Process optimization for biodiesel production from Tung *(Aleurites fordii.)* oil and its emissions characteristics

Thesis submitted in the partial fulfillment of requirement for award of the degree

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In

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DECLARATION

I undersigned, hereby declared that the research work present in the **Master of Technology thesis entitled "Process optimization for biodiesel production from Tung (*Aleurites fordii.*) oil and its emissions characteristics"** has been carried out by me under the supervision in guidance of **Mr K. S. Babu** Assistant Professor School of energy and environment Thapar University, Patiala and **Dr. Krishnendu Kundu** Scientist & Head, Department of Biofuel, CSIR-CMERI, Ludhiana.

Further I declared that no part of this theis has been submitted for a degree for any other qualification of any other university for examination body in India/elsewhere.

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CERTIFICATE

This is to certify that thesis entitled; **"Process optimization for biodiesel production from Tung (*Aleurites fordii.*) oil and its emissions characteristics"** by **Mr. Rajneesh Kumar** in partial fulfillment of the requirement for the award of **Master of Technology** degree in **Environmental Science and Technology** at **Thapar University, Patiala (Deemed University)** is an authentic piece of work carried out by him under my guidance and supervision.

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

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ABSTRACT

Biodiesel is receiving increased attention as an alternative, non-toxic, biodegradable, and renewable diesel fuel. It is derived from oils and fats by transesterification with alcohols. The present glut of energy crises due to continuous depletion of scarce fossil fuels has resulted in hike of global prices of crude petroleum which is bound to affect the economy of many countries. In a country like India, where edible oils are still imported, it would be worthwhile to explore the possibility of using such non edible oils in CI engines which are not in practice as cooking oil. Therefore, the study on Tung oil as fuel for CI engine was undertaken.

Tung oil was transesterified with methyl alcohol to obtain methyl ester of Tung oil to reduce its kinematic viscosity in the range of diesel fuel. The process parameters such as molar ratio, kaOH concentration and settling time were standardized to obtain higher recovery of esters. About 94 percent ester can be recovered if the Tung oil-methyl alcohol mixture of 5:1 molar ratio is preheated for 30 min at 60^0C and then reacted with 1.5 percent KOH for 1 h at 60^0C and then allowed to settle for 24 h in order to get methyl ester of 4.6 cS kinematic viscosity. Different blends of Tung biodiesel with diesel in proportion of 10:90, 15:85and 20:80 were prepared. The characteristic fuel properties such as kinematic viscosity, relative density, gross heat of combustion, cloud and pour point, flash and fire point, carbon and ash content and total acidity of refined Tung oil, its methyl esters and their blends with diesel were compared. The results of different fuel properties of blends of methyl ester of Tung oil with diesel were almost similar to diesel.

A 3.73 kW, constant speed compression ignition engine was tested on diesel, blends of methyl ester of Tung oil of 4.6. cS kinematic viscosity with diesel (10:90, 15:85, and 20:80). The study of engine exhaust emission reported lower emission compared to diesel . The CO emission on all fuel types was found to be lower. The emission of NO_x from the engine was found slightly higher on each fuel types under entire range of brake load conditions than that on diesel. The best performance in terms of various parameters of the engine was observed when a blend of 30 percent methyl ester of Tung oil with 70 percent diesel was used which enables 30 percent diesel replacement.

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NOTATIONS AND ABBREVIATIONS

NOTATION/ ABBREVIATION DISCRIPTION

ASTM = American Society for Testing Materials
BIS = Beauro of Indian Standards
BSFC = Brake specific fuel consumption
${}^{0}C$ = Degree Celsius
C = Carbon
cc = Centimeter cube
CFPP = Cold filter plugging point
CI = Compression ignition
CO = Carbon monoxide
CO_2 = Carbon dioxide
cS = Centistokes
EMA = Engine Manufacturer Association
FFA = Free Fatty Acid
Fig. = Figure
g = Gram
h = hour
HC = Hydrocarbon
HCl = Hydrochloric acid
HSD = High speed diesel
IC = Internal combustion
IP = Institute of Petroleum
IS = Indian Standards
kg = Kilogram
KOH = Potassium hydroxide
kW = Kilowatt
L = Litre
mg = Milligram
min. = Minute
ml = Milliliter

CHAPTER 1

INTRODUCTION

CHAPTER 1
INTRODUCTION

1.1 ORGANIZATION OF THESIS

Chapter 1

Covers brief introduction to biodiesel, different methods for its production, raw material required & its quality.

Chapter 2

Presents the extensive literature review of research work which has been done by different researchers in the past.

Chapter 3

Covers methodology adopted for the thesis work. It covers the methodology adopted for biodiesel production along with the experimental methodology.

Chapter 4

Presents the results and discussion of the experiments conducted.

Chapter 5

Discusses the conclusion of the research work and future scope related to it.

1.2 INTRODUCTION

The predicted shortage of fossil fuel has encouraged the search for substitutes for petroleum derivatives. This search has resulted in an alternative fuel called "biodiesel". Bio-diesel is an alternative to petroleum-based fuels derived from vegetable oils, animal fats, and used waste cooking oil including triglycerides. Since the petroleum crises in 1970s, the rapidly increasing prices and uncertainties concerning petroleum availability, a growing concern of the environment and the effect of greenhouse gases during the last decades, has revived more and more interests in the use of biodiesel as a substitute of fossil fuels**[1]**. Bio-diesel production is a very modern and technological area for researchers due to the relevance that it is winning everyday because of the increase in the petroleum prices and the environmental advantages biodiesel offers over diesel. Accordingly, many researchers around the world have dealt with these issues and in many cases devised unique solutions. Countless legislative and regulatory efforts around the world have helped pave the way toward the widespread application of the concept **[2]**.

1.3 BIODIESEL

The major components of vegetable oils and animal fats are triacylglycerols (TAG; often also called triglycerides). Chemically, TAG are esters of fatty acids (FA) with glycerol (1,2,3-propanetriol; glycerol is often also called glycerine). The TAG of vegetable oils and animal fats typically contain several different FA. Thus, different FA can be attached to one glycerol backbone. The different FA that are contained in the TAG comprise the FA profile (or FA composition) of the vegetable oil or animal fat. Because different FA have different physical and chemical properties, the FA profile is probably the most important parameter influencing the corresponding properties of a vegetable oil or animal fat. Biodiesel can be produced from a great variety of feedstocks. These feedstocks include most common vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut) and animal fats (usually tallow) as well as waste oils (e.g., used frying oils). In many countries, this has led to the use of blends of biodiesel with petrodiesel instead of neat biodiesel. It is important to note that these blends with petrodiesel are not biodiesel. Often blends with petrodiesel are denoted by acronyms such as B20, which indicates a blend of 20% biodiesel with petrodiesel **[2]**.

1.4 HISTORY OF BIODIESEL

The use of vegetable oils as alternative fuels has been around for one hundred years when the inventor of the diesel engine Rudolph Diesel first tested peanut oil, in his compression-ignition engine. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, but usually only in emergency situations. In 1940 first trials with vegetable oil methyl and ethyl esters were carried out in France and, at the same time, scientists in Belgium were using palm oil ethyl ester as a fuel for buses. Not much was done until the late 1970s and early 1980s, when concerns about high petroleum prices motivated extensive experimentation with fats and oils as alternative fuels. Bio-diesel (mono alkyl esters) started to be widely produced in the early 1990s and since then production has been increasing steadily. **[1]**

1.5 METHODS

Generally the direct use of vegetable oils in the diesel engine is not preferred due to their high viscosity.

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

- **Pyrolysis**
- **Micro-emulsification**
- **Dilution &**
- **Transesterification**

1.5.1 Pyrolysis [3][4]

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

1.5.2 Micro-emulsification [3][4]

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

1.5.3 Dilution [3]

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

1.5.4 Transesterification[2][3][5]

Although blending of oils and other solvents and microemulsions of vegetable oils lowers the viscosity, engine performance problems such as carbon deposit and lubricating oil contamination still exist. Pyrolysis produces more biogasoline than biodiesel fuel. Transesterification is by far the most common method for the production of biodiesel. As the name suggests it is the conversion of one ester into other. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess. Figure.1.1 describes the basic transesterfication process.

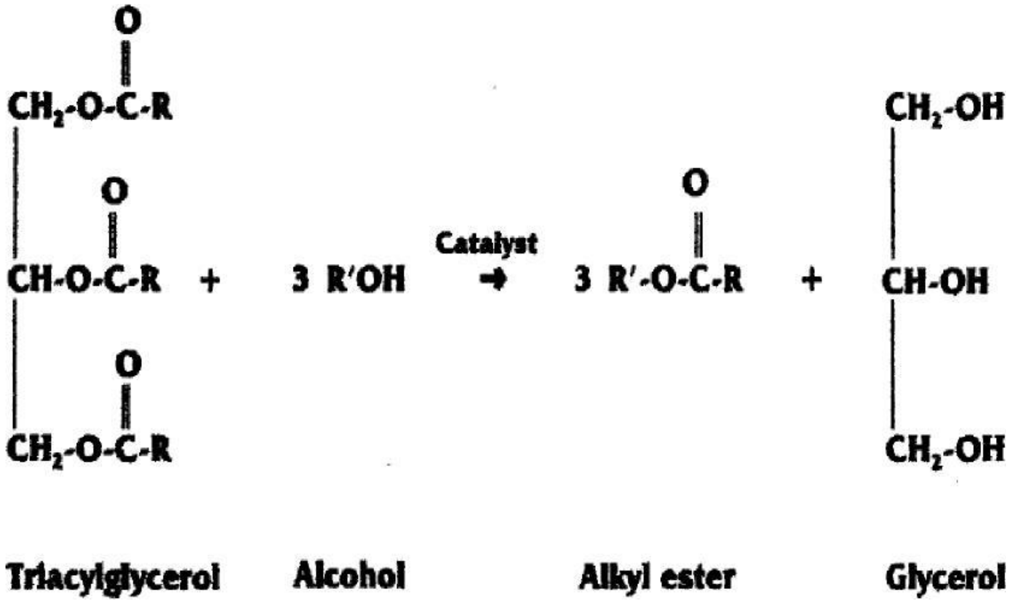


Figure-1.1 The transesterification reaction. R is a mixture of various fatty acid chains. The alcohol used for producing biodiesel is usually methanol (R′ = CH3).**[2]**

Generally, transesterification can proceed by base or acid catalysis. However, in homogeneous catalysis, alkali catalysis (sodium or potassium hydroxide; or the corresponding alkoxides) is a much more rapid process than acid catalysis.

