EXTRACTION OF BIODIESEL FROM PONGAMIA PINNATA (L) PIERRE AND ITS PERFORMANCE ANALYSIS

A Thesis Submitted to Gauhati University for the Degree of Doctor of Philosophy in Mechanical Engineering in the Faculty of Engineering

Submitted By

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June 2017

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Place……………...

DECLARATION BY THE CANDIDATE

I do hereby declare that the material presented in the thesis titled "**EXTRACTION OF BIODIESEL FROM PONGAMIA PINNATA (L) PIERRE AND ITS PERFORMANCE ANALYSIS"** in fulfillment of the requirement for the award of degree of Doctor of Philosophy and submitted to the Department of Mechanical Engineering, Assam Engineering College, Gauhati University is entirely my own account of research carried under the supervision of Dr. Dimbendra Kr. Mahanta, Professor, Mechanical Engineering Department, Assam Engineering College, Guwahati, Assam, India, PIN 781013 and contains as its main content work except where otherwise stated, which has not previously been submitted for a degree at this college/university or any other educational institution.

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This is to certify that the above statements made by the candidate are correct to the best of my knowledge.

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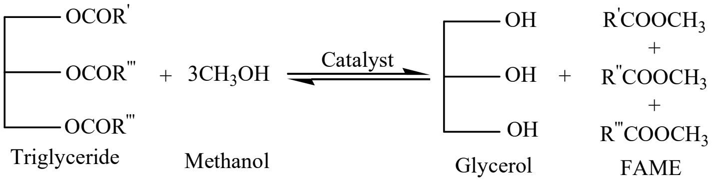
Abstract

EXTRACTION OF BIODIESEL FROM PONGAMIA PINNATA (L) PIERRE AND ITS PERFORMANCE ANALYSIS

The objective of the study is to determine biodiesel from the seed of Pongamia pinnata (L) pierre (Koroch) and determine the properties of the biodiesel and blending of the biodiesel with the diesel at different percentage of the biodiesel. The properties of the biodiesel and the blending of the biodiesel with the diesel are compared with those of diesel fuels and also with biodiesel standards such as ASTM D6751 and EN 14214. The biodiesel and blending of biodiesel with diesel is tested in the four stroke single cylinder compression ignition engine and the performance of the engine is studied, exergy of the engine is analyzed and exhaust gas parameters also studied.

The extraction of oil from the seed of the *Pongamia pinnata* is done in the vacuum evaporator apparatus in the laboratory of Chemistry, Bineswar Brahma Engineering College, Kokrajhar, BTAD, Assam, India. To produce oil from the seed, the fruit of the pongamia pinnata is collected from the Assam Engineering College campus, Jalukbari, Guwahati, Assam, India and dried the seed of the fruit for four days in the sunlight to remove the moisture of the seed. Around 48% moisture is removed from the seed, and then the dried seeds were grinded to powder size. Extraction of oil from the seeds of *Pongamia pinnata* was carried out with three different solvents namely diethyl ether, hexane, and petroleum ether (40-60 ^{o}C). The solvents are removed from the oil in the vacuum evaporator apparatus and the physiochemical properties like density, pour point, Kinematic viscosity, acidity, ash content, conradson carbon residue and caloric value (gross) etc of Koroch Seed Oil is determined by the Proximate Analysis. The properties of the oil are determined using standard methods in Bongaigaon Refinery and Petrochemicals Limited (BRPL), BTAD, Assam, India. The results are discussed in the thesis.

Biodiesel consists of alkyl esters of long chain fatty acids, more commonly methyl esters. Conversion of oil to biodiesel is achieved by transesterification process by reacting with methanol in the presence of catalyst. In this thesis, the seed oil from the pongamia pinnata oil is transesterified to fatty acid methyl esters (biodiesel) mixing with methanol (CH_3OH, 5ml/g of oil) and using K_2CO_3 catalyst (5 wt% of oil) is mechanically stirred at room temperature (32^{o}C). After completion of the reaction, the product mixture is partitioned between petroleum ether and water by adding petroleum ether and brine solution (10% of NaCl solution). The organic phase that is upper layer is then collected. This process is repeated for 2-3 times by taking the lower layer. The collected solution is then dried over anhydrous Na_2SO_4 and the solvent is removed under vacuum to yield the product.



Blending of the biodiesel is made with different percentage of biodiesel and petroleum diesel to produce different type of samples. More than one litre of biodiesel was prepared from an approximately equal volume of pongamia pinnata seed oil in several batches and prepared five samples of blends for determining the properties of diesel and biodiesel. The sample preparations by blending of diesel and biodiesel for the five samples of B00, B10, B20, B30 and B100, where "B" stands for biodiesel and double digit number followed by B stands for percentage of biodiesel and the remaining percentage is the petro diesel, required 480ml biodiesel and 1020ml petrodiesel and submitted for fuel properties determination in Bongaigaon Refinery and Petrochemicals Limited (BRPL) Dhaligaon, BTAD, Assam, India. The properties like Kinematic Viscosity at 40°C, Density at 15°C, Pour Point, Flash Point, Ramsbottom Carbon Residue, CFPP (Cold Filter Plugging Point), Total Sulfur, Acidity, Calorific Value of the samples are determined using standard methods in BRPL, Dhaligaon. Comparing with Indian automotive diesel fuel and biodiesel standards ASTM D6751 and EN 14214, it is found that the blend B10 is better than the other blending of the biodiesel and the diesel.

In order to perform the experiments for the analysis of CHN, GC-MS, FTIR, pH value analysis for five samples made from diesel, biodiesel and its blends, the following instruments were used – FTIR apparatus, CHN analyzer, GC-MS equipment and pH value analyzer in the laboratory of Tezpur University, Tezpur, Assam, India.

The Gas Chromatography and Mass Spectrometry (GC-MS) is used to identify the various chemical compounds present in the samples of diesel, biodiesel and its blends, biodiesel from the seed of pongamia pinnata. The peaks observed in the GC-MS spectrum of samples from diesel, biodiesel and its blends, biodiesel indicate the presence of various alcoholic compounds, ethyl, methyl, methoxy ketone, esters, aldehydes, and some aromatic hydrocarbons. The Fourier Transform Infrared (FTIR) analysis is used to determine the functional group present in the samples B00, B10, B20, B30, B100 which confirm the compounds seen in the GC-MS analysis with C=C, C=O, C – H, C – O stretching vibration and $-CH_2-$ and $-CH_3$ bending. The percentage of Carbon, Hydrogen and Nitrogen are determined by the CHN analyzer and the remaining percentage of the sample is the percentage of the Oxygen. The empirical formula of the samples is determined after getting the percentage of the carbon, hydrogen and oxygen and the characteristics of the samples. The pH values for the samples are determined in the Civil Engineering Department, Bineswar Brahma Engineering College, Kokrajhar and the results of the samples B00, B10, B20, B30, B100 were found. As per the range of the samples are from 7 to 9.4, so the samples have the basic in nature since the liquid with pH value less than 7 is the acidic and more than 7 it is basic.

In a single cylinder four stroke diesel engine made of Kirloskar AK65 was run using different types of sample that is petroleum diesel, blends of diesel and biodiesel, pure biodiesel made from the seed of pongamia pinnata at different loads to analyze the performance of the engine. To determine the performance of the engine, the values of the brake power, specific fuel consumption, heat supplied, brake thermal efficiency, heat lost in radiation and uncounted, volumetric efficiency were calculated.

According the result and discussion of different properties like brake power, specific fuel consumption, heat supply of the fuel, brake thermal efficiency, heat lost in radiation and uncounted, volumetric efficiency got from running the compression ignition engine using different samples from diesel and biodiesel, it is concluded that the sample B10 is the best among the fuel B00, B10, B20, B30, B100.

In the exergy analysis the various exergy properties of the smples are determined and the results are compared with the diesel. According the result and discussion of the different properties fuel energy, work energy, exhaust energy, and the fuel exergy, work exergy, heat loss exergy, exhaust exergy, exergy destroyed, efficiency of exergy and energy got from running the CI engine using different samples from diesel and biodiesel, it is concluded that the exergy efficiency is slightly less than the energy efficiency for all the samples and the loads.

In the exhaust gas analysis, the different parameters of the exhaust gas is determined and they are CO, CO_2, HC, NO, NO_2, NO_x, SO_x, Temperature and pressure. In exhaust gas analysis it is found that the value of CO_2 for biodiesel is much lower than the CO_2 value of the diesel fuel, that is the biodiesel fuel engine give an air/fuel imbalance or misfire. The other parameters except CO_2 remain almost same to the exhaust gas parameter of diesel. The compound SO_x is almost nil in quantity.

The entire work can be summarized into the steps as given below:

1. Extraction of oil from the seed of Pongamia pinnata and proximate analysis of the bio-oil.
2. Transesterification of oil to biodiesel and investigation of physical, chemical and thermal properties of the biodiesel and comparison with the ASTM D6751 and EN14214.
3. Investigation of compounds of the sample using CHN, GC-MS, FTIR and pH value analyzer.

4. Performance and exergy analysis of the biodiesel and its blends and diesel in the compression ignition engine.
5. Investigation of the exhaust gases from the CI engine.

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List of Abbreviation

ASTM = American Society for Testing and Materials

AV = Acid Value

BSII = Bharat Stage II

BSIII = Bharat Stage III

BSFC = Brake Specific Fuel Consumption

BSEC = Brake Specific Energy Consumption

BMEP = Brake Mean Effective Pressure

CO_2 = Carbon dioxide

CI = Compression Ignition

CO = Carbon Monoxide

CN = Cetane Number

CO_2 = Carbon dioxide

CFPP = Cold Filter Plugging Point

CP = Cloud Point

CH_3OH = Methanol

ENS = European Standards

EPA = Environmental Protection Authority

FFA = Free Fatty Acids

FAME = Fatty Acid Methyl Esters

FT-IR = Fourier Transform Infrared Spectroscopy

GC/MS = Gas Chromatography /Mass Spectrometry

g = Gram

H = Time in hours

HC = Hydrocarbon

HPLC = High Performance Liquid Chromatography

IV = Iodine Value

KOH = Potassium hydroxide

K_2CO_3 = Potassium carbonate

NaOH = Sodium hydroxide

NaCl = Sodium chloride

NO_x = Oxide of Nitrogen

NREL = National Renewable Energy Laboratory

OSI = Oil Stability Index

SFC = Specific Fuel Consumption

TLC = Thin Layer Chromatography

UK = United Kingdom

US = United State

UV = Ultra Violet

CHAPTER - 1

1.0 Introduction

1.1 Bio-fuels

All bio-fuels and bio-based products come from “biomass”, a term that coverts all living or recently living biological material which can be used as fuel or for industrial production. For example wood, corn, sugarcane and manure, fall in this category. Bio-fuels can be separated into three basic categories:

1.1.1 **Ethanol**: Ethanol is a type of alcohol, which is a substitute for petrol and is most commonly made from corn or sugarcane.

1.1.2 **Biodiesel**: Bio-diesel is a substitute for diesel fuel, which is most commonly made from soybeans. It is based on oils and used mostly in trucks in the US and also in an increasing number of diesel cars.

1.1.3 **Other biomass**: It is mostly used for generation of electricity or heat. Examples are burning wood chips to boil water and create steam, which spins turbines and creates electricity; collecting methane from manure piles to generate heat or electricity.

1.2 Biodiesel

Biodiesel is defined as monoalkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to ASTM D6751 specifications for use in diesel engines. Biodiesel is an energy rich biofuel made from fats and oils.

Biodiesel is a clean-burning diesel replacement fuel that can be used in compression-ignition (CI) engines, and which is manufactured from the following renewable, non-petroleum-based sources:

- Virgin vegetable oils such as soy, mustard, canola, rapeseed and palm oils;

- Animal fats such as poultry offal, tallow, and fish oils; and

- Used cooking oils and trap grease from restaurants.

Biodiesel is produced in pure form (100% biodiesel or B100), but is usually blended with petrodiesel at low levels, between 2% (B2) to 20% (B20) in the U.S., but at higher levels in other parts of the world, particularly in Europe, where higher-level blends up to B100 are used. Blends of biodiesel higher than B5 require special handling and fuel management as well as vehicle equipment modifications such as the use of heaters and changing seals/gaskets that come in contact with fuel, according to the National Renewable Energy Laboratory (NREL). The level of care needed depends on the engine and vehicle manufacturer.

Biodiesel refers to the pure fuel before blending with diesel fuel. Biodiesel, an alternative fuel resource for diesel engines, is of great interest because of its environmental benefits, such as its renewable, biodegradable, and nontoxic properties

They are mainly produced by alcoholysis or transesterification process wherein animal fats or vegetable oils are chemically reacted with small chain aliphatic alcohols. Biodiesel is mostly manufactured for fueling standard diesel engines. It can be used either in its pure form or blended with various chemical concentrations as per the requirements of specific applications. Biodiesel blends are denoted as “BXX” with “XX” representing the percentage of biodiesel contained in the blend (e.g. B30 is 30% biodiesel, 70% petroleum diesel, B100 is 100% biodiesel).

1.3 Need of the hour

The major need of bio-fuels has been driven by two very important factors.

- Depletion of non-renewable energy resources.
- Increase in pollution level.

1.3.1 Depletion of non-renewable energy resources:

Due to rampant use of non-renewable energy resources, i.e., the fossil fuels, the amount of fuel reserves left by the end of 20th century has raised an alarm worldwide as people have realized that the reserves will be over and done with in the future. This has forced humankind to move the attention towards renewable energy sources like solar energy, wind energy, geothermal energy, ocean thermal energy and energy from biomass. This has triggered the use of bio-fuel and biodiesel in the present time.

1.3.2 Increase in pollution level:

The increase in pollution level due to different gases and climate change by CO_2 emissions, basically from transport, has become a grave concern in the present age. A near-epidemic of asthma is closely linked to diesel exhaust and particulate matter. Oil spills, arctic oil drilling and strip mining for coal represent other potential environmental problem associated with fossil fuels. Hence, mankind has turned towards biodiesel, which does not contain sulphur or any other chemical pollutants. Due to this reason it does not produce any harmful poisonous gases during combustion.

In many ways biodiesel works better than diesel. Replacing diesel with biodiesel helps reduce smog, ozone, acid rain, cancer and asthma, some of the ills associated with burning petroleum diesel. Biodiesel burns up to 75% cleaner than the conventional diesel fuel and substantially reduce carbon monoxide and eliminate sulphur dioxide emissions. Arguably the largest benefit would be a reduction in greenhouse gases contributing the climate change.

1.4 Aim and Objectives of the research work

The undertaken research work aims demonstrate the production of biodiesel from the oil of the seeds of the fruit Pongamia pinnata, for analysis purpose, comparison of properties of biodiesel, performance analysis of the biodiesel and its blends in an Compression Ignition Engine, exergy analysis of the fuel and exhaust gas analysis of the CI Engine using the biodiesel and its blends.

1.4.1 Objectives:

The objectives of the research work are as given below:

1. Collection of seeds of *Pongamia pinnata*.
2. Extraction of oil from the seed of the fruit Pongamia pinnata.
3. Produce biodiesel from the extracted Pongamia pinnata oil.
4. Determination of composition of biodiesel by analytical techniques.
5. Comparison of the properties of biodiesel with ASTM D6751 and EN14214 standards.
6. Testing the biodiesel in Single Cylinder Compression Ignition Engine by blending it with the petroleum diesel.
7. Exergy analysis of the biodiesel and its blends fuel using the Single Cylinder Compression Ignition Engine.
8. Analysis of the exhaust gases from the Single Cylinder Compression Ignition Engine using the fuel petroleum diesel, the blending of the biodiesel and the petroleum diesel and pure biodiesel.

CHAPTER - 2

2.0 LITERATURE REVIEW

2.1 History

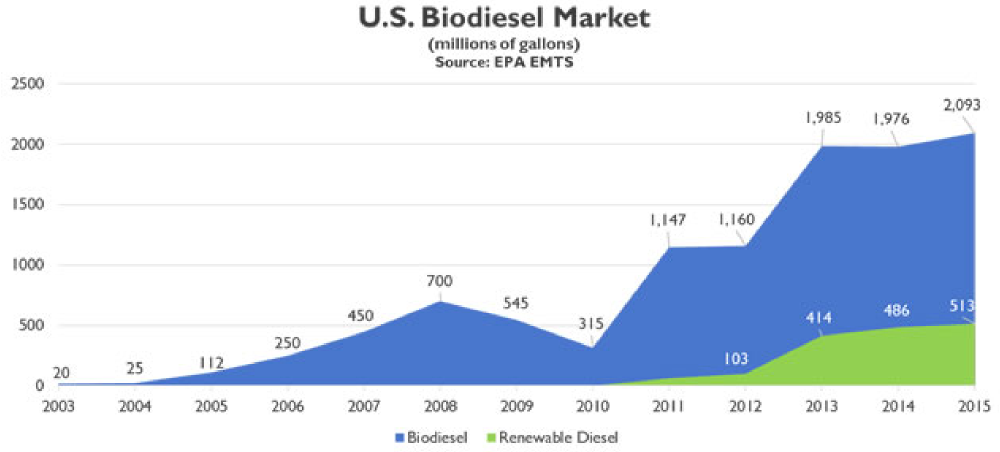
In 1897, Rudolph Diesel demonstrated that his engine could run on peanut oil. Nearly a century ago, the Model-T was designed and run on either gasoline or ethanol.(1) This marks the first use of the biofuels. Today following an twelve decade detour in the petroleum age, bio-fuels are back in demand, fueled by powerful combination of advancing technologies, depleting resources, rising environmental concerns, farmer support and soaring oil prices.

The biofuel industry has gained a head start in U.S. Presently U.S. is the pioneer user of biofuels, followed by U.K. and South Africa.

The biodiesel industry has steadily grown over the past decade, with commercial production facilities from coast to coast. Biodiesel production is a much smaller industry than ethanol, although it is growing very quickly. In U.S., the annual biodiesel production was 75 million gallons in 2005, up from 5,00,000 gallons in 1999 and 30 million gallons in 2004. The biodiesel tax incentive that went into effect January 1, 2005 is helping biodiesel demand to climb even more. The U.S. Energy Bill was supports the growth of annual biodiesel production to 5 billion gallons by 2012.(2). The industry reached a key milestone in 2011 when it crossed the billion gallon production mark for the first time. It repeated that in 2012 with more than 1.1 billion gallons and set a new record in 2013 by producing nearly 1.8 billion gallons, according to EPA figures. The industry's total production significantly exceeded the 2013 biodiesel requirement under the Federal Renewable Fuel Standard and was enough to fill the majority of the Advanced Biofuel requirement. (3)

The total Biomass-Based Diesel volume of 1.8 billion gallons is primarily biodiesel but also includes renewable diesel, a similar diesel alternative made with the same feed stocks but using a different technology.

According to a recent study, the industry supported more than 62,200 jobs nationwide. Biodiesel reduces greenhouse gas emissions by 57 percent to 86 percent, according to the EPA. Each of the last three years the industries has produced more than a billion gallons and has exceeded the minimum requirements under the RFS.



2.2 Literature Survey

Majority of the world's energy needs are supplied through petrochemical sources, coal and natural gases, with the exception of hydroelectricity and nuclear energy.(4) However, these energy resources are non-renewable and will be exhausted in the near future.

Pongamia pinnata or karanja or Indian beech is a medium sized glabrous tree. It is adaptable tree for tropical and subtropical regions which requires excellent drainage and sunny location. Its oil is a source of biodiesel. It has also alternative source of energy, which is renewable, safe and non pollutant.

Sabita Sangwan et al describe in their paper the reviews the botany, distribution, ecology, used of the plant and as a source of biodiesel(5). The pongamia pinnata seeds contain about 40% oil, which can be converted to biodiesel by transesterification method. Studied the nutrient levels in pongamia pinnata leaf and fruit, among the nutrients parameter of fruit (pod and seed) the fatty oil is 27.5% and moisture 19%. In comparison of properties of biodiesel and standard petroleum diesel, a slight difference is observed.

K. Sujatha et al studied the genetic variability and its association with oil content, seed and pod traits is mandatory for genetic improvement of Pongamia(6). They studied the oil content of Pongamia seeds of ten different trees collected from two locations and determined percentage of oil (w/w) ranging from 12.5 to

28.0 on the contrary, high degree of variability (76%) among the selected trees in variation analysis suggest applicability of the tissue culture techniques for multiplication of high oil-yielding Pongamia trees and exploration of desired wild germplasm characteristics.

The healthy and matured seeds of Trigonella foenum-graecum and Pongamia pinnata were collected from Amaravati during 2003 and dried at room temperature and later powdered in grinder. About 15g powder was used for aqueous extraction in Soxhlet. This oil is analyzed by GC/MS analysis. Pritee Wagh et al studied different concentration of oils obtained from the two plants after extraction**(7)**. They were evaluated for their antifungal and antibacterial activity against *Aspergillus niger, A.umigates, Staphylococcus aureus* and *Pseodomonus aeruginosa* by MIC determination and dry weight method. *A. niger* and *S aureu* were more sensitive to oil of Pongamia pinnata. Chemical analysis of oil performed by gas Chromatography (GC) and gas chromatography/mass spectrometry (GC-MS) showed the presence of fatty acid.

B. V. Mehta on his seminar paper he described that the Pongamia pinnata is the main species suitable for biodiesel extraction **(8)**. He described that with the present scenario petroleum product consumption; there is urgent need to develop attractive fuel such as biodiesel in the country. The potential demand for biodiesel at 20% blend is thus estimated at 13.38 million tons per annum by 2012.

A. J. Soloman Raju in his paper said that biodiesel which is an eco-friendly sustainable fuel source, renewable energy source, bio based, biodegradable, non toxic**(9)**. Blending of biodiesel with ordinary diesel may improve cetane rating and engine lubrication. Biodiesel is a fatty acid of ethyl ester made from virgin or used vegetable oils. The raw oil is subjected to chemical process “trans-esterification” in which oil is reacted with an alcohol (methanol or ethanol) in the presence of a catalyst such as sodium hydroxide to produce methyl or ethyl ester and glycerol. The methyl or ethyl ester formed in the process constitutes “bio-diesel”. Glycerol or glycerin is the byproduct, which also has commercial value, 100kg of crude oil, 24kg of methanol and 2.5kg of sodium hydroxide produce 100kg of biodiesel plus 26kg of glycerin.

H.N. Meenakshi et al on their article “Corrosion of metals in biodiesel from Pongamia pinnata” discussed the biodiesel as a new renewable energy source (10). And they discussed the corrosion rates of aluminium, copper, brass and carbon steel in biodiesel obtained from pongamia pinnata, since the tankers, storage tanks, pipes and pumping equipments are normally constructed using the above mentioned elements.

In the article “Biodiesel Safety and Best Management Practices for Small Scale Non-commercial Use and Production” said that the small scale biodiesel production can be conducted in a safe and environmentally responsible manner which generates a quality product (11). It is also important to ensure that best management practices are followed in order to protect the health and safety of the producer and the environment, and to minimize the risk of vehicle/machinery problems. All the points like fuel storage, cold temperature issue, economics, feedstock availability, chemical, waste, safety issues, process description, regulatory issues, process hazard, safety precautions, handling issues, byproduct handling and disposal, biodiesel quality test methods etc were discussed in the said article.

A.S.M.A. Haseeb et al (12) said that the biodiesel blend with the petroleum diesel cause corrosive and tribological attack on metallic components and degrade elastomer parts and these are varies with respect to the variation of the percentage of the blending. For gray cast iron no weight loss or corrosion in 20% biodiesel but moderate loses in 80% biodiesel. In their article they discussed the biodiesel of the peanut, rapeseed, calona, coconut, palm, soybean, sunflower and tallow. For biodiesel an alternative to diesel fuel, a higher CN is desirable whereas higher viscosity and higher cloud and pour points are undesirable. In wear analysis, Fe the main constituents of the most critical components in automobiles shows less or similar wear. Cu shows higher wear in many cases. Similar or less wear is found for the metal Pb and Al in biodiesel. It is evident that non ferrous metals suffer from higher wear loss compared with ferrous metals.

M. V. Nagarhalli et al analyzed the emission and performance characteristics of a single cylinder 3.76 kW, CI engine fueled with mineral diesel and diesel-biodiesel blends at an injection pressure of 200 bar(13). The performance parameters evaluated were break thermal efficiency, break specific energy consumption (BSEC) and the emission measured were carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbon (HC) and oxide of nitrogen (NO_x). The result of experimental investigation with biodiesel blends were compared with that of baseline diesel. The results indicates that the CO emissions were slightly higher, HC emissions decreased from 12.8% for B20 and 2.85% for B40, NO_x emissions decreased up to 39% for B20 and 28% for B40. The efficiency decreased slightly for blends in comparison with diesel. BSEC was slightly more for B20 and B40. They conclude that biodiesel can be used as an alternative to diesel in CI engine without any engine modification.

In “Experimental Investigation of Pongamia, Jatropha and Neem Methyl Esters as Biodiesel on CI engine” T. Venkateswara Rao et al studied the methyl esters of Pongamia (PME), Jatropha (JME), Neem (NME) which are derived through transesterification process (14). Experimental investigations have been carried out to examine properties, performance and emissions of different blends (B10, B20, B40) of PME, JME and NME in comparison to diesel using Single cylinder, four stroke, DI, water cooled engine of bore & stroke 80x110mm, compression ratio of 16.5:1, 3.7 kW at 1500 rpm rated power and 210bar injector opening pressure. In the result and discussion they got the following result: the kinematic viscosities (at room temperature of $35^{o}C$) of different blends of methyl esters are higher than the viscosity of diesel. The density of different blends of methyl esters are increased with increase in blend percentage. A slight drop in efficiency was found with methyl esters when compared with diesel. B20 biodiesel had equal efficiency with diesel. PME had better brake thermal efficiency than compared with the JME and NME. So B20 can be suggested as best blend for biodiesel preparation with pongamia oil. Biodiesel gives less smoke density compared to petroleum diesel. Biodiesel gives less CO than compared to petroleum diesel. When percentage of blend of biodiesel increases, CO decreases. Biodiesel gives fewer hydrocarbons than compared to petroleum diesel.

Madhavi Kamalvanshi et al mentioned that the Jatropha Curcas L. and P. pinnata Pierre is gaining importance as biodiesel crop in India(15). A study was conducted to identify common arbuscular mycorrhizal fungi present in its rhizosphere from different region of India. India has 146 m ha of wasteland of which 33 m ha can be reclaimed for plantation of the biodiesel plants, in addition to arable land that is being used for the plantation. The role of arbuscular mycorrhizal fungi in enhancing plant growth and yield, resistance to drought and salinity and tolerance to pathogens is well documented. The results showed that different arbuscular mycorrhizal fungal species were present at different locations in India.

In impact of biofuel production on food security, it said that by 2030, the global population is projected to increase by 17%, with majority of growth occurring in the poorer tropical regions, thus world food production must increase by 50% to satisfy these demands (16). Similar increases in demand are projected for energy and water. Impacts on food security will depend upon the biofuel crop grown and the context in which it is grown. Three contexts for biofuel production are: the use of existing arable land, expansion of agricultural frontier and the use of marginal land not otherwise suitable for crop production. These will be explored in more detail and effects on food security discussed.

Sudipta C. et al studied the fuel properties of esterified karanja oil and its blend with diesel fuel at different proportions, including engine tests (17). The straight karanja oil blend up to 25% with the petrodiesel meets the standard specification. However, blending of this oil with petrodiesel up to 20% (by volume) can be used safely in a conventional CI engine without any engine modification that could help in controlling air pollution. Different fuel properties like relative density, flash and fire point, cloud and pour point, caloric value, viscosity, cetane number are measured. Engine performances for diesel, B5, B10, B15, B20, B25 were checked at different engine load, BSFC, BSEC. The physical and chemical properties of karanja oil suggest that it cannot be used directly as CI engine fuel due to higher viscosity, density which will result in low volatility and poor atomization of oil during oil injection in combustion chamber causing incomplete combustion and carbon deposits in combustion chamber.

Meher L C et al study deals with the transesterification of pongamia pinnata oil by means of methanol to study the feasibility of methanolysis process by using potassium hydroxide catalysts (18). The yield of biodiesel obtained was >97% by using oil/methanol molar ratio 12:1, potassium hydroxide as catalyst, at 65°C and stirring at 360rpm in 3h. The biodiesel was characterized by TLC (thin layer chromatography) and HPLC (high performance liquid chromatography).

Paul T. Scott et al (19) and others discussed in their paper the important or use of pongamia pinnata in different field like biotic interactions, molecular and cytogenetics, propagation of pongamia pinnata, biomedical and biocidal properties, pongamia as an animal feed supplement, a renewable and sustainable source of biodiesel. The said pongamia pinnata has been identified as a resource for agro forestry, urban land scaping and the bioameloriation of degraded lands. It is nitrogen fixing tree and a member of the family Leguminosae.

The sources of livelihoods of village Kistanupur and Powerguda, Adilabad district, Andra Pradesh were investigated for details by Sreedevi T. K. et al (20). The activities in these villages such as growing nursery, collecting seeds and extracting oil in the village provide employment and livelihood during the off season in the village, which not only bring additional income but also gender equity, as the wage rates related to the pongamia seed collection are same for both male and female labourers. Participating evaluation of seed cake showed increase in crop yields significantly when applied alone or in the combination with normal natural fertilizers.

Refaat A. A. et al discussed the yield percentage obtained from waste vegetable oil is comparable to that obtained from neat vegetable oil which reached 96.15% under optimum condition (21). The biodiesel produced from neat vegetable oil or waste vegetable oil was within the recommended standard of biodiesel fuel. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. Best results were achieved with the neat vegetable oil followed by the domestic waste vegetable oil and the least results were achieved from the restaurant vegetable oil.

Gogoi P. wrote in his paper that the seed of pongamia have about 30-35% oil and upto 27-28% oil can be extracted in crusher and most of the physical and chemical properties of the oil is almost similar to those of the diesel, though 'conardson carbon' residue is higher in case of it and due to high viscosity preheating is needed to start a diesel engine **(22)**. The cost of pongamia cultivation in one hectare is calculated and got that from 15years onwards minimum seed yield will be 20kg per plant and total benefit will increase over the years and stabilized at 20years.

In pongamia's journey from forest to micro enterprise for improving livelihoods Wanni S. P. et al discuss that various statistical estimates of wastelands in India varies from 38.4mha to 187mha. Recently the National Mission on biofuels has identified 13.4mha land that can be readily utilized for biofuel plantation **(23)**. A comparison of biofuel and standard petroleum diesel properties are made and got the value of viscosity (c_p), (30^oC) 52.6, specific gravity ($15^oC/4^oC$), solidifying point (^oC), cetane value, flash point (^oC), carbon residue (%) for biofuel is more than the value of petroleum diesel and the biofuel distillation (^oC), sulfur (%) properties were less than the properties of petroleum diesel.

Xiaohu Fan et al studied the production of biodiesel from canola oil, due to its high FFA content, two step reactions was preferred to process recycled canola oil, that is, acid pretreatment followed by alkali-catalyzed transesterification **(24)**. The first acid catalyzed esterification step, carried out at 55^oC for 1.5 hours at 40/1 molar ratio of methanol to FFA and 5% sulfuric acid concentration (v/v based on FFA), reduced the FFA level from about 11% to 0.41%. The second alkali catalyzed transesterification step converted the esterified recycled canola oil into biodiesel under the following reaction conditions: 6/1 molar ratio of methanol to oil; 1% potassium hydroxide; 55^oC and 1.5 hours. GC analysis based on the ASTM D6584 standard confirmed the production of high quality FAME from recycled canola oil. The recycled canola oil biodiesel obtained has fuel properties that completely met and exceeded ASTM D6751 standard.

A biodiesel storage stability study was done by Farahani M et al on ULSDF petrodiesel and three B100s and fuel blends (B5 & B20) of Tallow based Methyl Ester (TME), a Canola based Methyl Ester (CME) and a Yellow Grease Methyl Ester (YGME) **(25)**. The storage stability study consisted of storing fuel samples in quarter filled plastic and steel Jerry cans, in a fuel shed for 11 months. Temperature and relative humidity in the outdoor storage facility range from 25°C to 35°C and 25% to 100% respectively. All fuels and blends proved to be very stable throughout the storage period. Acid number and the viscosity did not increase beyond the uncertainty of the method used. Sediment level remained low even when temperatures where below the cloud point.

Mahanta P et al extracted oil from the seed using Soxhlet apparatus and for production of biodiesel, the SVO of pongamia pinnata and jatropha curcus were transesterified with methyl alcohol in the presence of strong alkaline sodium hydroxide catalyst in a batch type transesterification reactor **(26)**. The physical and chemical properties test revealed that the pongamia pinnata methyl ester and jatropha curcus methyl ester (B5 and B20) have almost similar or better physical and chemical properties than the diesel oil, except the viscosity which is slightly higher than that of specified range of petrodiesel fuel. Both the blends are suitable as fuel for compression ignition engines without any engine modification. Brake thermal efficiency and SFC results show improvement for B5 and B20. Thermal efficiency was found to be highest with B20.

Sanjay B et al investigate yellow oleander (Thevetia peruviana schum) seed oil to produce biodiesel **(27)**. Transesterification of the oil to biodiesel was carried out in methanol by batch reaction using a heterogeneous catalyst derived from the trunk of Musa balbisiana (banana plant) 96 wt% of the oil is converted to biodiesel at 32°C in 3h. The wt% composition of the biodiesel is methyl oleate 43.72, methyl palmitate 23.28, methyl linoleate 19.85, methyl stearate 10.71

methyl arachidate 2.41. Fuel properties conform to standards sets for ASTM D6751, EN 14214, BSII and BSIII, and in certain aspects better. The biodiesel is free from sulfur and gas exhibited a high cetane number of 61.5.

Mushtaq A et al in their study, sunflower oil was investigated for biodiesel production (28). Sunflower is one of the leading oil seed crop, cultivated for the production of oil in the world. Electric oil expeller was used for the extraction of crude oil. Base catalyzed transesterification process is applied for optimum yield (80%) of biodiesel. Fuel properties of sunflower oil biodiesel were compared with American Society for Testing and Materials (ASTM) and found approximately within the range. Diesel fuel with high viscosity tends to form larger droplets on injection, which can cause poor combustion, increase exhaust smoke and emissions. The method of reducing the viscosity of vegetable oil is fuel blending.

Biodiesel derived from vegetable oil has been shown to be a viable alternative to the conventional transport fuel, petrodiesel for diesel engines and is receiving worldwide attention because of its renewability, biodegradability, nontoxicity and carbon neutrality (29-31). Biodiesel fuel has the potential to reduce the level of pollutants and potential or probable carcinogens and its usage will allow a balance to be sought between agriculture, economic development and the environment.

Biodiesel, an alternative and renewable fuel for diesel engines, consists of alkyl esters of long chain fatty acids, more commonly methyl esters and is typically made from nontoxic, biological resources such as vegetable oils, animal fats or even used cooking oils by transesterification with methanol.(32,33) Biodiesel has low emission profiles and so it is environmentally beneficial. The biodiesel is quite similar to conventional diesel fuel in its main characteristics.

