.1: Test engine Specification

Model	Z170f
Type	Single cylinder, horizontal,4-stroke
Combustion system	Swirl combustion chamber
Bore*stroke(mm)	70*70
Rated power	2.94kw/4hp
Rated speed(r/min)	2600
Max power	3.23kw/4hp
Cooling method	Air-cooled
Lubrication method	Centrifugal splashing
Starting method	Hand-cranking
Net weight(kg)	44

Fig 8.2: Engine testing setup

8.1 Exhaust Temperature Measurement

About 35% of the total fuel energy is converted to useful work and about 30% of the energy is expelled with the exhaust gas. EGT is an indication of how hot the combustion process is in the cylinders, and the amount of "afterburning" that is occurring in the exhaust manifold. EGT is also directly related to the air/fuel ratio. The richer the air/fuel ratio in a diesel, the higher the EGT will be. Two things can create a rich mixture under heavy loads or at full throttle: the first is too much fuel, and the second is not enough air.

K type thermocouple wire with stainless steel probe at exhaust manifold and other junction which was connected to Data Logger was used to measure exhaust gas temperature.

Calibration of Thermocouple

In order to achieve accurate readings from a thermocouple, it's essential to calibrate the device accordingly. Typically, thermocouples are standardized by using 0 degrees Celsius as a reference point, and many devices can adjust to compensate for the varying temperatures at thermocouple junctions. K type thermocouple is calibrated with respect to a temperature oil bath. Temperature of oil bath was increased from 50°C to 200°C at an interval of 10°c. Corresponding thermocouple temperature was noted.

This result was plotted in a X-Y curve. While TC temperature was kept at X-axis Oil bath temperature was kept at Y axis. Fig shows a straight line which gives the Thermocouple equation

y = 1.0054x - 0.1244

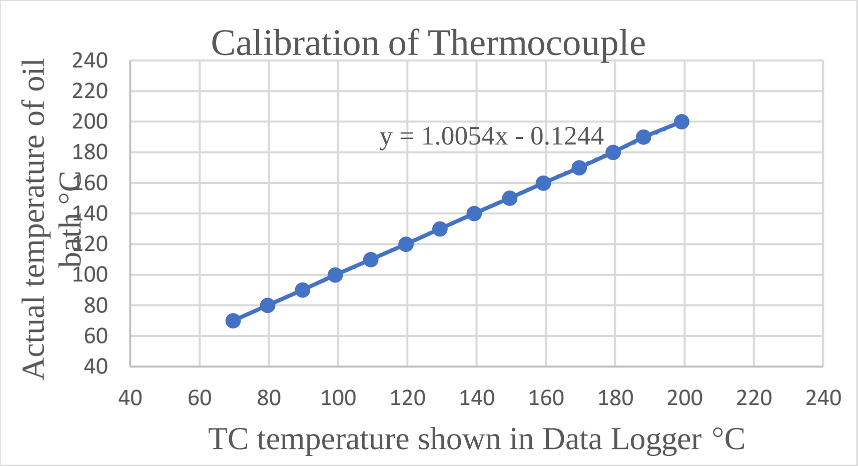


Fig: 8.1.1: Oil bath temperature vs Thermocouple temperature

8.2. Engine performance characteristic For Diesel Fuel

Table 8.2.1: experimental data for diesel fuel

Load (in Watts)	Duration (in minutes)	Oil Consumption (in milliliters)			Speed in RPM	Exhaust Temperature (in °C)	Specific fuel consumption (ml/kW-h)
		Start	Stop	Consumption			
200	10	500	453	47	2052	158	1410
500	10	450	400	50	1980	173	600
1000	10	395	335	60	1920	200	360
1500	10	330	265	65	1840	218	260
2000	10	260	182	78	1880	272	234

Specific fuel consumption (SFC) measures the amount of oil required to develop one kilowatt power. Taking second reading for calculation,

500 watts power developed for 10 mins, consume 50 ml of fuel.

1000 watts power will be produced for 60 mins consume $= \frac{50\times1000\times60}{500\times10}$ = 600 ml of fuel.

So, SFC for 500 watts Load is 600 ml/Kw-h.

In the same way, calculation are done for each reading to calculate SFC.

Also,

Load vs fuel consumption

Load vs Specific fuel consumption (SFC) and

Load vs Exhaust gas temperature has been plotted for each composition of oil experiment, for petroleum diesel, B10, B20, B30, B40 and B50.

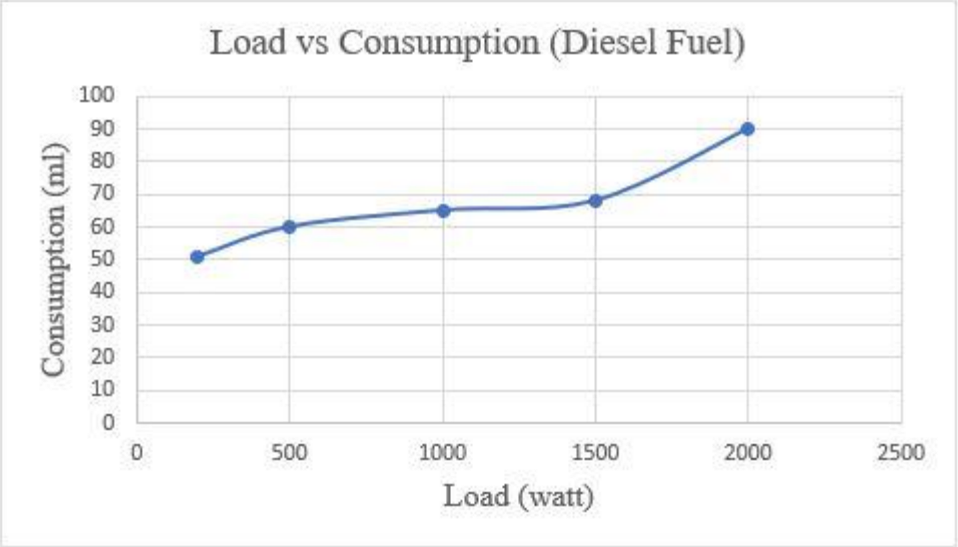


Fig 8.2.1: Load vs consumption graph for diesel fuel.

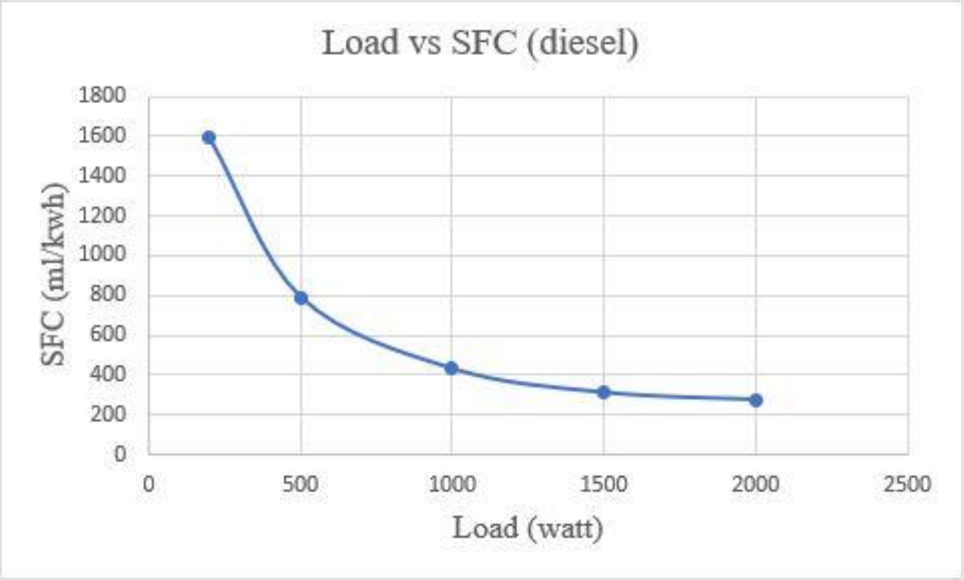


Fig 8.2.2: Load vs SFC graph for diesel fuel.