1.5.4.1 Different parameter selected for transesterification

Important parameter that influence transesterification reaction time and conversion are:

- Oil temperature
- Reaction temperature
- Ratio of alcohol to oil
- Catalyst type and concentration
- Mixing intensity
- Purity of reactants.

1.5.4.1.1 Oil Temperature

The temperature to which oil is heated before mixing with catalyst and methanol, affects the reaction. It was observed that increase in oil temperature marginally increases the percentage oil to bio-diesel conversion as well as the bio-diesel recovery. However, the tests were conducted up-to only 60°C as higher temperatures may result in methanol loss in the batch process.

1.5.4.1.2 Reaction temperature

The rate of reaction is strongly influenced by the reaction temperature. Generally, the reaction is conducted close to the boiling point of methanol (60 to 70°C) at atmospheric pressure. The maximum yield of esters occurs at temperatures ranging from 60 to 80°C at a molar ratio (alcohol to oil) of 6:1. Further increase in temperature is reported to have a negative effect on the conversion. Studies have indicated that given enough time, transesterification can proceed satisfactorily at ambient temperatures in the case of the alkaline catalyst. It was observed that bio-diesel recovery was affected at very low temperatures (just like low ambient temperatures in cold weather) but conversion was almost unaffected.

1.5.4.1.3 Ratio of alcohol to oil

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight. Higher molar ratio of alcohol to vegetable oil interferes in the separation of glycerol. It was observed that lower molar ratios required more reaction time. With higher molar ratios, conversion increased but recovery decreased due to poor separation of glycerol. It was found that optimum molar ratios depend upon type & quality of oil.

1.5.4.1.4 Catalyst type and concentration

Alkali metal alkoxides are the most effective transesterification catalyst compared to the acidic catalyst. Sodium alkoxides are among the most efficient catalysts used for this purpose, although potassium hydroxide and sodium hydroxide can also be used. Transesterification occurs many folds faster in the presence of an alkaline catalyst than those catalysed by the same amount of acidic catalyst. Most commercial transesterifications are conducted with alkaline catalysts. The alkaline catalyst concentration in the range of 0.5 to 1% by weight yields 94 to 99% conversion of vegetable oil into esters. Further, increase in catalyst concentration does not increase the conversion and it adds to extra costs because it is necessary to remove it from the reaction medium at the end. It was observed that higher amounts of sodium hydroxide catalyst were required for higher FFA oil. Otherwise higher amount of sodium hydroxide resulted in reduced recovery due to more quantity of glycerol being separated from the oil.

1.5.4.1.5 Mixing intensity

The mixing effect is most significant during the slow rate region of the transesterification reaction. As the single phase is established, mixing becomes insignificant. The understanding of the mixing effects on the kinetics of the transesterification process is a valuable tool in the process scale-up and design. It was observed that after adding methanol & catalyst to the oil, 5-10 minutes stirring helps in higher rate of conversion and recovery.

1.5.4.1.6 Purity of reactants

Impurities present in the oil also affect conversion levels. Under the same conditions, 67 to 84% conversion into esters using crude vegetable oils can be obtained, compared with 94 to 97% when using refined oils. The free fatty acids in the original oils interfere with the catalyst. However, under conditions of high temperature and pressure this problem can be overcome.

It was observed that crude oils were equally good compared to refined oils for production of bio-diesel. However, the oils should be properly filtered. Oil quality is very important in this regard. The oil settled at the bottom during storage may give lesser bio-diesel recovery because of accumulation of impurities like wax etc.

1.6 RAW MATERIAL AND ITS QUALITY FOR THE PRODUCTION OF BIODIESEL [3]

1.6.1 Vegetable Oil

The oil must be moisture-free because every molecule of water destroys a molecule of the catalyst thus decreasing its concentration. Any sediment would collect at the bottom of the reaction vessel during glycerol settling and at the liquid interface during washing. This would interfere with the separation of the phases and may tend to promote emulsion formation. The free fatty acid content should be less than 1%.

It was observed that lesser the FFA in oil better is the bio-diesel recovery. Higher FFA oil can also be used but the bio-diesel recovery will depend upon oil type and amount of catalyst used.

1.6.2 Alcohol

Methanol or ethanol, as near to absolute as possible. As with the oil, the water affects the extent of conversion enough to prevent the separation of glycerol from the reaction mixture.

1.6.3 Catalyst

Sodium or potassium hydroxide should be used as a catalyst, preferably the latter. The corresponding alkoxide also can be used, but prohibitively expensive. Best if it has 85% potassium hydroxide. Even best grades of potassium hydroxide have 14-15% water which cannot be removed. It should be low in carbonate, because the carbonate is not an efficient catalyst and may cause cloudiness in the final ester. Sodium hydroxide pellets have given very good results. Because quantity of catalyst used is quite less, good quality catalyst (in-spite of high cost) can be used.

1.6.4 Animal fats

The most prominent animal fat to be studied for potential biodiesel use is tallow. Tallow contains a high amount of saturated fatty acids, and it has therefore a melting point above ambient temperature.

1.6.5 Waste vegetable oils

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

1.6.6 Esters of vegetable oil

They make good biomass fuels as diesel substitutes, provided the following factors receive special attention:

- The yield of transesterified product should be >90%.
- The fuel should be as neutral as possible (pH 6.5-8.0)
- The fuel should be centrifuged at a temperature below the expected ambient operating temperature. Winterization has been suggested as the ideal solution.
- The neutralizing agent should form fuel in soluble salts, free from carbonate groups.
- Ash content should be 0.01%. The fuel should be free from alcohol as alcohol has an adverse effect on the rubber gaskets and piston rings in the engine.

Table 1.1 US and Indian standards for biodiesel

Source: http://www.svlele.com/biodiesel_std.htm

Standards for Biodiesel	**ASTM D-6751**	**IS 15607 : 2005**
Density	Not Mentioned	860 - 900 Kg / m3
Ester Content	Not Mentioned	96.5 %
Flash point (closed cup)	130°C min. (150°C average)	120°C
Water and sediment	0.050% by vol., max.	500 mg / Kg, max
Kinematic viscosity at 40°C	1.9-6.0 mm^2/s	2.5-6.0 mm^2/s
Oxidation Stability	Not Mentioned	6 hours min, at 110°C
Ramsbottom carbon residue, % mass	0.10	
Sulfated ash	0.020% by mass, max.	
Sulfur	0.05% by mass, max.	50 mg / Kg max
Copper strip corrosion 3 hrs. 50°C	No. 3 max	Class 1
Cetane Number	47 min.	51 min.
Carbon residue	0.050% by mass, max.	
Acid number, mg KOH/g	0.80 max.	0.50 max.
Methanol or Ethanol	Not Mentioned	0.2 % m/m, max
Free glycerin	0.020 % mass	0.020 % mass
Total glycerine (free glycerine and unconverted	0.24% by mass, max.	0.25% by mass, max.
Group I Metal (Na+K)	5 mg/Kg, max	5 mg/Kg, max
Group II Metal (Ca+Mg)	Not Mentioned	5 mg/Kg, max
Phosphorus content	0.001 max. % mass	10 mg/Kg, max
Distillation	90% @ 360°C	Not Mentioned

1.7 ADVANTAGES OF BIODIESEL

The advantages of biodiesel are as follows

- It is a renewable substitute for petroleum and diesel fuels.
- It has low sulphur and aromatic content.
- It is readily available and biodegradable fuel.
- It has higher flash point than diesel.
- Its combustion efficiency is high.
- It has better lubricity properties than diesel.
- It has lower HC, CO_2, CO emissions as compared to petroleum and diesel fuels.
- It has less particulate emissions than petroleum and diesel fuels.

1.8 TUNG OIL AS BIODIESEL [13][14]

Tung is produced in very large quantities in countries of South-east Asia. Considerable amounts are also produced in the USA, Europe and Latin America. China is the largest Tung oil producing country, In India Tung plantation found in North-east. The total expected availability of Tung oil in India is about 2 million tons [24]. The present production of Tung oil is low Tung oil is left unutilized due to various reasons. Thus the oil can be used for various purposes. One of the most effective ways is to use it for biodiesel production.

Tung (Aleurites fordii.) considering as a wild oilseed plant of the sub-tropical region is now been credited as a promising biofuel crop very much ideally suited for growing in the waste lands of the country. This potential biodiesel crop can be about major economic activity providing income and employments opportunities to the rural communities. The seeds of the oil seed plant Tung contain 20 to 35 per cent by weight viscous oil. It is a medium-sized deciduous tree growing upto 20m tall with spreading crown & belonging to the family of Euphorbiaceous. It is a plant with many attributes, multiple uses and potential.

Origin of Tung Tree

Tung tree originates from Central Asia and spread over a North-East Asia, In India mostly north east states.

Botanical Description

It is a medium sized deciduous tree growing upto 20m tall, with a spreading crown. The bark is smooth and thin, bleeds latex if cut. The leaves are alternate, 4-25 cm long and 4-22 cm broad, heart shaped. Tung fruit occurs in cluster, each bear 4-5 nuts.

The oil from the Tung is regarded as a potential fuel substitute. Diesel is a hydrocarbon with 8-10 carbon atoms per molecule, but Tung oil has 16-18 carbons. Thus, the nut oil is much more viscous than diesel. For this reason, using the oil directly in engines has not been fully used over long periods. Seed oils are usually transesterified to produce biodiesel; with properties similar to mineral diesel fuel. This reduces their viscosity and increase cetane number. For mitigating climate change by reducing emission of green house gases, meeting rural energy needs, protecting the environment and generating employment, jatropha curcas has multiple roles to play.

Production of biodiesel from the Tung plantation hold potential for at least partly remedying these stated problems. Tung tree grows on poor degraded soils and is able to ensure a reasonable production of seeds with very little inputs. It is not grazed by animals and is highly pest and dieses resistant. Time taken for nut yield is between 4 and 5 year based on soil and rainfall conditions. Yield varies from 4.5 to 5 t/year based on soil and rainfall condition. An average seed production of about 5 tones per hectare can be expected under optimum condition. A yield of 0.75 to 2 tons of biodiesel could be expected per hectare per year from fifth year onwards. Tung plantation yield over long periods of time. Tung tree cultivation generates an income of Rs.10,000- Rs.35,000 per hectare in a year, it can provide adequate employment to all landless workers all through the year.

1.9 OBJECTIVES OF PRESENT WORK

The proposed study has been carried out with biodiesel derived from Tung oil with the following objectives.