F. Ma et al state that there are four primary ways to make use of vegetable oils and animal fats.[34] They are (i) direct use and blending with diesel, (ii) microemulsions with solvents such as methanol, ethanol and/or other alcohols, (iii) thermal cracking (pyrolysis) by means of heat or by heat with the aid of a catalyst and (iv) transesterification (alcoholysis) with short chain alcohols in presence of a catalyst. The most commonly used method is transesterification with methanol or ethanol as the physical characteristics of fatty acid methyl or ethyl ester (biodiesel) are very close to those of diesel fuel, and the process is relatively simple.

S. Y. Li et al found that during transesterification, the backbone of triglyceride is replaced with three alkyl groups of the alcohol (35). Catalyst for transesterification can be alkali, acid, enzyme and heterogeneous catalysts. Since the base-catalyzed transesterification is rapid and easy to scale-up, it has been widely used in industry.

Biodiesel can be used alone or mixed in any ratio with petroleum based diesel fuel in most existing modern four stroke compression ignition diesel engines with very few technical adjustment or no modification.(36,37) Biodiesel as a neat can be used as a direct substitute for petrodiesel and is technically called B100. The preferred ratio of mixture ranges from 5% and 20%. The blending ratio has been investigated by various authors in CI engines. Up to 20% blending of biodiesel with diesel has shown no problems in engine parts. Even B20 biodiesel results in considerable reduction in pollutants emitted from the exhaust of CI engines.

Y. C. Sharma et al in their paper state that biodiesel along with bio-ethanol has the potential to replace approximately 10% of mineral diesel consumption in Europe and meets 5% of demand in Southwest Asia (38). Biodiesel must comply with fuel standards such as ASTM D6751 or EN 14214, before its commercial use is approved in diesel engines.

The Brazilian government authorized the use of biofuels to diversify the energy matrix, thereby inserting biodiesel fuel into the national fuel market. The initial commercial use of biodiesel was the addition of 2% biodiesel to mineral diesel. However, resolution no. 6 of the National Council of Energy Policy states that, beginning January 1st, 2010, diesel fuel sold in Brazil must contain 5% biodiesel.(39) In France, for example, biodiesel also has been used in urban busses, in proportion up to 30% in fossil diesel, in order to decrease vehicle emission in big cities.

Biodiesel, especially for the blends with small portion of biodiesel, is technically feasible as an alternative fuel in CI engines with no or minor modification to engine. Following in line with global trend, India declared its biofuel policy in which biodiesel, mainly from Jatropha, would meet 20% of the diesel demand beginning with 2011 – 2012 **(40)**.

The majority of studies have shown that SO_x, unburned hydrocarbons and particulate matter are significantly reduced for biodiesel when compared with conventional fossil based diesel fuel emissions. **[41-44]** CO emission reduces when using biodiesel due to higher oxygen content and the lower carbon to hydrogen ratio in biodiesel compared to diesel. There exists the inconsistent conclusions, some researches indicated that the CO_2 emission reduces for biodiesel as a result of low carbon to hydrocarbons ratio, and some researches shows that the CO_2 emission increases or keeps similar because of more effective combustion.

2.3 Production Process (45)

The first and foremost requirement of a production process is collection of raw material. The raw material for biodiesel production (may be seed e.g. soybean, rapeseed, cotton, etc or stem e.g. jatropha) is collected and dried to remove unbounded moisture. From the dried material, oil is extracted by the process of rotary vacuum evaporation. The oil is filtered and then taken for transesterification process to separate unblended biodiesel and glycerin.

2.3.1 Transesterification

Transesterification (also called alcoholysis) is the well established chemical reaction of vegetable oils and animal fats with an alcohol to form fatty acid alkyl esters and glycerol(45). Neat vegetable oil and animal fats cannot be used directly in diesel engine because of their high viscosity and low volatility and the major objectives of transesterification are to overcome these problem. A 3:1 M ratio of alcohol to oil (stoichiometrically) is required to complete the reaction. However, since the reaction is reversible, the excess alcohol is practically used to shift the equilibrium to the product side and raise the product yield. Methanol and ethanol are the most common alcohols used in transesterification, especially methanol due to its physical and chemical advantages (polar and shortest chain alcohol) and its low cost. In addition a catalyst is normally used to accelerate the reaction and improve the conversion yield.

Base, acid and enzyme are three types of catalyst which are usually used in the transesterification reaction. The transesterification reaction consists of a sequence of three reversible consecutive reactions. In the first step, triglycerides are converted to diglycerides; in the second, diglycerides are converted to monoglycerides. In the last step, monoglycerides are converted to glycerol. Three esters are obtained from one triglyceride molecule; one ester molecule for each glyceride at each step.

Several methods for production of biodiesel have been developed by scientists. In these methods, the transesterification process is carried out in the presence and absence of catalyst. The catalyst is applied to accelerate the reaction and produce biodiesel with higher quality.

The production of biodiesel from any fat or oil through a process is called transesterification. Transesterification or alcoholysis is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that alcohol is used instead of water (Fig. 2.1). In the production of biodiesel, oil and fats are transesterified with methanol in the presence of an acid, base or enzyme (lipase) catalyst to afford fatty acid methyl esters (FAME) and glycerol as a byproduct (Fig. 2.2) [46,47].

$$\underset{\text{Ester}}{\text{RCOOR'}} \quad + \quad \underset{\text{Alcohol}}{\text{R''OH}} \xrightleftharpoons{\text{Catalyst}} \underset{\text{Ester}}{\text{RCOOR''}} \quad + \quad \underset{\text{Alcohol}}{\text{R'OH}}$$

Figure 2.1 General Equation of Transesterification

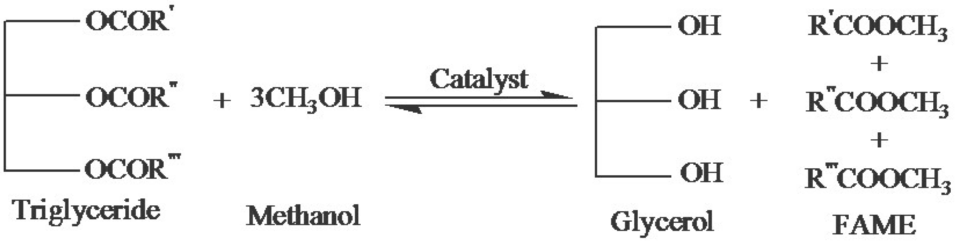


Figure 2.2 General Equation for Transesterification of a Triglyceride

Methanol, ethanol, propanol, butanol and amyl alcohol are the alcohol used in transesterification. For the purpose of low cost and its physical and chemical advantages, the methanol is used. This process has been widely used to reduce the high viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance [48].

Transesterification is a reversible reaction and proceeds by mixing the reactants. Transesterification consists of a number of consecutive and reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by conversion of diglycerides to monoglycerides and monoglycerides to glycerol, yielding methyl ester molecule per mole of glyceride at each step (Fig. 2.3).

$$\begin{aligned} &\text{Triglyceride} + \text{ROH} \rightleftharpoons \text{Diglyceride} + \text{R}'\text{COOR} \\ &\text{Diglyceride} + \text{ROH} \rightleftharpoons \text{Monoglyceride} + \text{R}''\text{COOR} \\ &\text{Monoglyceride} + \text{ROH} \rightleftharpoons \text{Glycerol} + \text{R}'''\text{COOR} \end{aligned}$$

Figure 2.3 Transesterification reactions of vegetable oil with alcohol to esters and glycerol.

The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. It is observed that transesterification is faster when catalyzed by alkali [34, 49].

2.3.2 Catalysts

Alkaline, acidic and enzymatic catalysts have been used, depending on the characteristics of feedstock. The use of each catalyst has some advantages and disadvantages. The alkaline catalysts are preferable in terms of their lower reaction temperature, higher reaction speed (lower reaction time) and higher conversion efficiency in comparison with the acid catalysts. However acid catalysts are intensive to FFA and are better than the alkaline catalysts for vegetable oils with FFA greater than 1%. The transesterification reaction can also be carried out by using enzymatic catalysts, which looks attractive and encouraging for reasons of easy product separation, purification, washing and neutralization. They can also be applied to high FFA feedstock. But the problems associated with enzyme catalysts are their higher cost and longer reaction time.

In all these methods, the transesterification process is carried out by using conventional heating, wherein, heat energy is transferred to the reaction mixture though convection, conduction and radiation from the surface of the reactor. Thus, in conventional heating, a large amount of the energy is needed to heat the media, which makes this method insufficient. In addition, a long reaction time (30 min to 8 h) is required to obtain a satisfactory conversion of oil (up to 95%).

For the acid catalyzed transesterification, the transesterification process is catalyzed by Bronsted acids, preferably by salfonic and sulfuric acids. These catalysts give very high yields of alkyl esters, but the reactions are slow, requiring typically temperature above 100°C and more than 3h to complete the conversion [50]. Although transesterification by acid catalysis is much slower than that by alkali catalysis [34, 51]; acid catalyzed transesterification is more suitable for glycerides that have relatively high free fatty acid contents and more water.

For the base catalyzed transesterification, the NaOH, KOH, carbonates and alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide were the bases used for transesterification. The base catalyzed transesterification of vegetable oils proceeds faster than that catalyzed by the same amount of an acidic catalyst [34, 50].

In the Enzyme catalyzed transesterification, uses the enzymes or lipases which are naturally occurring substances. Due to their ready availability and the ease with which they can be handled, enzymes have been widely applied in organic chemistry. They are widely employed to catalyze hydrolysis, alcoholysis, esterification and transesterification of carboxylic esters. Lipases have excellent catalytic activity and stability in non-aqueous media, which facilitate the esterification and transesterification process during biodiesel production. Enzyme based transesterification carried out at moderate temperatures with high yields, but this method cannot be used in industry today due to high enzyme costs and the problems related to its deactivation caused by feed impurities. [46]

In particular, the byproduct, glycerol can be easily removed without any complex process and also that free fatty acids contained in waste oils and fats can be completely converted to alkyl esters. On the other hand, in general the production cost of a lipase catalyst is significantly greater than that of a basic one.[52] If the enzyme-based transesterification is adopted at a large scale, a large demand would induce large-scale production of the enzyme and would result in lowering the market price of lipases. The existing usage of enzymes in several areas, such as detergents, dairy products and textile and leather processing reflect the soundness of such a strategic approach. [53]

2.3.3 Heterogeneously catalyzed transesterification

Transesterification using a conventional alkali catalyzed process may give high conversion levels of triglycerides to their corresponding methyl ester in short times, but the reaction has several drawbacks: it is energy intensive; recovery of glycerin is difficult; the catalyst has to be removed from the product; alkali waste –water requires treatment and free fatty acids and water interfere with the reaction.[34]

In order to minimize homogeneous process problems, and the present day high production cost of biodiesel, heterogeneous catalysts are promising for the transesterification reaction of vegetable oils to produce biodiesel. Unlike homogeneous, heterogeneous catalysts are environmentally benign and could be operated in continuous processes. Heterogeneous catalysts are advantageous for biodiesel production because of their reusability and consequently their more eco-friendly nature. These catalysts greatly simplify the post-treatment of the products (separation and purification) and they could give high quality of product. They can be easily separated from the system at the end of the reaction and could also be reused. Besides, the use of heterogeneous catalyst does not produce soaps through free fatty acid neutralization or triglyceride saponification. They can be designed to give higher activity, selectivity and longer catalyst lifetime. [54-58]

2.4 Recent Trends:

Recent advancement in technology and chemical process are revolutionizing the production process of biodiesel. Innovative techniques will reduce the time of production and complexity of the chemical processes involved, whose direct effect can be seen on the economy of production (59).

Some of the recent developments are Ultrasonic Assisted Production, Microwave Assisted Production and Production using Supercritical Fluid.

2.4.1 Ultrasonic Assisted Production(59)

Newly, the use of ultrasound has gained interest in biodiesel production. Ultrasonication (ultrasound) is producing a sound wave with a frequency higher than human audibility limits. Ultrasound provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction. Hence, the reaction time is shortened and the biodiesel yield is increased. The ultrasonication reactor was first introduced by Hielscher Ultrasound GmbH for biodiesel production in the year 2000. The Hielscher ultrasonic reactor adopts an ultrasonic processor, which operates at an ultrasonic frequency ranged from 18 to 20 kHz. Ultrasound waves at this frequency create an intense cavitations in liquids. The collapse of the cavitations bubbles creates emulsification of immiscible liquids. The collapse of the cavitations bubbles creates emulsification of immiscible liquids. The ultrasonic reactor is also capable of delivering a biodiesel yield of 99% at a reduced amount of catalyst and methanol required in the reaction. Furthermore, Hielscher ultrasonic reactor shows outstanding energy efficiency, when compared to high-shear mixing and hydrodynamic cavitations. The Hielscher ultrasonic reactor required 1.4kWh/m^3 (approximately) for biodiesel production. However, the hydrodynamic magnetic impulse cavitations require 32.0 kWh/m^3 (approximately) and the high-shear mixing requires 4.4kWh/m^3 (approximately) to achieve the related result.

The biodiesel yields achieved with heterogeneous catalyst, assisted by ultrasound were generally high and comparable with those of homogeneous catalysts. Conversely, the reaction temperatures were slightly higher while the reaction times were longer. Catalyst loading under ultrasonic field is usually higher than that for homogenous catalyst but this does not significantly affect the economics of the process because of simple separation and reusability of catalyst.

2.4.2 Microwave Assisted Production [60]

Microwave irradiation is an electromagnetic irradiation in the range of wavelength from 0.01 to 1m and corresponding frequency range of 0.3 to 300GHz. Generally radar transmissions use the wavelengths between 0.01 and 0.25m and telecommunications use the remaining wavelengths. All microwave reactors for chemical synthesis and all domestic microwave ovens operate at 2.45GHz frequency, which corresponds to a wavelength of 12.25cm. This is in order to avoid any interference with telecommunications and cellular phone frequencies. The microwave region of the electronic spectrum is shown in the fig. 2.4.

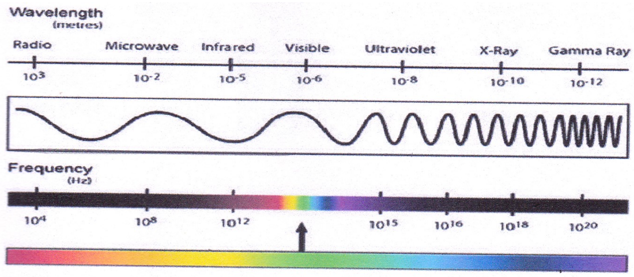


Figure: 2.4 Range of Wavelengths (Source: www.elsevier.com/locate/rser)

Microwave irradiation is a well-established method of accelerating and enhancing chemical reactions because it delivers the energy directly to the reactant. Therefore, heat transfer is more effective than in conventional heating and the reaction can be completed in a much shorter time. Thus microwave irradiation is one of the best methods of reducing the reaction time and obtaining higher yields in the production of biodiesel. It enhances the speed of the reaction and the makes the separation process easier in comparison with conventional heating.

A diagrammatic representation of microwave assisted biodiesel production is as shown in fig.2.5

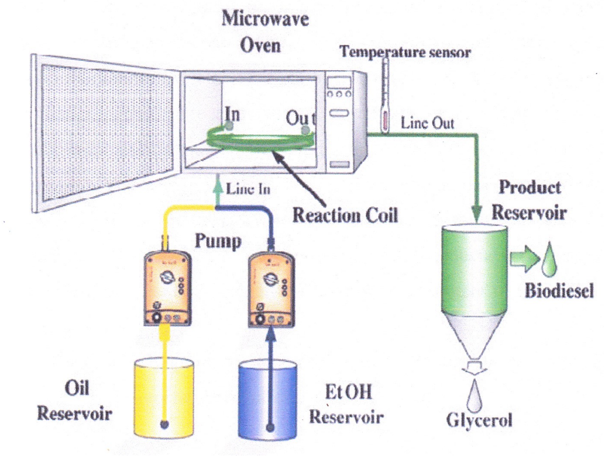


Figure 2.5 Microwave assisted production process (Source: www.elsevier.com/locate/rser)

2.4.3 Production using Supercritical Fluid

In conventional transesterification of fats and vegetable oil for biodiesel production, the production of free fatty acids and water are often undesirable because their presence causes soap formation and catalyst deactivation. However, the presence of water has positive effects in non-catalytic supercritical method because it promotes the mechanisms of reaction. The technology is able to overcome the reaction initiation lag time caused by the extremely low solubility of the alcohol.

Compared to chemical reactions using catalysts, the supercritical method offers three main advantages. First, it is environment friendly. Catalyst is not needed in the reaction, making the after production process much simpler since the separating process of the catalyst and saponified products from methyl esters become unnecessary. The waste water containing acid or alkali, resulted from the after production process can also be avoided. Second, supercritical reaction takes a shorter reaction time than the traditional catalytic transesterification reaction and the conversion rate is very high. The catalytic transesterification reaction requires several hours to reach reaction equilibrium, but the supercritical method only takes 2 to 4 minutes. Third, neither acidity nor water content influences the reaction in supercritical method. This allows a variety or resources to be used as feed materials.

The disadvantages of the supercritical methods stem mostly from high pressure and temperature requirement.

2.5 Feedstock in the production of biodiesel

Biodiesel is a mono alkyl ester mixture derived from oils and fats, which have characteristics similar to petroleum-derived diesel fuel. The source for biodiesel production is chosen according to climate and feedstock availability in each region or country. Any fatty acid source may be used to prepare biodiesel, but most research article have reported soybean as a biodiesel source. Generally, the most abundant vegetable oil in a particular region is the most common feedstock. Thus, soybean oil is the largest source of vegetable oil in the United States, while rapeseed and sunflower oils are the largest source in Europe. Similarly, palm oil in Southeast Asia (Malaysia and Indonesia) and coconut oil in the Philippines are the largest sources of vegetable oil.[61,62] Varied resources are used as feedstock for biodiesel production, some of them as mentioned in table 2.1. The common fatty acids found in vegetable oils and animal fats are shown in table 2.2.

Table 2.1 Feedstock used for biodiesel production [45, 60, 63]

Edible oils	*Non-edible oils*	*Animal fats*	*Other resources*
Soybeans	Almond	Lard	Bacteria
Rapeseed	Andiroba	Tallow	Algae
Canola	Babassu	Poultry fat	Fungi
Safflower	Camelina	Fish oil	Micro algae
Barely	Cumaru		Tarpenes
Coconut	Jatropha curcus		Latexes
Copra	Jatropha nana		Cooking oil
Cotton seed	Jatropha oil		
Groundnut	Pongamia glabra		
Oat	Mahua		
Rice	Palm		
Sorghum	Tobacco seed		
Wheat	Rubber plant		
Winter rapeseed oil	Rice bran		
	Sesame		
	Salmon oil		
	Piqui		
	Brassica carinata		
	Laurel		
	Lesquerella fendleri		
	Karang		
	Abutilon muticum		
	Cynara cardunculus		

Table 2.2 Common fatty acids found in vegetable oil and animal fats (61, 64)

Sl. No.	*Fatty acids*	*Number of Carbon and Double bonds*
1	Arachidic (eicosanoic) acid	C20:0
2	Arachidomic (5,8,11,14-eicosatetraenoic) acid	C20:4
3	Behenic (docosanoic) acid	C22:0
4	Capric (decanoic) acid	C20:0
5	Carotic acid (hexacosanoic) acid	C26:0
6	Eurcic (cis-13-docosenoic) acid	C20:1
7	Gadoleic (cis-9-eicosenoic) acid	C20:1
8	Gondoic (cis-11-eicosenoic) acid	C20:1
9	Lauric (dedecanoic) acid	C12:0
10	Linolenic (9,12,15 – octadecatrienoic) acid	C18:3
11	Linoceric (tetracosanoic) acid	C24:0
12	Myristic (tetradecanoic) acid	C14:0
13	Nerronic (cis – 15 – tetracosenic) acid	C24:1
14	Oleic (cis – 9 – octadecanoic) acid	C18:1
15	Palmitric (hexadecanoic) acid	C16:0
16	Palmitoleic (cis – 9 – hexadecanoic) acid	C16:1
17	Stearic (octadecanoic) acid	C18:0

Around 84% of the world biodiesel is produced from the rapeseed oil **(4)**. The remaining portion is from sunflower oil (13%), palm oil (1%) and soybean oil and others (2%). Since more than 95% of the biodiesel is made from edible oil, there are many claims that a lot of problems may arise. By converting the edible oils into biodiesel, food resources are actually being converted into automobile fuels. It is believed that large scale production of biodiesel from edible oils may bring global imbalance to the food supply and demand market. Recently, environmentalist have started to debate on the negative impact of biodiesel production from edible oil on our planet especially deforestation and destruction of ecosystem **(4)**. They claimed that the expansion of oil crop plantations for biodiesel production on a large scale has caused deforestation in countries such as Malaysia, Indonesia and Brazil since more and more forest have been cleared for plantation purposes. Although there is continuous increase in the production of the vegetable oil, the ending stocks of vegetable oils are however continuously decreasing due to increasing production of biodiesel. With the implementation of biodiesel as a substitute fuel for petroleum-derived diesel fuel, this may lead to the depletion of edible-oil supply worldwide. In order to overcome this, suggestion has been made and research has been conducted to produce biodiesel by using alternative or greener oil resources such as non-edible oils. Furthermore, most of the non-edible plants can be grown in wasteland and infertile land which otherwise would not have much use. This would not only allow wasteland utilization but at the same time would also be used to produce oil crops for biodiesel production without the need to compete with food crops for the limited arable land. Taking all these factors into consideration, non-edible oils definitely have the advantage over edible oils as biodiesel feedstock.

However, biodiesel production from conventional sources (soybean, rapeseed, sunflower, palm etc.) increasingly has placed strain on food production, price and availability **(4,33)**. Therefore, the search for additional regional biodiesel feedstock is an important objective. There are various biodiesel sources studied from less common or non-conventional oils. Reported non-conventional feedstock used for the production of biodiesel is shown in table 2.3.

Mahua oil was transesterified using methanol in presence of alkali and the biodiesel obtained was studied for fuel properties and exhaust emission characteristics (93). Engine performance test shows that MOME as a fuel do not differ greatly from that of diesel. A slight power loss, combined with an increase in fuel consumption, was experienced with MOME. This may be due to the lower heating value of the ester. Emission of CO, HC are too low for MOME. Oxides of nitrogen were slightly low for ester compared with diesel. The MOME could be used as alternative fuels in a diesel engine instead of diesel fuel.

Shang Q et al studied the process of transesterification between Tung oil and methanol catalyzed by KOH at 25°C, 40°C and 60°C (94). From UV, FT-IR and MG-MS they got the reaction temperature had little effect on the structure and composition of the Tung oil during transesterification. The properties of Tung oil biodiesel and its blends with O# diesel show that after a month, the acid value changed from 0.11 to 0.18mg KOH/g, the kinetic viscosity increased about 13% and cold filter plugging point (CFPP) increased from -19°C to -15°C. B20 or lower blends were more stable than Tung oil biodiesel.

Table 2.3 Non-Conventional seed oil

Sl. No.	Name	Oil content (wt%)
1	*Croton megalocarpus* [64]	32
2	Coriander (*coriandrum sativum L.*)[65]	26-29
3	Camelina (*camlina saliva L.*)[66,67]	30
4	*Euphorbia lathyris L.*[68]	48
5	Field pennycress (*Thlaspi arvense L.*)[29]	29
6	Guindila (*Guindila trinervis*)[69]	28-29
7	*Guizotia abyssinica*[70]	30
8	Hemp (*cannabis saliva L.*)[14]	26-38
9	Hazelnut oil[71]	60
10	Honne (*calophyllum inophylum L.*)[72,73]	75
11	*Idesia polycarpa* var[74]	26
12	*Jatropha curcas*[75-78]	30-50
13	*Moringa oleifera*[61]	35
14	Osaga orange (*Maclura pomifera)*[79]	32
15	*Pongamia glabra*[80,81,55]	33
16	*Pistacia chinensis*[12]	40
17	Parah (*Elateriospermum tap 03)*[82]	38
18	Rubber (*Hevea brasiliensis)*[83]	40-50
19	Rocket seed plant (*Eruca sativa Mill*)[84]	34
20	Roselle (*Hibiscus sabdariffa L.)*[85]	18
21	Stillingia (*Sapium sebiferum Roxb*)[86]	32

22	*Sapium sebiferum L.*[87]	29
23	*Syagrus coronota* (Mast.) Becc.[88]	39
24	*Schizochytrium limacinum*[89]	50
25	Terminalia (*Terminalia belerica* Robx),[90]	43
26	Tobacco seed,[91]	38
27	Yellow oleander (*Thevetia peruviana* Schum),[27]	63
28	*Zanthoxylum bungeanum* Maxim,[92]	24-28

The methyl esters are produced from transesterification of vegetable oils or animal fats with alcohol in the presence of acid or base catalyst **(95)**. In their work, biodiesel was obtained by a transesterification reaction of bovine fat with methanol using KOH as a catalyst. The blends diesel/biodiesel and biodiesel (B100) were also compared with diesel through consumption tests in a diesel engine used for energy generation. All tests demonstrated that biodiesel and its formulations with diesel can present similar results, or sometimes better results, to those of mineral diesel.

Single, binary, ternary and quaternary mixtures of canola (low erucic acid rapeseed), palm, soybean and sunflower oil methyl esters (CME, PME, SME & SFME respectively) were prepared and important fuel properties were measured, such as oil stability index (OSI), cold filter plugging point (CFPP), cloud point (CP), kinematic viscosity (40°C), lubricity, acid value (AV) and iodine value (IV) **(96)**. To the above properties the IV and OSI of SME was improved to satisfy EN 14214 specification through blending with CME, PME or SFME. The CFPP of PME was improved through blending with CME, SME and SFME; statistically significant relationship were discovered between OSI and IV, OSI and SFAME content, OSI and CFPP, CFPP and IV, CFPP and SFAME content. The fuel properties of biodiesel can be significantly modified through blending with biodiesel obtained from different feed stocks.

Investigate the oxidation stability of biodiesel produced from Manketti seeds oil **(97)** and determined the fuel related properties of MOME fulfilled the minimum requirements specified in global biodiesel standards, such as ASTM 6751 and EN 14214. However the oxidation stability of the MOME did not meet the EN 14214 specification (6h) because of the presence of unsaturated fatty acids, which is the primary reason for lower oxidation stability of biodiesel.

In their review paper they mentioned that waste cooking oil **(98)** is an economical choice for biodiesel production, because of its availability and low cost. The products formed during frying, such as free fatty acid and some polymerized triglycerides, can affect the transesterification reaction and the biodiesel properties. Apart from this phenomenon, the biodiesel obtained from waste cooking oil gives better engine performance and fewer emissions when tested on commercial diesel engine.

2.6 Specification of biodiesel and fuel properties:

Since biodiesel is produced in quite differently scaled plants from vegetable oils of varying origin and quality, it was necessary to install a standardization of fuel quality to guarantee engine performance without any difficulties. As standardization is a prerequisite for successful market introduction and penetration of biodiesel, standards or guidelines for the quality of biodiesel have also been defined in countries like Germany, Italy, France, the Czech Republic and in the United states. There are different parameters which define the quality of biodiesel.**(99,100)** In table 2.4, the limits for European (En 14214) and also for American specification (ASTM D6751) are shown. Some properties in the standard, such as cetane number or density, can reflect the properties of the chemical compounds that make up the biodiesel, and other properties provide an indication of the quality of the production process. Generally, biodiesel standards identify the parameters that pure biodiesel must meet before being used as a pure fuel or being blended with conventional diesel fuels.

Table 2.4 ASTM D6751 and EN 14214 biodiesel (B100) specification (99, 100)

Properties	*ASTM D6751*	*EN 14214*
Density at 15°C	870-890 kg/m^3	860-900 kg/m^3

Kinematic viscosity @ 40^{o}C	1.9-6.0 mm^2/s	3.5-5.0 mm^2/s
Cetane Number	47(minimum)	51(minimum)
Pour point (^{o}C)	Not Specified	Not Specified
Flash point	130 ^{o}C minimum	>101 ^{o}C minimum
Cloud point (^{o}C)	To report	Not Specified
Cold filter plugging point (^{o}C)	Not Specified	Not Specified
Lubricity (60^{o}C,µm)	Not Specified	Not Specified
Ramsbottom carbon residue (mass%)	Not Specified	Not Specified
Acid value	0.50 mg KOH/g maximum	0.50 mg KOH/g maximum
Iodine value	Not Specified	120 gI$_2$/100g maximum
Total sulphur (ppm)	15(max)	10(max)
Sulphated ash	0.02% m/m maximum	0.02% m/m maximum
Copper strip corrosion	Class 3 maximum	Class 1 rating
Water content and sediment	0.050 (%v) maximum	500mg/kg maximum
Free glycerine	0.02% m/m maximum	0.02% m/m maximum
Total glycerol	0.24% m/m maximum	0.025% m/m
Methanol content	0.20% m/m maximum	0.20% m/m maximum
Phosphorus	10 mg/kg maximum	10 mg/kg maximum
Distillation temperature	360 ^{o}C	–
Sodium and potassium	5.00 ppm maximum	5.00 mg/kg maximum

Oxidation stability	3h maximum	6h minimum
Carbon residue	0.05 wt% maximum	0.30% m/m maximum
Calcium and magnesium	5 ppm maximum	5 ppm maximum

Kinematic viscosity is one of the most important properties as it measures the resistance to flow due to internal friction(101). High values of kinematic viscosity give rise to poor fuel atomisation, incomplete combustion and carbon decomposition on the injectors. Therefore, the biodiesel viscosity must be low. Biodiesel fuel blends generally have improved lubricity; however their higher viscosity levels tend to form larger droplets on injection which can cause poor combustion and increased exhaust smoke. The viscosity of fatty acid methyl esters can go to very high levels and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore, the viscosity specifications proposed are nearly same as the diesel fuel.

Flash point of a fuel is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source under specified conditions (101). Flash point varies inversely with the fuel's volatility. Flash point minimum temperatures are required for proper safety and handling of fuels. It is noted that the biodiesel component must meet a flash point criteria, prior to blending, for the purpose of assuring that the biodiesel component does not contain methanol. The flash point of biodiesel is higher than the petrodiesel, which is safe for transport purpose. High values of flash point decreases the risk of fire.

Cold Filter Plugging Point (CFPP) of a fuel reflects its cold weather performance. At low operating temperature, fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pump and injectors. CFPP defines the fuel limit of filterability, having a better correlation than cloud point for biodiesel as well as petrodiesel. Normally either pour point or CFPP are specified (102). The cloud point of any petroleum fuel is defined as the temperature at which a cloud of wax crystals first appears in the oil when it is cooled at a specific rate. The pour point is the lowest temperature at which the oil specimen will flow. Both parameters are often used to specify cold temperature usability of fuel oils. The cloud and pour points are related to the cold start of the motor. Both points must be sufficiently low, because if the biodiesel is frozen, the motor will not start.

The cetane number is a prime indicator of fuel ignition quality in the realm of diesel engines. It is consequently similar to the octane number used for gasoline. Generally, a compound that has a high octane number tends to have a low cetane number and vice versa(103). The cetane number measures how easily ignition occurs and the smoothness of combustion. Higher is the cetane number better it is in its ignition properties. Cetane number affects a number of engine performance parameters like combustion, stability, driveability, white smoke, noise and emissions of CO and hydrocarbons. Biodiesel has higher cetane number than conventional diesel fuel, which results in higher combustion efficiency.

Acid number is a measure of acids in the fuel. These acids emanate from two sources: (i) acids utilized in the production of the biodiesel that are not completely removed in the production process; (ii) degradation by oxidation.(104) For biodiesel blends the acid number will change as a result of the normal oxidation process over time. Once purchased, biodiesel fuel blends that will not be utilized immediately should be monitored for changes in acid number as an indicator of fuel degradation.

The iodine value is related to the chemical structure of the fuel. The iodine value is a measure of the unsaturation in fats and oils. Higher iodine value indicates higher unsaturation in fats and oils(104). Standard iodine value for biodiesel is 120 for Europe’s EN 14214 specification. This requirement is limited by the standard limits of linolenic acid methyl ester composition for biodiesel. The limitation of unsaturated fatty acids is necessary due to the fact that heating higher unsaturated fatty acids results in polymerization of glycerides. This can lead to the formation of deposits or deterioration of the lubricating property. Fuel with this characteristic is also likely to produce thick sludge in the sump of the engine, when fuel seeps down the sides of the cylinder into the crankcase.

Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel(104). Conradsons carbon residue for biodiesel is more important than that in diesel fuel because it shows a high correlation with pressure of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities.

Lubricity is a measure of the fuel's ability to provide adequate lubrication of the components of the fuel system, including fuel pumps and injectors (104). The precision required in the manufacturing of these components and the significant influences of abnormal wear require that they may be adequately protected from scuffing, scratching, wearing etc. that may affect their fuel delivery characteristics. The level specified is consistent with that recommended by supplies of fuel injection equipment for modern diesel engines.

The presence of high level of alcohol in biodiesel causes accelerated deterioration of natural rubber seals and gaskets. Therefore control of alcohol content is required. Biodiesel fuel mainly consists of fatty acid alkyl esters and its quantities are specified according to the specifications of various countries. The presence of mono-di-and triglycerides cause engine problems like fuel filter plugging affecting the fuel properties and are specified in most of the biodiesel standards.

One of the main criteria for the quality of biodiesel is the storage stability. From the time of production, biodiesel fuels are unstable due to the natural oxidation process. The process involves a free radical chain reaction that continues until the reactive molecular links or available oxygen is depleted. Peroxides are reactive oxidizing agents formed during the first step of fuel oxidation. At high concentration, peroxides or the free radicals form can damage or degrade certain plastics and elastomers, particularly at higher temperatures. Subsequent steps in the oxidation process produce acids, gums, polymers and other insoluble. Polymers and other insoluble materials that are formed during oxidation result in fuel filter blockage. Fuel that meets the specified limit at the time of retail sale is expected to provide six months of storage capability, depending on storage conditions, before degradation occurs. Fuel should be monitored to determine if degradation has taken place and necessary steps taken to avoid the use of degraded fuel. It is important to note that the test method utilized must be modifies to use glass fibre filters to prevent degradation of the filter media by the biodiesel. If too high unsaturation results in an oxidation problem, a stabilizer (antioxidant) can be added to extend the storage life of the biodiesel.

The properties of biodiesel and diesel fuels show many similarities and therefore, biodiesel is rated as a strong candidate as an alternative to diesel. This is due to the fact that the conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-third, reduces the viscosity by about one-eighth, and increases the volatility marginally. Biodiesel contains 10-11% oxygen (w/w), thereby enhancing the combustion process in an engine. It has also been reported that the use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the biodiesel without having any negative effect on its cold flow properties. However, starting problems persist in cold conditions. Further, biodiesel has a high cetane number and a high flash point.