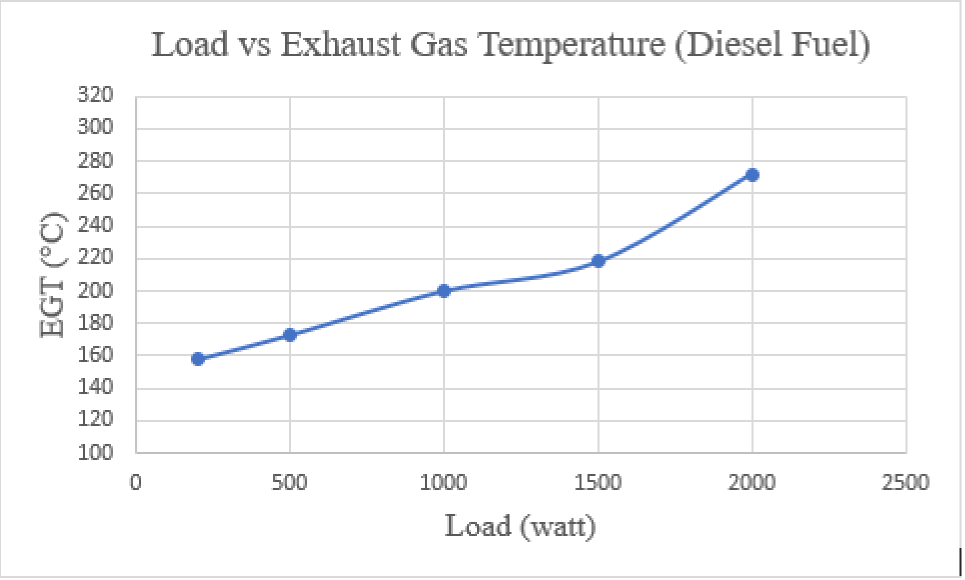


Fig 8.2.3: Load vs exhaust gas temperature graph for diesel fuel.

8.3 Engine performance characteristic for B10 (10% biodiesel, 90% Diesel)

Table 8.3.1: experimental data for B10

Load (in Watts)	Duration (in minutes)	Oil Consumption (in milliliters)			Speed in RPM	Exhaust Temperature (in °C)	Specific fuel consumption (ml/kW-h)
		Start	Stop	Consumption			
200	10	460	412	48	2306	166	1440
500	10	410	355	55	2218	184	660
1000	10	350	284	66	2130	213	396
1500	10	280	208	72	1905	238	288
2000	10	205	123	82	2050	288	246

Specific fuel consumption (SFC) measures the amount of oil required to develop one kilowatt power. Taking second reading for calculation,

500 watts power developed for 10 mins, consume 55 ml of fuel.

1000 watts power will be produced for 60 mins consume = $\frac{55\times1000\times60}{500\times10}$ = 660 ml of fuel.

So, SFC for 500 watts Load is 660 ml/kW-h.

In the same way calculation are done for each reading to calculate SFC.

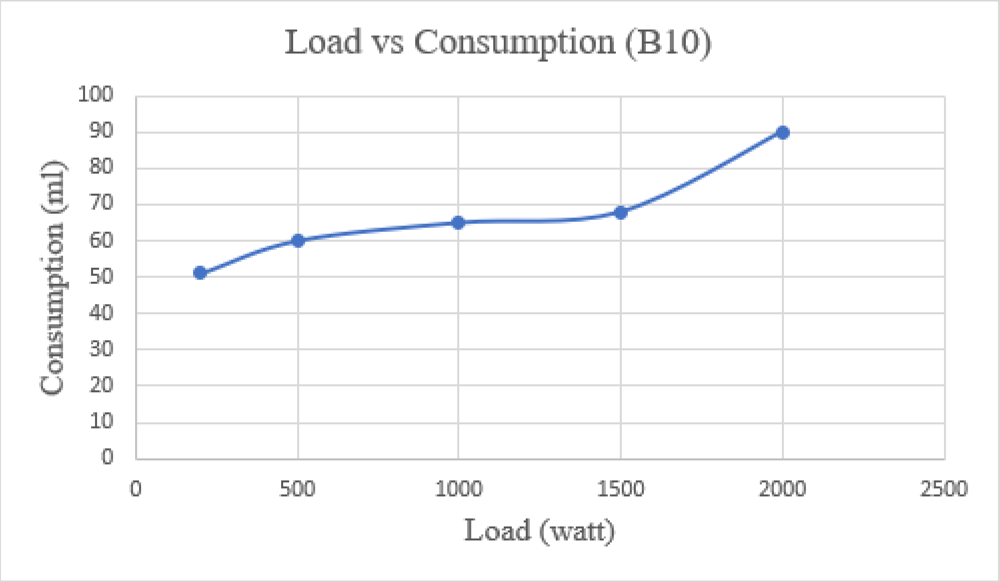


Fig 8.3.1: Load vs consumption graph for B10.

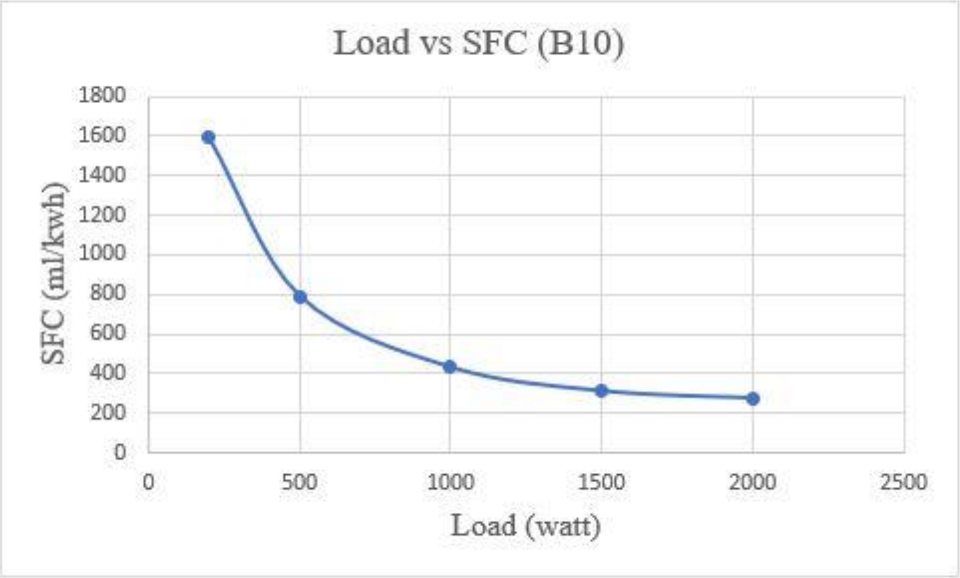


Fig 8.3.2: Load vs SFC graph for B10.