1. Standardization and optimization of transesterification process for biodiesiesl production.
2. Determination of the properties of optimized biodiesel produced from Tung oil.
3. Evaluation and comparison of various emission characteristics of Tung biodiesel such as hydrocarbon emissions, carbon dioxide emissions, carbon monoxide emissions and nitrogen oxide emissions with diesel fuel.

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2
LITERATURE REVIEW

2.1 REVIEW OF LITERATURE

A substantial amount of work has been done on various aspects of biodiesel. This chapter categorises the literatures into various parts. This chapter thus reviews the feasibility of this fuel source and some of the results obtained from investigations on the use of these fuels in compression ignition engines under the following heads:

- First part discusses the literature related to Chemistry of vegetable and Tung oils.
- Second part discusses the literature related to biodiesel and transesterification.
- Third part discusses the literature related to the production of biodiesel from Tung oil.
- Fuel properties of vegetable oils and their esters.
- Engine emission characteristics of vegetable oils and their esters.

Mustafa Balat , Havva Balat (2001)[1] described that the problems with substituting triglycerides for diesel fuels were mostly associated with their high viscosities, low volatilities and polyunsaturated character. The viscosity of vegetable oils, when used as diesel fuel, can be reduced in at least four different ways: (1) dilution with hydrocarbons (blending), (2) emulsification, (3) pyrolysis (thermal cracking), and (4) transesterification (alcoholysis). Transesterification was the most common method and leads to monoalkyl esters of vegetable oils and fats, now called bio-diesel when used for fuel purposes. The main factors affecting transesterification were molar ratio of glycerides to alcohol, catalyst, reaction temperature and pressure, reaction time and the contents of free fatty acids and water in oils. The commonly accepted molar ratios of alcohol to glycerides are 6:1–30:1. Bio-diesel is a cleaner-burning diesel replacement fuel made from natural, renewable sources such as new and used vegetable oils and animal fats. Just like petroleum diesel, bio-diesel operates in compression-ignition engines or Diesel engines. The bio-diesel was characterized by determining its density, viscosity, high heating value, cetane index, cloud and pour points, characteristics of distillation, and flash and combustion points according to ISO norms. Viscosity is the most important property of biodiesel since it affects the operation of the fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel.

Gerhard Knothe et al.(2005)[2] in their book described the technical concept of using vegetable oils or animal fats or even used oils as a renewable diesel fuel. Biodiesel is the form in which these oils and fats are being used as neat diesel fuel or in blends with petroleum-based diesel fuels. The concept itself may appear simple, but that appearance is deceiving since the use of biodiesel is fraught with numerous technical issues. Accordingly, many researchers around the world have dealt with these issues and in many cases devised unique solutions. This book was an attempt to summarize these issues, to explain how they have been dealt with, and to present data and technical information. Countless legislative and regulatory efforts around the world have helped pave the way toward the widespread application of the concept. This book addressed these issues also. To complete the picture, chapters on the history of vegetable oil-based diesel fuels, the basic concept of the diesel engine, and glycerol, a valuable byproduct of biodiesel production, were included.

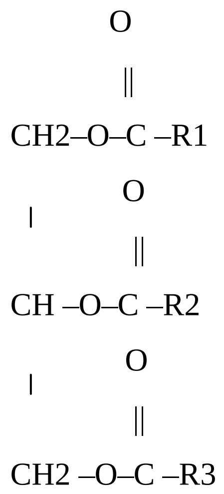
Codd *et al.* (1975) [3] reported that vegetable oils are natural products, therefore, subjected to some variation in composition and content of fatty acids. The most common fatty acids present in vegetable oils as reported are shown in Table 2.1. It is clear from the table that unlike diesel fuel, vegetable oils contain significant amount of oxygen in addition to carbon and hydrogen. The presence of different fatty acids is also dependent to a number of factors such as botanical variety, climatic conditions, soil composition, rainfall and temperature.

Fangrui Maa, Milford A. Hannab (1995)[4] described the four primary ways to make biodiesel, direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification. Of the several methods available for producing biodiesel, transesterification of natural oils and fats was the method of choice. The purpose of the process is to lower the viscosity of the oil or fat. Although blending of oils and other solvents and microemulsions of vegetable oils lowers the viscosity, engine performance problems, such as carbon deposit and lubricating oil contamination, still exist. Pyrolysis produces more biogasoline than biodiesel fuel. Transesterification is basically a sequential reaction.The commonly accepted molar ratio of alcohol to glycerides is 6:1. Base catalysts are more effective than acid catalysts and enzymes. The recommended amount of base used to use is between 0.1 and 1% w/w of oils and fats. Higher reaction temperatures speed up the reaction and shorten the reaction time. The reaction was slow at the beginning for a short time and proceeds quickly and then slowed down again. Base catalyzed transesterifications were basically finished within one hour.

Ulf Schuchardta et al. (1998)[5] reviewed the transesterification of vegetable oils with methanol as well as the main uses of the fatty acid methyl esters. The general aspects of this process and the applicability of different types of catalysts (acids, alkaline metal hydroxides, alkoxides and carbonates, enzymes and non-ionic bases, such as amines, amidines, guanidines and triamino(imino)phosphoranes) were described. Special attention was given to guanidines, which can be easily heterogenized on organic polymers. However, the anchored catalysts show leaching problems. New strategies to obtain non-leaching guanidine-containing catalysts are proposed. Finally, obtained by transesterification of vegetable oils, are described.

M.Mathiyazhagan et al.(2011)[6] researched on the non-edible oils as feed stocks for biodiesel production to reduce the cost of biodiesel. Normally alkali catalyzed method was followed for biodiesel production process. However the non-edible oils having high FFA content which is not suitable for normal transesterification process. Hence a two-step catalyzed method was used to prepare the biodiesel. High FFA content of non-edible oils were efficiently converted into biodiesel fuel. Figure 2.1 shows the flow diagram of biodiesel production from non-edible oils.

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

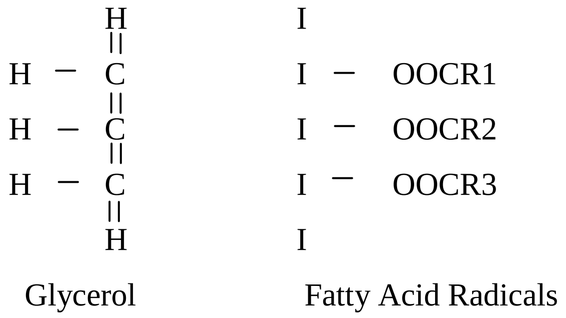


$$\begin{array}{l} \mathrm{CH2{-}O{-}\overset{\overset{O}{\|}}{C}{-}R1} \\ | \\ \mathrm{CH\ {-}O{-}\overset{\overset{O}{\|}}{C}{-}R2} \\ | \\ \mathrm{CH2\ {-}O{-}\overset{\overset{O}{\|}}{C}{-}R3} \end{array}$$

Fig. 2.1 Chemical Structure of Vegetable Oils

Gerhard Knothe (2005)[8] discussed that the fuel properties of biodiesel are strongly influenced by the properties of the individual fatty esters in biodiesel. Both moieties, the fatty acid and alcohol, can have considerable influence on fuel properties such as cetane number with relation to combustion and exhaust emissions, cold flow, oxidative stability, viscosity, and lubricity. Generally, cetane number, heat of combustion, melting point, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation. It therefore appeared reasonable to enrich (a) certain fatty ester(s) with desirable properties in the fuel in order to improve the properties of the whole fuel. For example, from the available data it appeared that iso-propyl esters had better fuel properties than methyl esters. The major disadvantage was the higher price of iso-propanol in comparison to methanol, besides modifications needed for the transesterification reaction. Similar observations likely hold for the fatty acid moiety.

Peterson (1986) [9] reported that the molecular weight of the glycerol portion (C3H5) in a triglyceride molecule is 41whereas the combined molecular weight of the fatty acid radicals (RCOO) comprising the remainder of the molecule varies with different fats from about 650 to 970 in molecular weight as shown in Fig. 2.2. Thus the fatty acids contribute 94 to 96 percent of the total weight of the molecule. This composition of fatty acid is crucial and it affects very much the chemical and physical properties such as viscosity, density, heat value of a fuel oil.



Molecular weight = 41 **Molecular weight = 650-970**

Fig. 2.2 Molecular Weight of Glycerol and Radical Fatty Acids of Triglyceride

Goering et al. (1981) [10] studied the content of different fatty acids in various vegetable oils as shown in Table 2.2. Since, fatty acid contents of vegetable oils have been found to be a significant factor in reducing carbon build up in the engine, therefore, the oils with lower level of saturation are more desirable for fuels.

Zhou Hui et al. . (2007) [11] tung oil was used to prepare the bio-diesel. In this study,the conditions of trans-esterification reaction were optimized.When the ratio of methanol to oil is higher than 6,the tung oil transformation ratio improved slightly.When there are small amounts of free fatty acids and water in the oil,the oil transformation ratio was not affected.However,large amounts of methyl ester were lost during the post treatment because of the emulsification.It was also found that the oil transformation ratio was greatly dependent on the reaction temperature.The low temperature property study indicated that the tung methyl ester could be blended with other biodiesel as low temperature property conditioner.The flash point is 194 ℃,and the sulfur content is 70.75 μg/g.

Li Lianhua et al. . (2011) [12] The effect of molar ratio of methanol to oil, temperature and space velocity (SV) on pre-esterification of Tung oil was carried out in pilot-scale fixed bed reactor, with solid acid catalysts. The molar ratio results showed the maximum acid value reduction efficiency (90.21%) was obtained at the molar ratio of 8:1, the acid value decreased sharply to 0.70 g kg^{-1} of KOH. And esterification reaction attained balance when space velocity was enough, so 0.029 h^{-1} was optimal space velocity. Furthermore, activity of reactant and rate of reaction increase with temperature increased, and the maximum conversion was achieved at 65 °C, the acid value of Tung oil could be reduced to 1.4 g kg^{-1} of KOH.

Gui zhuan et al . (2009) [13] The transesterification reaction conditions of tung oil with methanol have been studied in this article, with immobilized lipase NOVO435 as catalyst. The response surface methodology was used to optimize the transesterification reaction of tung oil in a nonsolvent system. The optimal conditions were rotation rate 200 r/min, molar ratio of methanol to oil 2.2:1, reaction temperature 43°C, and the catalyst amount 14% (based on the weight of oil). After reacting for 18 h, 67.5% of the oil was converted to its corresponding methyl esters (the theoretical ester conversion was 73.3%). The lipase was washed by organic solvents after each reaction and was reused again. The esters conversion of tung oil was decreased by 6% after the lipase was reused for 120 h. The theoretical amount of methanol was added in two steps, 85% ester conversion was obtained after 36 h of reaction (theoretical ester conversion was 100%). The molar ratio of methanol to oil, the catalyst amount, the reaction temperature, and reaction time were all highly significant factors, and there was a relative significant interaction between every two factors.