2.7 Performance Analysis

A study has been done to examine the work done on performance analysis of a compression ignition engine of internal combustion engine. This has been carried out to get an idea on the different method used for the performance analysis of the compression ignition engine. Few of the important works of researchers are discussed below.

Lebedevas S et al carried out research in to the change of parameters concerning the fuel economy thrust and harmful components of exhaust gases, namely hydrocarbon (HC), carbon monoxide (CO) and nitric oxide (NO_x) was carried out to evaluate the efficiency of fuel replacement; and that is, mineral diesel fuel, which is normally used by diesel engine fleets of agricultural machinery in Lithuania, was replaced with biofuel (biodiesel), which is rapeseed oil methyl ester (RME) and the research was done on a model diesel engine F2L511 and a single section of diesel engine A41 (105). Fuel blends of mineral diesel fuel and RME biodiesel fuel and pure RME were tested as B10, B15, B30, B100. A non-linear change of operational characteristics were determined depending on the loads of the diesel engine. From technical ecological parameters, B30 biodiesel fuel was acknowledged as the most convenient and reliable one being tested within a wide range of speed and load regimes. An improvement of all the ecological parameters was estimated by optimization of the diesel engine injection timing while running on RME.

Ozkan M did comparative study of the effect of biodiesel and diesel fuel on a four cylinder, four stroke, turbocharged IDI CI engine (106). The engine was operated with the same settings for both fuel types during the experiments and no alternation has been made in the fuel system elements.

Maximum brake mean effective pressure (BMEP) with biodiesel was 16% lower than obtained with diesel fuel, with the difference being 7.5% under maximum power while biodiesel reduced the maximum engine power by 8.6%, it increased the brake specific fuel consumption by 9.6%.

Exhaust emission showed that CO emission of biodiesel is lower than those of diesel fuel. In terms of HC emission, diesel fuel has produced better results than the biodiesel fuel.

Biodiesel results higher NO_x emission when the engine operation range is considered. The coefficient of variation of ignition delay of both fuels had similar characteristics.

Changes of maximum cylinder pressure have occurred at the same magnitude for both fuels for the same engine speed. The coefficient of variation of maximum cylinder pressure for both fuels had similar characteristics and considerably increased under maximum power conditions.

In this study an oxygenated additive diethyl ether (DEE) was blended with biodiesel in the ratio of 5%, 10%, 15% and 20% and tested their performance in a computerized Kirloskar diesel engine of AVI model, four stroke, direct injection, naturally aspirated, water cooled engine (107). The diesel engine is coupled with an eddy current dynamometer and data acquisition system, for saving data. The properties of biodiesel (Yellow oleander) were determined and the properties brake thermal efficiency (BTE), nitrogen oxide (NO_x), exhaust gas temperature

(EGT), hydrocarbon (HC), smoke opacity verses load (kg) were analyzed and cylinder pressure verses crank angle, rate of heat release verses crank angle for different blends of DEE and diesel were analyzed. From the detailed study of the mentioned above, they conclude that the 20% DEE blend with Thevetia perviana (Yellow oleander) biodiesel would result better performance and lesser emission.

Non-edible filtered viscous (72cst at 40^{o}C) and high acid value (44mg KOH/gm) polanga (Calophyllum inophyllum L.) oil based monoesters (biodiesel) produced by triple stage transesterification process and blended with high speed diesel (HSD) (20%, 40%, 60%, 80% and 100%) were tested for their use at varying loads (0%, 20%, 40%, 60%, 80% and 100%) as a substitute fuel of diesel in a single cylinder diesel engine **(108)**. The brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) were calculated from the recorded data. The engine performance parameters such as fuel consumption, thermal efficiency, exhaust gas temperature and exhaust emission (CO, CO_2, HC, NO_x, O_2) were recorded. The diesel engine can perform satisfactorily on biodiesel fuel without any engine hardware modification. The 100% biodiesel was found to be the best, which improved the thermal efficiency of the engine by 0.1%. Similar trend was shown by the brake specific energy consumption and the exhaust emissions were reduced. Smoke emissions also reduced by 35% for B60 as compared to neat petro-diesel. Decrease in the exhaust temperature of a biodiesel-fueled engine led to approximately 4% decrease in NO_x emissions for B100 biodiesel at full load. The performance of biodiesel-fueled engine was marginally better than the diesel fueled engine in terms of thermal efficiency, BSEC (Brake Specific Energy Consumption), smoke opacity and exhaust emissions including NO_x emissions for entire range of operations.

2.8 Exergy

A literature survey has been done to examine the work done on exergy analysis of a compression ignition engine of internal combustion engine. This has been carried out to get an idea on the different method and software used for the exergy analysis of the compression ignition engine. Few of the important works of researchers are discussed below.

The energy content of the universe is constant, just as its mass content is. What is not conserved is exergy, which is the useful work potential of the energy [109]. Once the exergy is wasted, it can never be recovered. Here the topics Exergy and dead state, Exergy forms, Exergy of kinetic energy, Exergy of potential energy, Useful work, Reversible work, Irreversibility, Second Law Efficiency, Exergy Change of a system, Exergy flow, Exergy Transfer by Heat, Work and Mass, the decrease of Exergy Principle and Exergy Destruction and Exergy Balance were discussed in detail.

The real useful energy loss cannot be justified by the first law of thermodynamics because it does not differentiate between the quality and quantity of energy. This study deals with the comparison of energy and exergy analysis of thermal power plants stimulated by coal and the gas [110]. By the exergy analysis they conclude that main energy loss in boiler, in coal based thermal power plant and combustion chamber in gas fired combined cycle thermal power plant. In every plant components such as boiler, combustion chamber there is some intrinsic irreversibility which cannot, owing to the present state of technological development, be eliminated. Exergy methods are useful in assessing which improvements are worthwhile, and should be used along with other pertinent information to guide efficiency improvement efforts for steam power plant.

They analysed the system components separately, then identify and quantify the sites having largest energy and exergy losses at different loads of Shobra El-Khima power plant in Cairo, Egypt [111]. The maximum energy loss was found in condenser where 56.4%, 55.2%, 54.4% of input energy was lost to the environment at 50%, 75%, full load respectively. The exergy analysis of the plant showed that lost exergy in the condenser is thermodynamically insignificant due to its low quality. In terms of exergy destruction, the major loss is found in the turbine were 46.1%, 59.6%, 42% of the fuel exergy input to the cycle was destroyed at 50%, 75%, full load respectively. Similarly percent exergy destruction in condenser was 23.8%, 20.3%, 28%, in all heaters and pumps 30.2%, 32.4%, 30% at 50%, 75%, full load respectively. The calculated second law efficiency of the power cycle was found to be 48.8%, 45.5%, 44.8% at 50%, 75%, full load respectively which is comparable to modern power plant.

In their study, energy and exergy analyses of Shobra EI-Khima power plant in Cairo, Egypt is presented. Their objectives were to analyse the system components separately and to identify and quantify the sites having largest energy and exergy losses at different load. The different loads they considered were maximum load (100%), 75% load and 50% load. The energy loses mainly occurred in the condenser, turbine and feed water heater. The percentage ratio of the exergy destruction to the total exergy destruction was found to be maximum in the turbine system followed by condenser and feed water heater respectively. In addition, the calculated thermal efficiency based on the specific heat input to the steam was ≈ 43% while the exergy efficiency of the power cycle was (44% - 48%).

The performance of an internal combustion engine is evaluated at the steady-state condition by application of energy and exergy analysis using the experimental test results [112]. The energy and exergy balances are calculated at different engine speeds. The results show that the heat rejection of energy and exergy flow increases with increasing engine speed. The exergy efficiencies are slightly higher than the corresponding energy efficiencies. The results of this study have revealed that the most important source of the system inefficiency is the destruction of exergy by irreversible processes, mostly by the combustion. One can conclude that the use of a combined energy and exergy analysis provides better criteria for the performance assessment of a thermal system.

The energy and exergy analyses were done in a four cylinder, direct injection diesel engine using petroleum diesel and biodiesel [113]. To do these analyses they collect the data like accurate measurements of air, fuel and cooling water flow rates, engine load and all the relevant temperatures using steady state tests. According to the study, using exergy as a measure of quality, the petroleum diesel fuel is greater quality fuel than biodiesel. Because of the net calorific value of diesel is greater than that of the biodiesel. It means that to cover the same distance, greater amount of diesel is needed. In addition to this, using biodiesel fuel shows the similar energetic performance values with that of diesel fuel. The important factor of the system inefficiency is the destruction of exergy by irreversible process. This mainly occurs by the combustion. Exergy losses due to the exhaust gas and heat transfer are other contributors in decreasing order.

2.9 Exhaust Gas Analysis

Some papers in connection with the exhaust gas analysis were studied and brief definitions related to the exhaust gas analysis were given below:

Leung DYC et al considered a single cylinder diesel engine, direct injection, water cooled engine for optimization of exhaust emission with biodiesel**(114)**. They optimized by varying the engine settings, including the injection timing, injection pressure and the fuel pump plunger diameter. The engine emissions were found to be lowered for particulate matters (PM) and hydrocarbon (HC) with the use of biodiesel, but an obvious increase in the oxides of nitrogen (NO_x) was observed, particularly at high engine loadings. For multi parameter engine, adjustment with the consideration of their cross interactive effects can keep the benefit of reducing PM and HC without increasing NO_x emission and sacrificing fuel combustion efficiency.

Breda Kegl investigates in his study the optimal timing of the diesel engine injection pump using biodiesel fuel from rapeseed**(115)**. He studied by running experiments on an NA diesel bus engine MAN D2 2566 with direct injection M system for the influence of biodiesel. Experiments with biodiesel and D2 diesel are run on several engine operating regimes and shown that with carefully optimized timing of the pump, the harmful emission of NO_x, smoke, HC and CO can be reduced essentially by keeping other engine characteristics within acceptable limits.

Zhang et al investigated the impact of biodiesel on NO_x emission in a 2.5L common rail direct injection diesel engine under both low load and high load conditions with different fuel injections strategies**(116)**. They used three fuels (i) an ultra low sulfur diesel fuel (BP15), (ii) a blend of 20 vol% biodiesel in BP15 and (iii) a blend of 40 vol% biodiesel in BP15 (B40). Biodiesel blends were found to generally produce slightly lower NO_x emissions than the baseline diesel fuel at the low load condition. Under the high load condition, evidently higher NO_x emissions for biodiesel blends were observed under both single and double injection conditions. Overall, biodiesel blends and the baseline diesel fuel had very similar heat release rate profile. For injection systems, retarding injection timing under single injection conditions was found to be the more effective approach to reduce the NO_x emissions than using pilot injection with retarded main injection in terms of NO_x and fuel consumption trade off. The performance of the 40 vol% biodiesel blend under various exhaust gas recirculation (EGR) rate condition was investigated, the biodiesel blend showed no further combustion deterioration compared to baseline diesel fuel. A low NO_x and fuel efficient engine operating condition was achieved with the 40 vol% biodiesel blend.

Cheng C. S. et al in their study aimed to investigate the effects of fumigation methanol on the emission of a diesel engine fueled with biodiesel as the baseline fuel**(117)**. The biodiesel used in this study was converted from waste cooking oil. Experiments were performed on a 4-cylinder naturally aspirated diesel engine operating at a constant speed of 1800 rev/min for three engine loads of 0.19 MPa, 0.38 MPa and 0.56 MPa. The results indicate no significant change in the brake thermal efficiency and carbon dioxide (CO_2) emission, an increase in both carbon monoxide (CO) and unburned hydrocarbon (HC) emission and a decrease in both nitrogen oxide (NO_x) and particulate matter (PM) emissions.

Their paper presents the results of investigations carried out in studying the fuel properties of karanja methyl ester (KME) and its blend with diesel from 20% to 80% by volume and running a diesel engine with these fuels**(118)**. Engine tests have been carried out with the air of obtaining comparative measures of torque, power, specific fuel consumption and emission such as CO, smoke density and NO_x to evaluate and compute the behavior of diesel engine running on the KME fuel. The reduction in exhaust emissions together with increase in torque, brake power, brake thermal efficiency and reduction in brake-specific fuel consumption made blends of karanja esterified oil (B20 and B40) a suitable alternative for diesel and could help controlling air pollution.

In their study, a number of experiments with 10 vol% (B10) biodiesel fuel of palm oil origin were performed on a light duty common-rail Euro 3 engine**(119)**. The measurements included in-cylinder pressure, pollutant emission and fuel consumption. Combustion effects were limited but changes in the start of ignition and heat release rate could be identified. Emission effects included both higher and lower smoke and NO_x, depending on the operation point. The results on the engine bench were compared against a Euro 3 common-rail high-duty vehicle driven on the chassis dynamometer, in order to include the effects of emission control system (EGR & oxidation catalyst). In addition to the palm biodiesel, an RME-diesel blends was also tested to examine the effect of a fuel with different characteristics. Both biodiesel blends reduced PM emissions and only marginal effects on NO_x over the certification test could be identified. The results of this study show that up to 10% biodiesel could be used on current diesel vehicles, without significantly affecting vehicle emission performance.

Blends of diesel oil and soybean biodiesel with concentration of 3% (B3), 5% (B5), 10% (B10) and 20% (B20) were used as fuel on a passenger vehicle and exhaust pollutant emissions were investigated **(120)**. The effects of anhydrous ethanol as an additive to B20 fuel blend with concentration of 2% (B20E2) and 5% (B20E5) were also studied. The emissions tests were carried out following New European Driving Cycle (NEDC). Results shows that increasing biodiesel concentration in the fuel blend increase CO_2 and oxides of nitrogen (NO_x) emissions, while carbon monoxide (CO), Hydrocarbon (HC) and particulate matter (PM) emissions are reduced. The addition of anhydrous ethanol to B20 fuel blend proved it can be a strategy to control exhaust NO_x and global warming effects through the reduction of CO_2 concentration.

2.9 Advantages and disadvantages

Biodiesel can be considered as a new and clean replacement for diesel fuel. Using biodiesel as fuel has some advantages and disadvantages.

2.9.1 Advantages

The following are some advantages of using biodiesel:

i. It is biodegradable, non-toxic, environmental friendly and renewable resource.

ii. It can reduce the amount of greenhouse gas emissions and it emits less CO_2, SO_2, CO, HC and PM in comparison to conventional diesel.

iii. It decreases the vibrations, smoke and noise produced.

iv. The energy security of the country will be increased and there can be a reduction in fossils fuel use.

v. Biodiesel is more cost efficient because it is produced locally.

vi. Biodiesel has high flash point, which makes it a safer fuel.

vii. It does not need engine modification up to B20.

viii. Production of biodiesel is easier than production of diesel fuel and it creates a brand new job infrastructure and will help local economies.

2.9.2 Disadvantages

On the other hand, there are several concerns about biodiesel:

i. It emits higher NO_x emissions in comparison with conventional diesel.

ii. Its higher pour and cloud points create problems in cold weather.

iii. It has a corrosive nature against copper and brass.

iv. It has a higher viscosity in comparison with diesel fuel.

v. It has low volatility.

CHAPTER – 3

3.0 Methods and Materials

3.1 Introduction

In this chapter different method and the materials used for the production of biodiesel from the seed of pongamia pinnata and different material for the analysis of the biodiesel, blending biodiesel with the petroleum diesel will be discussed. The different methods and materials used for the production, analysis and performance analysis is given as follows.

3.2 Feedstock Used

The fruits of Koroch (Pongamia pinnata) were collected at the Assam Engineering College Campus, Jalukbari, Guwahati, Assam, India from the Koroch tree (fig. 3.1). The seeds of koroch or pongamia pinnata were produced by removing the upper crust part of the fruits which is around 1.5cm long, light brown, oval and contained in clusters of brown, eye-shaped pods (fig. 3.2).

Figure 3.1 Mature Pongamia pinnata tree

Figure 3.2 Seed of Pongamia pinnata

3.3 General Procedure for Extraction of oil from seeds

The seeds were dried in the sunlight and the percentage of moisture removal is shown in the table 3.1, fig. 3.3 and fig. 3.4. The dry seeds were grinded and powdered (fig. 3.5) with the help of grinder (fig. 3.6) made from Philips Classic 500W. 50ml of solvent (5ml/g) and 10g of powdered seed were taken in a round bottom flask. The mixture is stirred by using magnetic stirrer with hot plate for 2, 3 and 4 hours as shown in fig. 3.7. Then the mixture of powdered seed and solvent is filtered fig. (3.8) and filtrate is taken in a round bottom flask (pre-weighted). The solvent present in the oil is removed under reduced pressure using a rotary vacuum evaporator to obtain the crude oil as shown in the fig 3.9. The process is repeated for three solvents viz. diethyl ether, hexane and petroleum ether. Three extractions were carried out for each solvent with different duration of stirring viz. 2, 3 and 4hours.

3.4 Extraction of Oil

Extraction of oil from the seeds of Pongamia pinnata was carried out with three different solvents namely diethyl ether, hexane, and petroleum ether (40-60 ^{o}C). With each solvent, three experiments were done allowing different times for stirring the mixture of grinded seeds and the solvents. Results are shown in table 3.3. It can be seen from the table that stirring for three hours increases the yield of oil only marginally over that with two hours of stirring. Extending time beyond three hours does not increase the yield. Therefore three hour time can be considered as optimum time.

With three hours stirring, it is seen that hexane and petroleum ether (40-60 ^{o}C) give almost equal yield of oil, i.e., about 23% in each case. But with diethyl ether yield of oil is slightly lower i.e. about 20%. Thus, it appears that increase in solvent polarity has no beneficial effect in the extraction of oil by solvent. Among the two solvents, hexane and petroleum ether, the former is more expensive and therefore, petroleum ether is a better choice for extraction of oil from the grinded seeds. The extraction of pongamia pinnata seed oils with different solvents are shown in the fig. (3.10-3.15). The koroch oil found from the seed was submitted for determination fuel properties by proximate analysis in Bongaigaon Refinery and Petrochemicals Limited (BRPL) Dhaligaon, BTAD, Assam, India and the properties

Table 3.1 Moisture removal from Pongamia pinnata seeds in 3rd and 6th Day

Sample	1	2	3	4
Initial weight (gm)	100.39	100.29	100.32	100.12
3rd Day weight (gm)	58.11	60.20	59.87	54.13
Moisture remove (gm) (for 3 days)	42.28	40.09	40.45	45.99
Average moisture remove (gm)	42.20			
Percentage of moisture remove(for 3 days)	42.11	39.97	40.32	45.93
Average percentage moisture remove	42.08			
6th Day or Final weight (gm)	53.32	53.23	52.64	51.32
Moisture remove (gm) (for 6 days)	47.07	47.06	47.68	48.80
Average moisture remove(gm)	47.65			
Percentage of moisture remove(for 6 days)	46.89	46.92	47.52	48.74
Average percentage moisture remove	47.52			

like density, pour point, Kinematic viscosity, acidity, ash content, conradson carbon residue and caloric value (gross) etc of Koroch Seed Oil were determined by the Proximate Analysis.

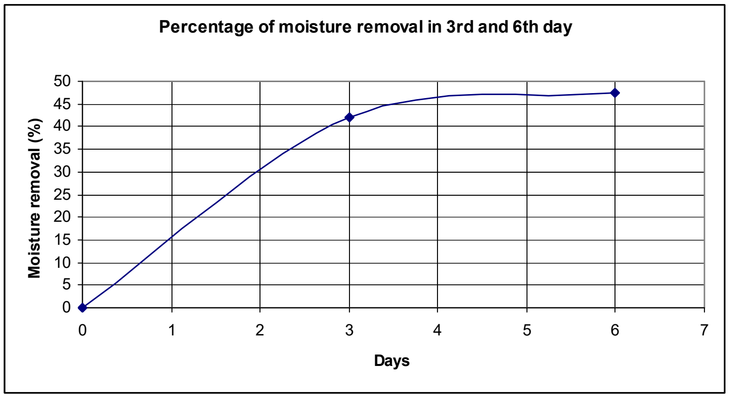


Figure 3.3 Percentage of moisture removal in 3rd and 6th Day

Table 3.2 Moisture removal from Pongamia pinnata seeds

No. (Sample)	Initial weight (gm)	Final weight (gm)	Moisture remove (gm)	Average moisture remove(gm)	Percentage of moisture remove	Average percentage moisture remove
1	100.39	53.32	47.07	47.65	46.89	47.52
2	100.29	53.23	47.06		46.92	
3	100.32	52.64	47.68		47.52	
4	100.12	51.32	48.80		48.74	

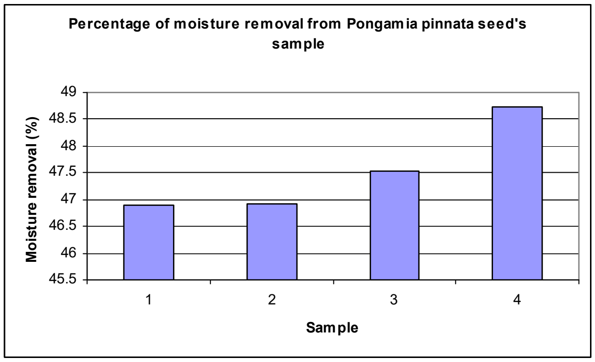


Figure 3.4 Percentage of moisture removal from the seeds of Pongamia pinnata


Figure 3.5 Grind seed of Pongamia pinnata

Fig. 3.6 Grinding Machine

Fig. 3.7 Magnetic Stirrer with hot plate

Fig. 3.8 Filtration

Fig.3.9 Solvent removal (Rotary Vacuum Evaporator)

Table 3.3 Extraction of Pongamia pinnata seed oils with different solvents

Solvent	Weight of seed (g)	Stirring time (h)	Weight of crude oil (g)	Yield of oil (wt.%)
Diethyl ether	10.040	2	2.048	20.40
	10.050	3	2.067	20.57
	10.070	4	2.081	20.66
Hexane	10.040	2	2.116	21.08
	10.060	3	2.223	22.09
	10.050	4	2.138	21.27
Petroleum ether	10.030	2	2.030	20.24
	10.015	3	2.307	23.04
	10.020	4	2.265	22.60

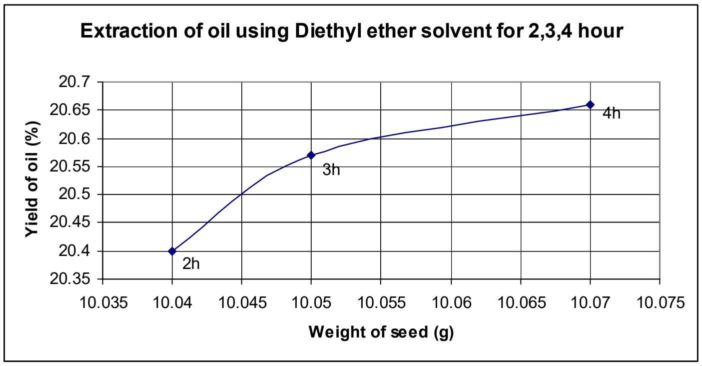


Figure 3.10 Extraction of oil using Diethyl ether solvent for 2,3,4 hour

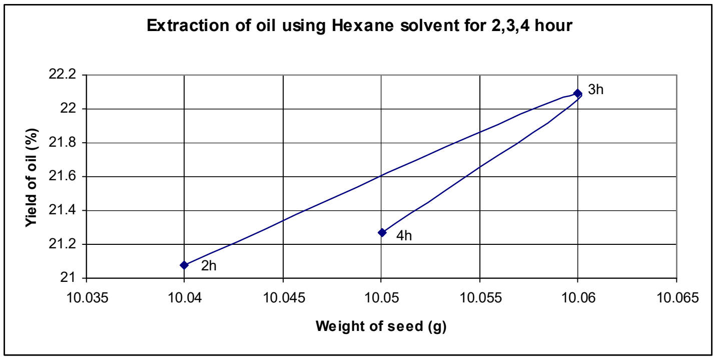


Figure 3.11 Extraction of oil using Hexane ether solvent for 2,3,4 hour

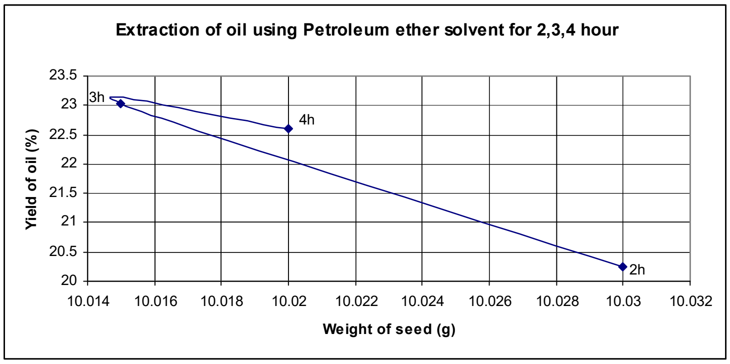


Figure 3.12 Extraction of oil using Petroleum ether solvent for 2,3,4 hour

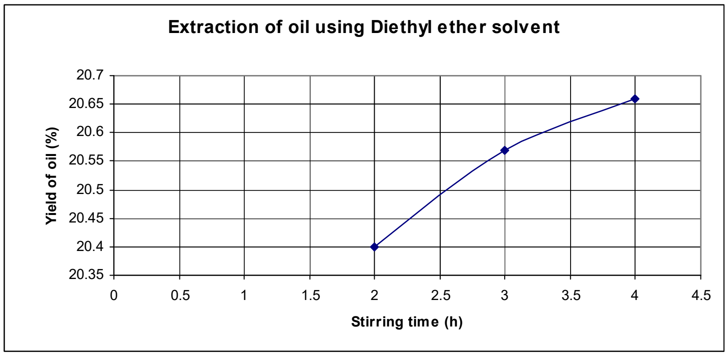


Figure 3.13 Extraction of oil using Diethyl ether solvent

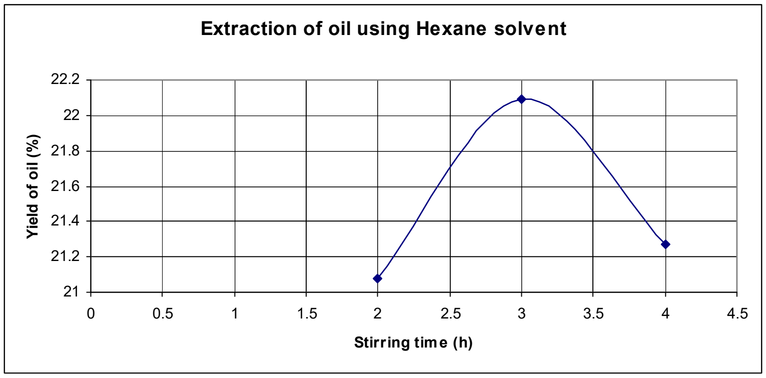


Figure 3.14 Extraction of oil using Hexane solvent

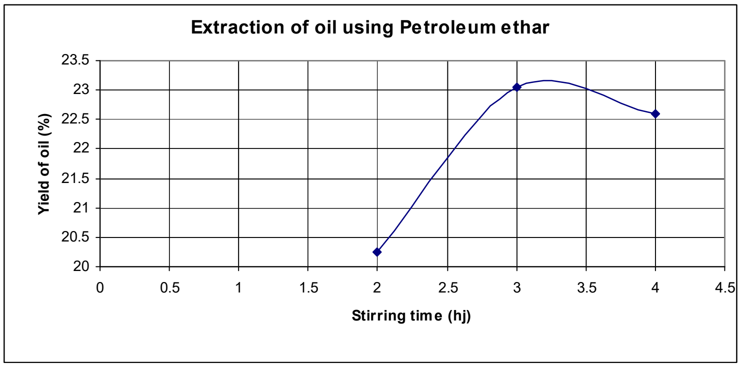


Figure 3.15 Extraction of oil using Petroleum ether solvent

3.5 Transesterification of seed oil to Biodiesel

Biodiesel consists of alkyl esters of long chain fatty acids, more commonly methyl esters and is typically made from non-toxic, biological resources such as vegetable oils, animal fats or even used cooking oils. A conversion of oil to biodiesel is achieved by reacting with methanol in the presence of catalyst.

In the production of biodiesel from the seed of pongamia pinnata, the oil and fats are transesterified with methanol in the presence of catalyst to afford fatty acid methyl esters (FAME) and glycerol as by-product(121, 122).

Here, the seed oil from the pongamia pinnata oil is transesterified to fatty acid methyl esters (biodiesel) mixing with methanol (CH_3OH, 5ml/g of oil) and using K_2CO_3 catalyst (5 wt% of oil) is mechanically stirred (fig. 3.16) at room temperature (32°C)

Figure 3.16 Mechanically stirred

After completion of the reaction, the product mixture is partitioned between petroleum ether and water by adding petroleum ether and brine solution (10% of NaCl solution). The organic phase that is upper layer (fig. 3.17) is then collected. This process is repeated for 2-3 times by taking the lower layer. The collected solution is then dried over anhydrous Na_2SO_4 and the solvent is removed under vacuum to yield the product (fig. 3.9).

Figure 3.17 Separations after Transesterification

Calculation for percentage yield of oil:

For a sample of Pongamia pinnata oil of weight 96gm.

Amount of methanol CH_3OH at the 5ml/gm of oil = 96x5

= 480ml

Amount of catalyst K_2CO_3 at the 5wt% of oil = $96\text{x}\frac{5}{100}$

= 4.80gm

Yield of biodiesel = 88.320gm

Percentage of yield = $\frac{88.32}{96}\text{x}100\%$

= 92%

3.6 Blending of Biodiesel

More than one litre of biodiesel was prepared from an approximately equal volume of pongamia pinnata seed oil in several batches and prepared five samples of blends (table 3.4) for determining the properties of diesel, biodiesel and its blends. The sample preparations by blending of diesel and biodiesel for the five samples of B00, B10, B20, B30 and B100 required 480ml biodiesel and 1020ml petrodiesel (table 3.5) and submitted for fuel properties determination in Bongaigaon Refinery and Petrochemicals Limited (BRPL) Dhaligaon, BTAD, Assam, India. The properties like Kinematic Viscosity at 40°C, Density at 15°C, Pour Point, Flash Point, Ramsbottom Carbon Residue, CFPP (Cold Filter Plugging Point), Total Sulfur, Acidity, Calorific Value of the samples were determined.

The blends considered are as follows:

Table:3.4 Blending Ratios of Biodiesel

Sample No.	*Sample*	*Particulars*

1	B00	100% Diesel
2	B10	10% Biodiesel & 90% Diesel
3	B20	20% Biodiesel & 80% Diesel
4	B30	30% Biodiesel & 70% Diesel
5	B100	100% Biodiesel

Fig.3.18 Different types of samples

3.6.1 Sample Preparation

For 300ml sample

Table: 3.5 Sample preparations of 300ml

Sample	*Biodiesel (ml)*	*Petroleum Diesel (ml)*
B00	00	300
B10	30	270
B20	60	240
B30	90	210
B100	300	00
Total	480	1020

3.7 Measuring Instruments

To determine the different properties of the koroch oil and the biodiesel and its blending some instruments are used which are discussed as follows.

3.7.1. Density

The density or more precisely, the volumetric mass density of a substance is its mass per unit volume. The symbol most often used for density is ρ. Mathematically, density is defined as mass divided by volume.

$$\rho=\frac{m}{V}$$

Where ρ is the density, m is the mass and V is the volume

3.7.2 Dynamic viscosity

The dynamic (shear) viscosity of a fluid expresses its resistance to shearing flows, where adjacent layers move parallel to each other with different speeds.

3.7.3 Kinematic viscosity

The kinematic viscosity is the ratio of the dynamic viscosity to the density of the fluid. The measurement of kinematic viscosity and density of the koroch oil and biodiesel, its blending and diesel were measured with the help of a digital viscosity and measuring device with LEMIS Instrument; Model: VDM-300, (fig. 3.19).

Fig. 3.19 Viscosity and density measuring instrument

3.7.4 Pour point

The pour point of a liquid is the temperature at which it becomes semi solid and losses its flow characteristics.

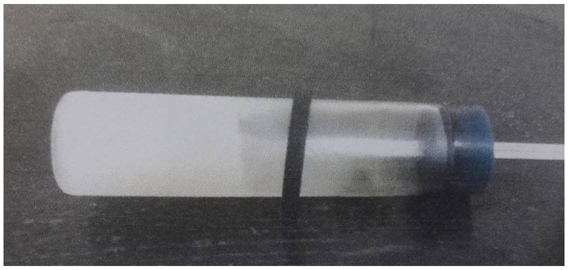


Fig. 3.20 Pour point tester

3.7.5 Flash point

It is the temperature at which a particular organic compound gives off sufficient vapour to ignite in air. The flash point of the biodiesel and its blends were measured using an open cup digital tester made of Reico Equipment and Instrument Pvt. Ltd. (fig. 3.21).

Fig. 3.21 Flash and Fire Point Tester

3.7.6 pH Value

The acidity or bacisity (alkalinity) of any liquid is determined with reference to the pH value. The pH value less than 7 gives the acidic and more than 7 gives the basic. The pH value of the biodiesel and its blends were determined using the pH measuring instrument of Butech, PC650 (fig. 3.22)

Fig. 3.22 pH measuring instrument

3.7.7 Carbon residue

The carbon residue of a fuel is the tendency to form carbon deposits under high temperature conditions in air inert atmosphere.

Fig. 3.23 Carbon Residue Tester

3.7.8 Caloric value

It is the energy contained in a fuel or food, determined by measuring the heat produced by the complete combustion of a specified quantity of it.The calorific values of all the samples of biodiesel and its blends were determined in a Automatic Calorimeter made of M/S. Changsha Kaiyun Instruments Co. Ltd., Changsha China of Model: SE-1AC/ML as shown in fig. 3.24.

Fig. 3.24 Bomb Calorimeter

3.7.9 Cloud point

Cloud point refers to the temperature below which wax in diesel or bio – wax in biodiesels form a cloudy appearance.

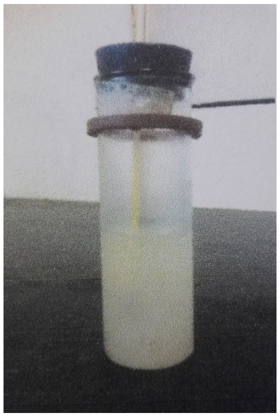


Fig. 3.25 Cloud point tester

3.7.10 CHN Analysis

CHN (carbon, hydrogen, nitrogen) analysis is a common form of elemental or ultimate analysis which is accomplished by combustion analysis. This analysis can be determined the element presents that is qualitative and how much of each present that is quantitative of the compounds. The CHN analysis of the sample of biodiesel and its blends were conducted in a CHN analyser made of Perkin Elmer, USA, Model 2400 series – ii as shown in fig. 3.26.

Fig. 3.26 CHN Analyser

3.7.11 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

To analyze and quantify of organic volatile and semi volatile compounds the GC-MS technique is used. The GC-MS is an effective instrument in separating compounds into their various components and used to identify various components from their mass spectra. The GC-MS analyser can be used to work on liquids, gases and solids.