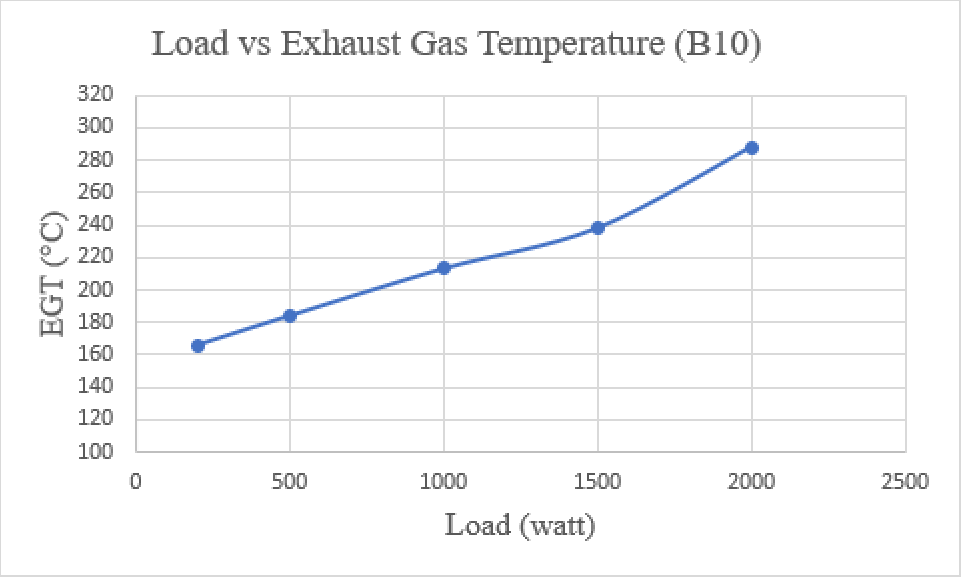


Fig 8.3.3: Load vs exhaust gas temperature graph for B10.

8.4 Engine performance characteristic for B20 (20% biodiesel, 80% Diesel)

Table 8.4.1: experimental data for B20

Load (in Watts)	Duration (in minutes)	Oil Consumption (in milliliters)			Speed in RPM	Exhaust Temperature (in °C)	Specific fuel consumption (ml/Kw-h)
		Start	Stop	Consumption			
200	10	430	380	50	2298	167	1500
500	10	375	317	58	2180	182	696
1000	10	310	240	70	2065	220	420
1500	10	235	160	75	1840	234	300
2000	10	155	70	85	2025	295	255

Specific fuel consumption (SFC) measures the amount of oil required to develop one kilowatt power. Taking second reading for calculation,

500 watts power developed for 10 mins, consume 58 ml of fuel.

1000 watts power will be produced for 60 mins consume $= \frac{58\times1000\times60}{500\times10}$ = 696 ml of fuel.

So, SFC for 500 watts Load is 696 ml/kW-h.

In the same way calculation are done for each reading to calculate SFC.

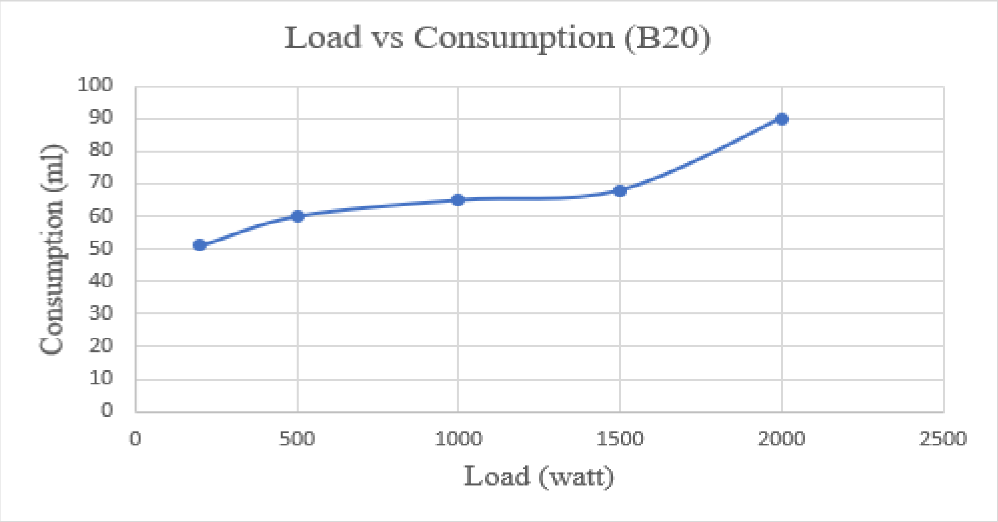


Fig 8.4.1: Load vs consumption graph for B20.

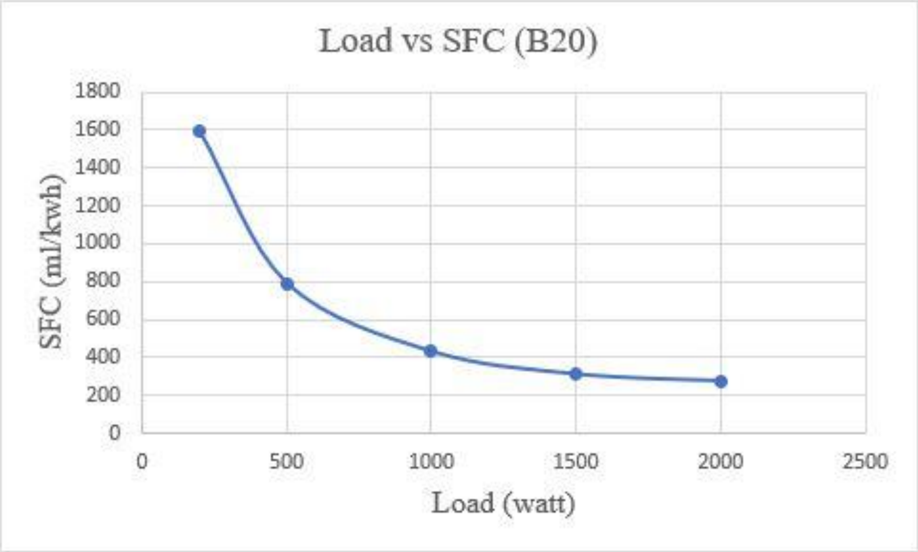


Fig 8.4.2: Load vs SFC graph for B20.

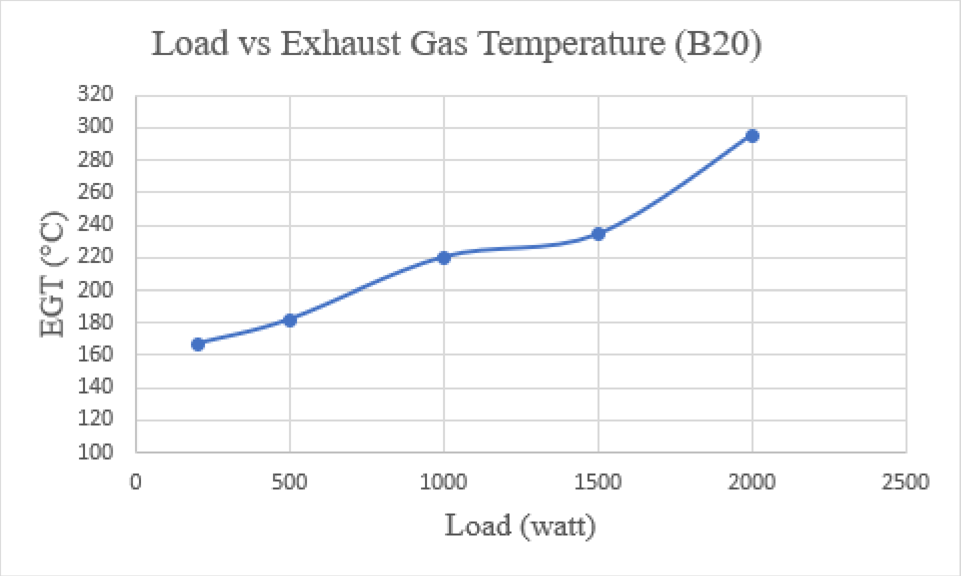


Fig 8.4.3: Load vs exhaust gas temperature graph for B20.