Don van Manh et all. . (2012) [14] The effects of ultrasonic irradiation time (tUS) on the transesterification yield (YF) of biodiesel from Tung (Vernicia fordii) and blended oils with CH3OH and KOH, and on some properties of biodiesel such as acid value (AV), iodine value (IV), kinematic viscosity (KV), density and cold filter plugging point (CFPP) were investigated. The blended oil is consisted of 20, 50 and 30% of Tung, canola and palm oils, respectively. Tung oil should be blended with other oils in order to produce biodiesel satisfying the biodiesel standards. Moreover, the results indicated that a certain enough time, say 5 min, is needed to provide sufficient cavity heating and mixing via ultrasonic wave ensuring good properties of biodiesel produced. The KV of biodiesel using blended oil decreases from 6.26 mm2/s at tUS = 1 min to 5.54 mm2/s at tUS = 5 min, thus meeting the ASTM-D6751 value of 1.9–6.0 mm2/s. The information obtained in this study is useful for the proper use of Tung oil in conjunction with other edible oils for the production of biodiesel with satisfactory qualities and the rational design and operation of ultrasonically catalytic transesterification process

Clark *et al*. . (1984) [15] used a John Deere, 4239TF, four cylinder, DI, turbo-charged, CI engine to study emissions from both methyl and ethyl esters of soybean. The measurements of HC, CO, CO_2, NO_X and O_2 were made. It was found that CO was very low, with no difference between fuels. Soybean ethyl and methyl esters had slightly lower HC levels than the diesel fuel. Methyl and ethyl ester of soybean oil had consistently higher levels of NO_X than the reference fuel. Ethyl esters were lower in NO_X than methyl esters.

Zubik *et al*. (1984) [16] studied exhaust emission from a CASE 188 D four cylinder, naturally aspirated, four stroke diesel engine operating on a blend of 25 percent sunflower oil with diesel fuel and 100 percent sunflower methyl ester. It was reported that emissions of CO and NO_X were essentially the same for all the fuels at constant speed (1800 rpm) operation of the engine. Emission of smoke was the lowest for the ethyl ester and highest for pure diesel fuel. It was also mentioned that throughout the operating range, lowest HC emission was on diesel, however, at the lightest loads HC emissions was more on diesel compared to that observed on methyl ester and blended fuels.

Wagner *et al*. (1985) [17] compared emission from a John Deere 4239TF engine fueled with methyl, ethyl and butyl esters. It was reported that all regulated emission levels for the ester fuels were similar to diesel fuel except for NO_X. It was stated that smoke was definitely less visible under full rack conditions for the methyl and ethyl esters compared to diesel fuel but for the butyl ester it was more. Carbon dioxide, carbon monoxide and oxygen emissions were very similar for all four fuels at both the 2200 and 1500 rpm speed settings. The NO_X emissions for the esters measured two to five times that of the diesel fuel. The emission of NO_X from the methyl esters was highest followed by butyl esters and was lowest on ethyl ester at the above mentioned engine speed settings. Visible smoke was less for the methyl and butyl esters at full rack compared to diesel fuel.

Alfuso *et al*. (1993) [18] carried emission tests of a direct injection, compression ignition diesel engine on rapeseed methyl ester. It was reported that rapeseed methyl ester promoted a rise in NO_X, decrease in HC and CO and reduction in smoke. Particulate matter produced by rapeseed methyl ester in transient cycles was higher than that obtained with diesel fuel. The contribution of soluble organic fractions was reported to be higher at low loads. The rapeseed methyl ester produced more soluble organic fractions and particulate matter than the diesel fuel at lighter loads while as in proximity of full load the trend was the opposite. The emission of hydrocarbon from diesel was higher at lighter loads and lower at higher loads. Carbon monoxide emission was about the same at different loads on diesel but it reduced with rapeseed methyl ester and nitrogen oxide production was generally higher on biofuel.

Gupta (1994) [19] reported that for some combination of load and fuel injection timing, the Tung oil ester gave best engine performance in form of lower smoke number, lower exhaust gas temperature and lower CO/HC emission. It was closely followed by cotton seed oil ester and Tung oil oil ester. The values of CO emissions for Tung oil ester were 0.12, 0.12, 0.15, 0.20, 0.60 and 1.2 percent at loads of 8.4, 25.4, 50.7, 76, 98.5 and 107 percent respectively. There was abrupt increase in CO emission when the load was increased beyond 76 percent.

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

2.1CONCLUSION

It appears from the past research that the approaches of using vegetable oils as diesel engine fuel include use of neat vegetable oil, esterified vegetable oil and blends of vegetable oils or vegetable oil esters with diesel fuel. Over a short period of time, an unmodified engine can perform satisfactorily on neat vegetable oils or their blends with diesel but there is a decrease in maximum power and about 10 percent increase in fuel consumption relative to diesel. However, use of vegetable oils or their blends with diesel is associated with both short term and long term problems. The short term problems include difficult cold starting, plugging and degumming of filters, line and injectors and engine knocking. Though these problems are not universal but have been noted in different places. The potential long term problems include coking of injector nozzles, carbon deposits on the piston and cylinder head, dilution of the crankcase lubricating oil, excess wear on the rings, pistons and cylinders and failure of the engine lubricating oil due to oxidation and polymerization. These problems are correlated to basic properties of vegetable oils such as naturally occurring gums, high viscosity, acid composition, free fatty acids content and low cetane ratings.

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

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

Further, emission characteristics of ethyl and methyl esters of vegetable oils have been found essentially similar to diesel fuel. The studies indicate reduction in emission of HC and CO on esterified vegetable oils compared to diesel. The NO_X and particulate matter are related and tend to change inversely with each other, differing from diesel by al most 10 to 15 percent. In view of the above, use of either esterified vegetable oils alone or their blends with diesel appear to be promising alternative fuels of the future. The present study was therefore, undertaken to use pure Tung oil with diesel and also its methyl ester with diesel.

2.2 GAP IN LITERATURE

A lot of work has been done on transesterification of edible oils. Limited amount of work is done for the extraction of the biodiesel through transesterification from non-edible oils. In India, the high cost of edible oils prevents their use in biodiesel preparation. But non-edible oils are affordable for biodiesel production. Cost associated with biodiesel is reduced due to the low cost of the non edible oils. Awareness of the biodiesel production from Tung oil is very less. Limited amount of work has been done on standardization and optimization of tung biodiesel using basic catalyst, the engine emission analysis fuelled with methyl ester of Tung oil is not done very extensively. India is the major producer of tung in the world and its present production of Tung oil is about 50,000 tons of which is non edible in nature. The total available Tung oil is left unutilized due to various reasons. Thus due to the unawareness of the benefits of this unutilized oil to extract biodiesel limited amount of research work has been done on its use in diesel engines.

CHAPTER 3

METHODOLOGY

CHAPTER 3

METHODOLOGY

In this chapter the techniques and procedures adopted and the equipment and material used during the experiment have been discussed. Fuel characteristics and other laboratory tests were conducted in the Department of Biofuel CSIR-CMERI (FORMERLY MERADO) Ludhiana. Details on the above aspects have been presented under the following heads:

- Fatty acids composition of Tung oil
- Development of transesterfication process for Tung oil
- Estimation of conversion to ester
- Measurement of fuel properties
- Fuels selected for engine test
- Exhaust emissions measurement

3.1 Fatty Acids Composition of Tung oil

Tung oil contains various fatty acids as mentioned in Table 2.2, Section 2.1.2 was selected for the study. The estimation of fatty acids present in the refined Tung oil was done using a Hewlett Packard make, 5890 series II model gas chromatograph. The following procedure was adopted to determine different fatty acids present in the refined Tung oil selected for the study:

- preparation of a sample by taking 1 ml of refined Tung oil into a centrifuge glass tube
- addition of 0.5 ml petroleum ether (40 – 60°C) to the sample
- addition of 1.5 ml of methylating solution to the mixture
- thoroughly mixing of refined Tung oil, petroleum ether and methylating solution and allowing it to remain at room temperature (22^0C) for 50 minutes

- addition of 1 ml of distilled water and centrifuging the mixture for a while and leaving it for 10 min
- taking 0.75 μl of supernatant using a micro litre syringe from centrifuge tube which is methyl ester
- injecting the gas into gas chromatograph set to run on conditions described in Table 3.1
- analyzing the peaks eluded for identification and estimation of different fatty acids

Since the sequence of fatty acids elution is based on their carbon number and the acids having lowest carbon number elude first followed by others, therefore, the type and content of different acids was observed based on sequence of peaks and the percent area under respective eluded peak.

Table 3.1 Conditions Set for Gas Chromatograph for Fatty Acids Estimation

Column	DB – Waxeter, 30 m long, internal diameter, 0.5 μm film thickness
Detector	Thermal Conductivity Detector
Carrier gas	Nitrogen
Carrier gas flow rate, ml/min	30
Oven temperature, °C	250
Detector temperature, °C	280
Injector temperature, °C	260
Detector Current, m A	5
Attenuation	2X

3.2 Transesterification Process for Tung oil

Transesterification process is defined as the chemically reacting triglycerides such as one of the vegetable oil with an alcohol in presence of an alkaline or acidic catalyst to produce glycerol and fatty acids ester. In this process the ester is produced when vegetable oil combines with a simple alcohol in the presence of a catalyst. The fatty acids of vegetable oil exchange places with the (OH) groups of the alcohol producing glycerol and methyl, ethyl or butyl fatty acids ester depending on the type of alcohol used. The four distinct stages in the preparation of an ester are namely:

- heating oil at a desired temperature
- stirring and heating of alcohol-oil mixture with an alkaline or acidic catalyst
- separation of glycerol and washing of ester with water
- evaporating traces of water from ester recovered

The following parameters affect the level of ester recovery:

- molar ratio of Tung oil – methanol mixture
- preheating time
- percentage amount of catalyst (KOH) or concentration of KOH
- reaction time
- reaction temperature
- settling time
- method of removal of traces of water from washed ester either by heating or absorbing using a suitable chemical

The methyl esters of Tung oil were prepared for the experiment. Since the recovery of ester from transesterification process is affected by the parameters described above, the process was carried out as per steps described . The effect of process parameters shown in Table 3.2 was studied to standardize the transesterification process for estimating recovery of ester as well as recovering ester of lowest possible viscosity.