Here, the GC-MS instrument is conducted to elucidate the molecular identity of compounds in the liquid samples biodiesel and its blends. The instrument GC-MS made Perkin Elmer, USA; of model: GC-Clarus 600, MS-Clarus 600 C; Software: TURBOMASS-VER, as shown in fig. 3.27, is equipped with a quadruple ion trap mass detector coupled with Elite-5 MS with dimension of 0.25 mm ID × 30 m length capillary column, Ionization energy of 70 eV, with scan interval of 1.5 second and mass range of 50–600amu was used. The oven temperature was programmed at 120 °C for 1.0 min with 20 °C min^{-1} increment and held at 270 °C for 10 min. The temperature of both the detector and the injector was kept at 270 °C.

Fig. 3.27 GC–MS Instrument

Table 3.6. Analysis parameters of GC-MS

Parameter	Specification
GC Line temperature	250 °C
Source temperature	150 °C
Oven temperature	120-270 °C, 20 °C /min
Carrier gas	Helium
Carrier gas flow rate	1 ml/min
Split ratio	50:1
Acquisition mode	Threshold
Capillary Column	30 m x 0.25 mm, and 0.25μm film thickness (Elite-5 MS)
Electron energy	70eV

3.7.12 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

This analysis is used to obtain an infrared spectrum of absorption or emission of a gas, liquid or solid. The term FTIR originated from the fact that Fourier Transform is required to convert the raw data into actual spectrum. When Infra-Red (IR) is passed through the sample some of the radiation is absorbed and some of it passed through i.e. transmittance which result the molecular absorption and transmission, creating molecular fingerprint of the sample. The FTIR spectrum gives sufficient information about the structure of a compound.

The Fourier Transform Infrared Spectroscopy that used to analyse the sample of biodiesel and its blend in the range of 4000-500 cm^{-1} at the resolution of 4 cm^{-1} is made of Perkin Elmer Frontier FTIR, Ncolet, USA; Model: IMPACT 410; Software: OMNIC E.S.P.5.0, as shown in fig. 3.28.

Fig. 3.28. Fourier Transform Infrared Spectroscopy (FTIR) Instrument

3.8. Experimental Studies

In a diesel engine the compression stroke only compresses air and not fuel. In the ignition stroke compressed air is present with very high pressure and then fuel is injected into the engine cylinder with the help of an injector, resulting in generating enormous heat, which then ignites the fuel that is injected into the combustion chamber at that precise moment of maximum pressure. There is no need for a spark plug in a diesel engine. The compressed air is hot enough to cause the fuel to explode. This is because a diesel engine has a far higher “compression ratio” that does a petrol engine.

3.8.1 Experimental Set-up

The engine performance tests were conducted with a single cylinder four stroke diesel engine Test Rig set up as shown in fig. 3.29 and the block diagram of the two views were shown in fig. 3.30 and 3.31. The specification the test engine is as given below:

Engine Type : Make Kirloskar AK65
Stroke Diameter : 0.08m

Stroke Length : 0.11m
No. of Cylinder : 1
No. of Stroke : 4
Type of cooling : Water cooled
Rated Power : 4.8kW at 1500 RPM
Engine Capacity : 553cc
Compression ratio : 17.5
Variable CR range : 12 to 18
Fuel used : Diesel, Blends of diesel and biodiesel, Biodiesel
BHP : 6.5

The parameters like fuel consumption, speed of engine, torque and etc. were measured at different loads for diesel and with various combinations of biodiesel from pongamia pinnata with the petroleum diesel. Brake power, brake specific fuel consumption, brake thermal efficiency, heat carried out by water from calorimeter, heat carried away by engine jacket, heat carried out by exhaust gases and air consumption were calculated using the collected test data.

3.8.2 Description of the test rig

Single cylinder four stroke diesel engine test rig with rope brake dynamometer arrangement mainly consists of:

a. Loading arrangement: A rope brake dynamometer arrangement with a brake drum coupled to the engine shaft and provided with a cooling water arrangement and spring balances. The load can be varied by increasing the rope tension on the brake drum with revolving the hand wheel provided on the top of frame as shown in block diagram fig. 3.30 and 3.31.

b. A fuel input measuring arrangement: This arrangement consists of a fuel tank of suitable capacity mounted on a stand. The fuel goes to the engine through a burette. The burette facilitates the measurement of fuel consumption for a definite period with the help of stopwatch (fig. 3.31).

c. Air intake measuring arrangement: It consists of an orifice, a diaphragm base manifold and a U-tube manometer. With the help of orifice and manometer, the volume of the air sucked can be calculated.

Fig. 3.29 Set up of Single Cylinder Four Stroke Diesel Engine Test Rig (With Rope Brake Dynamometer)

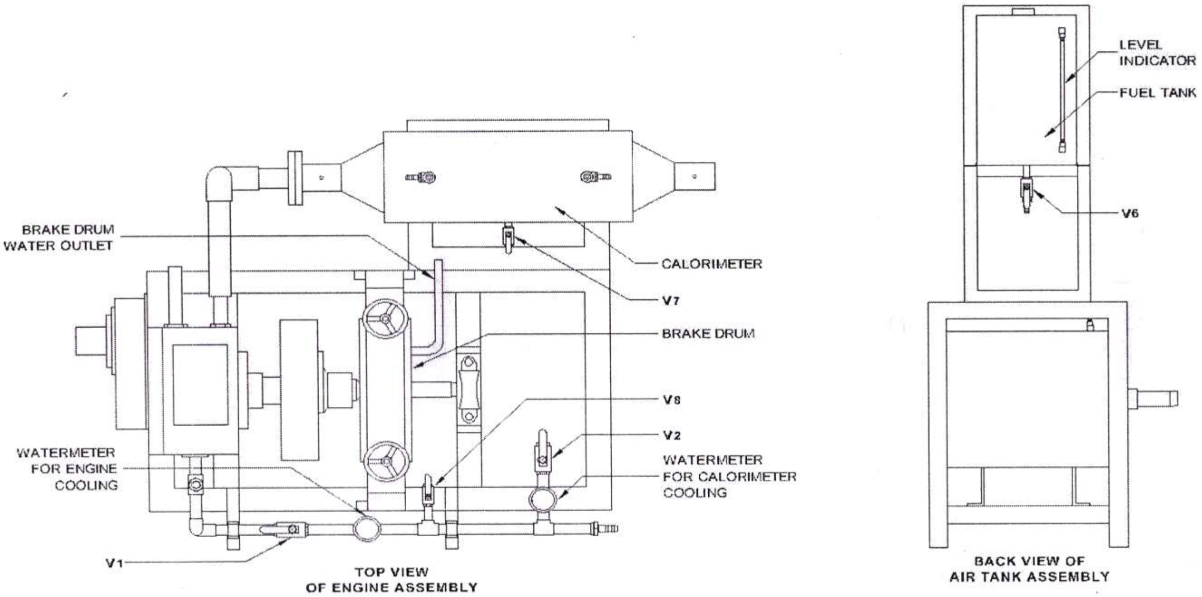


Fig 3.30 Single Cylinder Four Stroke Diesel Engine Test Rig (With Rope Brake Dynamometer) Top View (courtesy: KC Engineers Pvt. Ltd. Ambala)

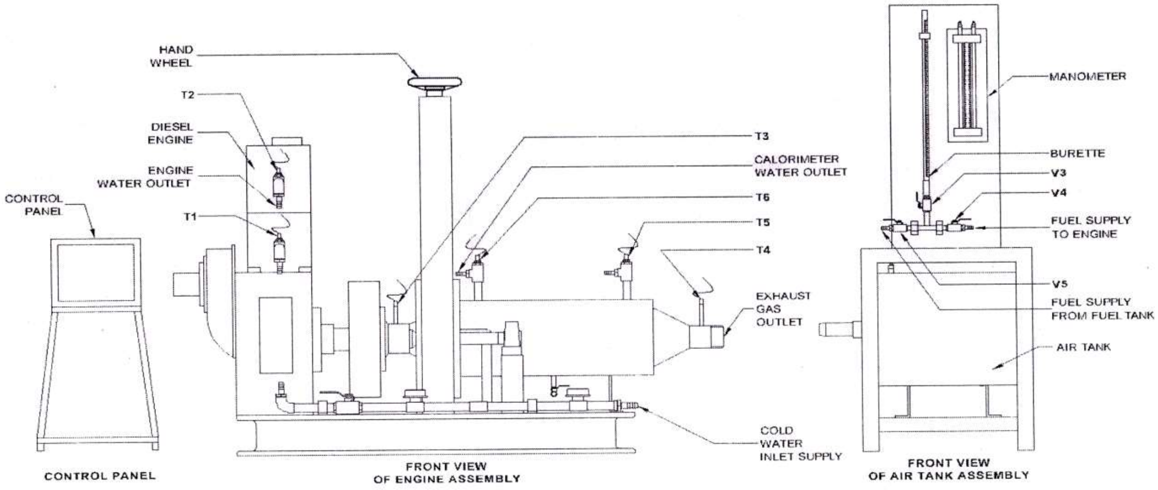


Fig 3.31 Single Cylinder Four Stroke Diesel Engine Test Rig (With Rope Brake Dynamometer) Front View (courtesy: KC Engineers Pvt. Ltd. Ambala)

d. An arrangement for measuring the heat carried away by cooling water from engine jacket: Suitable pipe fitting is provided for circulating the cooling water into the engine water jacket. For measuring the rate of flow of cooling water, a water meter is provided. With these entire arrangements, one can find the heat carried away by cooling water. The temperature of the inlet and outlet water can be directly read from the digital temperature indicator.

e. An arrangement for measuring the heat carried away by cooling water from exhaust gases: It consists of exhaust gas calorimeter to measure the heat carried away by exhaust gases. Exhaust gas calorimeter consists of a central tube and an outer jacket. Exhaust gases passes through central tube and water is circulated in outer jacket to get the maximum temperature difference of exhaust gases at inlet and outlet of calorimeter. The volume of water circulation is measured with the help of water meter and stopwatch. Thermocouples are provided to get the inlet and outlet temperature of exhaust gases and water circulated.

f. A control panel.

3.8.3 Engine Setup

Experiments were conducted on an existing test unit. The test unit was a Single Cylinder, Naturally Aspirated, Direct Injection, and Compression Ignition Engine using standard diesel fuel

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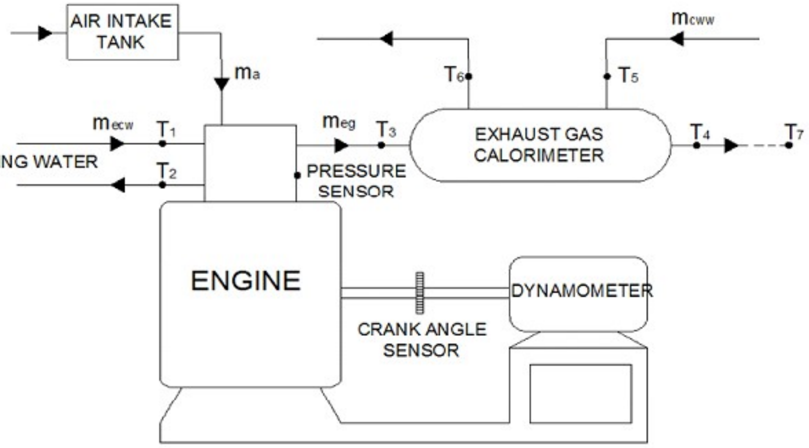

Fig.3.32 Schematic diagram of engine test unit (Source: www.elsevier.com/locate/pecs)

3.8.4 Performance Analysis

In a single cylinder four stroke diesel engine made of Kirloskar AK65 was run using different types of sample that is petroleum diesel, blends of diesel and biodiesel, pure biodiesel made from the seed of pongamia pinnata at different loads to analyse the performance of the engine. To determine the performance of the engine, the values of the brake power, specific fuel consumption, heat supplied, brake thermal efficiency, heat lost in radiation and uncounted, volumetric efficiency were calculate. The performance of the engine using the samples from the biodiesel, diesel and blends were used to run the engine at different loads and their performance like fuel energy, effective power, energy losses, energy efficiency and the fuel exergy, work exergy, exergy losses, exergy destroyed and exergy efficiency were analysed.

3.9 Exhaust Gas Analysis

Exhaust emissions are produced during combustion and the emissions are harmful. In addition to these harmful emissions, both carbon dioxide (CO_2) and oxygen (O_2) readings can provide additional information on what’s going on inside the combustion chamber.

Fig. 3.33 Exhaust Gas Analyser

The exhaust gas analysis of the sample of biodiesel and its blends were conducted in a exhaust gas analyser made of KM Quintox Gas Analyser, Kane May Pvt. Ltd. as shown in fig. 3.33.

CHAPTER – 4

4.0 Characterization of Biodiesel

The koroch oil is extracted from the seed of koroch using the petroleum ether solvent and then the biodiesel of the oil is produced by transesterification of the oil using the solvent and etc. The characterization of the various properties of the koroch oil and the sample from biodiesel and its blends were discussed in the following sections.

4.1 Properties of oil

The physiochemical properties like density, pour point, Kinematic viscosity, acidity, ash content, conradson carbon residue and caloric value (gross) etc of Koroch Seed Oil is determined by the Proximate Analysis and the respective values of the properties were shown in the table 4.1.

4.2 Result and Discussion (oil)

Oil extraction from the seed is carried out by the Rotary Vacuum Evaporator extraction method. The solvents like hexane, diethyl ether and petroleum ether were used as extracting solvent seeds. Seeds were soaked into the solvents and extraction carried out for three hours for the each case. The solvents were evacuated under the vacuum and pure oil is dried. It was thick acrid smell having yield of 23.04%. Physiochemical analysis were carried out and it was given density value at 15^{o}C 929.3kg/m^{3}, pour point +6, Kinematic viscosity at 40^{o}C 33.42cst, acidity (Inorganic) Nil, Acidity (Total) 2.14 mg KOH/g, ash content 0.047 % mass, conradson carbon residue 0.80% mass and caloric value (gross) 10573 cal/g.

Table 4.1 Proximate Analysis of Koroch Seed Oil

No.	Test parameters	units	Test method IS 1448/ASTM	Results

1	Density at 15^{o} C	kg/m^{3}	P:16	929.3
2	Pour Point	^{o}C	P:10	+6
3	Kinetic Viscosity at 40 ^{o}C	Cst	P:25	33.42
4	Acidity (Inorganic)	mg KOH/g	P:2	Nil
5	Acidity (Total)	mg KOH/g	P:2	2.14
6	Ash content	%mass	P:4	0.047
7	Conradson carbon residue	%mass	D 189	0.80
8	Caloric value (gross)	cal/g	P:7	10573

4.3 Transesterification

Biodiesel consists of alkyl esters of long chain fatty acids, more commonly methyl esters and is typically made from non-toxic, biological resources such as vegetable oils, animal fats or even used cooking oils. Here, the seed oil from the pongamia pinnata is transesterified to fatty acid methyl esters (biodiesel) mixing with methanol (CH_3OH, 5ml/g of oil) and using K_2CO_3 catalyst (5 wt% of oil) is mechanically stirred at room temperature (32^{o}C). After completion of the reaction, the product mixture is partitioned between petroleum ether and water by adding petroleum ether and brine solution (10% of NaCl solution). The organic phase that is upper layer is then collected. The collected solution is then dried over anhydrous Na_2SO_4 and the solvent is removed under vacuum to yield the product.

4.4 Properties of Biodiesel

The sample preparations by blending of diesel and biodiesel for the five samples of B00, B10, B20, B30 and B100 required 480ml biodiesel and 1020ml petrodiesel and submitted for fuel properties determination in Bongaigaon

Refinery and Petrochemicals Limited (BRPL) Dhaligami, BTAD, Assam, India. The properties like Kinematic Viscosity at 40°C, Density at 15°C, Pour Point, Flash Point, Ramsbottom Carbon Residue, CFPP (Cold Filter Plugging Point), Total Sulfur, Acidity, Calorific Value of the samples are determine and given in the table 4.2 and Comparison of the properties of biodiesel from Karanja seed oil with Indian automotive diesel fuel and biodiesel standards is given in table 4.3 and the corresponding figures of sample verses the property were shown in the fig. 4.1 to 4.8.

Table 4.2 Properties of biodiesel from Karanja seed oil

Sl. No.	**Property**	**Sample**				
		B00	**B10**	**B20**	**B30**	**B100**
1	Kinematic Viscosity at 40 °C, cst	2.38	2.50	2.64	2.75	3.67
2	Density at 15 °C, g/mL	0.8289	0.8324	0.8363	0.8393	0.8572
3	Pour Point, °C	<0	<0	-6	-6	-6
4	Flash Point, °C	40	32	<20	<20	<20
5	Ramsbottom Carbon Residue, %w	0.042	0.053	0.055	0.072	0.37
6	Calorific Value, kJ/kg	43500	42738	41956	40995	35879
7	CFPP (Cold Filter Plugging Point), °C	-1	-2	-2	-5	+5
8	Total Sulfur, mg/kg	257	224	193	169	7
9	Acidity, mg KOH/g	0.027	0.05	0.081	0.106	0.41

Table 4.3 Comparison of the properties of biodiesel from Koroch seed oil with Indian automotive diesel fuel and biodiesel standards.

Sl. No.	Properties	KME	BS II	BS III	BS IV	BS VI	ASTM D6751	EN 14214
1	Kinematic Viscosity at 40 °C, cst	3.67	2.0-5.0	2.0-4.5	2.0-4.5	2-4.5	1.9-6.0	3.5-5.0
2	Density at 15 °C, g/mL	0.8572	0.82-0.86[a]	0.82-0.845[a]	0.82-0.845	0.82-0.86	NS	0.86-0.90
3	Pour Point, °C	-6	3[c]/15[d]	3[c]/15[d]	3[c]/15[d]	NS	NS	NS
4	Flash Point, °C	<20	35 min	35 min	35	35	130 min	120 min

5	Ramsbottom Carbon Residue, max, %w	0.37	0.30	0.30	0.30	0.30	NS	NS
6	Calorific Value, kJ/kg	35879	NS	NS	NS	NS	NS	NS
7	CFPP (Cold Filter Plugging Point), °C	+5	6[c]/18[d]	6[c]/18[d]	6[c]/18[d]	6[c]/18[d]	NS	NS
8	Total Sulfur, max, mg/kg	7	500	350	50	10	15	10
9	Acidity, mg KOH/g	0.41	To report	To report	To report	To report	0.50max	0.50max

KME: Karanja Methyl Ester; NS: Not Specified; min: Minimum; max: Maximum; BS II: Bharat Stage II; BS III: Bharat Stage III; BS IV: Bharat Stage IV; BS VI: Bharat Stage VI; a: For fuel processed from Assam crude; c: Maximum in winter; d: Maximum in summer

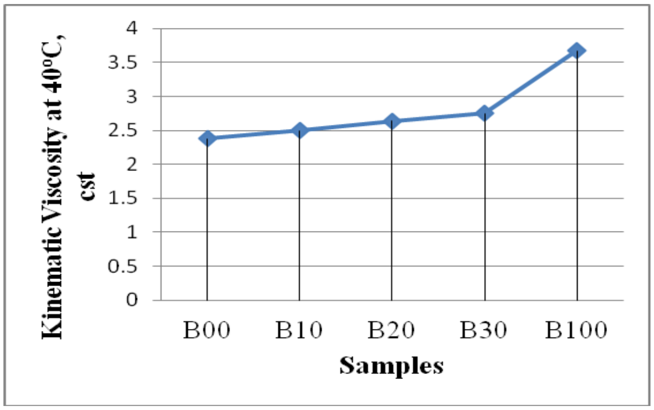

Figure 4.1 Kinematic viscosity at 40°C for different samples

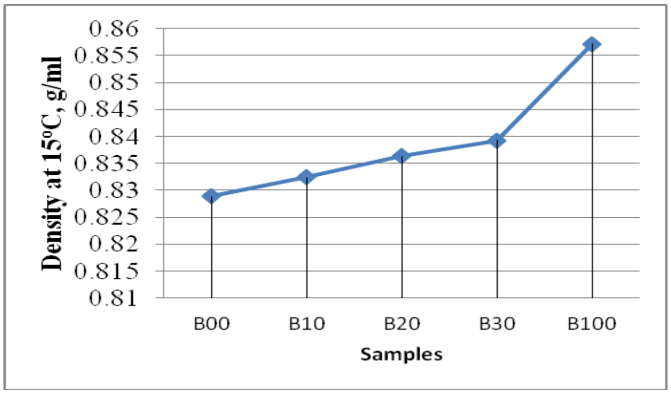

Figure 4.2 Density at 15°C for different samples

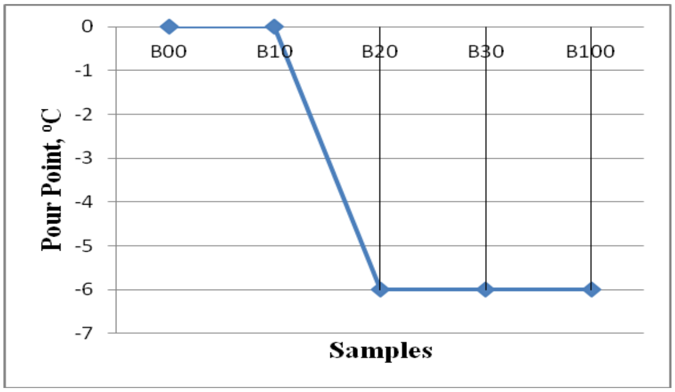

Figure 4.3 Pour Point (°C) for different samples

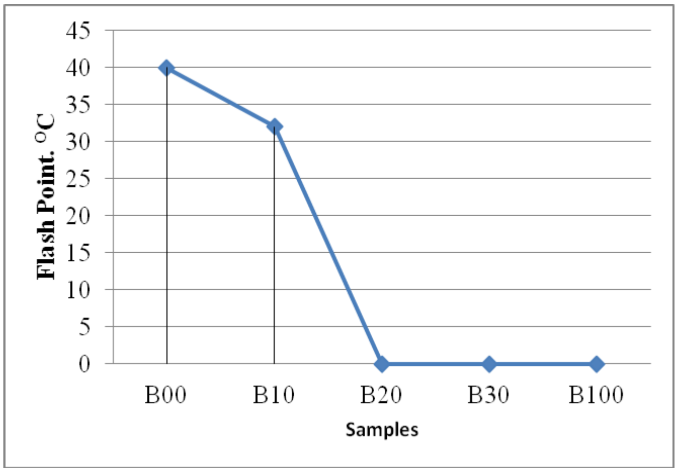

Figure 4.4 Flash point (°C) for different samples

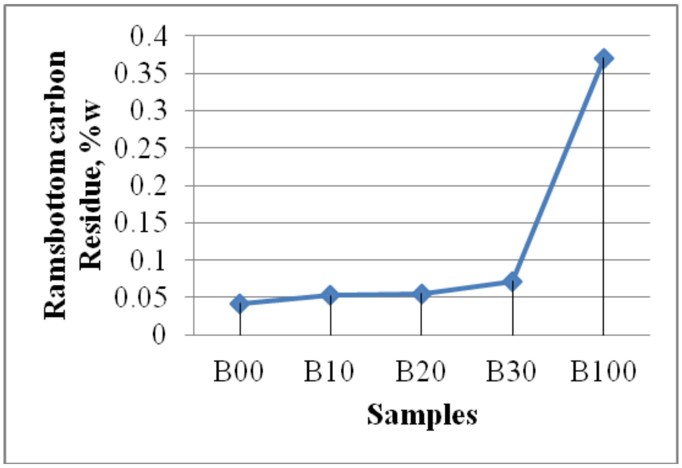

Figure 4.5 Ramsbottom Carbon Residue (%w) for different samples

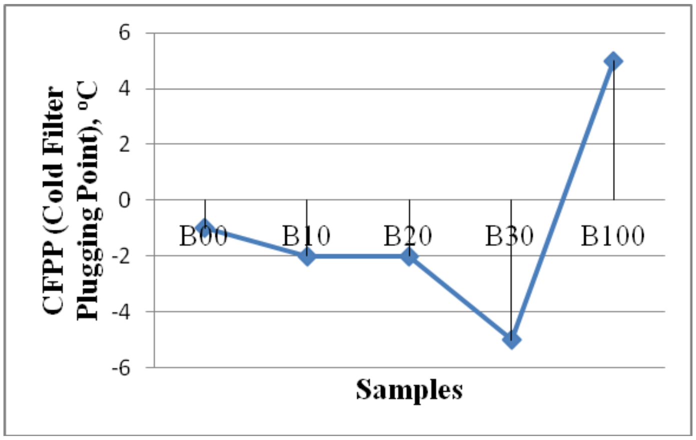

Figure 4.6 Cold Filter Plugging Point (°C) for different samples

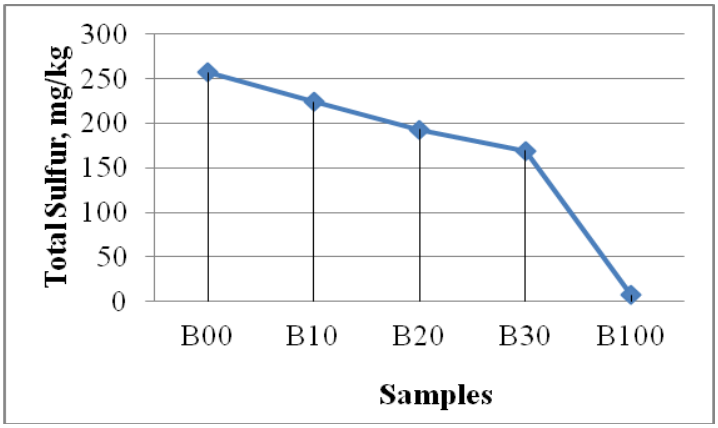

Figure 4.7 Total Sulfur (mg/kg) for different samples

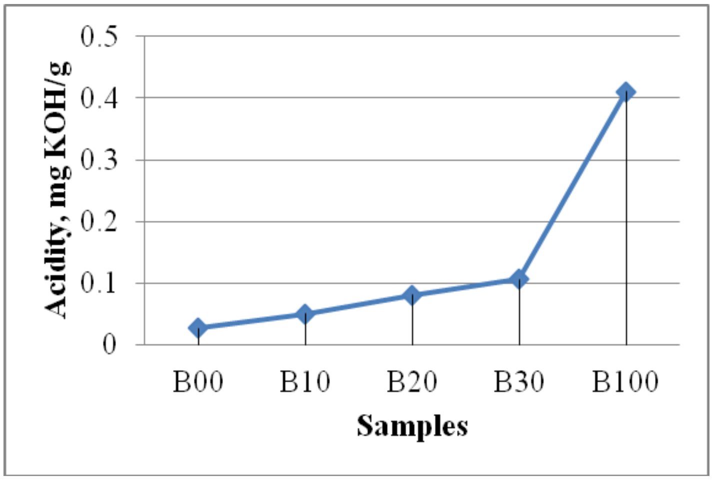

Figure 4.8 Acidity (mg KOH/g) for different samples

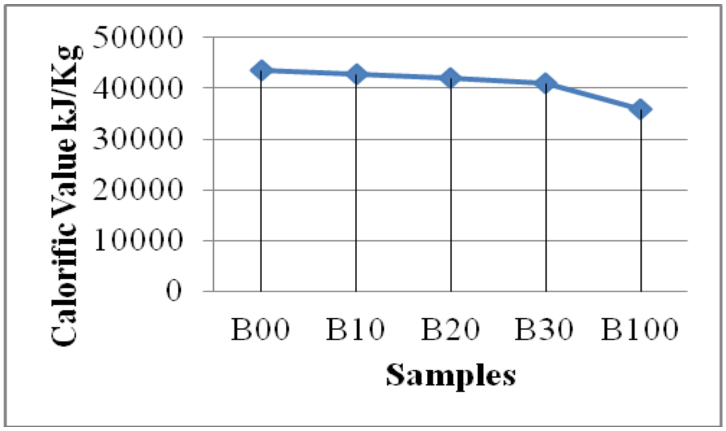

Figure 4.9 Calorific Value (kJ/kg) for different samples

4.5 Result and Discussion

The changes of the properties of the fuel with respect to the blending of biodiesel with the petroleum diesel is done for the properties like Kinematic viscosity at 40^{o}C, Density at 15^{o}C, Pour Point (°C), Flash point (°C), Ramsbottom Carbon Residue (%w), Cold Filter Plugging Point (°C), Total Sulfur (mg/kg), Acidity (mg KOH/g), Calorific Value (kJ/kg) and these were compared with the Indian automotive diesel fuel and biodiesel standards (table 4.3) .

Kinematic viscosity is an important fuel property since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. The biodiesel having higher viscosity does not burn completely and forms deposits in the fuel injector of diesel engine and hence, the biodiesel viscosity must be low (14). The kinematic viscosity of KME (Karanja Methyl Ester) at 40^{o}C is 3.67 cst which is in the range of specified in biodiesel fuel standards such as ASTM D6751, EN14214, BS II and BS III. The values of kinematic viscosity of blending B30, B20, B10 decreases gradually as shown in fig. 4.1. The kinematic viscosity for the samples is within the range of ASTM D6751, EN14214, BS II and BS III, therefore the blends of biodiesel and the diesel and the biodiesel can be used directly to the diesel engine.

Density value of KME at 15^{o}C is found to be 0.8572 which is within the range of specified by BS II and EN14214 and comparable to the values prescribed for BS III. The values of B30, B20, B10 decreases and march to the value of B00, i.e., pure diesel (fig. 4.2). Therefore the blends of biodiesel and pure biodiesel may be used directly as per the values were within the range.

The pour point of KME is found less than zero, i.e., -6 for biodiesel and remain constant for B30 and B20 and for B10 and B00 it comes in between 0 and -6 which is below the specified BS II and BS III (fig. 4.3). According the BS II and BS III, the value of pour point is 3 it can be considered the fuel of B10 blends.

The flash point of the KME is lower than the prescribed value of BS II and BS III, ASTM D6751 and EN14214. As the percentage value of biodiesel decreases the value of flash point increase (fig. 4.4). The minimum value of flash point for the BS II and BS III is 35, so it can be considered for the fuel of B10 blends.

The Ramsbottom carbon residue for the KME is little above the value for BS II and BS III. On blending with diesel at B30, B20, B10 its value become much below the value of BS II and BS III (fig. 4.5). The maximum value of ramsbottom carbon residue for BS II and BS III is 0.30, so it can be considered the fuel of B10 blends.

The Cold Filter Plugging Point ^{o}C (CFPP) is used to determine whether the biodiesel produced is suitable for the cold climate regions. The value of CFPP for KME is +5 and blending with the petrodiesel its value decreases up to -5 (B30). The maximum value of CFPP for winter is +6 in case of BS II and BS III. For ASTM D6751 and EN14214 it is not specified (fig. 4.6). Therefore, according to the BS II and BS III the pure biodiesel is better on consideration of CFPP.

Total sulphur value of KME is much lower, up to 7 whereas in case of BS II and BS III its value is 500 max and 350 max respectively. For ASTM D6751 and EN14214 its value is 15 max and 10 max respectively. So in this case the biodiesel from pongamia pinnata have good property with reference to diesel fuel (fig. 4.7).

Acidity of the KME is much below the specified value of ASTM D6751 and EN14214. The value of acidity is not reported for the BS II and BS III. The value of acidity decreases with the decreasing of biodiesel percentage up to petrodiesel (fig. 4.8). Here B10 blends of diesel and biodiesel can be considered as best blend as per acidity.

The calorific value for biodiesel is lower than that of petrodiesel. But with blending of biodiesel and petrodiesel, respectively B30, B20, B10, the calorific value increases and B10 is give the good result (fig. 4.9).

4.6 CHN Analysis

The physical properties and the chemical properties of the biodiesel from the seed of pongamia pinnata and its blends and the diesel were evaluated and comparative studies of these five samples are performed. The CHN analysis or elemental analysis of any fuel is used to investigate the samples in quantitative and qualitative manner. Element presents in the sample is determine by the qualitative analysis and the percentage of the elements in the sample is determine with the help of the quantitative analysis. The percentage of Carbon, Hydrogen and Nitrogen are determined by the CHN analyser and the remaining percentage of the sample is the percentage of the Oxygen. The empirical formula of the samples is determined after getting the percentage of the carbon, hydrogen and oxygen and the characteristics of the samples. The results obtained from the elemental analysis are shown in the table. The calorific value of the biodiesel and its blends show that the sample B10 has the highest calorific value as the carbon content of this sample is highest and the oxygen content of this sample is lowest (table 4.4).

Table 4.4 CHN analysis of Biodiesel and its blends

Sl No.	Particulars	B00	B10	B20	B30	B100
1	Carbon (%)	81.65	83.13	80.79	77.43	71.96
2	Hydrogen (%)	12.55	12.79	12.48	12.11	11.51
3	Nitrogen (%)	0	0	0.20	0	0
4	Oxygen (calculated)	5.80	4.08	6.53	10.46	16.53
5	Calorific value	43.5	42.7	41.9	41.0	35.9

	(MJ/kg)					
6	H/C ratio	1.82	1.83	1.84	1.87	1.91
7	O/C ratio	0.05	0.04	0.06	0.10	0.17
8	Empirical formula	$C_{18.9}H_{34.5}O$	$C_{26.6}H_{48.7}O$	$C_{16.4}H_{30.2}O$	$C_{9.9}H_{18.5}O$	$C_{5.8}H_{11.1}O$

4.7 pH Value

The acidity or basicity (alkalinity) of any liquid is determined in reference to the pH value of that liquid. The pH values for the samples are determined in the Civil Engineering Department, Bineswar Brahma Engineering College, Kokrajhar and the results of the samples B00, B10, B20, B30, B100 were tabulated as below. As the range of the samples are from 7 to 9.4, the samples are basic in nature since the liquid with pH value less than 7 is the acidic and more than 7 it is basic. The pH values of the biodiesel and its blends represent the basic in nature that’s why these fuels were directly useable to compression ignition engines.

Table 4.5 pH value of the samples

Particular	B00	B10	B20	B30	B100
pH	7.05	9.4	8.2	7.5	7.1

4.8 GC-MS Analysis:

This analysis is used to determine the major compounds and the chemical structure in the samples of biodiesel, blends of biodiesel-diesel and diesel. The results of the GC-MS analysis in the five samples are represented with the help of GC-MS chromatograms in the fig. 4.10 to 4.14 and their chemical compounds, molecular weight and the respective formula are shown in the table 4.5 to 4.9.