8.5 Engine performance characteristic for B30 (30% biodiesel, 70% Diesel)

Table 8.5.1: experimental data for B30

Load (in Watts)	Duration (in minutes)	Oil Consumption (in milliliters)			Speed in RPM	Exhaust Temperature (in °C)	Specific fuel consumption (ml/Kw-h)
		Start	Stop	Consumption			
200	10	470	419	51	2270	166	1530
500	10	415	355	60	2140	180	720
1000	10	350	285	65	1970	206	390
1500	10	280	212	68	1820	230	272
2000	10	200	110	90	2130	302	270

Specific fuel consumption (SFC) measures the amount of oil required to develop one kilowatt power. Taking second reading for calculation,

500 watts power developed for 10 mins, consume 60 ml of fuel.

1000 watts power will be produced for 60 mins consume $= \frac{60\times1000\times60}{500\times10}$ = 720 ml of fuel.

So, SFC for 500 watts Load is 720 ml/kW-h.

In the same way calculation are done for each reading to calculate SFC.

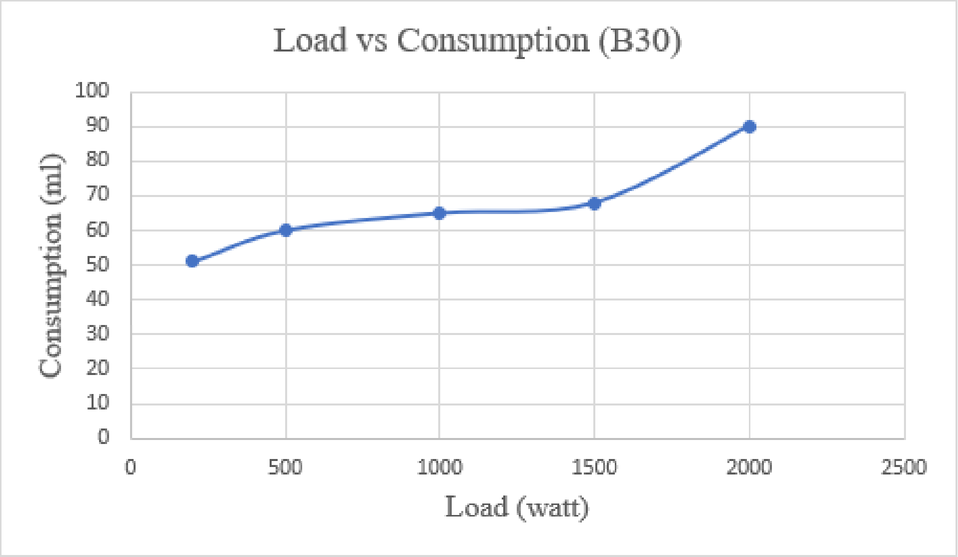


Fig 8.5.1: Load vs consumption graph for B30.

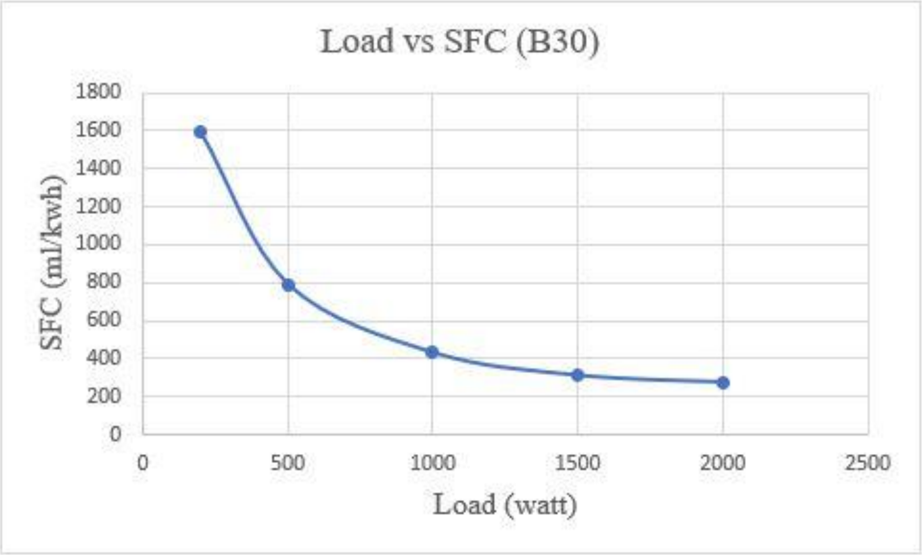


Fig 8.5.2: Load vs SFC graph for B30.

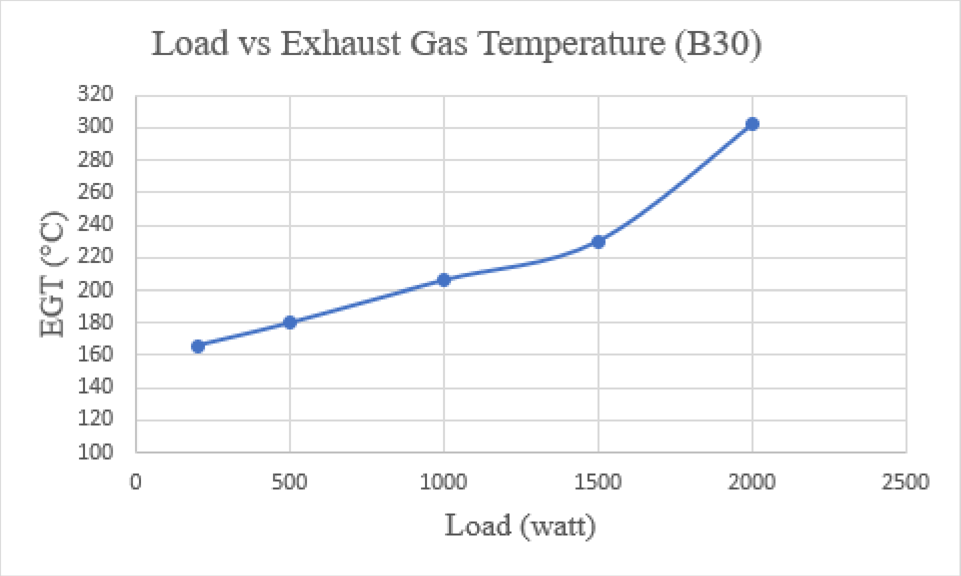


Fig 8.5.3: Load vs exhaust gas temperature graph for B30.