The transesterification process was carried out as per the procedure outlined below:

- take 100 g refined Tung oil in a 100 ml capacity conical flask
- heat the oil at 60°C selected reaction temperature for 30 min preheating time

- take 25, 20 and 16ml of methyl alcohol to obtain molar ratio of 4:1, 5:1, and 6:1 respectively . Add selected quantity of Potassium hydroxide (KOH) and mix thoroughly
- add this mixture to 100 g preheated oil
- add this mixture to oil to obtain an oil- methyl alcohol mixture of above selected molar ratio.
- place the mixture having selected molar ratio in a shaking water bath to carry out reaction
- carry out reaction for a period of 1 hour in the shaking water bath at the selected reaction temperature
- place the sample which is now a mixture of ester and glycerol in a separating funnel and leave it for the selected settling time to observe separation of ester and glycerol
- separate the glycerol settled at the bottom of separating funnel from ester by draining it
- wash the ester with distilled water and allow it to settle for 10 min
- drain the water accumulated along with traces of glycerol at the bottom of the separating funnel and again wash the ester
- carry out washing of ester three times to obtain an ester free of glycerol, excess of alcohol and KOH.
- heat the washed ester at 100^0C for 10 min to evaporate traces of water from the ester

In all 27 samples of refined Tung oil -methyl alcohol having different molar ratio were transesterified to study the effect of four levels of selected molar ratio of Tung oil-methyl alcohol, three level of KOH concentration and three levels of selected settling time on ester recovery and subsequent measurement of their kinematic viscosity.

Table 3.2 Process Parameters Selected for Standardization of Transesterification Process

Sl. No.	Name of Parameter	Levels Selected
1	Molar Ratio (Tung oil : Methanol)	4:1, 5:1 and 6:1
2	Preheating time, min	30
3	KOH concentration	1, 1.5 and 2%

4	Reaction Temperature, °C	60
5	Reaction Time, min	60
6	Settling Time, h	24,

3.3 Measurement of Fuel Properties

The kinemetic viscosity of ester produced from selected molar ratio was measured. It was observed that the ester of lowest kinematic viscosity (4.6 cS) was obtained at the molar ratio of 5:1 when the KOH concentration was kept to 0.33 percent and settling time 24 h. The Table 3.3 shows the standardized process parameters obtained in the experiment. Further, observations in the experiment were made using this ester of lowest kinematic viscosity. The fuel types as shown in Table 3.4 were selected for the measurement of characteristics fuel properties to enable the selection of a suitable fuel blend for engine testing.

Table 3.3 Transesterification Process Parameters Selected to Produce Methyl Ester of Tung oil of 4.6 cS Kinematic Viscosity

Sl. No.	Process Parameters	Standardized Value
1	Molar Ratio	5:1
2	Preheating Time, min	30
3	Preheating Temperature, ^{0}C	60
4	Reaction Temperature, ^{0}C	60
5	Reaction Time, h	1
6	Settling Time,	24
7	KaOH Concentration	1.5%

3.3.1 Kinematic viscosity

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

A Redwood Viscometer No.1 of Widson make as shown in Plate 3.3 was used for measurement of kinematic viscosity of selected fuel samples as well as the methyl ester obtained from selected molar ratio of 5:1, 6:1, 7:1 and 8:1. The instrument measures the time of gravity flow in seconds of a fixed volume of the fluid (50ml) through specified orifice made in an agate piece as per **IS: 1448 [P : 25] 1976**. The apparatus could be used for flow time between 30 to 2000 seconds. The fuel was filled in a cup fitted with an agate jet at the bottom up to a specified level indicated in the cup. The cup was surrounded by water jacket having an immersion heater. The water was heated to 38^{0}C by regulating the rate of heating using a voltage regulator of the instrument. A silver plated metallic ball was used to open and close the agate jet. A standard 50 ml volumetric glass was kept below the agate jet to collect a falling fuel sample. Each test was replicated thrice. Kinematic viscosity in centistokes was then calculated from time units by using the relationships given by **Guthrie (1960)**:

$$V = 0.26\ t - \frac{179}{t} \qquad ...3.1$$

When 34 < t < 100 and

$$V = 0.24\ t - \frac{50}{t} \qquad ...3.2$$

When t > 100

where,

V = Kinematic viscosity in centistokes, cS

t = Time for flow of 50 ml sample, s

3.3.2 Relative density and API gravity

The relative density of the selected fuels as mentioned above at 15^0C was determined as per **IS: 1448 [P: 32]: 1992**. The empty pyknometers (Plate 3.4) were weighed on an Adair Dutt make, MJ 500 series electronic balance of range 0 - 500g, having readability of 0.001 g. The pyknometers were then filled with fuel samples and weighed. The samples were maintained at 15^0C by keeping them in a Saveer Biotech make walk-in temperature control chamber. A mercury thermometer of 0 – 100^0C range was also used to measure the temperature of fuels kept inside the temperature control chamber.

The weights of the empty pyknometers were subtracted from the weights of the filled ones to get the weight of the fuel samples. Three replicates were taken for each samp kle and their mean was calculated. This value when divided by the volume of the fuel sample gave the density of the fuel sample. The density of distilled water at 15^0C was also determined.

The equation 3.1 was used to calculate the relative density.

$$\text{Relative density} = \frac{\text{Density of the fuel at } 15^0\text{ C}}{\text{Density of the water at } 15^0\text{ C}}$$

The API (American Petroleum Institute) gravity, which is an indicator of heat content and lightness of a fuel, was also calculated. The higher the API gravity, the lighter is the fuel. The following relationship was used to determine the API gravity of diesel, Tung oil, and its methyl esters of 6.49 cS kinematic viscosity and their blends with diesel.

$$\text{API Gravity} = \frac{141.5}{\text{Relative density at } 15^0\text{C}} - 131.5$$

3.3.3 Heat of combustion

The heat of combustion or calorific value of a fuel is an important measure since it is the heat produced by the fuel within the engine that enables the engine to do the useful work. The gross heat of combustion of fuel samples was determined as per **IS: 1448 [P : 6] : 1984** with the help of a Widson Scientific Works make Isothermal Bomb Calorimeter (Plate 3.5). A 2 ml fuel sample was burnt in the bomb of calorimeter in the presence of pure oxygen. The sample was ignited electrically. As the heat was produced, the rise in temperature was measured. The water equivalent (effective heat capacity of the calorimeter) was also determined using pure and dry benzoic acid as test fuel. Each sample was replicated three times.

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

$$H_c = \frac{W_C \times \Delta T}{M_S}$$

where,

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

W_c = Water equivalent of the calorimeter, Cal / ^{0}C

ΔT = Rise in temperature, ^{0}C

M_s = Mass of sample burnt, g

3.3.4 Cloud and Pour point

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

The Cloud and Pour point of fuel samples were determined as per **IS: 1448 [P : 10] : 1970** using the Cloud and Pour point apparatus as shown in Plate 3.6. The apparatus mainly consists of 12 cm high glass tubes of 3 cm diameter. These tubes are enclosed in an air jacket which is filled with a freezing mixture of crushed ice and sodium chloride crystals. The glass tube containing fuel sample is taken out from the jacket at every 1^{0}C interval as the temperature falls and is inspected for cloud formation. The point at which a haze was first seen at the bottom of the sample was taken as the Cloud Point.

The apparatus and the procedure for the Pour Point was same as for Cloud Point, only the sample was pre-heated to 48^{0}C and then cooled to 35^{0}C in air before it was filled in the glass tube. Thereafter, the cooled samples were placed in the apparatus and withdrawn from the cooling bath at 1^{0}C interval for checking its flowability. The Pour Point was taken to be the temperature 1^{0}C above the temperature at which no motion of fuel was observed for five seconds on tilting the tube to a horizontal position. Three replications were made for each fuel type.

3.3.5 Flash and Fire Point

Flash Point measures the tendency of a fuel to form a flammability mixture with air under controlled laboratory conditions. This is the property that must be considered in assessing the over all flammability and hazard of material. Flash Point can indicate the possible presence of highly volatile and flammable material in relatively non volatile material. It is defined as the lowest temperature at which the fuel gives off enough vapours and ignites for a moment. The Fire Point is an extension of Flash Point in a way that it reflects the condition at which vapour burns continuously for five seconds. The Fire Point is always higher than flash point by 5 to 8^0C.

A Pensky Martin Flash Point (closed) apparatus as shown in Plate 3.7 was used for measuring the Flash and Fire Point of the fuel samples. The sample was filled in the test cup up to the specified level and heated by heating the air bath with the help of a heater. The fuel sample was stirred at a slow constant rate. The sample was heated in such a way that rate of temperature rise was approximately 5^0C per min. The temperature was measured with the help of a thermometer of -10 to 400^0C range. At every 1^0C temperature rise, flame was introduced for a moment with the help of a shutter. The temperature at which a flash appeared in the form of sound and light was recorded as flash point. The Fire Point was recorded as the temperature at which fuel vapour catches fire and stays for minimum of five seconds.

3.3.6 Ash content

Ash in a fuel can result from oil, water soluble material compounds or extraneous solids, such as dirt and rust. The ash content of diesel, Tung oil, methyl ester of Tung oil and their blends with diesel fuel was measured as per the standard **ASTM D482-IP 4** of Institute of Petroleum, London. An electric Muffle Furnace of Wiswo make was used in the experiment as shown in Plate 3.8. In order to measure the ash content, sample was taken in a silica dish. The dish was first weighed empty and then with the fuel sample. The sample weight was obtained from the difference between the initial and final weight of the dish. The sample was then placed in the muffle furnace and heated at 775 ± 25^0C for two hours. The dish was then cooled to room temperature in a desiccator. Thereafter, the dish was weighed to the nearest 0.01 mg using an electronic balance described in Section 3.3.2. Each sample was replicated three times. The ash content was obtained using the equation given below

$$A_s = \frac{Wa}{Ws} \times 100$$

where,

A_s = Ash content, %

W_a = weight of ash, g

W_s = weight of sample, g

3.3.7 Carbon residue

Carbon residue was determined for different fuels by the method specified in the standard **ASTM D189–IP 13** of Institute of Petroleum, London. This procedure determines the amount of carbon residue left after evaporation and pyrolysis of an oil. It is intended to provide some indication of relative coke forming properties. In this method, 10 g weight to the nearest 5 mg of each fuel sample was weighed free of moisture and other suspended matter into an iron crucible of the apparatus. The crucible was then placed in the center of skidmore crucible of the apparatus and the sand was leveled in the large sheet iron crucible and then the skidmore crucible was set on it in the exact centre of the iron crucible. Thereafter, the covers were applied to both skidmore and iron crucible loosening the latter fitting to allow free exit to the vapours as it is formed. The fuel sample was then heated with a high strong flame from gas burner for 20 min. When the smoke appeared on the chimney, immediately the burner was moved or tilted so that the gas flame plays on the sides of the crucible for the purpose of igniting the vapours. After that the ignited vapour was burnt uniformly with the flame above the chimney for another period of time. When the vapour ceased to burn and no further smoke was observed, the burner was adjusted and the heat was held as at the beginning to make the bottom and the lower part of the sheet iron crucible a cherry red for about 15 min. Thereafter, the burner was removed and allowed to cool until no smoke appeared. The cover of skidmore was then removed with a tong and was cooled and weighed. The percentage of carbon residue on the original sample was then calculated using the equation as given below:

$$C_r = \frac{W_c}{W_s} \times 100$$

where,

C_r = carbon residue, %
W_c = weigh of carbon residue, g
W_s = weight of the sample, g