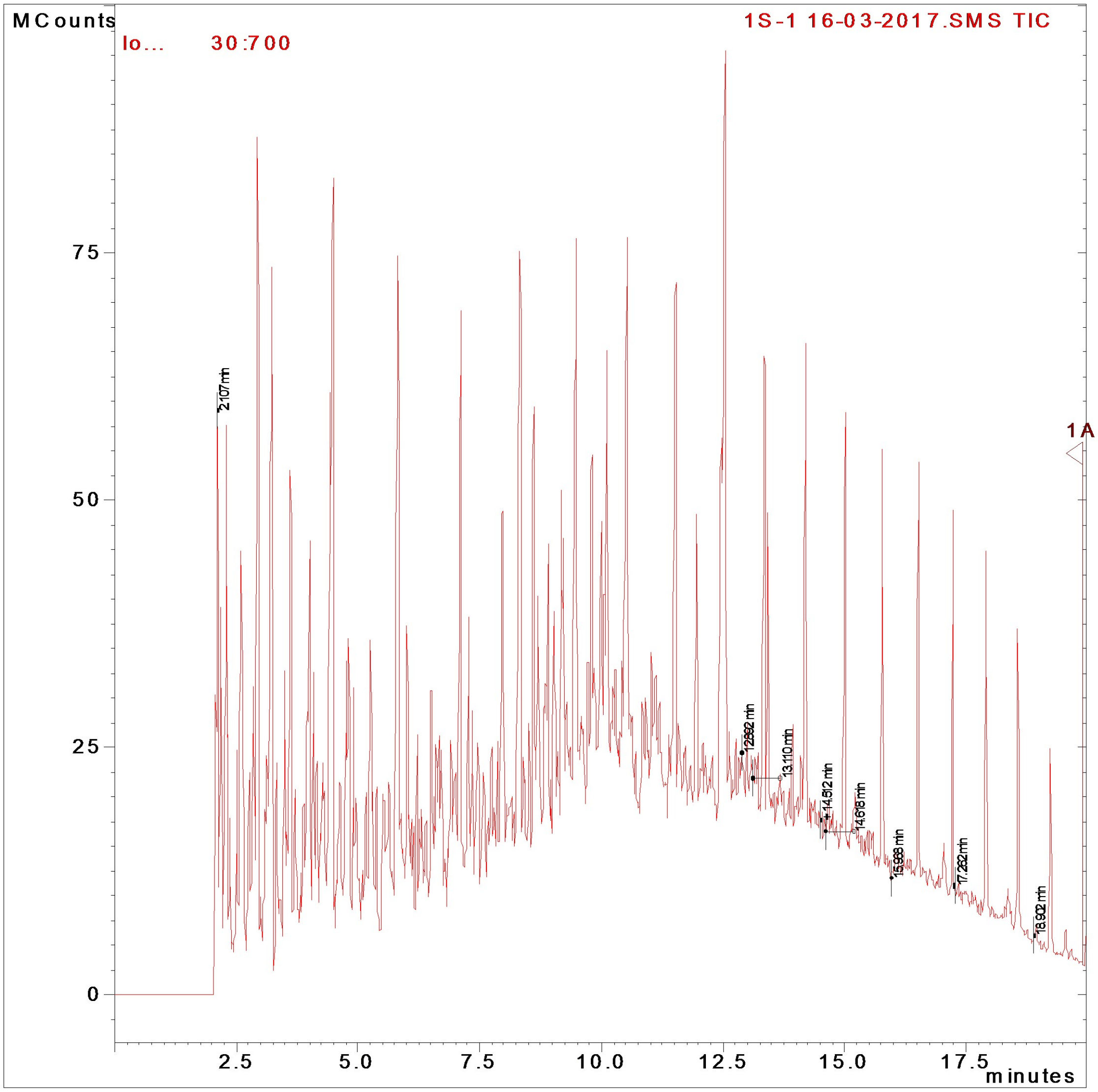

Fig. 4.10 GC-MS spectrum of diesel

Table 4.6 GC-MS compounds of diesel (B00)

Sl No	*Retention time (min)*	*Compounds*	*Molecular weight (g/mol)*	*Formula*
1	2.106	Benzene, (3-octylundecyl)	344	$C25H_{44}O$
2	2.176	1-(Trimethylsilyl)-1-propyne 1-	112	$C_6H_{12}Si$
3	2.281	Sulfurous acid, 2-ethylhexyl nonyl	320	$C_{17}H3_6O_3S$
4	2.597	Dodecylcyclohexane	252	$C_{18}H_{36}$
5	2.937	Di-tungsten, tris(cyclooctatetraene)	680	$C_{24}H_{24}W_2$
6	3.229	Sulfurous acid, 2-ethylhexyl hexyl	278	$C_{14}H_{30}O_3S$
7	3.604	Undecane, 5-cyclohexyl	238	$C_{17}H_{34}$
8	3.990	Benzene, 1,2,4-trimethyl	120	C_9H_{12}
9	4.481	Nonane, 3-methyl-5-propyl	184	$C_{13}H_{28}$
10	4.809	Mesitylene	120	C_9H_{12}
11	4.902	Cyclohexane, tetradecyl	280	$C_{20}H_{40}$
12	5.253	Benzene, 1,2,3,5-tetramethyl	134	$C_{10}H_{14}$
13	5.815	Dodecane, 2,6,10-trimethyl	212	$C_{15}H_{32}$
14	6.002	trans-Decalin, 2-methyl	152	$C_{11}H_{20}$
15	7.114	Tetratetracontane	618	$C_{44}H_{90}$
16	7.968	2-Ethyl-2,3-dihydro-1H-indene	146	$C_{11}H_{14}$
17	8.331	Tetratetracontane	618	$C_{44}H_{90}$
18	8.611	2,5,6-Trimethylbenzimidazole	160	$C_{10}H_{12}N_2$
19	8.705	Benzene, 1-(1-methylethenyl)-3-(1-methylethyl)	160	$C_{12}H_{16}$
20	8.904	3-Buten-2-one, 3-methyl-4-phenyl	160	$C_{11}H_{12}O$
21	9.185	Nonadecane	268	$C_{19}H_{40}$
22	9.477	Tetratetracontane	618	$C_{44}H_{90}$
23	9.805	3-Oxatricyclo[20.8.0.0(7,16)]triaconta-	406	$C_{29}H_{42}O$
24	10.121	Sulfurous acid, decyl 2-pentyl ester	292	$C_{15}H_{32}O_3S$
25	10.530	Tetratetracontane	618	$C_{44}H_{90}$
26	11.525	9-methylheptadecane	254	$C_{18}H_{38}$
27	11.969	Nonadecane	268	$C_{19}H_{40}$

28	12.554	Tetratetracontane	618	$C_{44}H_{90}$
29	13.350	Tetratetracontane	618	$C_{44}H_{90}$
30	13.431	Sulfurous acid, butyl decyl ester	278	$C_{14}H_{30}O_3S$
31	14.304	Tetratetracontane	618	$C_{44}H_{90}$

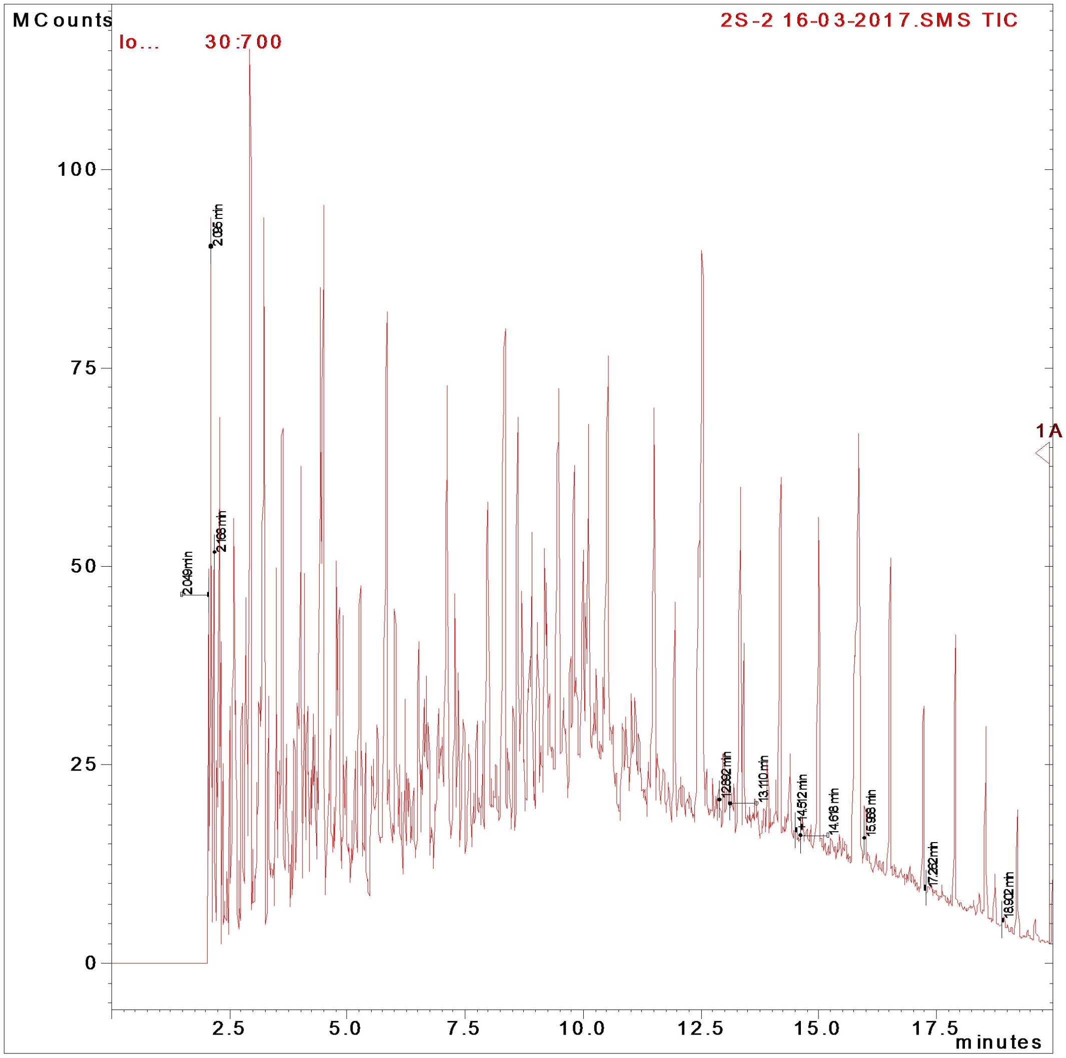

Fig. 4.11 GC-MS spectrum of sample B10

Table 4.7 GC-MS Compounds of Biodiesel and its blends B10

Sl. No.	*Retention time (min)*	*Compounds*	*Molecular weight (g/mol)*	*Formula*
1	2.047	Benzene, (2-methyloctyl)	204	$C_{15}H_{24}$
2	2.059	Heptane, 3,3,5-trimethyl	142	$C_{10}H_{22}$
3	2.094	Benzene, (3-octylundecyl)	344	$C_{25}H_{44}$
4	2.164	2,4,4,6,6,8,8-Heptamethyl-2-nonene	224	$C_{16}H_{32}$
5	2.281	Sulfurous acid, 2-ethylhexyl nonyl ester	320	$C_{17}H_{36}O_3S$
6	2.597	Cyclohexane, tetradecyl	280	$C_{20}H_{40}$
7	2.936	Palladium(0), bis(η-2-butadiene) 1,1,4,5,8,8-hexa(tert.-butyl)-1,4,5,8-tetraphosphaoctane	842	$C_{36}H_{74}P_4Pd_2$
8	3.229	Tridecane	184	$C_{13}H_{28}$
9	3.615	Tetratetracontane	618	$C_{44}H_{90}$
10	4.001	Pregn-5-en-20-one, 3,16,17,21-tetrakis[(trimethylsilyl)oxy]-, O-(phenylmethyl)oxime, (3β,16α)	757	$C_{40}H_{71}NO_5Si_4$
11	4.423	β,.Psi.-Carotene, 3’,4’-didehydro-1’,2’-dihydro-1’,2’-dihydroxy-, (2’R)-	568	$C_{40}H_{56}O_2$
12	4.493	Nonane, 3-methyl-5-propyl-	184	$C_{13}H_{28}$
13	5.827	Tetratetracontane	618	$C_{44}H_{90}$
14	7.125.	Tetratetracontane	618	$C_{44}H_{90}$
15	7.968	Benzene, 2-ethenyl-1,3,5-trimethyl-	146	$C_{11}H_{14}$
16	8.342	Tetratetracontane	618	$C_{44}H_{90}$

17	8.611	2,5,6-Trimethylbenzimidazole	160	$C_{10}H_{12}N_2$
18	8.915	Naphthalene, 1,2,3,4-tetrahydro-2,6-dimethyl-	160	$C_{12}H_{16}$
19	9.184	Tetratetracontane	618	$C_{44}H_{90}$
20	9.477	Tetratetracontane	618	$C_{44}H_{90}$
21	9.804	Silane, (cyclohexylamino)(1H-inden-1-yl)	271	$C_{17}H_{25}Nsi$
22	10.120	Tetratetracontane	618	$C_{44}H_{90}$
23	10.530	Tetratetracontane	618	$C_{44}H_{90}$
24	11.512	Heptadecane, 9-hexyl	324	$C_{23}H_{48}$
25	11.957	Tetratetracontane	618	$C_{44}H_{90}$
26	12.530	Tetratetracontane	618	$C_{44}H_{90}$
27	13.338	Tetratetracontane	618	$C_{44}H_{90}$
28	14.192	2,2-Dimethylpropanoic acid, 4-hexadecyl ester	326	$C_{21}H_{42}O_2$
29	15.865	8-Octadecenoic acid, methyl ester, (E)	296	$C_{19}H_{36}O_2$
30	19.212	1-Decanol, 2-hexyl	242	$C_{16}H_{34}O$

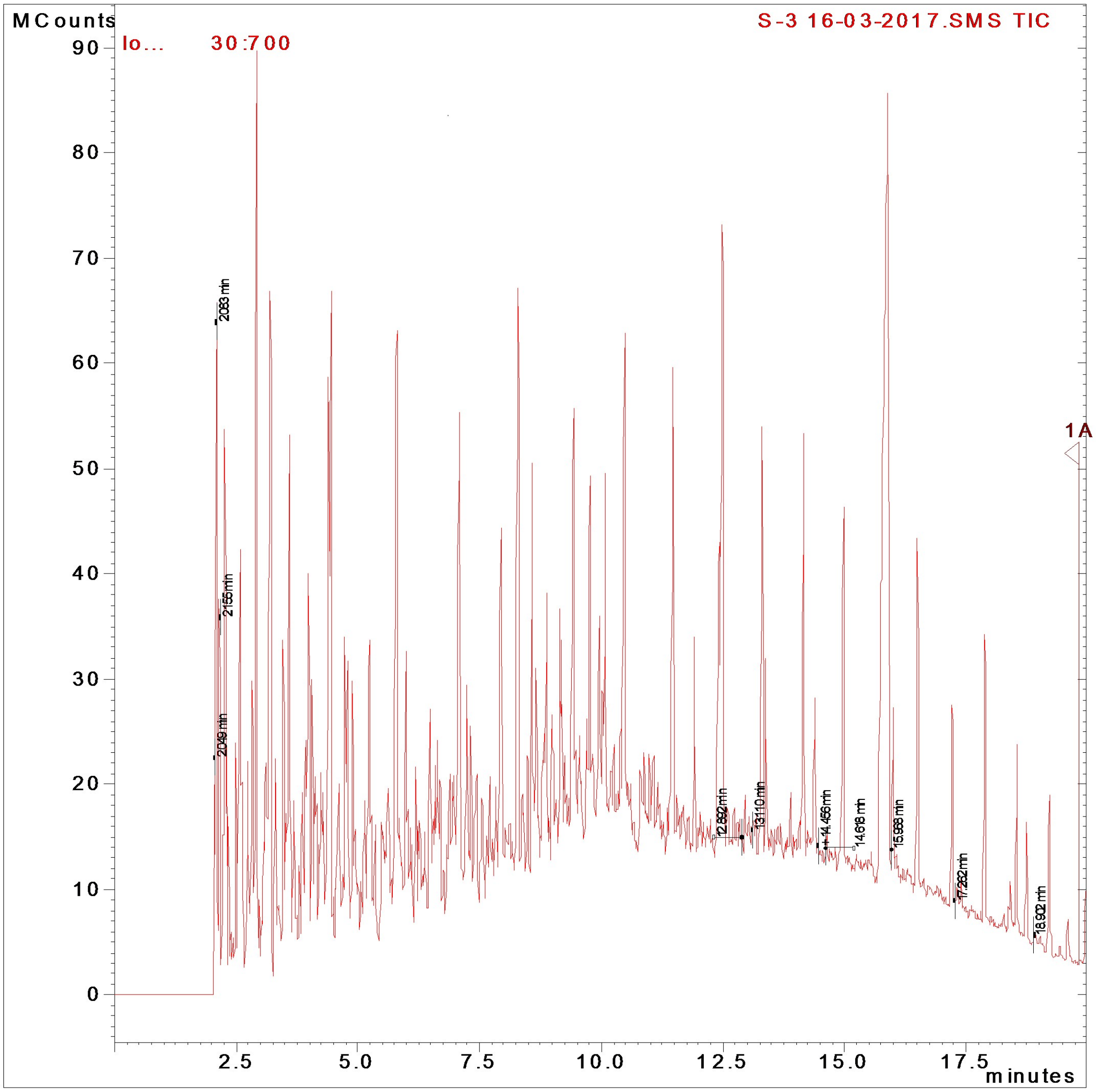

Fig. 4.12 GC-MS spectrum of sample B20

Table 4.8 GC-MS Compounds of Biodiesel and its blends B20

Sl.	*Retention*	*Compounds*	*Molecular*	*Formula*

No.	*time (min)*		*weight (g/mol)*	
1	2.047	Benzene, (2-methyloctyl)	204	$C_{15}H_{24}$
2	2.082	Benzene, (3-octylundecyl)	344	$C_{25}H_{44}$
3	2.152	1-(Trimethylsilyl)-1-propyne	112	$C_6H_{12}Si$
4	2.258	Sulfurous acid, 2-ethylhexyl nonyl ester	320	$C_{17}H_{36}O_3S$
5	2.547	Cyclohexane, undecyl	238	$C_{17}H_{34}$
6	2.913	Pregn-5-en-20-one, 3,16,17,21-tetrakis[(trimethylsilyl)oxy]-, O-(phenylmethyl)oxime, (3β,16α)	757	$C_{40}H_{71}NO_5Si_4$
7	3.194	Decane, 2,3,5-trimethyl	184	$C_{13}H_{28}$
8	3.580	Dodecane, 3-cyclohexyl	252	$C_{18}H_{36}$
9	3.967	Chloro-1,5-(cyclooctadiene)iridium(I) dimer	672	$C_{16}H_{24}Cl_2\ Ir_2$
10	4.400	Benzene, 1,2,4-trimethyl	120	C_9H_{12}
11	4.446	Heptane, 2,2,3,3,5,6,6-heptamethyl	198	$C_{14}H_{30}$
12	5.792	Nonane, 3-methyl-5-propyl	184	$C_{13}H_{28}$
13	7.079	Tetratetracontane	618	$C_{44}H_{90}$
14	7.933	2,3,4,5,6,7-Hexahydro-1H-cyclopenta[a]pentalene	146	$C_{11}H_{14}$
15	8.296	Palladium(0), bis(η-2-butadiene) 1,1,4,5,8,8-hexa(tert.-butyl)-1,4,5,8-tetraphosphaoctane	842	$C_{36}H_{74}P_4Pd_2$
16	8.577	2,5,6-Trimethylbenzimidazole	160	$C_{10}H_{12}N_2$
17	9.431	Tetratetracontane	618	$C_{44}H_{90}$
18	9.770	Naphthalene, 1,2-dimethyl	156	$C_{12}H_{12}$
19	10.086	Sulfurous acid, decyl pentyl ester	292	$C_{15}H_{32}O_3S$
20	10.484	Tetratetracontane	618	$C_{44}H_{90}$
21	11.478	Tetratetracontane	618	$C_{44}H_{90}$

22	12.496	Tetratetracontane	618	$C_{44}H_{90}$
23	13.315	Tetratetracontane	618	$C_{44}H_{90}$
24	14.169	9-methylheptadecane	254	$C_{18}H_{38}$
25	14.977	Tetratetracontane	618	$C_{44}H_{90}$
26	15.889	Rhodopin	554	$C_{40}H_{58}O$
27	16.509	Tetratetracontane	618	$C_{44}H_{90}$
28	17.211	2-methylhexacosane	380	$C_{27}H_{56}$
29	17.890	1-Decanol, 2-hexyl	242	$C_{16}H_{34}O$
30	18.756	Glaucine	355	$C_{21}H_{25}NO_4$
31	19.213	1-Decanol, 2-hexyl	242	$C_{16}H_{34}O$

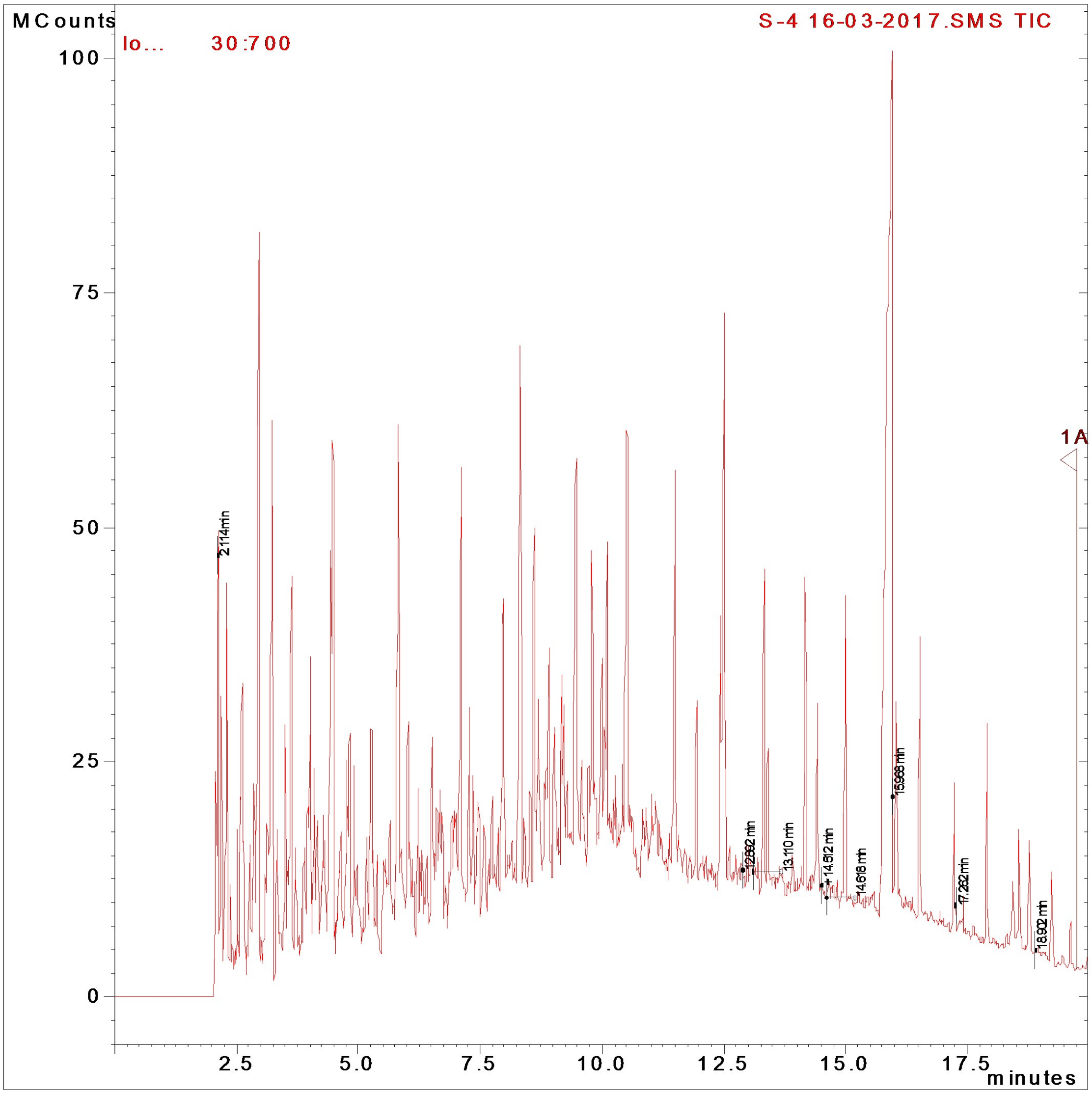

Fig. 4.13 GC-MS spectrum of sample B30

Table 4.9 GC-MS Compounds of Biodiesel and its blends B30

Sl.	*Retention*	*Compounds*	*Molecular*	*Formula*

No.	*time (min)*		*weight (g/mol)*	
1	2.117	Benzene, (3-octylundecyl)	344	$C_{25}H_{44}$
2	2.293	Sulfurous acid, 2-ethylhexyl nonyl ester	320	$C_{17}H_{36}O_3S$
3	2.609	Cyclohexane, (1-methylpropyl)	140	$C_{10}H_{20}$
4	2.948	Pregn-5-en-20-one, 3,16,17,21-tetrakis[(trimethylsilyl)oxy]-, O-(phenylmethyl)oxime, (3β,16α)	757	$C_{40}H_{71}NO_5Si_4$
5	3.229	Decane, 2,3,5-trimethyl	184	$C_{13}H_{28}$
6	3.616	Undecane, 5-cyclohexyl	238	$C_{17}H_{34}$
7	4.002	Mesitylene	120	C_9H_{12}
8	4.470	Dodecane, 2,6,10-trimethyl	212	$C_{15}H_{32}$
9	5.816	Tetratetracontane	618	$C_{44}H_{90}$
10	7.115	Tetratetracontane	618	$C_{44}H_{90}$
11	7.969	2,3,4,5,6,7-Hexahydro-1H-cyclopenta[a]pentalene	146	$C_{11}H_{14}$
12	8.331	Tetratetracontane	618	$C_{44}H_{90}$
13	8.612	2,5,6-Trimethylbenzimidazole	160	$C_{10}H_{12}N_2$
14	9.466	Tetratetracontane	618	$C_{44}H_{90}$
15	9.794	Naphthalene, 1,5-dimethyl	156	$C_{12}H_{12}$
16	10.110	Tetratetracontane	618	$C_{44}H_{90}$
17	10.508	Tetratetracontane	618	$C_{44}H_{90}$
18	11.502	2-Hexyl-1-octanol	214	$C_{14}H_{30}O$
19	12.520	Tetratetracontane	618	$C_{44}H_{90}$
20	13.327	9-methylheptadecane	254	$C_{18}H_{38}$
21	15.948	Rhodopin	554	$C_{40}H_{58}O$
22	16.533	9-methylheptadecane	254	$C_{18}H_{38}$

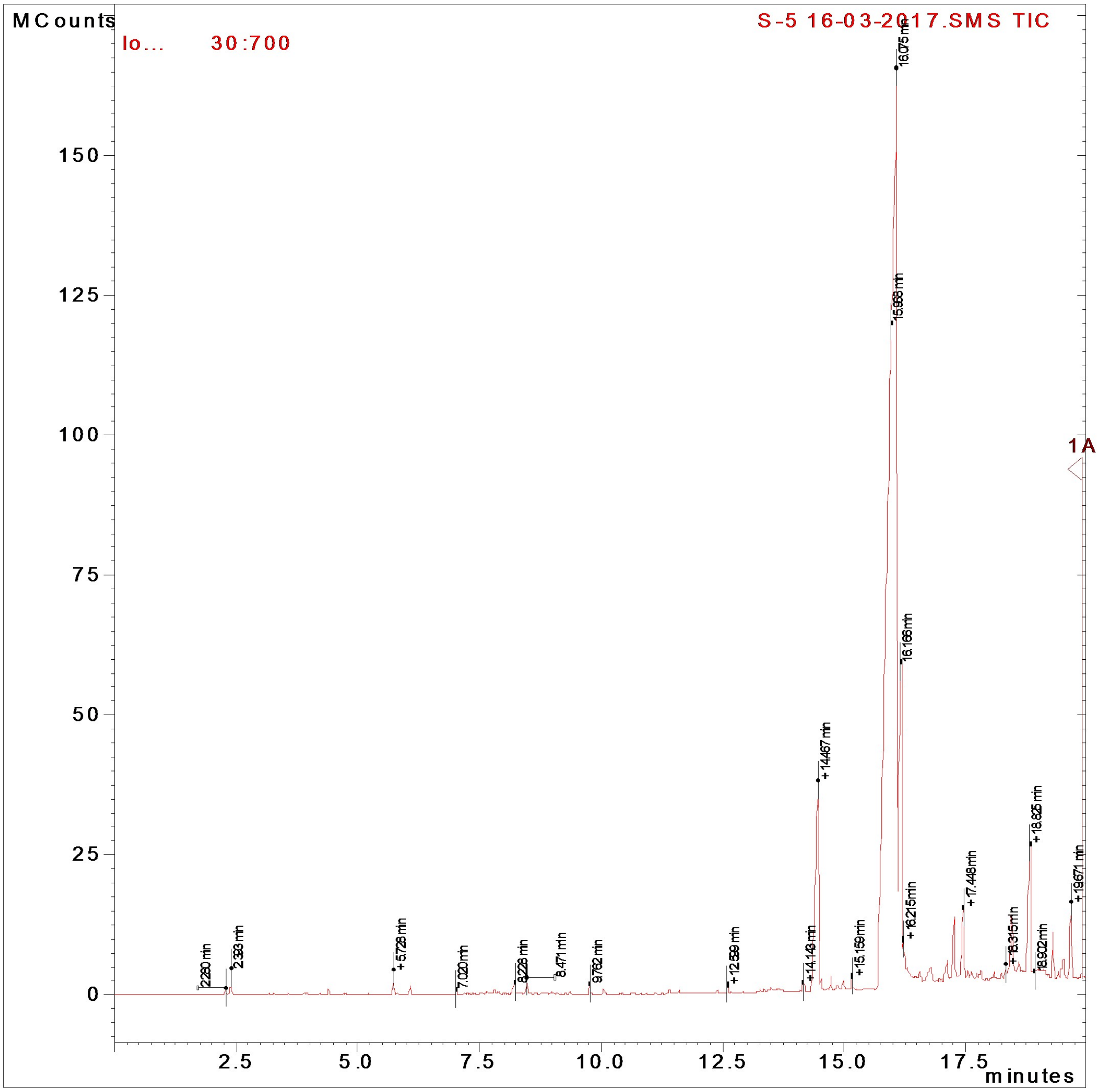

Fig. 4.14 GC-MS spectrum of sample B100

Table 4.10 GC-MS Compounds of Biodiesel (B100)

Sl. No.	*Retention time*	*Compounds*	*Molecular weight*	*Formula*

	(min)		*(g/mol)*	
1	2.377	Tetrachloroethylene	164	C_2Cl_4
2	14.460	9-Borabicyclo[3.3.1]nonane, 9-[[[2-[(9-borabicyclo[3.3.1]non-9-yloxy)methyl]phenyl]thioxomethyl]thio]	424	$C_{24}H_{34}B_2OS_2$
3	16.068	Rhodopin	554	$C_{40}H_{58}O$
4	16.080	Triolein	884	$C_{57}H_{104}O_6$
5	16.161	3-Pyridinecarboxylic acid, 2,7,10-tris(acetyloxy)-1,1a,2,3,4,6,7,10,11,11a-decahydro-1,1,3,6,9 –pentamethyl-4-oxo-4a,7a-epoxy-5H-cyclopenta[a]cyclopropa[f]cycloundecen-11-yl ester, [1aR-(1aR*,2R*,3S*, 4aR*,6S*,7S*,7aS*,8E,10R*,11R*,11aS*)]	597	$C_{32}H_{39}NO_{10}$
6	17.438	Benzocycloheptano[2,3,4-I,j]isoquinoline, 4,5,6,6a-tetrahydro-1,9-dihydroxy-2,10-dimethoxy	327	$C_{19}H_{21}NO_4$
7	18.831	Glaucine	355	$C_{21}H_{25}NO_4$
8	19.674	9H-Carbazole, 9-(1-naphthalenyl)	293	$C_{22}H_{15}N$

4.9 FTIR Analysis

The functional group and structure of the compounds present in the samples are found from the shape, position and intensity of the peaks in the FTIR spectrum. The functional groups identified from the peaks observed in FTIR spectrum are confirmed the compounds detected in GC-MS analysis. The IR spectrums of the samples are given in the fig. 4.15 to 4.19.

The FTIR spectrum of diesel in fig. 4.15 shows the strong and sharp signals at 2926 and 2856 cm^{-1} are due to C-H stretching frequencies. The signals at 1457 and 1377 cm^{-1} may be due to $–CH_2$- and $–CH_3$ bending.

The FTIR spectrum of B10 in fig. 4.16 shows a signal at 1748 cm^{-1} is due to C=O stretching frequency of methyl esters (RCOOMe) and signal at 1024 cm^{-1} may be due to C-O stretching frequency. The signals at 1456 and 1378 cm^{-1} may be due to $–CH_2$- and $–CH_3$ bending. Strong and sharp signals at 2922 and 2854 cm^{-1} are due to C-H stretching frequencies.

In the FTIR spectrum of B20 in fig. 4.17 shows a sharp signal at 1747 cm^{-1} is due to C=O stretching frequency of methyl esters (RCOOMe) and signals at 1165 and 1019 cm^{-1} may be due to C-O stretching frequencies. The signals at 1456 and 1377 cm^{-1} may be due to $–CH_2$- and $–CH_3$ bending. Strong and sharp signals at 2923 and 2855 cm^{-1} are due to C-H stretching frequencies.

In the FTIR spectrum of B30 in fig. 4.18 shows a sharp signal at 1747 cm^{-1} is due to C=O stretching frequency of methyl esters (RCOOMe) and signals at 1163 and 1021 cm^{-1} may be due to C-O stretching frequencies. The signals at 1460 and 1378 cm^{-1} may be due to $–CH_2$- and $–CH_3$ bending. Strong and sharp signals at 2925 and 2855 cm^{-1} are due to C-H stretching frequencies.

In the FTIR spectrum of B100 in fig. 4.19 shows IR spectrum of biodiesel showed a C=O stretching band of methyl esters (RCOOMe) at 1747 cm^{-1} and C-O stretching bands at 1173 and 1023 cm^{-1}. The weak signal at 1646 cm^{-1} is due to C=C stretching frequency. The signals at 1464 and 1377 cm^{-1} may be due to $–CH_2$- and $–CH_3$ bending. The observation of an absorption peak at 723 cm^{-1} suggested the CH_2 rocking. Strong and sharp signals at 2924 and 2856 cm^{-1} are due to C-H stretching frequencies. The weak signal at 3451 cm^{-1} may be due to O-H stretching frequency of water.