8.6 Engine performance characteristic for B40 (40% biodiesel, 60% Diesel)

Table 8.6.1: experimental data for B40

Load (in Watts)	Duration (in minutes)	Oil Consumption (in milliliters)			Speed in RPM	Exhaust Temperature (in °C)	Specific fuel consumption (ml/Kw-h)
		Start	Stop	Consumption			
200	10	450	398	52	2150	163	1560
500	10	395	333	62	1960	176	744
1000	10	330	260	70	1930	210	420
1500	10	250	174	76	1910	241	304
2000	10	160	72	88	2023	291	264

Specific fuel consumption (SFC) measures the amount of oil required to develop one kilowatt power. Taking second reading for calculation,

500 watts power developed for 10 mins, consume 62 ml of fuel.

1000 watts power will be produced for 60 mins consume $= \frac{62\times1000\times60}{500\times10}$ = 744 ml of fuel.

So, SFC for 500 watts Load is 744 ml/kW-h.

In the same way calculation are done for each reading to calculate SFC.

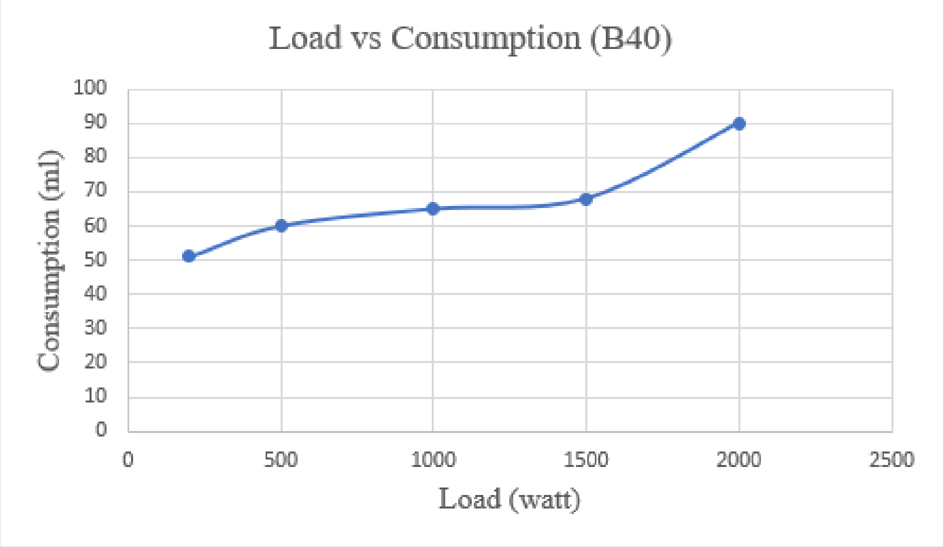


Fig 8.6.1: Load vs consumption graph for B40.

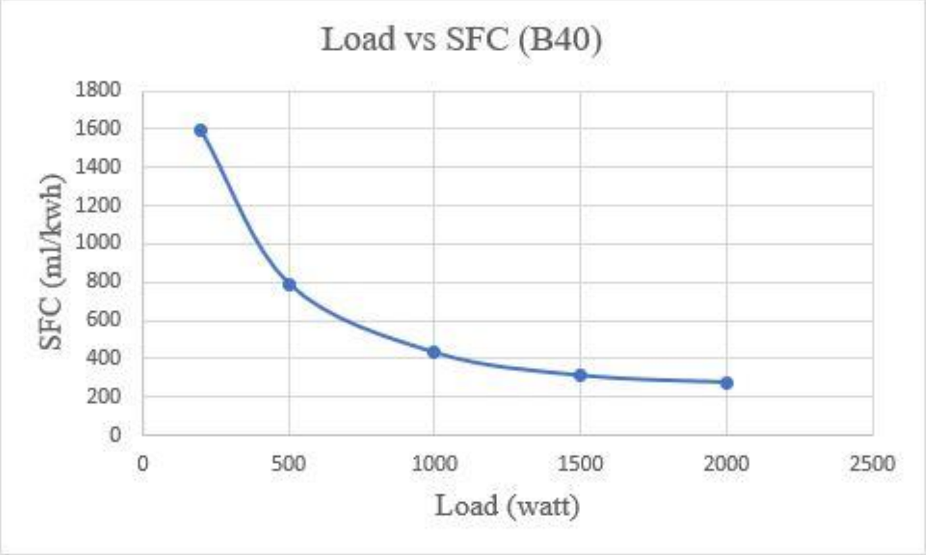


Fig 8.6.2: Load vs SFC graph for B40.

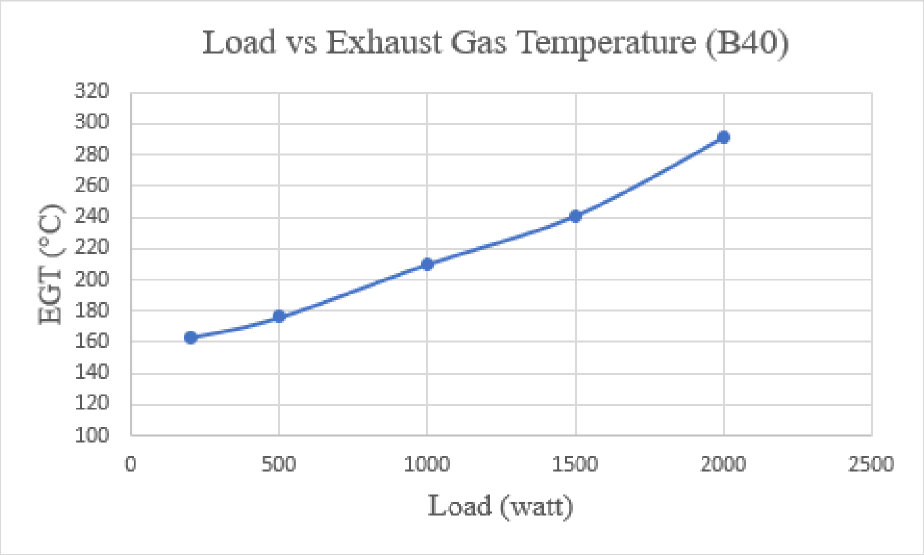


Fig 8.6.3: Load vs exhaust gas temperature graph for B40.

8.7 Engine performance characteristic for B50 (50% biodiesel, 50% Diesel)

Table 8.7.1: experimental data for B50

Load (in Watts)	Duration (in minutes)	Oil Consumption (in milliliters)			Speed in RPM	Exhaust Temperature (in °C)	Specific fuel consumption (ml/Kw-h)
		Start	Stop	Consumption			
200	10	480	427	53	2150	161	1590
500	10	425	359	66	2030	175	792
1000	10	355	283	72	1990	215	432
1500	10	280	202	78	1830	235	312
2000	10	190	98	92	2040	288	276

Specific fuel consumption (SFC) measures the amount of oil required to develop one kilowatt power. Taking second reading for calculation,

500 watts power developed for 10 mins, consume 66 ml of fuel.

1000 watts power will be produced for 60 mins consume = $\frac{66\times1000\times60}{500\times10}$ = 792 ml of fuel.

So, SFC for 500 watts Load is 792 ml/kW-h.

In the same way calculation are done for each reading to calculate SFC.