3.3.8 Acid value

Free fatty acids present in a vegetable oil or their esters may be corrosive to some engine parts. At elevated temperatures, free fatty acids may react with many metals producing fatty acid metal salts thus increasing wear. Acid value is, therefore, an important characteristic to be measured. The acid value is measured in terms of total acidity which is defined as a measure of combined organic and inorganic acidity. The inorganic acidity is a measure of the mineral acids present whereas the organic acidity is obtained by deducting the inorganic acidity from the total acidity. The total acid value of different fuel samples was measured as per **ASTM D974–IP 1/64** of Institute of Petroleum, London. The procedure described below was followed in order to determine total acidity of various fuels selected for the study:

- Prepare standard of potassium hydroxide reagent in the following manner:
    - dissolve 1.5 g silver nitrate in 3 ml of water and add 1 litre of 95 percent alcohol to it.
    - dissolve 3 g of potassium hydroxide in 10 – 15 ml of warm alcohol and add it to alcoholic silver nitrate solution with slight stirring.
    - allow the mixture to settle for a week.
    - thereafter distill the clear supernatant solution off the alcohol on a steam bath to recover the reagent.
    - now dissolve 6 g solid potassium hydroxide in 1 litre of purified alcohol reagent as proposed above.
    - allow the solution to settle in dark place for 24 hours and calculate the normality.
- Analyze total acidity of a fuel sample in the following manner:
    - weigh 10 ml sample in to 250 ml conical flask.
    - add 1 ml of phenolphthalein solution to 50 ml of alcohol in another flask and heat it to 50^0C and neutralize with potassium hydroxide reagent as proposed above.
    - add neutralized alcohol and phenolphthalein solution to the fuel sample.
    - heat the mixture to the boiling point on a water bath for 5 min.
    - add 1 ml of phenolphthalein to the mixture and cool it to 40 -50^0C.

- titrate as quickly as possible the sample with the potassium hydroxide reagent.

During the course of study, each sample was replicated three times. The total acidity of a fuel sample was then calculated using equation given below:

$$A_t = \frac{56.1 N \times V}{W}$$

where,

A_t = total acidity, mg of KOH/g

V = volume of potassium hydroxide solution, ml

N = normality of the potassium hydroxide solution

W = weight of sample, g

3.4 Fuels selected for Engine Test for Exhaust Emissions Measurement

The kinematic viscosity of 15 fuels as shown in Table 3.4 indicates that some fuel blends had the viscosity above 7.5 cS which is the upper limit specified for diesel by **IS: 1460- 1974.** In view of this the fuel types as shown in Table 3.5 were selected for the engine test which had kinematic viscosity with in the range specified in the BIS Standard.

Table 3.4 Fuel Types Selected for Engine Test

SL. No	**Fuel Type**	**Fuel content (%, v/v)**	
		Diesel	**Tung Biodiesel/Methyl ester**
1	Diesel	100	0
2	Tung biodisel: Diesel (B10)	90	10
3	Tung biodisel: Diesel (B15)	85	15
4	Tung biodisel: Diesel (B20)	80	20

3.4.1 Engine specification

Details of the engine and other components of the test set up used alongwith general procedure are described. The performance evaluation of a 3.73 kW engine on selected fuels was carried out. The engine specification is shown in Table 3.6.

Table 3.5 Engine Specification

Parameters	Details
Make	Kirloskar
Model	AVI
Rated Engine Brake Power, kW	3.73
Rated Engine Speed, rpm	1500
Number of Cylinder	1
Bore, mm	80
Stroke, mm	110
Displacement Volume, cc	252.9
Compression Ratio	16.5:1
Cooling System	Water Cooled
Lubricating System	Force Feed
Standard Injection Advance, ^{0}BTDC	27

3.4.2 Experimental set-up

The engine test set-up available in the Department of Biofuel CSIR-CMERI, Ludhiana was used. The set-up includes the following facilities:

- a SAJ make, EC–15 eddy current dynamometer with electronic controller .
- a Kirloskar make, 3.73 kW, constant speed engine .
- a SAJ make, SFV–75 model electronic volumetric fuel consumption measuring unit .
- a Nucon make, model 4900 hydrocarbon analyzer.
- a Nucon make, model 500, nitric oxide analyzer.
- a Nucon make, model 500, nitrogen dioxide analyzer.
- digital temperature indicators with chromal-alumal thermocouples for measurement of

3.4.3 Exhaust Emissions Measurement

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

The exhaust emission parameters were analyzed by the horiba and flue gas analyzer. The exhaust emissions parameters with their respected test methods are given in Table 3.2

Table 3.6 Emission parameter test method

S.NO.	Parameters	Test methods
1.	Hydro carbon as HC (ppm)	Nucon analyzer.
2.	Carbon monoxide as CO (ppm)	Nucon GC
3.	Nitrogen oxides (NO) as NO_X (ppm)	Nucon gas analyzer
4.	Carbon dioxide as CO_2 (%)	Nucon gas analyzer

3.4.3.1 Carbon monoxide emission

The CO contents of exhaust gases emanating from burning of different fuel types at different load conditions were analyzed using a Nucon – 5700 gas chromatograph **Fig** having conditions set for analysis as shown in Table 3.7

In order to determine the CO content at different load conditions, the exhaust gas samples were collected in 20 ml syringe as shown in Plate 3.13. The gas chromatograph was calibrated by injecting 1 ml standard CO sample having 1.05 percent CO in nitrogen using a Hamilton make gas tight syringe. The elution times as well as peak obtained as shown in Fig.3.2 were recorded. Thereafter, 1 ml sample from the exhaust gas samples already collected in 20 ml syringe was injected in to the chromatograph. The elution times as well as peak obtained were again recorded (Fig. 3.3). The amount of CO in the unknown sample was determined by comparing the peak of unknown sample with that of standard one. Each sample was replicated thrice and the average was calculated.

Fig.3.1 Gas Liquid Chromatograph Used for Measurement of Carbon Monoxide

Table 3.7 Conditions of Gas Chromatograph Set for CO Analysis

Column	Stainless Steel, 1800 mm long, 3 mm Outer Diameter, 60 / 80 mesh Porapack Q
Detector	Flame Ionization Detector with Methanizer
Carrier Gas	Nitrogen
Carrier Gas Flow Rate, ml/min	36
Oven Temperature, ^{0}C	80
Detector Temperature, ^{0}C	50
Injector Temperature, ^{0}C	50
Methanizer Temperature, ^{0}C	200

3.4.3.2 Unburnt hydrocarbon emission

The measurement of unburnt hydrocarbon in the exhaust gases was made using a Nucon make, model 4900 hydrocarbon analyzer (Plate 3.14). The exhaust gas sample was fed into the analyzer through a pump. The pump operating on 230V AC draws the sample from the exhaust manifold through a 3 mm diameter PVC tube and supplies it to the analyzer. The analyzer has an electrochemical sensor and indicates the percent unburnt hydrocarbon in exhaust gas. The total range of the analyzer was 0–10 percent. The measurements of unburnt hydrocarbon were made at different load conditions.

Fig.3.2 Unburnt Hydrocarbon Analyser

3.4.3.3 Nitric oxide emission

A Nucon make nitric oxide analyzer, model 500–NO (Plate 3.15) was used for the measurement of nitric oxide in the exhaust gas. The instrument uses an electrochemical transducer that operates on 230V AC. It has a range of 0 -1999 ppm. An exhaust gas sample drawn through a pump operating on 230V AC was fed to the analyzer for the measurement of nitric oxide content in exhaust gas. The exhaust gas sample was directly drawn from exhaust gas manifold using a 3 mm PVC pipe. The measurements were made under all the selected load conditions.

3.4.3.4 Nitrogen dioxide emission

The nitrogen oxide content in engine exhaust gas emanating from burning of different fuels samples was measured with the help of a Nucon make, model 500-NO_2 analyzer (Plate 3.16). The samples were drawn from the exhaust pipe of the engine using 3 mm diameter PVC pipe through a pump operating on 230V AC and fed in to the electrochemical sensor of the analyzer. The analyzer used had a range of 0–199.9 ppm. The measurements were carried out under different load conditions.

3.4.4 Operation

3.2.2.2.1 Experimental procedure

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

CHAPTER 4

RESULT AND DISCUSSIONS

CHAPTER 4

RESULTS AND DISCUSSIONS

4 Experimental Result

The recovery of ester as well as its kinematic viscosity is affected by the esterification process parameters such as catalyst concentration, reaction temperature and molar ratio of oil and methanol used. The above parameters were standardized to obtain biodiesel of coconut oil and cottonseed oil with lowest possible kinematic viscosity and highest level of recovery. The fuel properties such as kinematic viscosity, relative density, gross heat of combustion, cloud and pour point, flash and fire point, ash content, carbon content and total acidity of Tung biodiesel were calculated.

The objective of the experiments can be categorised in the following manner:

- Optimizing of tranesterification of Tung oil.
- Comparison of diesel and its blends on emissions parameters.