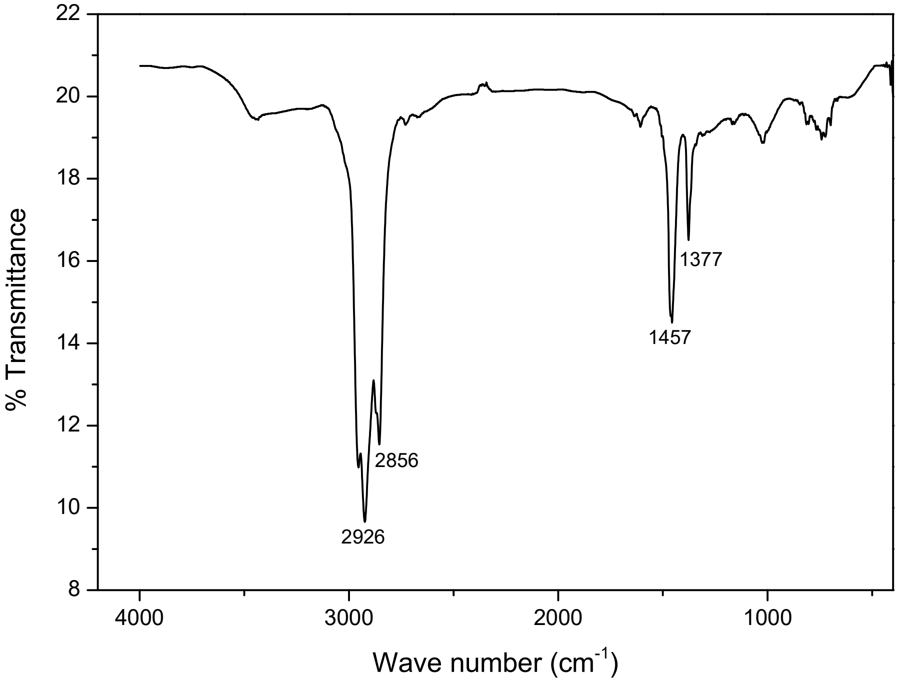

Fig. 4.15 FTIR of Diesel (B00)

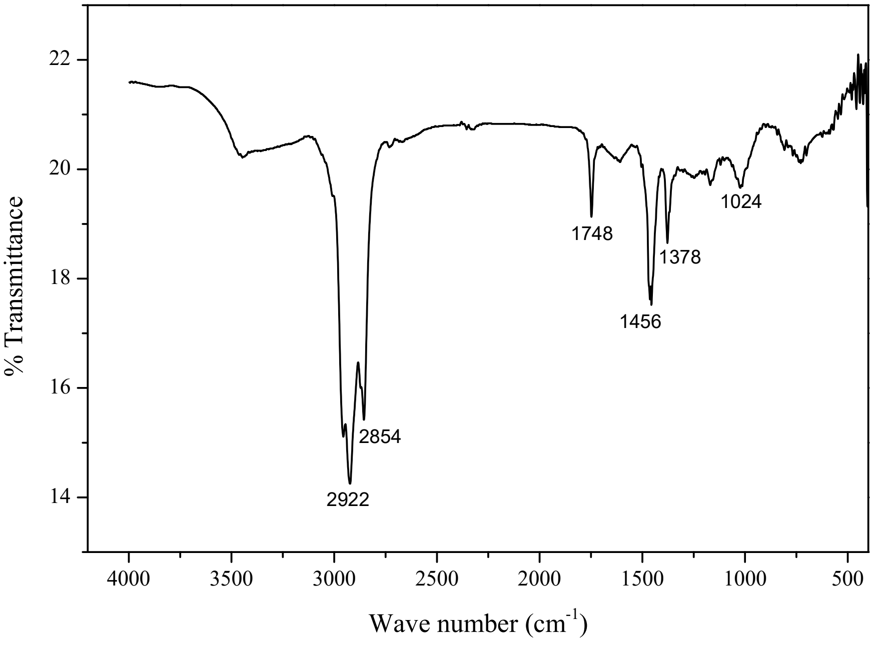

Fig. 4.16 FTIR of Biodiesel and its blend (B10)

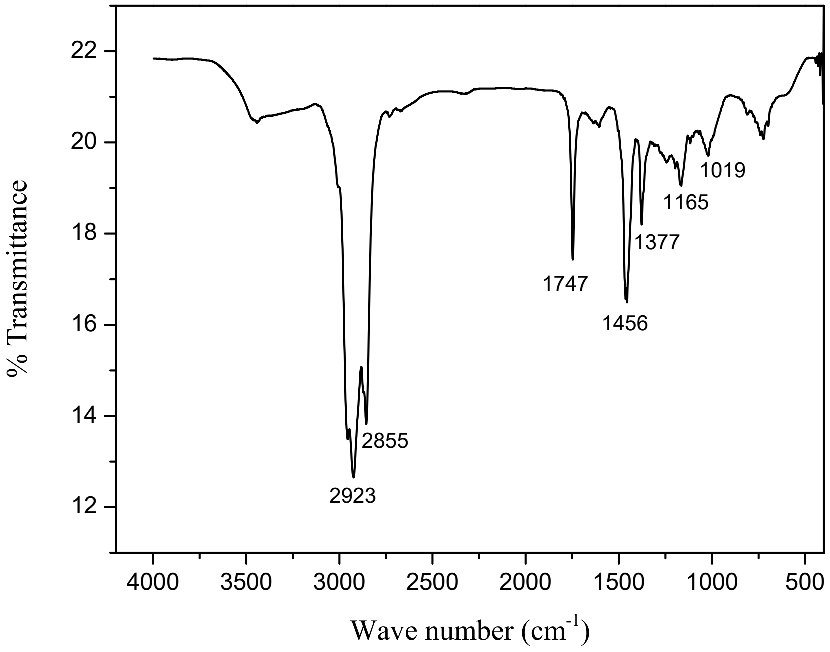

Fig. 4.17 FTIR of Biodiesel and its blend (B20)

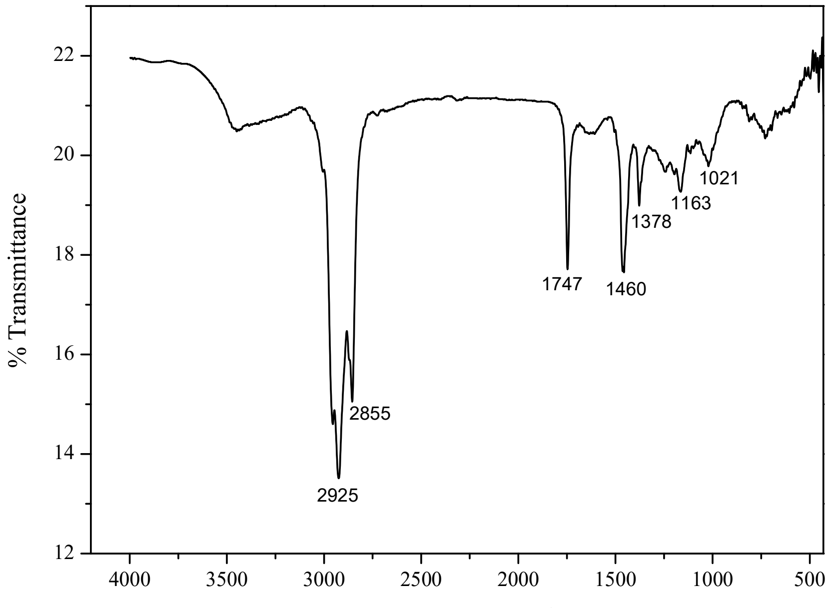

Fig. 4.18 FTIR of Biodiesel and its blend (B30)

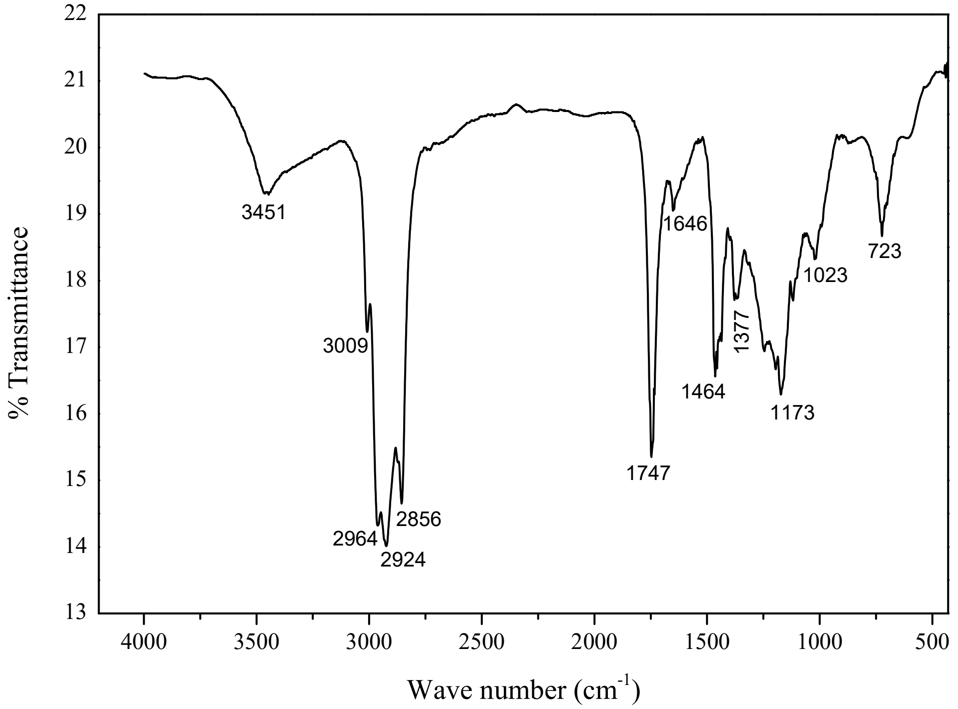

Fig. 4.19 FTIR of Biodiesel (B100)

CHAPTER – 5

5.0 Performance Analysis

A diesel engine is almost the same as a petrol engine but it burns a different type of fuel. Diesel is named after its inventor Rudolf Diesel, a German who first developed this type of fuel in the early 1900's. Diesel engines have mainly been used in Lorries and buses because of their increased power and their reliability. They tend to be noisy and smelly compared to a petrol engine, but are more economical to run. The performance analyses of a compression ignition engine for different samples were discussed as follows:

5.1 Observation

Data for water and the other samples of blends and the diesel were given below:

Specific Heat of water C_p = 4.186 kJ/kg^{o}C
Density of air ρ_a = 1.21 kg/m^3
Density of water ρ_w = 1000 kg/m^3
Diameter of the brake drum d_B = 0.2 m
Diameter of the rope d_R = 0.012 m
Diameter of orifice d_O = 0.015 m
Diameter of piston D = 0.08 m
Stroke length of piston L = 0.11 m
Number of cylinder (N_C) = 1
Number of cycles (n) = 2

Table 5.1 Data for different samples (diesel, blends of biodiesel and diesel, biodiesel)

Sl. No.	*Particulars*	*Sample 1 B00*	*Sample 2 B10*	*Sample 3 B20*	*Sample 4 B30*	*Sample 5 B100*
1	Acceleration due to	9.81	9.81	9.81	9.81	9.81

	gravity, g (m/sec^2)					
2	Caloric Value of fuel C_v (kJ/kg)	43500	42738	41956	40995	35879
3	Co-efficient of discharge for orifice C_d	0.64	0.64	0.64	0.64	0.64
4	Density of fuel ρ_f (kg/m^3)	828.9	832.4	836.3	839.3	857.2

5.2 Relations for calculations

Mean effective radius, $R_e = \frac{d_B+2D_R}{2}$ (m)

Torque, $T = (W_1 - W_2) \times g \times R_e$ (N-m)

Brake Power, $\dot{E}_w = BP = \frac{2\times\pi\times N\times T}{60\times 1000}$ (kW)]

Fuel Consumption, $W_f = \frac{x}{t} \times \frac{\rho_f}{10^6}$ (kg/sec)

Specific fuel consumption, $W_{sf} = \frac{W_f}{BP}$ (kg/kW sec)

Heat supplied, $\dot{E}_f = H_f = W_f \times C_v$ (kW)

Brake thermal efficiency, $\eta_{BT} = \frac{BP}{H_f} \times 100\%$

Mass of water entering the engine cooling jacket,

$$m_{ew} = \frac{V_E}{t_E} \times \frac{\rho_W}{10^3} \text{ kg/sec}$$

Heat carried out by water from engine cooling jacket,

$$\dot{E}_L = H_{ecw} = m_{ew} \times C_p \times (T_2 - T_1) \text{ (kW)}$$

Mass of water entering the calorimeter,

$$m_{cw} = \frac{V_C}{t_C} \times \frac{\rho_W}{10^3} \text{ kg/sec}$$

Heat carried out by water from calorimeter,

$$\dot{E}_c = H_{ccw} = m_{cw} \times C_p \times (T_6 - T_5) \text{ (kW)}$$

Heat carried out by exhaust gas,

$$\dot{E}_g = H_{exh} = \frac{H_{ccw}}{T_3 - T_4} \times (T_3 - T_a) \text{ (kW)}$$

Heat lost in radiation and uncounted heat,

$$\dot{E}_r = H_{un} = H_f - (BP + H_{ecw} + H_{exh}) \text{ (kW)}$$

Cross sectional area of the orifice,

$$a_o = \frac{\pi}{4} d_o^2 \ (m^2)$$

Head causing flow of air through orifice,

$$H = \frac{h_1 - h_2}{100}\left(\frac{\rho_w}{\rho_a} - 1\right) \ (m)$$

Air consumption, $Q_a = C_d \times a_o \sqrt{(2gH)} \ (m^3/sec)$

Swept Volume, $V_s = \dfrac{\pi \times D^2 \times L \times N \times N_c}{4 \times 60 \times n} \ (m^3/sec)$

Volumetric efficiency, $\eta_{vol} = \dfrac{Q_a}{V_s} \times 100\%$

Where:

x = Volume of the fuel consumed

t = Time taken for x ml

V_E = Volume of water flow through the engine jacket

t_E = Time for V_E

V_C = Volume of water flow through the calorimeter

t_C = Time for V_C

h_1, h_2 = Manometer reading (high and low level respectively)

Table 5.2 Observation table for sample 1 (B00)

T_a=23°C (Reading of Sensor T_3/T_4 before starting engine)			
Sl. No.	*1*	*2*	*3*
N(RPM)	1572	1564	1551
h_1 (cm)	29	29	29
h_2 (cm)	11	11	11
W_1 (kg)	5	10	15
W_2 (kg)	0.5	1.0	1.8

x (ml)	10	10	10
t (sec)	67	51	44
T_1 (°C)	34	35	35
T_2 (°C)	55	58	64
T_3 (°C)	157	175	202
T_4 (°C)	58	61	66
T_5 (°C)	34	35	35
T_6 (°C)	40	42	44
V_E (ltrs)	1	1	1
t_E (sec)	48	48	48
V_c (ltrs)	1	1	1
t_c (sec)	48	48	48

Table 5.3 Result for the sample 1 (B00)

Sl. No.	*Particulars*	*Load 5kg*	*Load 10kg*	*Load 15kg*
1	Brake Power (kW)	0.814	1.619	2.356
2	Fuel Consumption (kg/h)	0.445	0.585	0.678
3	Specific fuel consumption (kg/kWh)	0.546	0.369	0.287
4	Heat supplied (kW)	5.377	7.069	8.193
5	Brake thermal efficiency (%)	15.13	22.44	28.76
6	Heat carried out by water from engine cooling jacket (kW)	1.828	2.006	2.525

7	Heat carried out by water from calorimeter (kW)	0.522	0.609	0.784
8	Heat carried out by exhaust gas (kW)	0.685	0.791	1.009
9	Heat lost in radiation and uncounted (kW)	2.020	2.653	2.303
10	Air consumption (m^3/sec)	6.107×10^{-3}	6.107×10^{-3}	6.107×10^{-3}
11	Swept Volume (m^3/sec)	7.243×10^{-3}	7.206×10^{-3}	7.146×10^{-3}
12	Volumetric efficiency (%)	84.33	84.69	85.40

Table 5.4 Observation table for sample 2 (B10)

T_a=23°C (Reading of Sensor T_3/T_4 before starting engine)			
Sl. No.	*1*	*2*	*3*
N(RPM)	1582	1566	1555
h_1 (cm)	29	29	29
h_2 (cm)	11	11	11
W_1 (kg)	5	10	15
W_2 (kg)	0.5	1.0	1.8
x (ml)	10	10	10
t (sec)	67	51	44
T_1 (°C)	34	35	35

T_2 (^{o}C)	56	59	65
T_3 (^{o}C)	161	182	203
T_4 (^{o}C)	58	63	69
T_5 (^{o}C)	34	35	35
T_6 (^{o}C)	41	43	45
V_E (ltrs)	1	1	1
t_E (sec)	48	48	48
V_c (ltrs)	1	1	1
t_c (sec)	48	48	48

Table 5.5 Result for the sample 2 (B10)

Sl. No.	*Particulars*	*Load 5kg*	*Load 10kg*	*Load 15kg*
1	Brake Power (kW)	0.819	1.622	2.362
2	Fuel Consumption (kg/h)	0.447	0.588	0.681
3	Specific fuel consumption (kg/kWh)	0.546	0.363	0.288
4	Heat supplied (kW)	5.307	6.981	8.085
5	Brake thermal efficiency (%)	15.43	23.23	29.21
6	Heat carried out by water from engine cooling jacket (kW)	1.916	2.090	2.612
7	Heat carried out by water from calorimeter (kW)	0.609	0.697	0.871
8	Heat carried out by exhaust gas (kW)	0.792	0.908	1.144

9	Heat lost in radiation and uncounted (kW)	1.780	2.361	1.967
10	Air consumption (m^3/sec)	6.107x10^{-3}	6.107x10^{-3}	6.107x10^{-3}
11	Swept Volume (m^3/sec)	7.289x10^{-3}	7.216x10^{-3}	7.165x10^{-3}
12	Volumetric efficiency (%)	83.76	84.57	85.28

Table 5.6 Observation table for sample 3 (B20)

T_a=23^{o}C (Reading of Sensor T_3/T_4 before starting engine)			
Sl. No.	*1*	*2*	*3*
N(RPM)	1583	1568	1559
h_1 (cm)	29	29	29
h_2 (cm)	11	11	11
W_1 (kg)	5	10	15
W_2 (kg)	0.5	1.0	1.8
x (ml)	10	10	10
t (sec)	67	51	44
T_1 (^{o}C)	34	35	35
T_2 (^{o}C)	56	59	65
T_3 (^{o}C)	163	187	206
T_4 (^{o}C)	60	66	74

T_5 (^{o}C)	34	35	35
T_6 (^{o}C)	42	44	46
V_E (ltrs)	1	1	1
t_E (sec)	48	48	48
V_c (ltrs)	1	1	1
t_c (sec)	48	48	48

Table 5.7 Result for the sample 3 (B20)

Sl. No.	*Particulars*	*Load 5kg*	*Load 10kg*	*Load 15kg*
1	Brake Power (kW)	0.820	1.624	2.368
2	Fuel Consumption (kg/h)	0.449	0.590	0.684
3	Specific fuel consumption (kg/kWh)	0.548	0.363	0.289
4	Heat supplied (kW)	5.233	6.879	7.972
5	Brake thermal efficiency (%)	15.67	23.61	29.70
6	Heat carried out by water from engine cooling jacket (kW)	1.916	2.090	2.612
7	Heat carried out by water from calorimeter (kW)	0.697	0.784	0.958
8	Heat carried out by exhaust gas (kW)	0.920	1.037	1.299
9	Heat lost in radiation and uncounted (kW)	1.577	2.128	1.693
10	Air consumption (m^3/sec)	6.107×10^{-3}	6.107×10^{-3}	6.107×10^{-3}

11	Swept Volume (m^3/sec)	7.294×10^{-3}	7.224×10^{-3}	7.183×10^{-3}
12	Volumetric efficiency (%)	83.76	84.45	85.04

Table 5.8 Observation table for sample 4 (B30)

T_a=23°C (Reading of Sensor T_3/T_4 before starting engine)			
Sl. No.	*1*	*2*	*3*
N(RPM)	1590	1573	1562
h_1 (cm)	29	29	29
h_2 (cm)	11	11	11
W_1 (kg)	5	10	15
W_2 (kg)	0.5	1.0	1.8
x (ml)	10	10	10
t (sec)	67	51	44
T_1 (°C)	34	35	35
T_2 (°C)	56	61	66
T_3 (°C)	169	190	211
T_4 (°C)	62	69	76
T_5 (°C)	34	35	35
T_6 (°C)	43	46	48
V_E (ltrs)	1	1	1

t_E (sec)	48	48	48
V_c (ltrs)	1	1	1
t_c (sec)	48	48	48

Table 5.9 Result for the sample 4 (B30)

Sl. No.	*Particulars*	*Load 5kg*	*Load 10kg*	*Load 15kg*
1	Brake Power (kW)	0.823	1.629	2.372
2	Fuel Consumption (kg/h)	0.451	0.592	0.687
3	Specific fuel consumption (kg/kWh)	0.548	0.363	0.290
4	Heat supplied (kW)	5.136	6.741	7.823
5	Brake thermal efficiency (%)	16.02	24.16	30.32
6	Heat carried out by water from engine cooling jacket (kW)	1.916	2.264	2.699
7	Heat carried out by water from calorimeter (kW)	0.784	0.958	1.132
8	Heat carried out by exhaust gas (kW)	1.040	1.291	1.543
9	Heat lost in radiation and uncounted (kW)	1.357	1.557	1.209
10	Air consumption (m^3/sec)	6.107×10^{-3}	6.107×10^{-3}	6.107×10^{-3}
11	Swept Volume (m^3/sec)	7.326×10^{-3}	7.248×10^{-3}	7.197×10^{-3}
12	Volumetric efficiency (%)	83.42	84.22	84.81

Table 5.10 Observation table for sample 5 (B100)

$T_a=23^{o}C$ (Reading of Sensor T_3/T_4 before starting engine)			
Sl. No.	*1*	*2*	*3*
N(RPM)	1592	1577	1564
h_1 (cm)	29	29	29
h_2 (cm)	11	11	11
W_1 (kg)	5	10	15
W_2 (kg)	0.5	1.0	1.8
x (ml)	10	10	10
t (sec)	67	51	44
T_1 (^{o}C)	34	35	35
T_2 (^{o}C)	57	62	67
T_3 (^{o}C)	170	192	213
T_4 (^{o}C)	63	72	78
T_5 (^{o}C)	34	35	35
T_6 (^{o}C)	44	47	49
V_E (ltrs)	1	1	1
t_E (sec)	48	48	48
V_c (ltrs)	1	1	1
t_c (sec)	48	48	48

Table 5.11 Result for the sample 5 (B100)

Sl. No.	*Particulars*	*Load 5kg*	*Load 10kg*	*Load 15kg*
1	Brake Power (kW)	0.824	1.633	2.375
2	Fuel Consumption (kg/h)	0.461	0.608	0.701
3	Specific fuel consumption (kg/kWh)	0.559	0.372	0.295
4	Heat supplied (kW)	4.595	6.060	6.986
5	Brake thermal efficiency (%)	17.93	26.95	34.00
6	Heat carried out by water from engine cooling jacket (kW)	2.003	2.351	2.786
7	Heat carried out by water from calorimeter (kW)	0.871	1.045	1.219
8	Heat carried out by exhaust gas (kW)	1.164	1.437	1.679
9	Heat lost in radiation and uncounted (kW)	0.604	0.639	0.146
10	Air consumption (m^3/sec)	6.107×10^{-3}	6.107×10^{-3}	6.107×10^{-3}
11	Swept Volume (m^3/sec)	7.335×10^{-3}	7.266×10^{-3}	7.206×10^{-3}
12	Volumetric efficiency (%)	83.19	83.99	84.69

Table 5.12 Result for the samples B00, B10, B20, B30, B100 at different loads.

Sl. No.	*Particulars*	*Load (kg)*	*Samples*				
			B00	*B10*	*B20*	*B30*	*B100*
1	Brake Power (kW)	5	0.814	0.819	0.820	0.823	0.824
		10	1.619	1.622	1.624	1.629	1.633
		15	2.356	2.362	2.368	2.372	2.375
2	Fuel Consumption (kg/h)	5	0.445	0.447	0.449	0.451	0.461
		10	0.585	0.588	0.590	0.592	0.608
		15	0.678	0.681	0.684	0.687	0.701
3	Specific Fuel Consumption (kg/kWh)	5	0.546	0.546	0.548	0.548	0.559
		10	0.361	0.363	0.363	0.363	0.372
		15	0.287	0.288	0.259	0.290	0.295
4	Heat supplied (kW)	5	5.377	5.307	5.233	5.136	4.595
		10	7.069	6.981	6.879	6.741	6.060
		15	8.193	8.085	7.972	7.823	6.986
5	Brake thermal efficiency (%)	5	15.13	15.43	15.67	16.02	17.93
		10	22.90	23.23	23.61	24.16	26.95
		15	28.76	29.21	29.70	30.32	34.00
6	Heat carried out by water from engine cooling jacket (kW)	5	1.828	1.916	1.916	1.916	2.003
		10	2.006	2.090	2.090	2.264	2.351
		15	2.525	2.612	2.612	2.699	2.786
7	Heat carried out by water from calorimeter (kW)	5	0.522	0.609	0.697	0.784	0.871
		10	0.609	0.697	0.784	0.958	1.045
		15	0.784	0.871	0.958	1.132	1.219
8	Heat carried out by exhaust gas (kW)	5	0.685	0.792	0.920	1.040	1.164
		10	0.791	0.908	1.037	1.291	1.437
		15	1.009	1.144	1.299	1.543	1.679
9	Heat lost in radiation and uncounted (kW)	5	2.050	1.780	1.577	1.357	0.604
		10	2.653	2.361	2.128	1.557	0.639
		15	2.303	1.967	1.693	1.209	0.146
10	Volumetric efficiency (%)	5	84.33	83.76	83.76	83.42	83.19
		10	84.69	84.57	84.45	84.22	83.99
		15	85.40	85.28	85.04	84.81	84.69

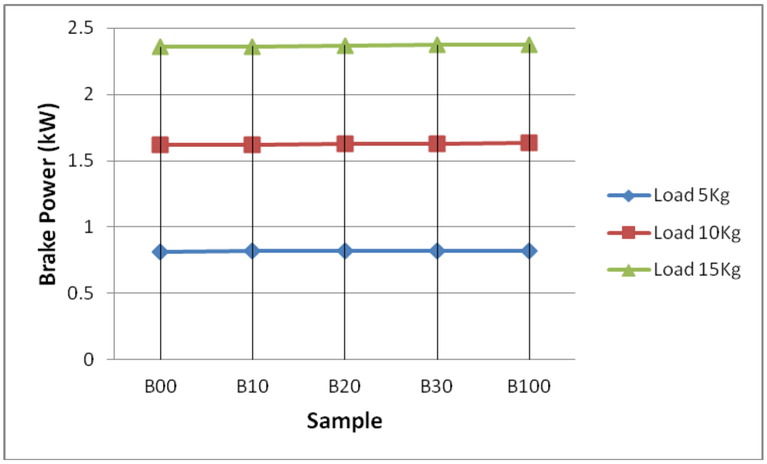

Fig.5.1 : Brake power for different sample at different load

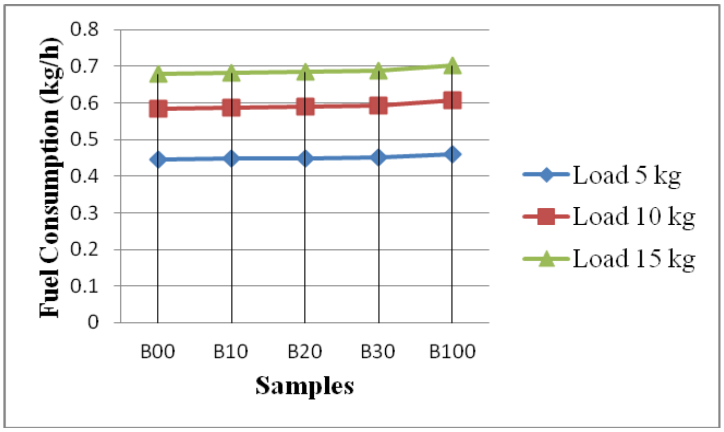

Fig.5.2 : Fuel consumption for different sample at different load

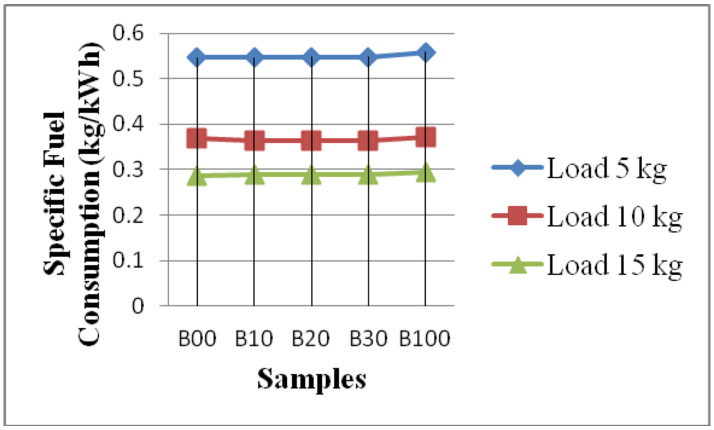

Fig.5.3 : Specific fuel consumption for different sample at different load

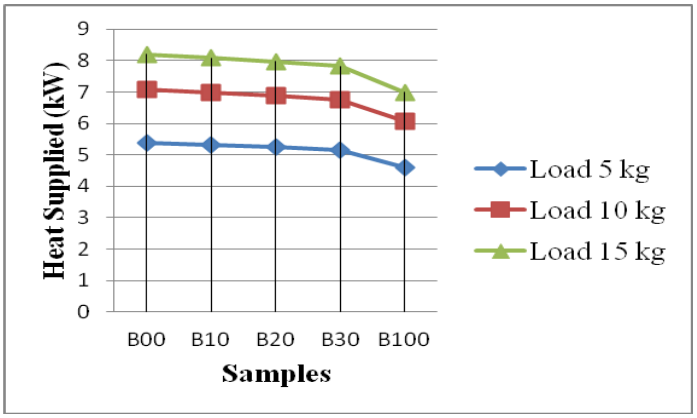

Fig.5.4: Heat supplied for different sample at different load

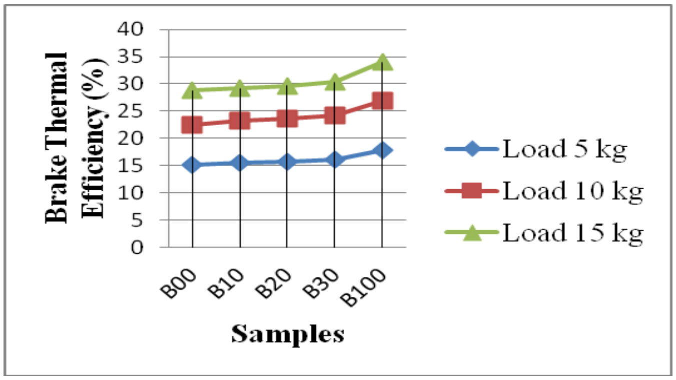

Fig.5.5 Brake thermal efficiency for different sample at different load

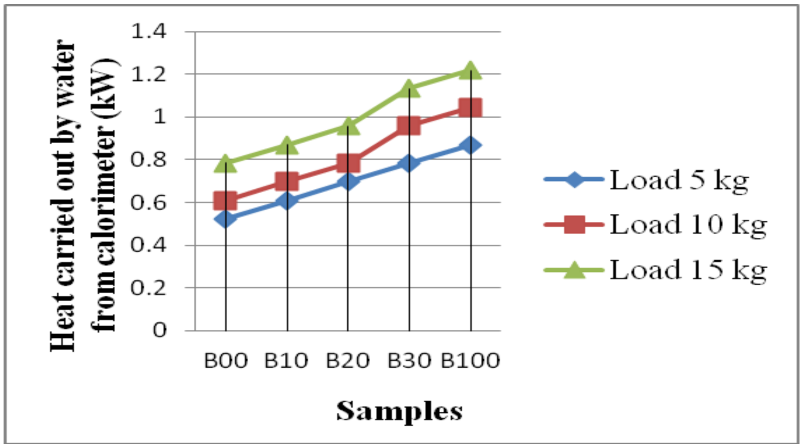

Fig.5.6 Heat carried out by water from calorimeter for different sample at different load

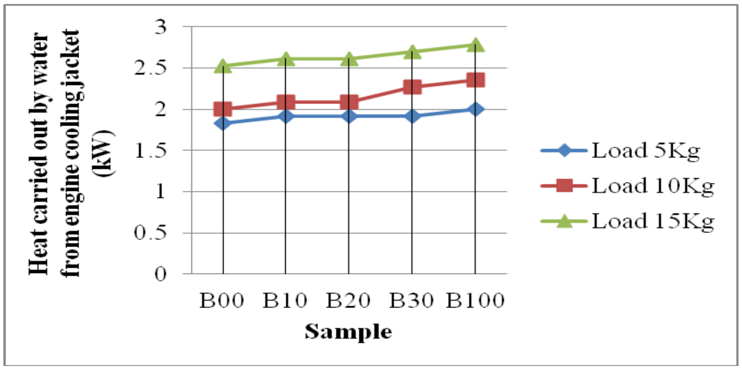

Fig.5.7 Heat carried out by water from engine cooling jacket for different sample at different load

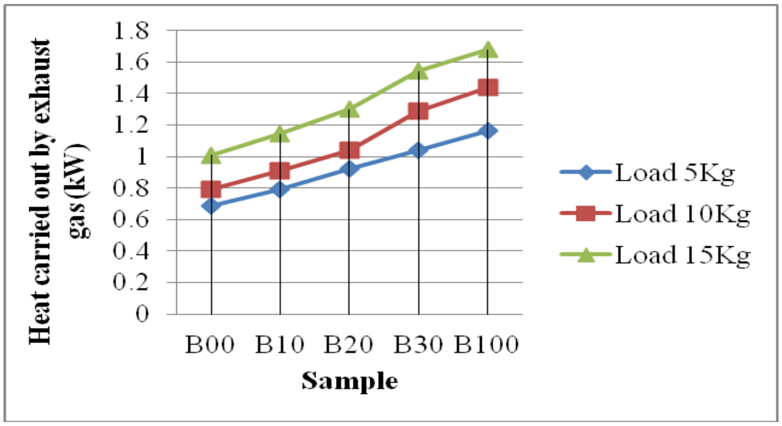

Fig.5.8 Heat carried out by exhaust gas for different sample at different load

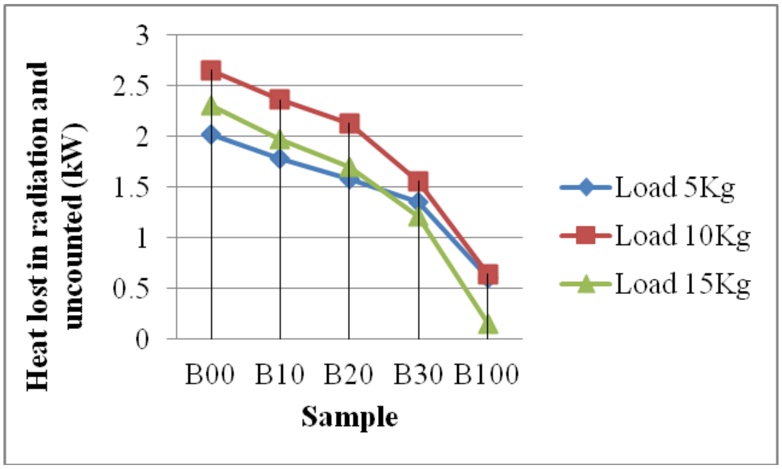

Fig.5.9 Heat lost in radiation and uncounted for different sample at different load.