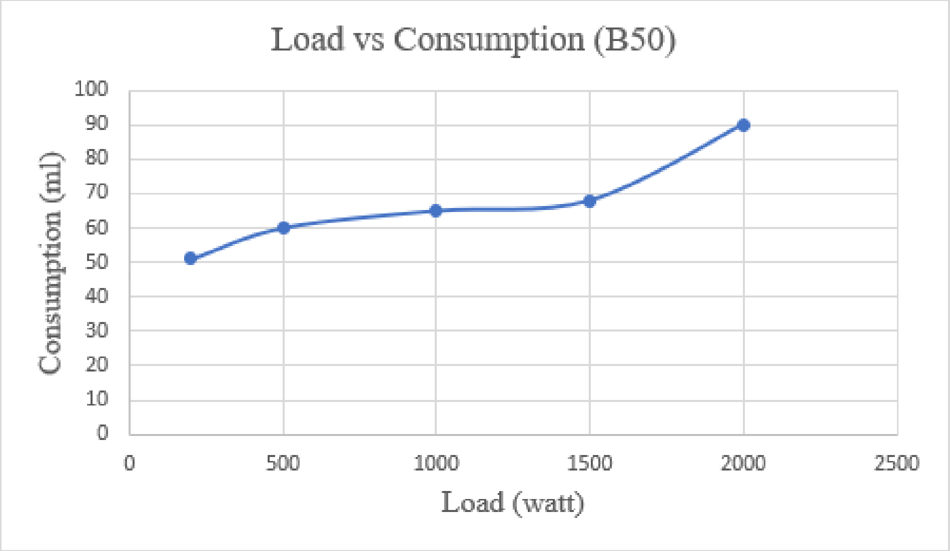


Fig 8.7.1: Load vs consumption graph for B50.

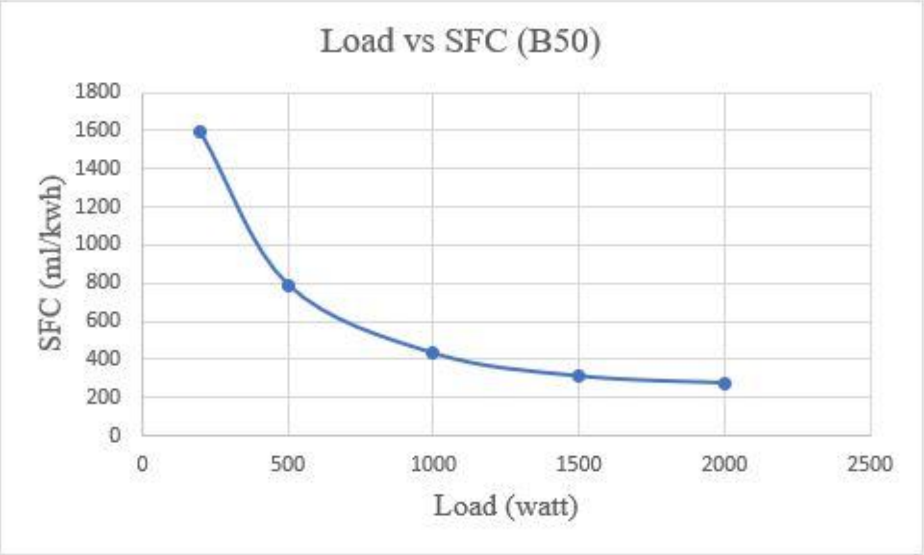


Fig 8.7.2: Load vs SFC graph for B50.

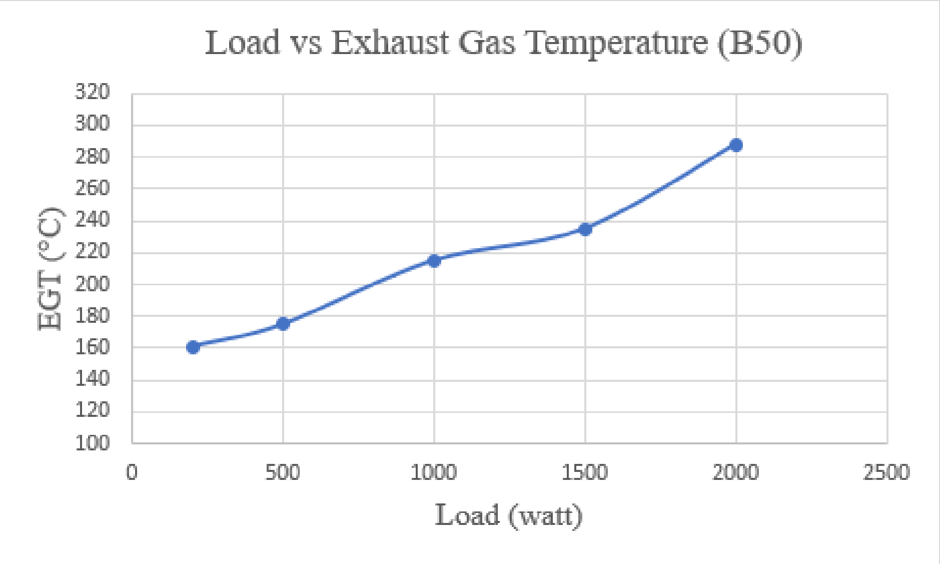


Fig 8.7.3: Load vs exhaust gas temperature graph for B50.

CHAPTER 9: RESULTS AND DISCUSSION

9.1 Optimization

Optimization of transesterification reaction parameters of waste cooking oil WCO (mixture of soybean oil and sunflower oil) to bio-diesel has been done based on one factor at a time method. The transesterification was carried out with stirring rate of 700 rpm using magnetic stirrer, which is lower than the rpm used by others. Methanol and KOH is used for transesterification reaction. The optimized amount of methanol to oil molar ratio is 9:1 and amount of KOH is optimized at 1% wt/wt. the other parameters time and temperature are optimized at 90 minutes and 55°C respectively.

9.2 Properties of Biodiesel

The properties of biodiesel produced from mix waste cooking oil of used sunflower oil and waste soybean oil have been measured. The measuring apparatus, procedure and the results were discussed in chapter 7. Here the properties of biodiesel are compared with diesel oil and also with the Indian standard specification for biodiesel, IS 15607:2005*

.

Table 9.1: Biodiesel property comparison

Fuel Property	WCO biodiesel	IS 15607:2005*	Diesel
Density, gm/cm^3	0.874	0.86 - 0.90	0.8211
Kinematic Viscosity at 40°C	4.82	2.5 – 6.0	2.5 – 3.5
Calorific Value, MJ/ kg	38.36		42.7
Flash Point, °C	178	120 min	52
Cetane Number	52	51 min	49 - 55

*Indian standard specification for biodiesel.

It is seen that all the properties are follow the range mentioned in Indian standard specification for biodiesel. It is observed that the value of the properties of biodiesel are different from the properties of diesel fuel. Thus density, cetane number are very nearer to diesel fuel, kinematic viscosity is little more than diesel and calorific value of biodiesel is less than diesel. Flashpoint of biodiesel is much higher than diesel fuel.

9.2 Fuel consumption with varying load at different blend

Fuel consumption of the test engine is the amount of fuel consumed for a particular load at a particular time. Specific fuel consumption can be calculated from these results. Thus, it is checked for different type of fuel blend and also for mineral diesel. All the experiment results have been given and the respective graphs are shown in chapter 8. Fuel consumption results for different blends are plotted in a single graph.