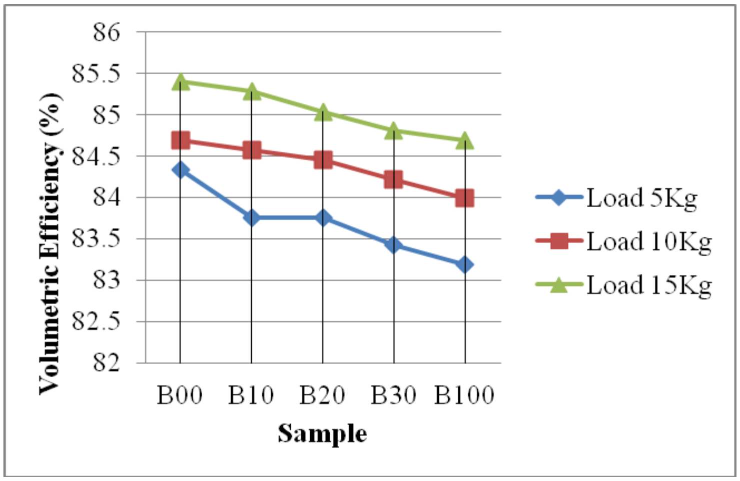

Fig.5.10: Volumetric efficiency for different sample at different load.

5.3 Result and Discussion

A single cylinder four stroke diesel engine made of Kirloskar AK65 was run using different types of samples that is petroleum diesel, blends of diesel and biodiesel, pure biodiesel made from the seed of pongamia pinnata at different loads to analyse the performance of the engine. To determine the performance of the engine, the values of the brake power, specific fuel consumption, heat supplied, brake thermal efficiency, heat lost in radiation and uncounted, volumetric efficiency were calculated (table 5.12).

Brake power (kW), as shown in the fig.5.1, increases as load of the compression ignition engine increase. The values of brake power are small at the low load and at high load the brake power is higher. The brake power remains almost same for all the sample and from the fig. 5.1 it can be concluded that we may use the B10 blend of diesel and biodiesel which has the almost same value for all the samples.

Specific fuel consumption (fig. 5.3) is almost same for all samples to the respective load. It is the lowest for maximum load that at 15kg and highest at lowest load (5kg). The specific fuel consumption is better for the all samples; therefore, B10 will be the considered for the purpose of the practical application.

Heat release pattern of the fuel of different sample from the fig. 5.4 shows that the sample B00 fuel is better than the sample B100 fuel, where as in between these two the sample B10 provides more efficient heat release by the fuel. With increase in load it is seen that B10 and B20 will remain same fuel heat supply. Therefore, the sample B10 fuel is more efficient fuel for the compression ignition engine or any other engine run by the diesel fuel.

Brake thermal efficiency increases with respect to load increased as shown in the fig. 5.5. The B100 or pure biodiesel gives better brake thermal efficiency with comparison to other sample. In between the sample B00 and B100, it may consider any sample of the blending.

In reference to the fig. 5.9, it is seen that the heat lost in radiation and unaccounted ht loss decreases as load and blending increases. With this scene it may conclude that the blends from B10 to B100, all are applicable.

The volumetric efficiency of the single cylinder four stroke compression ignition engine using the fuel of petroleum diesel, blends of diesel and biodiesel, pure biodiesel is shown in fig. 5.10. The volumetric efficiency decreases with respect to load, at low load the B10 shows the slidely down efficiency and with increase in load it becomes gradually decrease to all samples of the diesel, blends of diesel and biodiesel, biodiesel as shown in fig. 5.10. With respect to the changes of efficiency, the sample B10 gives uniform values and therefore it may be useable for the practical purposes.

CHAPTER –6

6.0 Exergy

6.1 Introduction

An exergy-based performance analysis is the performance analysis of a system based on the second law of thermodynamics that overcomes the limit of an energy-based analysis. Exergy is defined as the maximum theoretical useful work obtained as a system interacts with an equilibrium state. Exergy is generally not conserved as energy but destroyed in the system. Exergy destruction is a measure of irreversibility that is the source of performance loss. Therefore, an exergy analysis assessing the magnitude of exergy destruction identifies the location, the magnitude and the source of thermodynamic inefficiencies in a thermal system. This provides useful information to improve the overall efficiency and cost effectiveness of a system and/or comparing the performance of the two systems.

Internal combustion engine simulation modeling has long been established as an effective tool for studying engine performance and contributing to evaluation and new developments. Thermodynamic models of the real engine cycle have served as effective tools for complete analysis of engine performance and sensitivity to various operating parameters. On the other hand, it has long been understood that traditional first-law analysis, which is needed for modeling the engine processes, often fails to give the engineer the best insight into the engine’s operation. In order to analyze engine performance—that is, evaluate the inefficiencies associated with the various processes—second-law analysis must be applied. For second-law analysis, the key concept is ‘availability’ (or exergy) .The availability content of a material represents its potential to do useful work. Unlike energy, exergy can be destroyed which is a result of such phenomena as combustion, friction, mixing and throttling. The destruction of availability—often termed irreversibility—is the source for the defective exploitation of fuel into useful mechanical work in a compression or spark ignition engine. The reduction of irreversibilities can lead to better engine performance through a more efficient exploitation of fuel. To reduce the irreversibilities, we need to quantify them. That is we need to evaluate the availability destructions-we need the second-law analysis.

6.2 Objectives

a. To weigh the various processes and devices, calculating the ability of each one of these to produce work.

b. To identify those processes in which destruction or loss of exergy occurs. To quantify the various losses and destructions.

c. To propose methods for exploitation of losses—most notably exhaust gas to ambient and heat transfer to cylinder walls—now lost or ignored.

d. To define efficiencies so that different applications can be studied and compared, and possible improvements measured.

6.3 Exergy of a system

The exergy or availability of a system in a given state can be defined as the maximum useful work that can be produced through interaction of the system with its surroundings, as it reaches thermal, mechanical and chemical equilibrium. Usually, the terms with thermo mechanical and chemical equilibration are differentiated and calculated separately.

For a closed system experiencing heat and work interactions with the environment, the following equation holds, for the thermo mechanical exergy.

$$\chi^{tm} = (E-U_o) + p_o(V-V_o) - T_o(S-S_o) \qquad (1)$$

where $E = E_{kin} + E_{pot} + U$ with E_{kin} the kinetic energy and E_{pot} the potential energy, p_o and T_o are the fixed pressure and temperature of the environment; and U_o , V_o and S_o are the internal energy, volume and entropy of the contents were they brought to p_o and T_o.

Exergy is an extensive property with a value greater than or equal to zero. It is obvious that exergy is a property, the value of which depends not only on the state of the system, but also on the ambient properties. As stated above, there is no exergy in a system when thermal, mechanical and chemical equilibrium exists with the environment. Thermal equilibrium is achieved when the temperature of the system is equal to the temperature of the surrounding environment. In the same way, mechanical equilibrium is achieved when there is no pressure difference between the working medium and the environment.

6.3.1 Chemical equilibrium

Chemical equilibrium is achieved only when there are no components of the working medium, which could interact with those of the environment to produce work. In the case of engines, all the components of the working medium must be either oxidized (e.g. fuel, CO, H), or reduced (e.g. NO, OH), in a reversible way as the system reaches the dead state (see following section for dead state definition). The only components of the system, which cannot react chemically with the atmosphere and therefore, constitute the components of the mixture at the dead state are O_2, N_2, CO_2 and H_2O. Chemical exergy take into account the capacity to produce work because of the difference between the partial pressures of the components (when in thermal and mechanical equilibrium with the environment) and the partial pressures of the same components in the atmosphere.

6.3.2 Dead state

The choice of a reference dead state is of paramount importance when dealing with exergy calculations since this will determine what kind of equilibrium will be established with the environment and consequently, the calculated values of exergy. In general, a system is considered to be at the so called ‘restricted’ dead state when no work potential exists between the system and the environment due to temperature or pressure differences. This is the dead state reached when calculating the thermo mechanical exergy. On the other hand, if chemical equilibrium with the environment is of concern, then we refer to the ‘true’ or ‘unrestricted’ dead state, where the chemical potentials of the system also equal those of the environment. For engine applications the (environmental) pressure and temperature conditions of the dead state are usually taken to be p_o = 1.01325 bar and T_o = 298.15 K and if chemical availability is also taken into account, then the molar composition of the environment is: 20.35% O_2, 75.67% N_2, 0.03% CO_2, 3.03% H_2O and 0.92% various other substances. Changes in the dead state conditions are reflected by changes in the value of the system availability.

6.4 General energy balance equation

For an open system experiencing mass exchange with the surrounding environment, the following equation holds for the total energy on a time basis:

$$\frac{dE_{CV}}{dt} = \sum_j \dot{Q}_j - \dot{W}_{CV} + \dot{m}_i . e_i - \dot{m}_e . e_e \qquad (2)$$

Where

a) Q_j represents the time rate of heat transfer at the boundary of the control volume.

b) $\dot{W}_{CV}$ mechanical work transfer from control volume.

c) $\dot{m}_i . e_i$ $\dot{m}_e . e_e$ are the energy terms associated with inflow and outflow of masses, respectively. In particular, the terms and refer to the flow or energy of the incoming and the outgoing cylinder mass flow rates, respectively, given by e = c_p.T (neglecting kinetic and potential energy contribution).

6.5 General exergy balance equation

For an open system experiencing mass exchange with the surrounding environment, the following equation holds for the total exergy on a time basis:

$$\frac{dX_{cv}}{dt} = \int_j \left(1 - \frac{T_0}{T_j}\right) . \dot{Q}_j - \left(\dot{W}_{CV} - p_o . \frac{dV_{CV}}{dt}\right) + \sum_i \dot{m}_i b_i - \sum_e \dot{m}_e b_e - \dot{x}_d \qquad (3)$$

Where

(a) $\frac{dX_{cv}}{dt}$ is the time rate of change in the exergy of the control volume content (i.e. engine cylinder, or exhaust manifold, etc.).

(b) $\int_j \left(1 - \frac{T_0}{T_j}\right) . \dot{Q}_j$ is the exergy term for heat transfer, with the temperature at the boundary of the system, which in general, is different from the temperature level of a process (although these two temperatures are the same when applying the most usual simulation approach of internal combustion engines operation, i.e. single-zone oronate).

(c) $\left(\dot{W}_{CV} - p_o.\frac{dV_{CV}}{dt}\right)$ is the exergy term associated with (mechanical or electrical) work transfer $p_o.\frac{dV_{CV}}{dt}$ denotes the dead state work.

(d) $\sum_i \dot{m}_i b_i - \sum_e \dot{m}_e b_e$ are the exergy terms associated with inflow and outflow of masses, respectively. In particular, the terms b_i and b_e in refer to the flow or stream exergy (or exergy) of the incoming and the outgoing cylinder mass flow rates, respectively, given by (neglecting kinetic and potential energy contribution):

$$b = h - h_o - T_o(s - s_o) \qquad (4)$$

with s_o the entropy of (cylinder) flow rate were it brought to p_o and T_o. Flow exergy is defined as the maximum work output that can be obtained as the fluid passes reversibly from the given state to a dead state, while exchanging heat solely with the environment.

(e) $\dot{x}_d$ is the rate of exergy destroyed due to irreversibility production inside the control volume due to combustion, throttling, mixing, heat transfer under finite temperature difference to cooler medium, etc. $\dot{x}_{gen} = T.\dot{S}_{gen}$ based on an entropy balance, with $\dot{S}_{gen}$ denoting the rate of entropy creation due to irreversibilities.

6.6 Engine Modelling of Compression Ignition engines

In a single-zone model the working fluid in the engine is assumed to be a thermodynamic system that undergoes energy and mass exchange with the surroundings, where the energy released during the combustion process is obtained by applying the first law of thermodynamics to the system. The heat release rate as a function of crank angle was deduced from experimentally obtained in-cylinder pressure data, which was then used as an input to the in-cycle calculations.

6.7 Assumptions included while doing calculations

a. Spatial homogeneity of pressure ,

b. Spatial homogeneity of temperature (for the whole cylinder or for each zone considered),

c. Working fluid is considered an ideal gas,

d. Gas properties (enthalpy, internal energy, etc.) are modelled using polynomial relations with temperature (and pressure),

e. Heat released from combustion is distributed evenly throughout the cylinder,

f. Blow-by losses are not taken into account,

g. Enthalpy associated with pressure of injected fuel is usually not significant and hence ignored,

h. No heat transfer occurs between burned and unburned zones,

i. Work required to transfer fluid from the unburned zone to the burned zone is negligible.

6.8 Engine analysis

In the following subsections, the equations will be given that deal with the exergy balance applied to the engine cylinder in order to evaluate the various processes irreversibilities.

6.8.1 Fuel exergy

The chemical exergy of fuel of type C_zH_y is approximated by:

$$\psi_{fch} = LCV\left(1.04224 + 0.011925\frac{y}{z} - \frac{0.042}{z}\right) \quad (5)$$

where LCV is the fuel lower calorific value.

6.8.2 Engine cylinder exergy balance

For the engine cylinder on crank angle basis, we have:

$$\frac{d\chi_{cyl}}{d\varphi} = \frac{\dot{m}_i b_i - \dot{m}_g b_g}{6N} - \frac{d\chi_W}{d\varphi} - \frac{d\chi_L}{d\varphi} + \frac{d\chi_f}{d\varphi} - \frac{d\chi_d}{d\varphi}$$

where the terms on the right hand side are:

a) $\dot{m}_i$ is the incoming flow rate form the inlet manifold and $\dot{m}_g$ outgoing flow rate to the exhaust manifold.

b) $\frac{d\chi_W}{d_\varphi}$ is the exergy rate of work transfer, given by

$\frac{dX_w}{d\varphi} = (p_{cyl} - p_o)\frac{dV}{d\varphi}$ where p_{cyl} is the instantaneous cylinder pressure.

c) $\frac{dX_L}{d\varphi}$ is the exergy rate of the heat transfer to the cylinder walls, given by

$\frac{dX_L}{d\varphi} = \frac{dE_L}{d\varphi}(1 - \frac{T_o}{T_{cyl}})$ where T_{cyl} is the in cylinder temperature.

d) $\frac{dX_f}{d\varphi}$ is the fuel exergy rate, given by $\frac{dX_f}{d\varphi} = \psi_{fch} . \frac{dm_f}{d\varphi}$

where $\psi_{fch} = 1.0599LHV$ for diesel fuel.

e) $\frac{dX_d}{d\varphi}$ is the rate exergy generation due to irreversibility production within the cylinder, which consists of combustion (dominant contribution), viscous dissipation, turbulence, inlet valve throttling and mixing of the incoming air or air– fuel mixture with the cylinder residuals.

And the term on the left hand side is expressed explicitly as,

$$\frac{dX_{cyl}}{d\varphi} = \frac{dU}{d\varphi} + p_o\frac{dV}{d\varphi} - T_o . \frac{dS}{d\varphi}$$

representing the rate of change in the total exergy of the cylinder contents.

As regards cumulative terms, these are defined after integration of the respective rate terms over an engine cycle. Especially, for steady-state operation, the cumulative value for the cylinder exergy is

$$\int_0^{720} \frac{dX_{cyl}}{d\varphi} . d\varphi = 0$$

6.8.3 Second-law or exergy or exergetic efficiencies

For the cylinder alone, the following second-law efficiency is used:

$$\varepsilon = \frac{W_{br}}{m_f(1.06LHV)}$$

with W_{br} the brake work production and M_f the total mass of fuel entering the cylinder per cycle.

Efficiency can be then compared to a first-law one, such as:

$$\eta = \frac{W_{br}}{m_f . LCV}$$

6.8.4 Energy Analysis of the engine at different loads

Energy content of fuel:

$$\dot{E}_f = LCV.\dot{m}_f$$

CV = calorific value of fuel

Effective power of engine:

$$\dot{E}_w = \frac{\pi.N.\tau}{30}$$

N = rpm of engine ; τ = Torque applied by dynamometer

Energy loss in exhaust gases:

$$\dot{E}_e = m_{eg}.c_{pg}(T_3 - T_4) = m_{ccw}.c_{pw}.(T_6 - T_5)$$

Energy loss to cooling water:

$$\dot{E}_L = m_{ecw}.c_{pw}.(T_2 - T_1)$$

Energy Balance

$$\dot{E}_f = \dot{E}_w + \dot{E}_e + \dot{E}_L + \dot{E}_r$$

Energy Efficiency:

$$\eta_{energy} = \frac{E_W}{E_f}$$

6.8.5 Exergy Analysis of the system

Exergy of fuel:

$$X_f = 1.06 \times LCV \times m_f$$

Work exergy:

$$X_w = \dot{E}_w$$

Exergy of heat lost to exhaust gases:

$$X_e = \dot{E}_e \left(1 - \frac{T_u}{T_3}\right)$$

Exergy of heat lost to cooling water:

$$X_L = \dot{E}_L \left(1 - \frac{T_o}{T_2}\right)$$

Exergy of heat lost to radiation:

$$X_r = \dot{E}_r \left(1 - \frac{T_o}{T_w}\right)$$

Exergy Balance:

$$X_f = X_w + X_e + X_L + X_r + X_{des}$$

Exergy Efficiency:

$$\eta_{exergy} = \frac{x_w}{x_f}$$

6.9 Engine Setup

Experiments were conducted on an existing test unit. The test unit was a Single Cylinder, Naturally Aspirated, Direct Injection, Compression Engine using standard diesel fuel

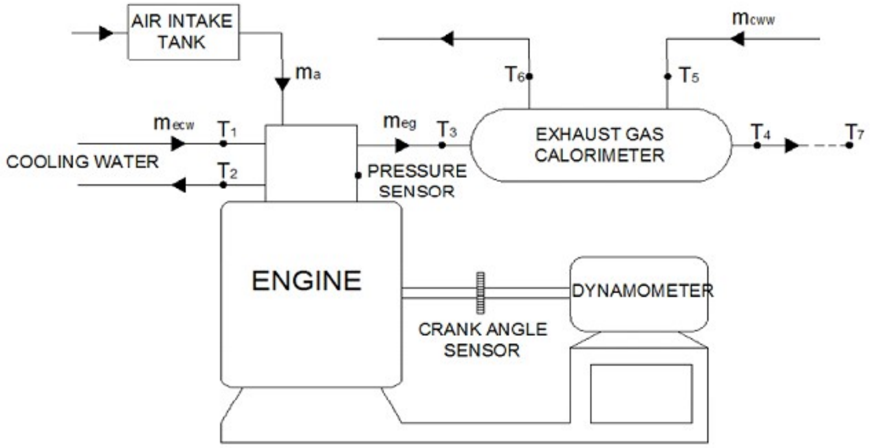

Fig.6.1 Schematic diagram of engine test unit. (Source: www.elsevier.com/locate/pecs)

6.10 Procedure

The set up enabled measurement of in-cylinder pressure and volume as a function of crank angle; fuel rate, air flow rate, cooling water flow rates to engine and gas calorimeter, engine load; and inlet and outlet temperatures for each stream.

m_{ecw} = engine cooling water flow rate (kg/s)
m_{ccw} = calorimeter water flow rate (kg/s)
m_a = air flow rate (kg/s)
m_{eg} = exhaust gas flow rate (kg/s)

m_f = fuel flow rate (kg/s)

T_1 = Inlet engine cooling water temperature (°C)

T_2 = Outlet engine cooling water temperature (°C)

T_3 = Exhaust gas temperature at inlet of calorimeter (°C)

T_4 = Exhaust gas temperature at outlet of calorimeter (°C)

T_5 = Inlet calorimeter cooling water temperature (°C)

T_6 = Outlet calorimeter cooling water temperature (°C)

T_7 = Ambient temperature (°C)

Results Energy and Exergy balances at different loads:

The data for different samples from the biodiesel and its blends are applied to the mentioned relations for different loads and the results of the energy and the exergy are tabulated in the tables 6.1 to 6.20 and the exergy terms depicted in figs. 6.2 to 6.20.

Table 6.1 Energy balance at different loads for B00

Load (kg)	$\dot{E}_f$(kW)	$\dot{E}_w$(kW)	$\dot{E}_g$(kW)	$\dot{E}_L$(kW)
5	5.377	0.814	0.685	3.878
10	7.069	1.619	0.791	4.659
15	8.193	2.356	1.009	4.828

$\dot{E}_L$= Total heat loss (cooling water +radiation)

Table 6.2 Energy balance at different loads for B10

Load (kg)	$\dot{E}_f$(kW)	$\dot{E}_w$(kW)	$\dot{E}_g$(kW)	$\dot{E}_L$(kW)
5	5.307	0.819	0.792	3.696
10	6.981	1.621	0.908	4.452
15	8.085	2.362	1.144	4.579

Table 6.3 Energy balance at different loads for B20

Load (kg)	$\dot{E}_f$(kW)	$\dot{E}_w$(kW)	$\dot{E}_g$(kW)	$\dot{E}_L$(kW)
5	5.233	0.820	0.920	3.493
10	6.876	1.624	1.037	4.215
15	7.972	2.368	1.299	4.305

Table 6.4 Energy balance at different loads for B30

Load (kg)	$\dot{E}_f$(kW)	$\dot{E}_w$(kW)	$\dot{E}_e$(kW)	$\dot{E}_L$(kW)
5	5.136	0.823	1.040	3.273
10	6.741	1.629	1.291	3.821
15	7.823	2.372	1.543	3.908

Table 6.5 Energy balance at different loads for B100

Load (kg)	$\dot{E}_f$(kW)	$\dot{E}_w$(kW)	$\dot{E}_e$(kW)	$\dot{E}_L$(kW)
5	4.595	0.824	1.164	2.607
10	6.060	1.633	1.437	3.000
15	6.986	2.375	1.679	2.932

Table 6.6 Energy breakdown at different loads for B00

Load (kg)	Fuel Energy	Energy Efficiency %	Exhaust heat loss %	Heat loss %
5	100.00	15.14	12.74	72.12
10	100.00	22.90	11.19	65.91
15	100.00	28.76	12.32	58.92

Table 6.7 Energy breakdown at different loads for B10

Load (kg)	Fuel Energy	Energy Efficiency %	Exhaust heat loss %	Heat loss %
5	100.00	15.43	14.92	69.65
10	100.00	23.23	13.01	62.62
15	100.00	29.21	14.15	56.64

Table 6.8 Energy breakdown at different loads for B20

Load (kg)	Fuel Energy	Energy Efficiency %	Exhaust heat loss %	Heat loss %
5	100.00	15.67	17.58	66.75

10	100.00	23.61	15.08	61.31
15	100.00	29.70	16.29	54.01

Table 6.9 Energy breakdown at different loads for B30

Load (kg)	Fuel Energy	Energy Efficiency %	Exhaust heat loss %	Heat loss %
5	100.00	16.02	20.25	63.73
10	100.00	24.16	19.15	56.69
15	100.00	30.32	19.72	49.96

Table 6.10 Energy breakdown at different loads for B100

Load (kg)	Fuel Energy	Energy Efficiency %	Exhaust heat loss %	Heat loss %
5	100.00	17.93	25.33	56.74
10	100.00	26.95	23.71	49.34
15	100.00	34.00	24.40	41.60

Table 6.11Exergy balance at different loads for B00

Load (kg)	X_f (kW)	X_w (kW)	X_e (kW)	X_L (kW)	X_{des} (kW)
5	5.700	0.814	0.207	0.157	4.522
10	7.493	1.619	0.261	0.188	5.425
15	8.685	2.356	0.372	0.277	5.680

X_L= Total heat loss (cooling water +radiation)

Table 6.12 Exergy balance at different loads for B10

Load (kg)	X_f (kW)	X_w (kW)	X_e (kW)	X_L (kW)	X_{des} (kW)
5	5.625	0.819	0.245	0.169	4.392
10	7.400	1.621	0.309	0.201	5.269
15	8.570	2.362	0.423	0.294	5.491

Table 6.13 Exergy balance at different loads for B20

Load (kg)	X_f (kW)	X_w (kW)	X_e (kW)	X_L (kW)	X_{des} (kW)
5	5.547	0.820	0.287	0.169	4.271
10	7.291	1.624	0.361	0.201	5.105
15	8.450	2.368	0.485	0.294	5.303

Table 6.14 Exergy balance at different loads for B30

Load (kg)	X_f (kW)	X_w (kW)	X_e (kW)	X_L (kW)	X_{des} (kW)
5	5.444	0.823	0.334	0.169	4.118
10	7.145	1.629	0.454	0.230	4.832
15	8.292	2.372	0.587	0.311	5.022

Table 6.15 Exergy balance at different loads for B100

Load (kg)	X_f (kW)	X_w (kW)	X_e (kW)	X_L (kW)	X_{des} (kW)
5	4.871	0.824	0.376	0.182	3.489
10	6.424	1.633	0.510	0.246	4.035
15	7.405	2.375	0.643	0.328	4.059

Table 6.16 Exergy breakdown at different loads for B00

Load (kg)	Fuel exergy %	Exergy efficiency %	Exhaust exergy %	Heat loss exergy %	Exergy destroyed %
5	100.00	14.28	3.63	2.75	79.34
10	100.00	21.61	3.48	2.51	72.39
15	100.00	27.13	4.28	3.19	65.40

X_L= Total heat loss (cooling water +radiation)

Table 6.17 Exergy breakdown at different loads for B10

Load (kg)	Fuel exergy %	Exergy efficiency %	Exhaust exergy %	Heat loss exergy %	Exergy destroyed %
5	100.00	14.56	4.36	3.00	78.08
10	100.00	21.91	4.16	2.51	71.42
15	100.00	27.56	4.94	3.43	64.07

Table 6.18 Exergy breakdown at different loads for B20

Load (kg)	Fuel exergy %	Exergy efficiency %	Exhaust exergy %	Heat loss exergy %	Exergy destroyed %
5	100.00	14.78	5.17	3.05	77.00
10	100.00	22.27	4.95	2.76	70.02
15	100.00	28.02	5.74	3.48	62.76

Table 6.19 Exergy breakdown at different loads for B30

Load (kg)	Fuel exergy %	Exergy efficiency %	Exhaust exergy %	Heat loss exergy %	Exergy destroyed %
5	100.00	15.12	6.14	3.10	75.64
10	100.00	22.80	6.35	3.22	67.63
15	100.00	28.61	7.08	3.75	60.56

Table 6.20 Exergy breakdown at different loads for B100

Load (kg)	Fuel exergy %	Exergy efficiency %	Exhaust exergy %	Heat loss exergy %	Exergy destroyed %
5	100.00	16.92	7.72	3.74	71.62
10	100.00	25.42	7.94	3.83	62.81
15	100.00	32.07	8.68	4.43	54.82

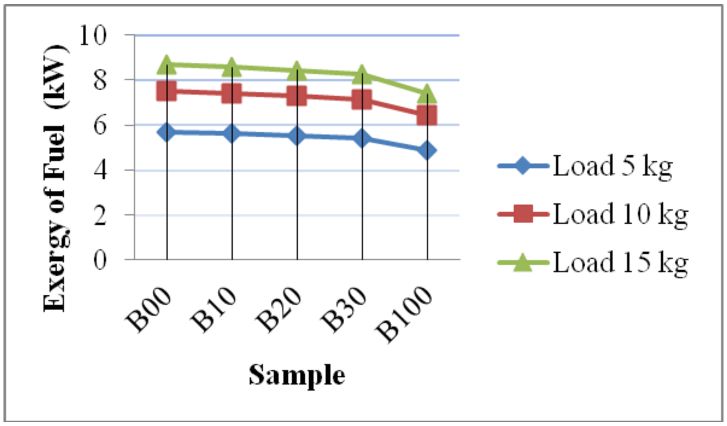

Fig 6.2 Fuel exergy for different samples at different loads.

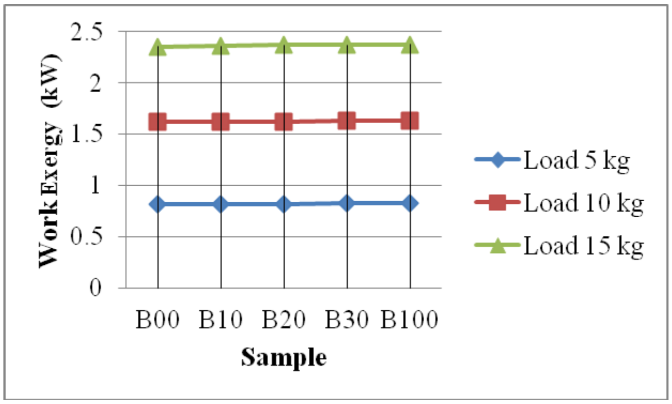

Fig 6.3 Work exergy for different samples at different loads.

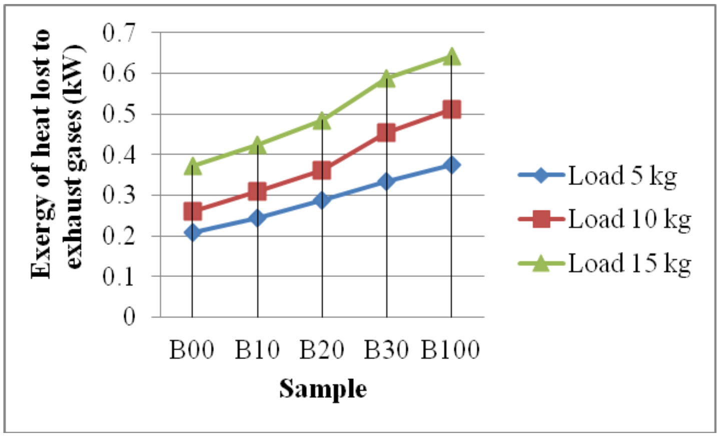

Fig 6.4 Exhaust exergy for different samples at different loads.

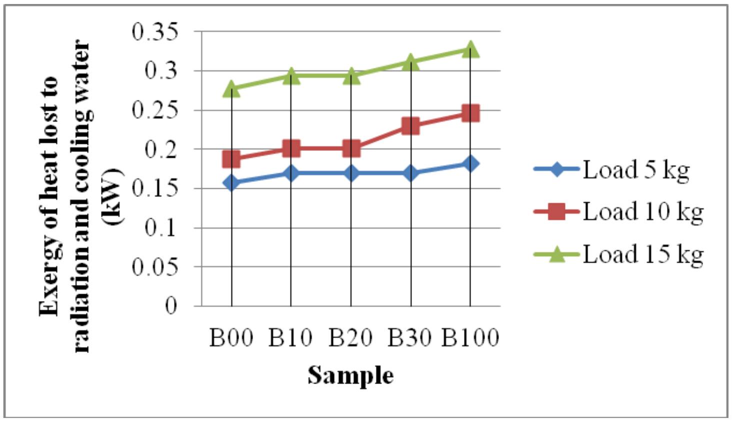

Fig 6.5 Exergy of heat loss to radiation and cooling water for different samples at different loads.

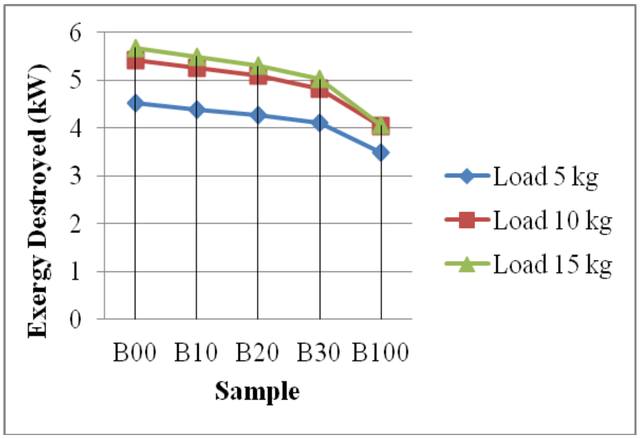

Fig 6.6 Exergy destroyed for different samples at different loads.

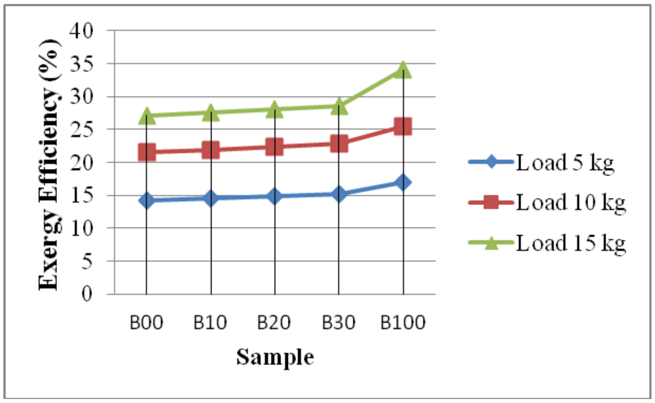

Fig 6.7 Exergy efficiency for different samples at different loads.

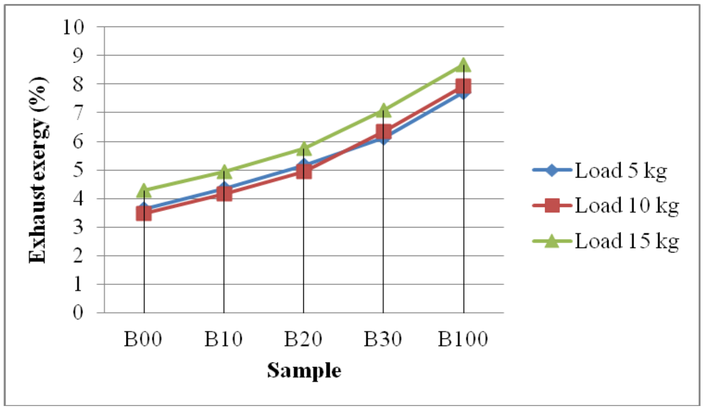

Fig 6.8 Exhaust exergy for different samples at different loads.

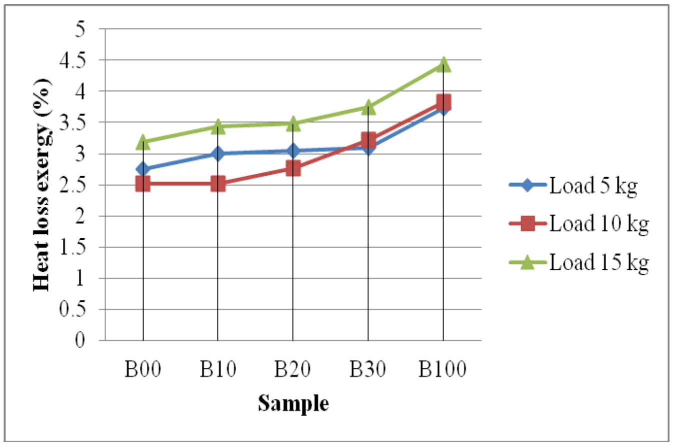

Fig 6.9 Heat loss exergy for different samples at different loads.