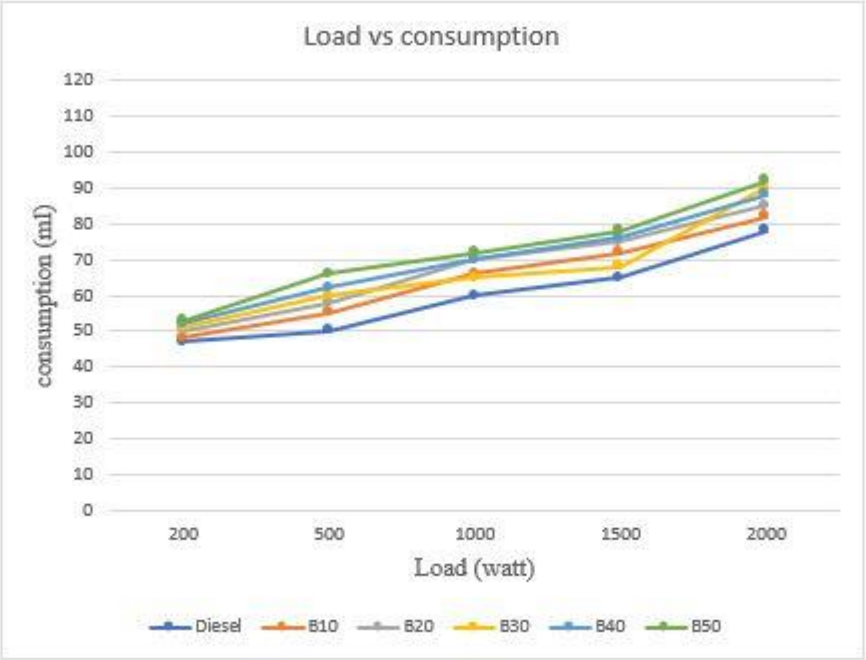


Fig 9.2.1: Load vs. fuel consumption graph for Diesel, B10, B20, B30, B40 & B50

From the above graph, it is shown that the fuel consumption is increase by increasing the amount of load, because applying more load increases the resistance hence increases the power demand and to supply the required power, the engine has to produce more power thus consume more fuel.

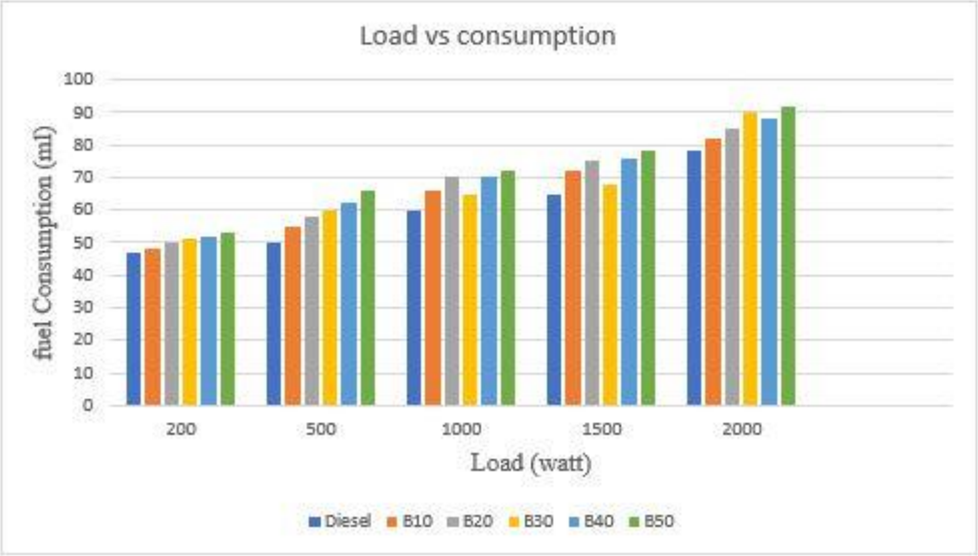


Fig 9.2.2: Load vs. fuel consumption column chart for Diesel, B10, B20, B30, B40 & B50

It is also observed from the line graph and from the column chart, that the fuel consumption for a particular load is less for ultralow sulfur diesel or petroleum diesel and maximum for B50. The reason is that the calorific value of diesel is more than biodiesel. B30 blend shows different results for two particular load 1000 watt and 1500 watt, the fuel consumption of B30 blend is less than the other blends but not less than diesel.

9.3 Specific fuel consumption (SFC) with varying load at different blend

Specific fuel consumption (SFC) measures the amount of fuel required to develop one-kilowatt power. The SFC is an important parameter of an engine because it takes care of both mass flow rate and heating value of the fuel. In the experiment, SFC of different biodiesel blend has been calculated for different Load. In a single graph, SFC of all WCO biodiesel blend has been represented for different Load. Engine specific fuel consumption decreases with engine Load because the ratio of friction to brake power goes down. Interaction among these factors results in lowest value of specific fuel consumption at higher Load.