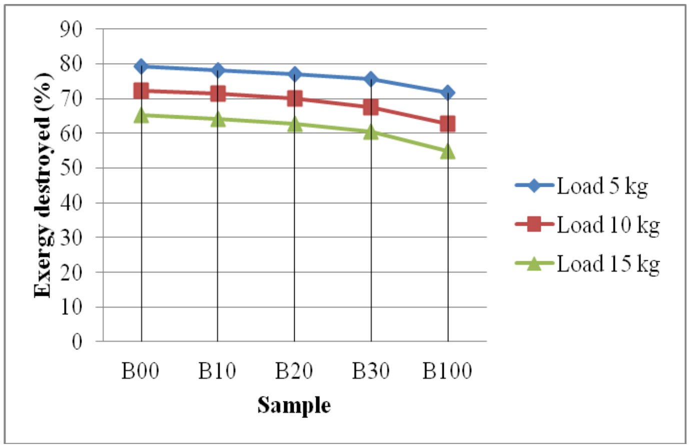

Fig 6.10 Exergy destroyed for different samples at different loads.

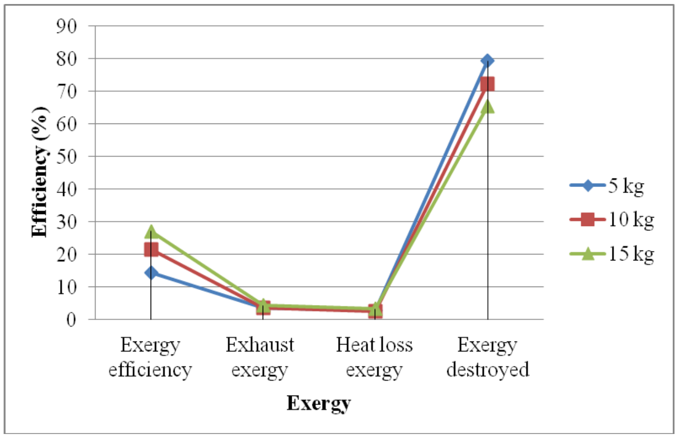

Fig 6.11 Efficiency of different exergy of sample B00 at different loads.

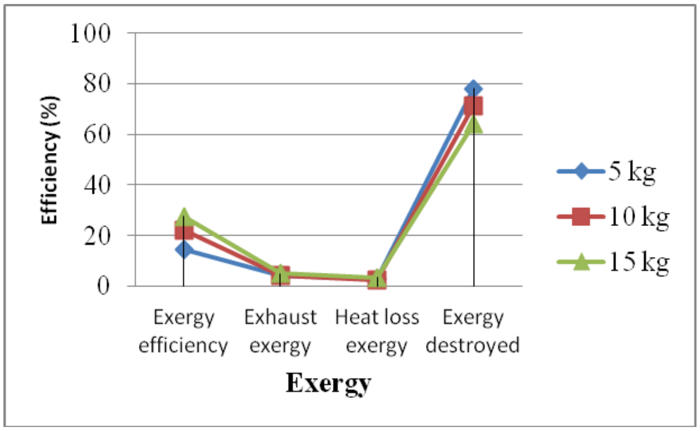

Fig 6.12 Efficiency of different exergy of sample B10 at different loads.

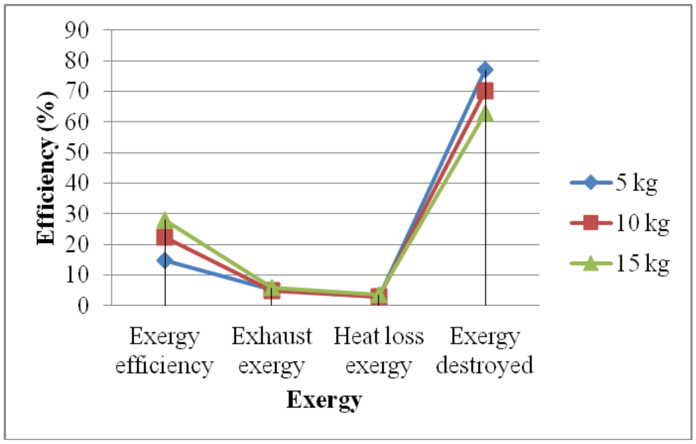

Fig 6.13 Efficiency of different exergy of sample B20 at different loads.

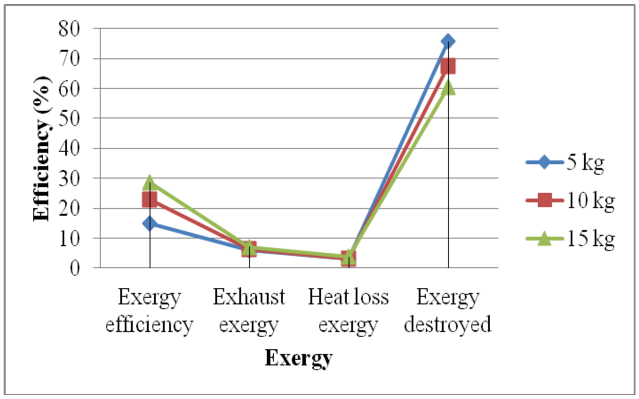

Fig 6.14 Efficiency of different exergy of sample B30 at different loads.

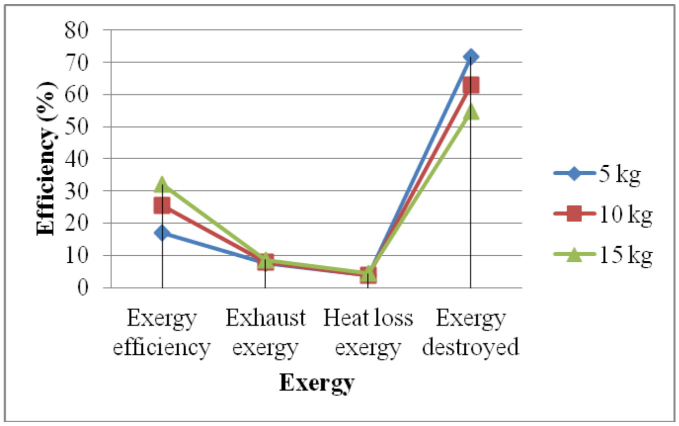

Fig 6.15 Efficiency of different exergy of sample B100 at different loads.

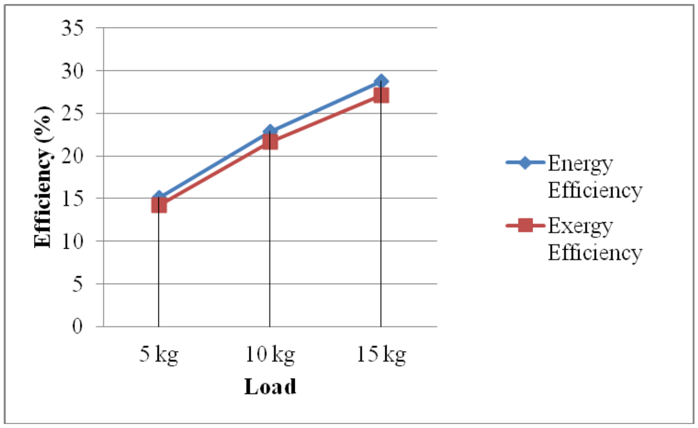

Fig 6.16 Efficiency for B00 at different load.

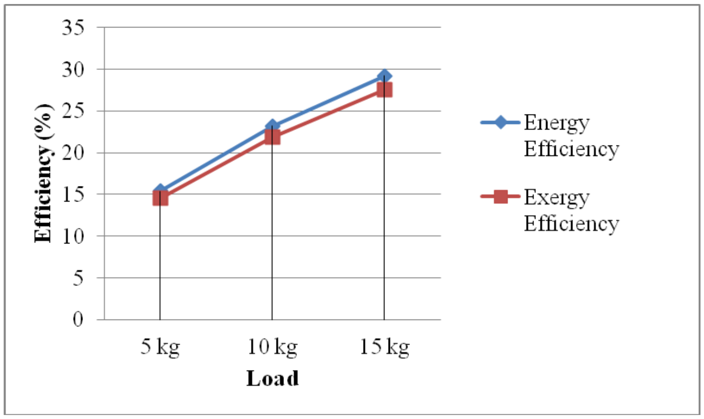

Fig 6.17 Efficiency for B10 at different load.

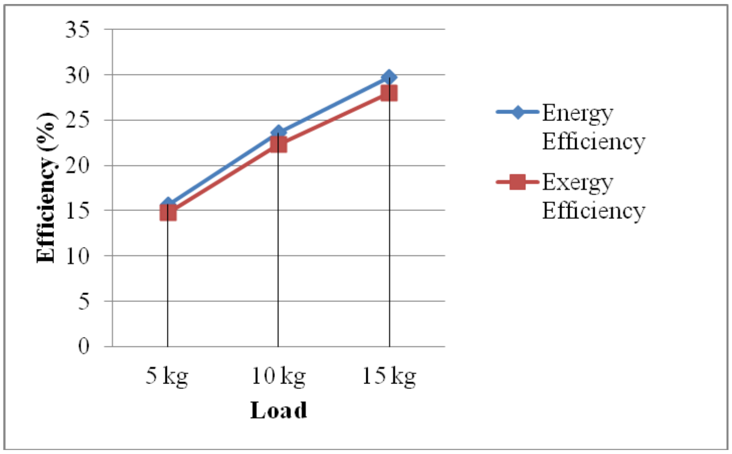

Fig 6.18 Efficiency for B20 at different load.

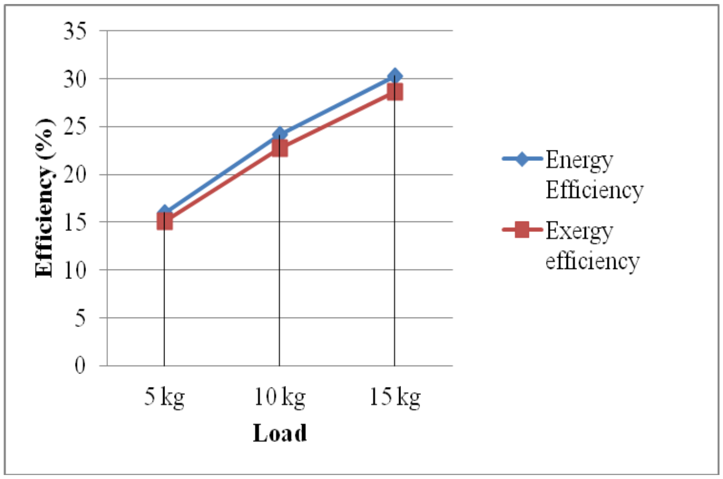

Fig 6.19 Efficiency for B30 at different load.

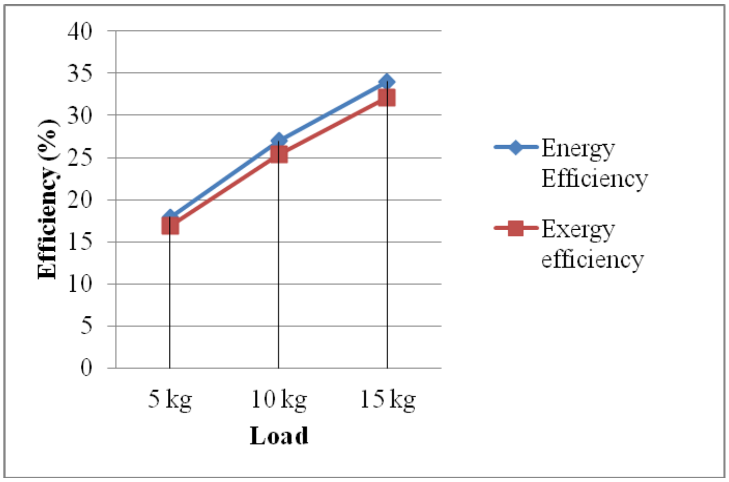

Fig 6.20 Efficiency for B100 at different load.

6.11 Results and Discussion

Figures 6.11, 6.12, 6.13, 6.14, 6.15 show that the efficiency of different exergy of samples at different loads. From these figures it shows that the exergy destruction decreases, because combustion irreversibility decreases with increasing load. Greater load results in less degradation of the fuel chemical exergy when transferred to the exhaust gases and also less mixing of exhaust gases with air.

Figure 6.16, 6.17, 6.18, 6.19, 6.20 shows the efficiency of the samples at different loads. In these figures both energy efficiency and the exergy efficiency increases with increasing load. The exergy efficiency is lower than the energy efficiency for the five samples for the same power output. This is due to the fact that the input fuel exergy of the fuel is slightly higher than its input fuel energy.

CHAPTER – 7

7.0 Exhaust Gas Analysis

7.1 Introduction

Exhaust emissions are produced during combustion and the emissions are harmful. In addition to these harmful emissions, both carbon dioxide (CO_2) and oxygen (O_2) readings can provide additional information on what's going on inside the combustion chamber.

Carbon dioxide (CO_2) is a desirable by-product that is produced when the carbon from the fuel is fully oxidized during the combustion process. As a general rule, the higher the carbon dioxide reading, the more efficient the engine is operating. Therefore air/fuel imbalances, misfires or mechanical problems will causes CO_2 to decrease. It is noted that "ideal" combustion produces large amount of CO_2 and H_2O (water vapour)

Oxygen (O_2) readings provide a good indication of a lean running engine, since O_2 increase with leaner air/fuel mixtures. Lean air/fuel mixtures and misfires typically cause high O_2 output from the engine.

There are a few other exhaust emission components which impact driveability and/or emissions diagnosis, that are not measured by shop analysers. They are (a) water vapour (H_2O), (b) sulphur dioxide (SO_2), (c) hydrogen (H) and (d) particulate carbon soot (C).

Sulphur dioxide (SO_2) is sometimes created during the combustion process from the small amount of sulphur present in the gasoline. During certain conditions the catalyst oxidizes sulphur dioxide to make SO_3, which then reacts with water to make H_2SO_4 or sulphuric acid. Finally, when sulphur and hydrogen react, it forms hydrogen sulphide gas. This process creates the rotten egg odour we sometimes smell when following vehicles in the highway. Particulate carbon soot is the visible black smoke we see from the tailpipe of a vehicle that's running very rich.

The quantity of NO_x varies from a few hundred to well over 1000 ppm in diesel exhaust. Oxides of nitrogen which also occur only in the engine exhaust are combination of nitric oxide (NO) and nitrogen dioxide (NO_2). Nitrogen and oxygen reacts at relatively high temperatures. Therefore high temperature and availability of oxygen are the two main reasons for the formation of $NO_{x.}$ When the proper amount of the oxygen is available the higher the peak combustion temperature the more is the NO formed. The NO_x is formed in the atmosphere as NO oxidizes. The combination of HC and NO_x in the presence of sunlight and certain atmospheric condition produce photochemical smog. The conditions that cause highest local peak temperature and have sufficient oxygen give highest NO_x concentration in diesel exhaust.

A pre-combustion chamber engine produces less NO_x than a direct injection engine due to lower peak temperature. The effect of fuel-air ratio is same that on a gasoline engine. At high fuel-air ratio the additional fuel tends to cool the charge, so the localized peak temperatures are lowered resulting in drop in

NO_x concentration. The NO_x production is also significantly affected by injection system and time. Also, variations in fuel characteristics such as cetane number, viscosity, modulus of elasticity and rate of burning, etc., all contribute to differences in NO_x levels obtained from different levels.

7.2 Analysing Exhaust Emission Readings

Hydrocarbons are measured by an exhaust analyser in parts per million (ppm). It is known that HC is unburned fuel that remains as a result of a misfire. When combustion does not take place or when only part of the air/fuel charge burns, hydrocarbon levels goes up.

Carbon monoxide (CO) is measured by an exhaust analyzer in percent (%) or parts per hundred. CO is a by-product of combustion; therefore, if combustion does not take place, carbon monoxide will not be created. Based on this premise, when a misfire occurs, the carbon monoxide that would have normally been produced during the production process is not produce. Generally speaking, on fuel injected vehicles, high CO means too much fuel is being delivered to the engine for the amount of air entering the intake manifold.

Nitrogen oxide measured by an exhaust analyser in parts per million (ppm). Nitrogen oxides are a by-product of combustion. NO_x is formed in large quantities when combustion temperatures exceed about 1370^{o}C (2500^{o}F). Anything which causes combustion temperatures to rise will also cause NO_x emissions to rise. Misfire can also cause NO_x to rise because of the increase in oxygen that it causes in the catalytic converter feed gas.

Carbon Dioxide measured by an exhaust analyser in percent (%) or parts per hundred. Carbon dioxide is a by-product of efficient and complete combustion. Near perfect combustion will result in carbon dioxide levels which approach the theoretical maximum of 15.5%. Carbon dioxide levels are affected by air/fuel ratio, spark timing and any other factors which affect the combustion efficiency.

Oxygen is measured by an exhaust analyzer in percent (%) or parts per hundred. The amount of oxygen produced by an engine is affected by how close the air/fuel ratio is to stoichiometry. As the mixture goes lean of stoichiometry, oxygen increases. As mixture goes rich of stoichiometry, oxygen falls to zero.

Because oxygen is used up in the combustion process, concentrations at the tailpipe will be very low. If misfire occurs, however, oxygen will increase dramatically as it passes unused through the combustion chamber.

7.3 General Rules of Emission Analysis

If CO goes up, O_2 goes down and conversely if O_2 goes up, CO goes down. It is noted that CO readings are indicator of a rich running engine and O_2 readings are an indicator of a lean running engine.

If HC increases as a result of a lean misfire, O_2 will also increases.

CO_2 will decrease in any of the above cases because of an air/fuel imbalance or misfire.

An increase in CO does not necessarily mean there will be an increase in HC. Additional HC will only be created at the point where rich misfire begins (3% to 4% CO).

High HC, low CO and high O_2 at same time indicates a misfire due to lean or EGR diluted mixture.

High HC, high CO and high O_2 at same time indicate a misfire due to excessively rich mixture.

High HC, Normal to marginally low CO, High O_2, indicates a misfire due to mechanical engine problem or ignition misfire.

Normal to marginally high HC, Normal to marginally low CO and high O_2 indicates a misfire due to false air or marginally lean mixture.

Ambient values of the exhaust parameters are given below:

$CO = 6\ mg/m^3$
$CO_2 = 0\%$
$HC = 0\ ppm$
$NO = 1\ mg/m^3$
$NO_2 = 0\ mg/m^3$
$NO_x = 1\ mg/m^3$
$SO_x = 0\ mg/m^3$

Ambient temperature = 24 ^oC

The different values of the exhaust gas elements are shown in the following tables and the respective figures are shown as belows:

Table 7.1 Exhaust gas parameters for the sample B00

Sl. No.	Load Parameters	5kg	10kg	15kg
1	CO (mg/m^3)	81	80	79
2	CO_2 (%)	1.2	1.3	1.5
3	HC (ppm)	25	25	25
4	NO (mg/m^3)	59	88	133
5	NO_2 (mg/m^3)	43	45	55
6	NO_x (mg/m^3)	106	133	188
7	SO_x (mg/m^3)	3	3	3

Table7.2 Exhaust gas parameters for the sample B10

Sl. No.	Load Parameters	5kg	10kg	15kg
1	CO (mg/m^3)	76	76	75
2	CO_2 (%)	1.1	1.3	1.5
3	HC (ppm)	25	25	25
4	NO (mg/m^3)	64	87	168
5	NO_2 (mg/m^3)	45	49	51
6	NO_x (mg/m^3)	109	136	219
7	SO_x (mg/m^3)	-	-	-

Table 7.3 Exhaust gas parameters for the sample B20

Sl. No.	Load Parameters	5kg	10kg	15kg
1	CO (mg/m^3)	61	61	63
2	CO_2 (%)	1.1	1.3	1.5
3	HC (ppm)	27	26	26
4	NO (mg/m^3)	60	101	139
5	NO_2 (mg/m^3)	47	57	58
6	NO_x (mg/m^3)	112	142	219
7	SO_x (mg/m^3)	-	-	-

Table 7.4 Exhaust gas parameters for the sample B30

Sl. No.	Load Parameters	5kg	10kg	15kg
1	CO (mg/m^3)	36	36	38
2	CO_2 (%)	1.1	1.3	1.5
3	HC (ppm)	28	27	26
4	NO (mg/m^3)	60	101	140
5	NO_2 (mg/m^3)	49	57	58
6	NO_x (mg/m^3)	115	152	271
7	SO_x (mg/m^3)	-	-	-

Table 7.5 Exhaust gas parameters for the sample B100

Sl. No.	Load Parameters	5kg	10kg	15kg
1	CO (mg/m^3)	34	34	33
2	CO_2 (%)	1.2	1.3	1.4
3	HC (ppm)	28	27	27

4	NO (mg/m^3)	60	101	145
5	NO$_2$ (mg/m^3)	49	59	60
6	NO$_x$ (mg/m^3)	121	163	288
7	SO$_x$ (mg/m^3)	-	-	-

Table 7.6 Particulars of exhaust gas for the samples at different loads.

Sl. No.	*Particulars*	*Load (kg)*	*Samples*				
			B00	*B10*	*B20*	*B30*	*B100*
1	CO (mg/m^3)	5	81	76	61	36	34
		10	80	76	61	36	34
		15	79	75	63	38	33
2	CO$_2$ (%)	5	1.2	1.1	1.1	1.2	1.2
		10	1.3	1.3	1.3	1.3	1.3
		15	1.5	1.5	1.5	1.5	1.4
3	HC (ppm)	5	25	25	27	28	28
		10	25	25	26	27	27
		15	25	25	26	26	27
4	NO (mg/m^3)	5	59	60	60	60	60
		10	88	97	101	101	101
		15	133	136	139	140	143
5	NO$_2$ (mg/m^3)	5	43	45	47	49	49
		10	45	49	57	57	59
		15	55	56	58	58	60
6	NO$_x$ (mg/m^3)	5	106	109	112	115	121
		10	133	135	142	152	163
		15	188	219	249	271	288
7	SO$_x$ (mg/m^3)	5	3	-	-	-	-
		10	3	-	-	-	-
		15	3	-	-	-	-

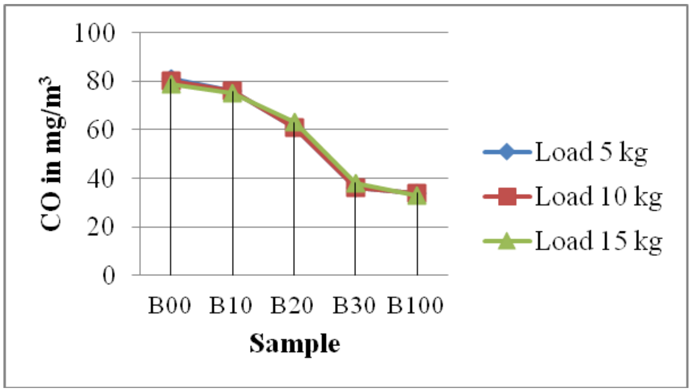

Figure 7.1 Change of CO with respect to load for different samples

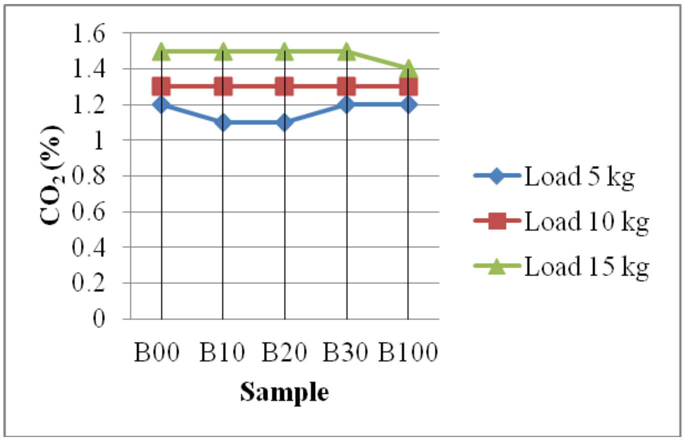

Figure 7.2 Change of CO_2 with respect to load for different samples

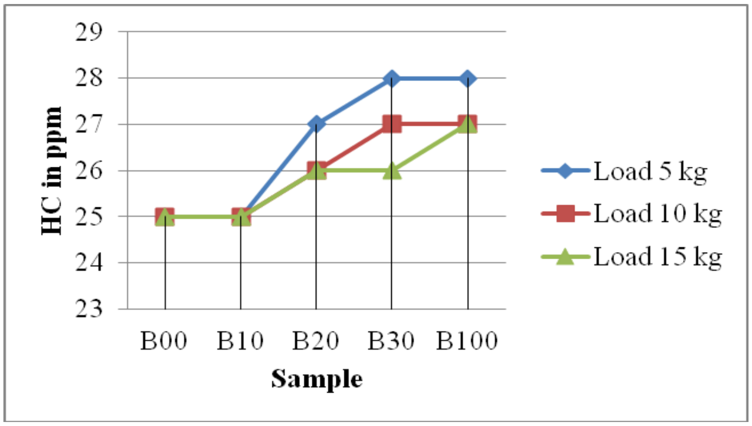

Figure 7.3 Change of HC with respect to load for different samples

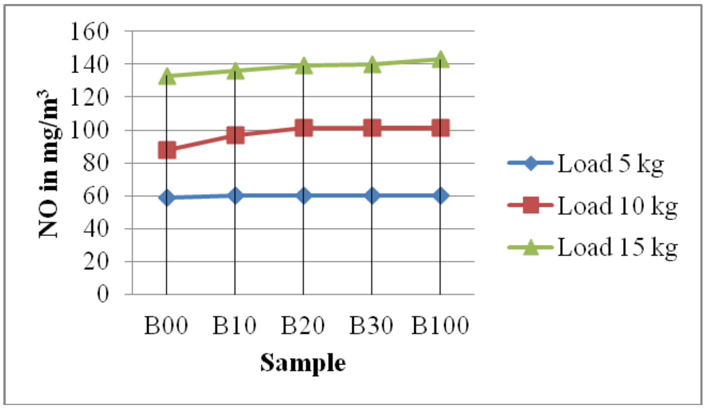

Figure 7.4 Change of NO with respect to load for different samples

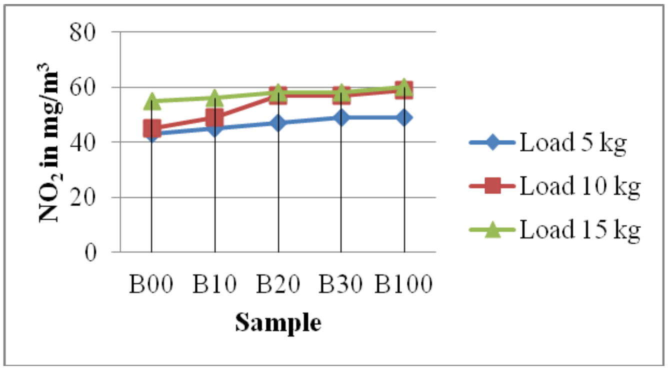

Figure 7.5 Change of NO_2 with respect to load for different samples

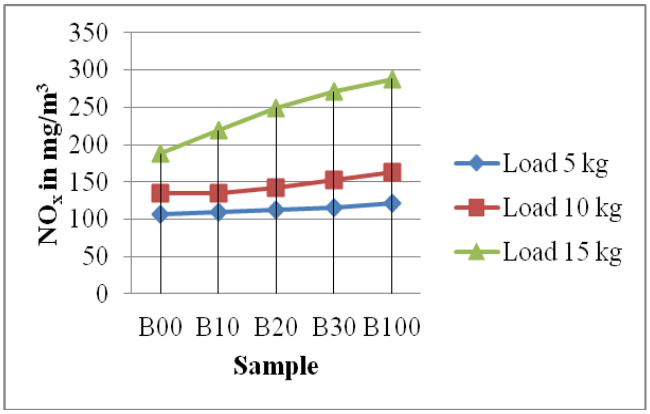

Figure 7.6 Change of NO_x with respect to load for different samples

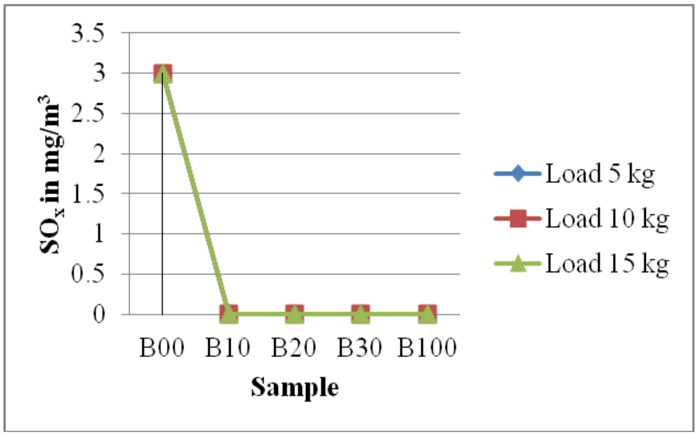

Figure 7.7 Change of SO_x with respect to load for different samples

7.4 Result and Discussion

In figure 7.1 the change of CO with respect to load for different samples are decreasing as the content of biodiesel increases. That means the diesel give rich running engine and it becomes lean running at biodiesel fuel. It is noted that CO readings are indicator of a rich running engine. In fig. 7.2, 7.4, 7.5 it is seen that the values of the CO_2, NO, NO_2, with respect to different load for different samples remains mostly equal, so it may conclude that the biodiesel and its samples can used directly to the compression ignition engine. In fig. 7.3 it is seen that the value of HC remain same for the sample B00 and B10 and then increases with increase the increase value of the biodiesel in diesel. The values of NO_x remain almost same for different samples at lower load and at high load it increases with increase in value of biodiesel blending as shown in the fig. 7.6. In fig. 7.7 it is observed that the blending of diesel and biodiesel gives nil value of the SO_x for different sample at all loads.

CHAPTER – 8

Conclusion

Biodiesel, an alternative and renewable fuel for diesel engines, is receiving worldwide attention because of its renewability, biodegradability, no toxicity and carbon neutrality. It is typically made from biological resources such as vegetable oils, animal fats or even used cooking oils by transesterification with methanol. The biodiesel is quite similar to conventional diesel fuel in its main characteristics.

In this work, excellent quality of biodiesel has been prepared in yield of biodiesel from the seed oil of Pongamia pinnata of 92%. The fuel properties of the biodiesel and blends with diesel for five samples like Kinematic Viscosity at 40°C, Density at 15°C, Pour Point, Flash Point, Ramsbottom Carbon Residue, CFPP (Cold Filter Plugging Point), Total Sulfur, Acidity, Calorific Value are evaluated and recorded. The biodiesel is free from sulphur. The properties of the biodiesel are within the range specified by ASTM D6751, EN 14214, BS II and BS III. The investigation has established the pongamia pinnata oil seed as highly promising feedstock for biodiesel industries.

GC-MS analysis, CHN analysis and FTIR analysis were carried out for detailed characterization of the biodiesel. GC-MS analysis gives the major compound and the chemical structure in the samples like the chemical compound, molecular weight and the respective formula. CHN analysis gives the percentage of the Carbon, Hydrogen and Oxygen in a sample, the H/C, O/C ratio and the empirical formula of the samples. The functional group and the structure of the compounds present in the samples are found from the shape, position and intensity of the peaks in the FTIR analysis.

In a single cylinder four stroke diesel engine made of Kirloskar AK65 was run using different types of sample that is petroleum diesel, blends of diesel and biodiesel, pure biodiesel made from the seed of pongamia pinnata at different loads to analyze the performance of the engine. To determine the performance of the engine, the values of the brake power, specific fuel consumption, heat supplied, brake thermal efficiency, heat lost in radiation and uncounted, volumetric efficiency were calculate. After calculating all these values and comparing with the properties of the petrodiesel it may conclude that the sample B10 gives the most comfortable for running the engine.

The efficiency of exergy, exhaust exergy, heat loss exergy and exergy destroyed of different samples of biodiesel and its blends at different loads were determined. From these investigations it shows that the exergy destruction decreases, because combustion irreversibility decreases with increasing load. Greater load results in less degradation of the fuel chemical exergy when transferred to the exhaust gases and also less mixing of exhaust gases with air.

The energy efficiency and exergy efficiency of the samples at different loads were investigated. Both energy efficiency and the exergy efficiency increases with increasing load. The exergy efficiency is lower than the energy efficiency for the five samples for the same power output. This is due to the fact that chemical availability or exergy of the fuel is slightly higher than its input fuel energy.

The changes of CO with respect to load for different samples are decreasing as the content of biodiesel increases. That means that diesel give rich running engine and it becomes lean running at biodiesel fuel. It is noted that CO readings are indicator of a rich running engine. The values of the $CO_{2,}$ NO, NO_2, with respect to different load for different samples remains mostly equal, so it may conclude that the biodiesel and its samples can be used directly to the compression ignition engine. It is seen that the value of HC remain same for the sample B00 and B10 and then increases with increase value of the biodiesel in diesel. The values of NO_x remain almost same for different samples at lower load and at high load it increases with increase in value of biodiesel blending. The blending of diesel and biodiesel gives nil value of the SO_x for different samples at all loads.

It may conclude that the biodiesel and its samples, the sample B10 can be used directly to the compression ignition engine

Contributions of the work:

Following are the contributions of the work:

1) A detailed characterization of the biodiesel has been carried out. CHN analysis has been done to determine the percentage of the Carbon, Hydrogen and Oxygen in a sample, the H/C, O/C ratio and the empirical formula of the samples. GC-MS analysis has been carried out to find the major compound and the chemical structure in the samples like the chemical compound, molecular weight and the respective formula. The functional group and the structure of the compounds present in the samples have been found from the shape, position and intensity of the peaks in the FTIR analysis.

2) Exergy analyses for the Compression Ignition Engine have been carried out for pure diesel, pure biodiesel and their various blendings to determine the blending that provide the maximum possible work output of the engine.

3) Exhaust analyses have been carried out to determine the pollution characteristics of the fuels and blendings.

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LIST OF PUBLICATIONS

Journal Publications:

1. Brahma K.K., Mahanta D. K., Basumatary S *Bio-oil from the seed of pongamia pinnata found in Assam, North-east India* Technical Research Organization, India, 1, 84-86, 2014, ISBN 978-81-930280-2-5

2. Brahma K.K., Mahanta D. K. *Blending properties of petro-diesel and biodiesel from the seeds of pongamia pinnata* Material Today: Proceeding (Elsevier) Accepted

3. Brahma K.K., Mahanta D. K. *Performance analysis of CI engine using biodiesel from pongamia pinnata* Int. Journal of Mech. Engg. and Technology, 8(1), 281-291, 2017, ISSN-0976-6359

Papers presented in conferences:

1. "Blending properties of petro-diesel and biodiesel from the seeds of pongamia pinnata" in the proceeding of International Conference on Advanced Material Technologies – 2016 on 27th and 28th December 2016 at Dadi Institute of Engineering and Technology, Vishakhapatnam, Andhra Pradesh.

2. "Bio-oil from the seed of Pongamia pinnata found in Assam, North-east India" in the proceeding of International Conference on Mechatronics and Mechanical Engineering held at Warangal on 30th November 2014.