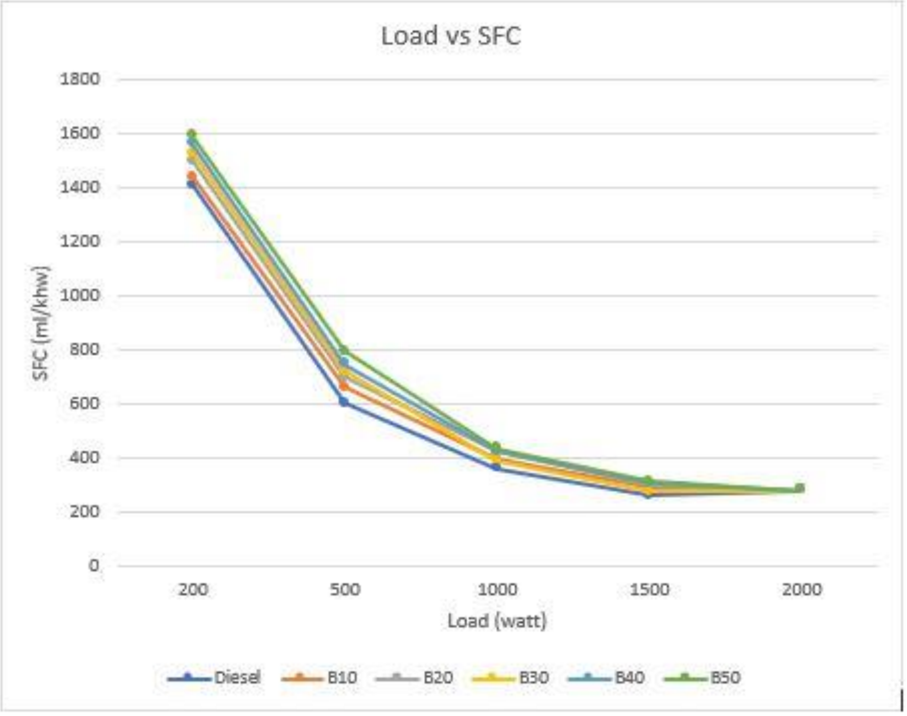


Fig 9.3.1: Load vs. SFC graph for Diesel, B10, B20, B30, B40 & B50

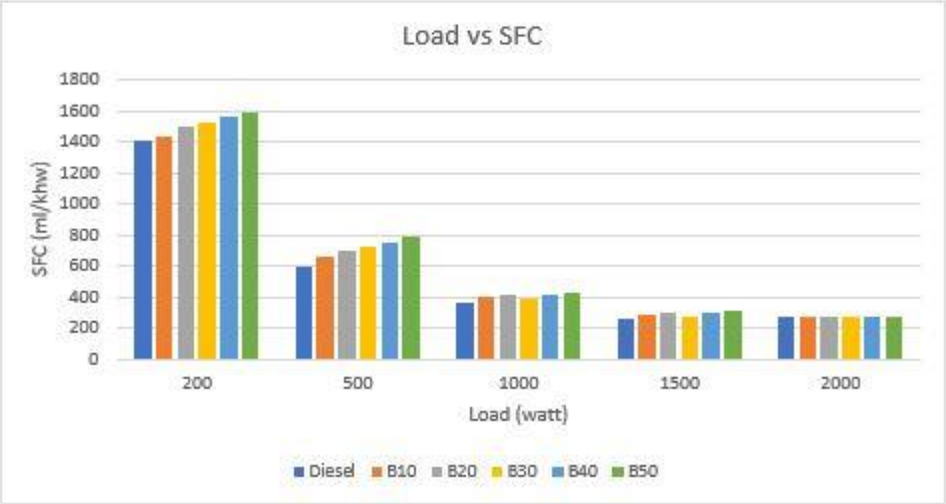


Fig 9.3.2: Load vs. SFC column chart for Diesel, B10, B20, B30, B40 & B50

As shown in Figure the SFC initially decreases with increasing of engine Load until it reaches a maximum value and then increases slightly with further increasing engine Load for all kind of fuels. In the using of blends B30, the SFC of the engine is lower than that of other blends. B20, B40 and B50 the brake specific fuel consumption is more than the diesel fuel because of lower heating value of biodiesel. With increase the biodiesel percentage in fuel this reason is more predominant. From the graph it is clear that at 2 Kw Load SFC is minimum for diesel as well as all the blend of biodiesel, SFC is minimum for B30 WCO biodiesel among all.

9.4 Exhaust gas temperature with varying load at different blend

Exhaust gas temperature indicates the quality of combustion in the combustion chamber. More amount of fuel is required to produce the additional power to take up the increase in loading. This is the reason for increase in exhaust gas temperature with increase in Load. The exhaust temperatures of biodiesel blends are lower than those of conventional diesel due to their lower heating value.

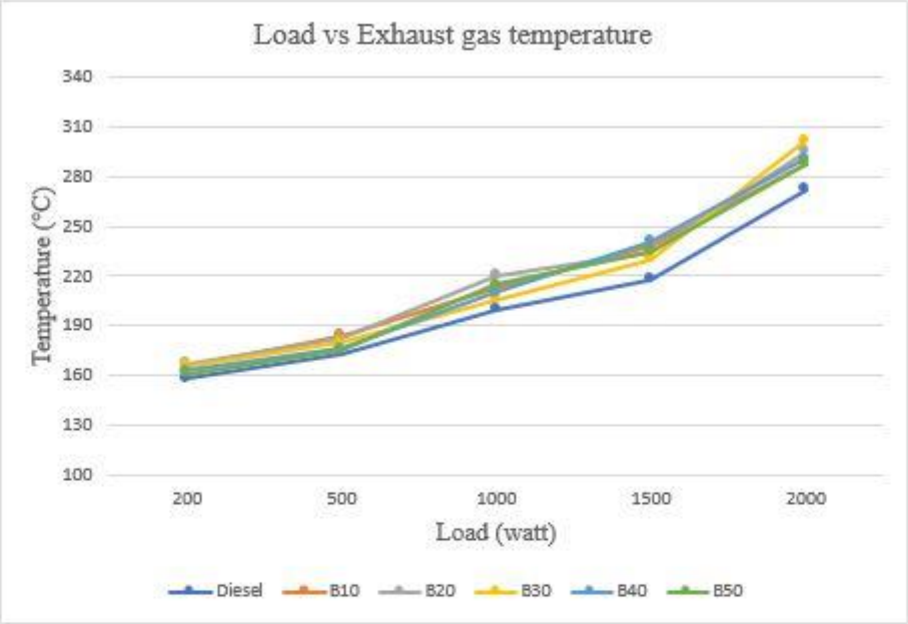


Fig 9.4.1: Load vs. Exhaust gas temp graph for diesel, B10, B20, B30, B40 & B50

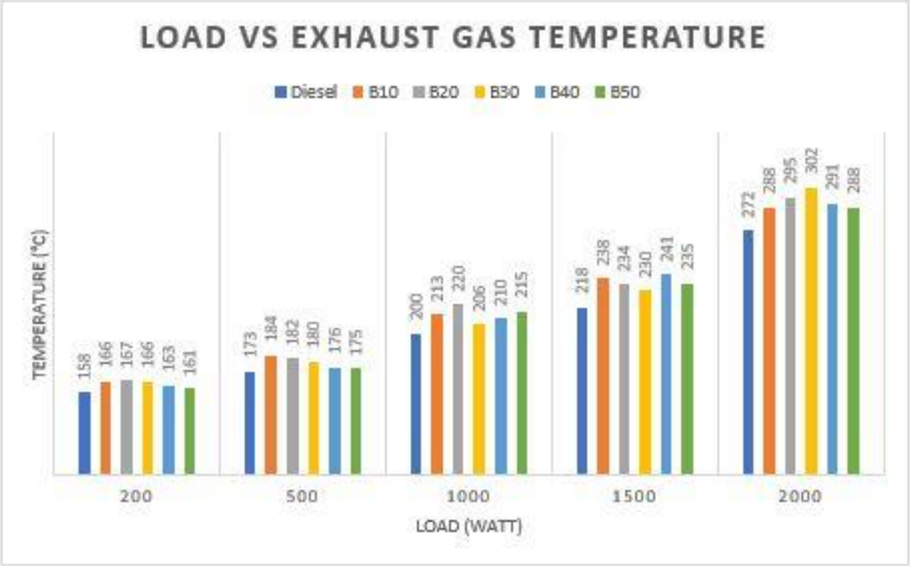


Fig 9.4.2: Load vs. Exhaust gas temp column chart for diesel, B10, B20, B30, B40 & B50

It is clearly shown in the above two graphs that the exhaust gas temperature increases with increasing load, this is due to decreased rate of heat transfer through the cylinder wall at higher load.

It is also observed that using higher blend results lower exhaust gas temperature than the other blends. It is an important advantage of using biodiesel as an alternative fuel.

CHAPTER 10: CONCLUSIONS

WCO (Mixture of used sunflower oil and soybean oil) are used for production of biodiesel. The reaction parameters are optimized for maximum biodiesel yield. The properties of biodiesel are measured and compared with diesel and with Indian standard specification for biodiesel. Biodiesel is blend with diesel fuel at various percentages and engine testing are carried out at different loads. The following points are concluded.

1. It observed that biodiesel can be produced from the mixture of different oils. Maximum biodiesel yield is 95%. The optimized parameters to get maximum yield for biodiesel production from mix WCO were carried out and the values are.

   methanol to oil molar ratio - 9:1. Time – 90 minutes.
   Amount of KOH as catalyst – 1% w/w. Temperature – 55 °C.

   The transesterification reaction for biodiesel production has been carried out at 700 rpm which is lower than others and the reaction time is less.
2. The properties of biodiesel have been measured and compared with diesel and the values are within the range of Indian standard specification for biodiesel.

3. From the results of engine testing data, the fuel consumption for a particular load is less for ultralow sulfur diesel or petroleum diesel and maximum for B50. The SFC initially decreases with increasing of engine load until it reaches a maximum value and then increases slightly with further increasing engine Load for all kind of fuels. using blends B30, the SFC of the engine is lower than that of other blends. B20, B40 and B50 the brake specific fuel consumption is more than the diesel fuel. Increase in exhaust gas temperature with increase in Load. The exhaust temperatures of biodiesel blends are lower than those of conventional diesel fuel.

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