4.1 Standardization and Optimizing of tranesterification of Tung oil

The effect of selected level of parameters was investigated to standardize the esterification process for Tung oil. The standirization and optimization of process for biodiesel via transesterification was evaluated on various parameter such as molar ratio, KOH concentration and reaction time . by varying these parameter, a total 27 sample were prepared. The reaction temperature was kept 60^{O}C. out of these sample a best combination with maximum yield and low vicoscity were selected as optimum parameter for transesterification. On comparision , the optimized result were obtained at mplar ratio 5:1, 1.5% KOH and at 60 min reaction time. The maximum yield 94% was obtained. The FFA content and viscosity were evaluated as o.o6 and 4.6 Cs respectively

Table 4.1 Optimization table for the production of biodiesel from Tung oil

S.N0.	molar ratio	Tung oil sample (ml)	KOH (%)	methanol (ml)	reaction time (min.)	reaction temp(^{O}C)	yield (%)	FFA	Viscosity (centi stokes)
1	4:1	100	1	17	30	60	57	0.197	-------
2	4:1	100	1.5	17	30	60	81	0.141	5.204
3	4:1	100	2	17	30	60	86	0.169	5.063
4	4:1	100	1	17	45	60	90	0.141	4.8246
5	4:1	100	1.5	17	45	60	85	0.169	4.3378
6	4:1	100	2	17	45	60	65	0.141	--------
7	4:1	100	1	17	60	60	91	.0705	4.376
8	4:1	100	1.5	17	60	60	92	0.112	4.202
9	4:1	100	2	17	60	60	70	-------	--------
10	5:1	100	1	21	30	60	73	0.098	5.899
11	5:1	100	1.5	21	30	60	84	0.084	4.717
12	5:1	100	2	21	30	60	78	0.112	4.674
13	5:1	100	1	21	45	60	96	0.126	5.611
14	5:1	100	1.5	21	45	60	68	0.112	--------
15	5:1	100	2	21	45	60	78	0.846	4.254
16	5:1	100	1	21	60	60	86	0.169	4.932
17	**5:1**	**100**	**1.5**	**21**	**60**	**60**	**94**	**0.120**	**4.6.00**
18	5:1	100	2	21	60	60	84	0.126	4.097
19	6:1	100	1	25	30	60	75	0.098	4.531
20	6:1	100	1.5	25	30	60	79	0.169	4.624
21	6:1	100	2	25	30	60	74	0.112	4.537
22	6:1	100	1	25	45	60	95	0.112	6.104
23	6:1	100	1.5	25	45	60	83	0.155	4.865
24	6:1	100	2	25	45	60	90	0.098	4.531
25	6:1	100	1	25	60	60	83	0.169	4.932
26	6:1	100	1.5	25	60	60	81	0.098	4.133
27	6:1	100	2	25	60	60	73	0.112	4.388

The various properties of optimized biodiesel were compared with those of diesel and according to the specifications provided by ASTM standards. It was observed that properties of Tung biodiesel given in Table 3.4 were conforming to the latest biodiesel standards. The calorific value of optimized Tung oil biodiesel was 9100 kcal/kg which is lower than diesel fuel. The flash and fire point of Tung seed biodiesel were observed to be higher than of diesel fuel. The cloud and pour point were also observed to be lower for biodiesel fuel.

Table 4.2 Properties of diesel and Tung oil biodiesel according to ASTM standards.

Property of oil	ASTM standards	Diesel	Tung oil(B100)biodiesel
Density kg/m^3	------------	850	885.8
Kinematic viscosity (cSt)	1.9-6.0	2.049	4.60
Flash point, ^{O}C	>130	78	194
Fire point, ^{O}C	>53	83	180
Cloud point, ^{O}C	-3 to 12	<10	-2
Pour point, ^{O}C	-15 to 10	-6	-6
Calorific value, kJ/kg	> 33000	42000	39000.0
Carbon residue, (%)	<0.05	0.0214	0.0150%
Ash content,%	0.02% max	0.02	0.02
FFA, %	<2.5	-----	0.12
pH	-----	-------	7.5

4.2 Effect of parameters on transesterification of Tung oil.

The effect of various parameters such as catalyst concentration, reaction time, molar ratio etc. on production of biodiesel from Tung oil oil through transesterification process is presented in this section.

4.2.1 Effects of catalyst concentration and reaction time on methyl ester formation.

In the present study, KOH was chosen to catalyze the reaction due to its relatively low cost. The experiments were conducted with varying catalyst concentrations and reaction times using a methanol-to-oil molar ratio of 5:1 and a reaction temperature of 60°C. The effects of these variables on the methyl ester formation are shown in Fig. 4.1

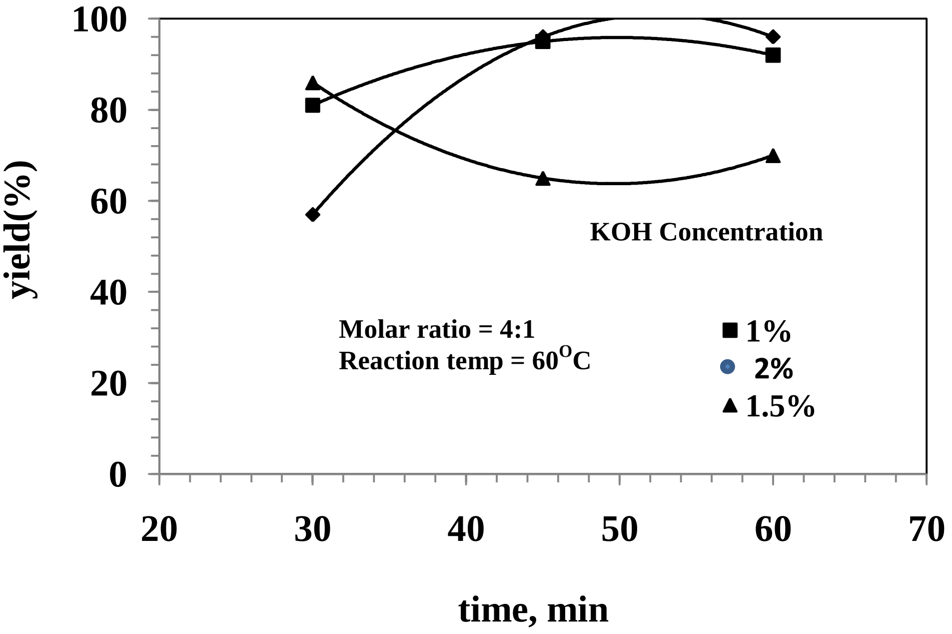


Fig 4.1 Variation of ester yield with reaction time and KOH concentration at 5:1 molar ratio

catalyst concentration is increased from 1 to 2%, the methyl ester content increases from 57% to 94% at a reaction time of 60 minutes. Further increase in catalyst concentration decreases the ester yield because of incomplete reaction due to soap formation at higher catalyst concentrations. The reason is that high FFA content in the oil deactivates the catalyst and the addition of excess catalyst as compensation gives rise to the formation of emulsion (Ma and Hanna, 1999) which increases the viscosity, leading to the formation of gels and problem associated with glycerol separation and loss

Fig 4.2Variation of ester yield with reaction time and KOH concentration at 4:1 molar ratio

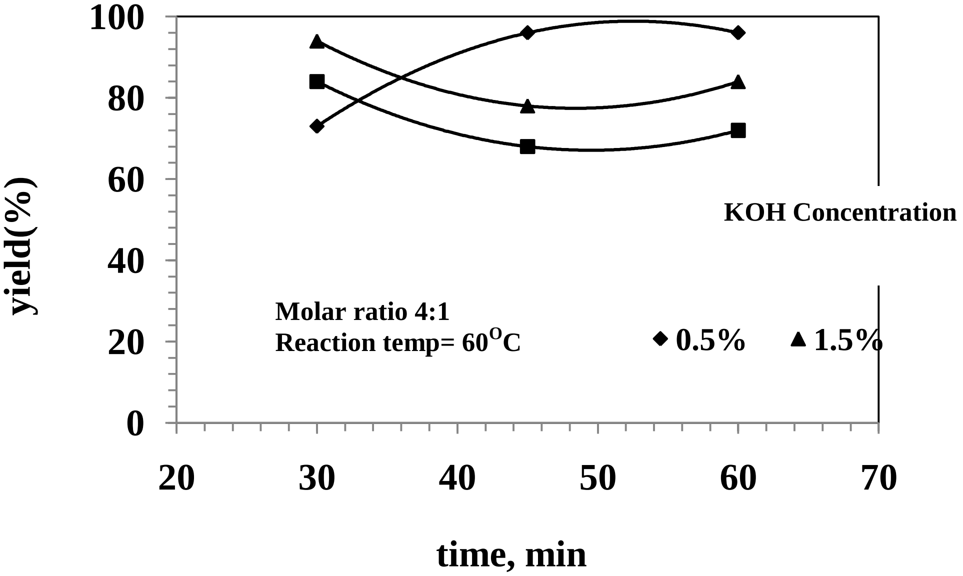
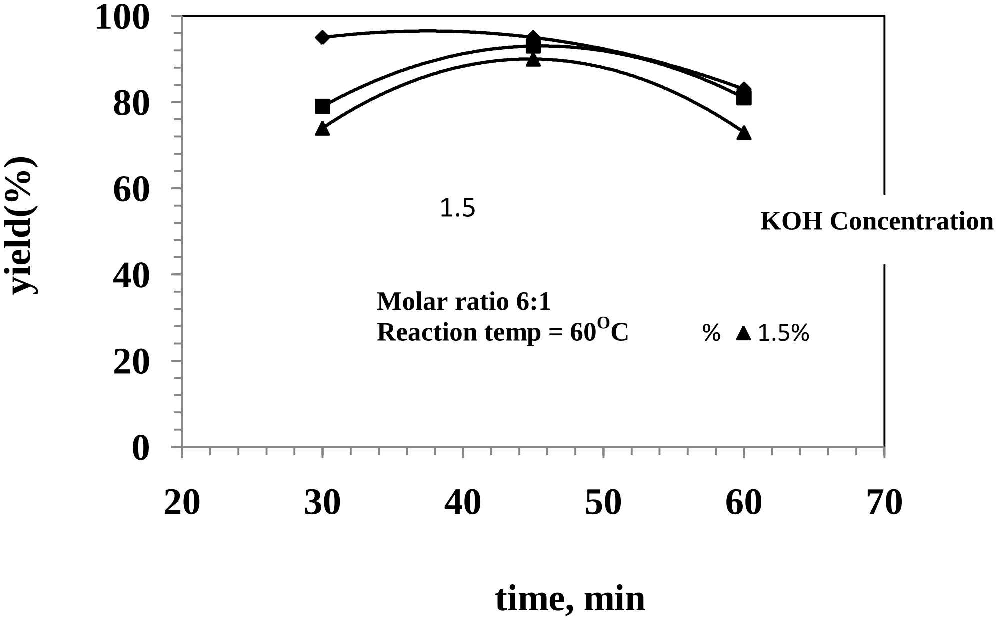


Fig 4.3 Variation of ester yield with reaction time and KOH concentration at 6:1 molar ratio



4.2.2Effects of molar ratio and reaction time on methyl ester formation:

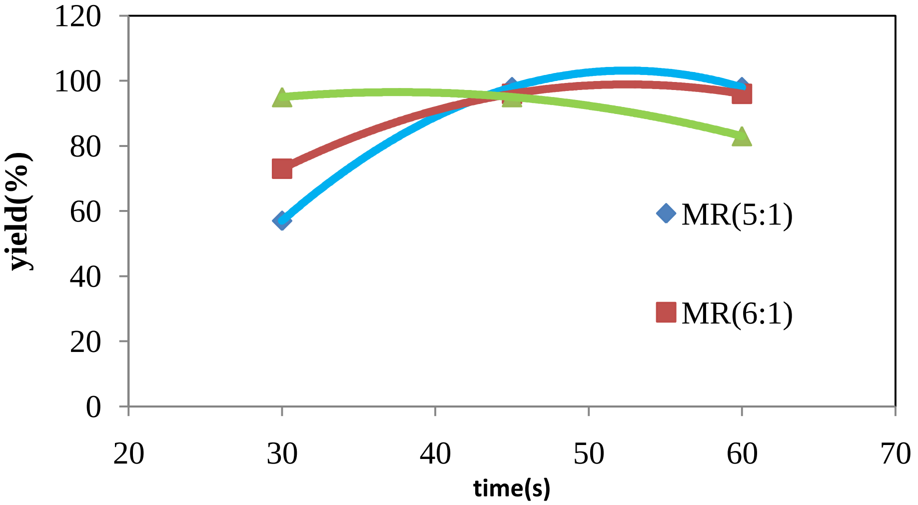


Fig4.4 Variation of ester yield with reaction time and molar ratio at 1% KOH concentration

The effect of increasing molar ratio and reaction time is illustrated in the fig. It was observed the on increasing the molar ratio the yield was increased at reaction time of 30 minutes. A maximum yield of 98 % with molar ratio (5:1), at reaction time (45min) was observed.

4.2.3 Effects of KOH concentration and molar ratio on viscosity of methyl ester

The effect of increasing KOH concentration and molar ratio on viscosity is illustrated in the figure. It was observed that with increase in molar ratio viscosity was increased and with increase in KOH concentration the viscosity was decreased.

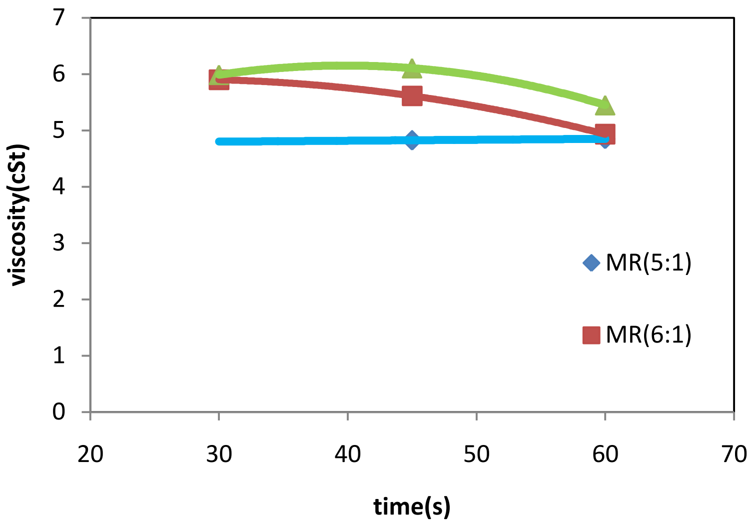


Fig4.5 Variation of viscosity with time and molar ratio

4.2.4 Effects of reaction time and molar ratio on viscosity of methyl ester

The viscosity was observed to be decreased with increase in reaction time and increased with increase in MR.

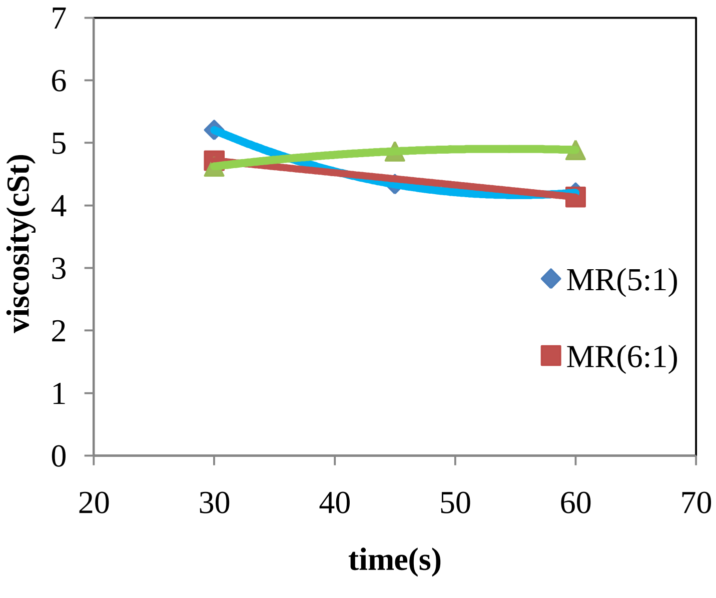


Fig 4.6 Variation of viscosity with reaction time and molar ratio.

4.3 EMISSION PARAMETERS

43.1 HYDROCARBON EMISSIONS (HC)

The variation of hydrocarbon emissions with load for diesel, B10, B15, B20 are compared at two different compression ratios. It was observed that with increase in load the hydrocarbon emission increases .It is due to entering of rich fuel air mixture in the combustion chamber because of increase in fuel consumption. This leads to improper combustion due to which unburnt hydrocarbon emissions increases. It was also observed that with increase in blend content the HC emission decreases. This is due to the high cetane no of biodiesel blends. Higher cetane no lowers the combustion delay which improves the combustion. Another reason for low hydrocarbon emission with the increase in blend content is due to more oxygen content than diesel fuel. It was observed that HC emissions for diesel fuel were highest and for B20 blend it was lowest. The HC emissions for different fuels with load at two different compression ratio is illustrated in the following figures.

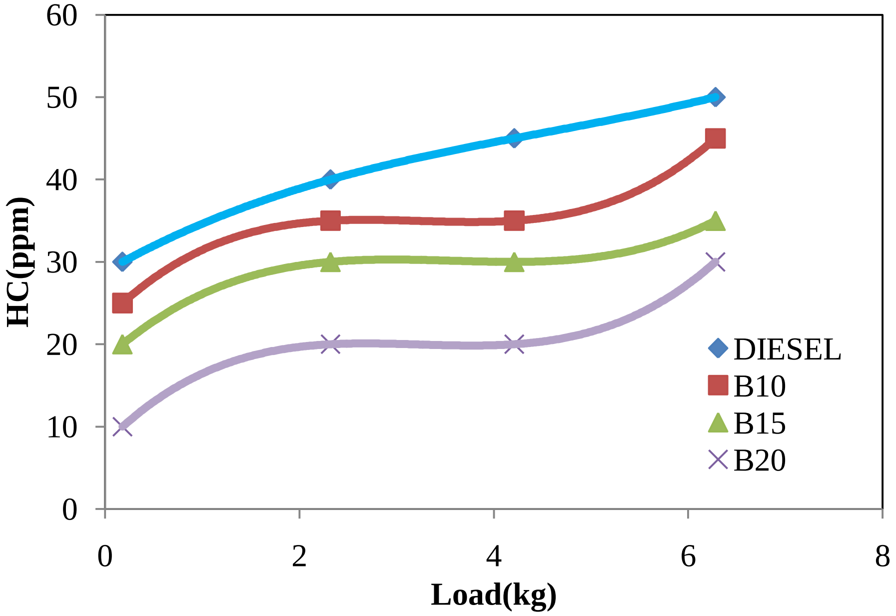


Fig 4.7 Variation of hydrocarbon emissions with compression ratio 16

4.4.2 CARBON MONOXIDE (CO) EMISSIONS

The carbon monoxide emissions results from incomplete combustion. The CO emissions for diesel fuel, B10, B15, B20 with load are compared at CR16

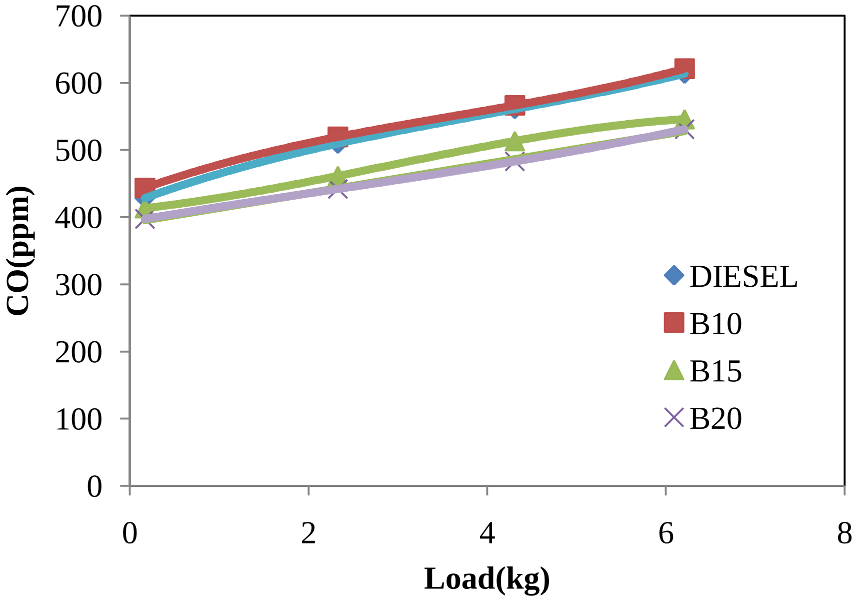


Fig4.8 Variation of carbon monoxide emissions with load at compression ratio 16

It was observed that with increase in load the CO emissions increased .This is due the injection of rich air fuel mixture which led to incomplete combustion of fuel. It was observed the CO emissions of B10 blend were nearly same as that of diesel fuel. But with further increase in blend content the emissions were observed to be decreased. This may be due to the higher oxygen content which leads to complete combustion. The CO emissions were decreased with increase in compression ratio because of increase in air temperature which lowers the delay period and improves the combustion. The CO emissions for the B20 blend at CR16 were found to be the lowest among all fuels. The CO emissions for Diesel, B10, B15, and B20 with load at CR14 compression ratios are illustrated in the fig 4.32.

4.4.3 NO_x EMISSIONS

The NO_x emissions of diesel, B10, B15, B20 with load at compression ratios CR14 and CR16 were compared. NO_x emissions are temperature dependent. It was observed that NO_x emissions increase with increase in load. This is because of increase in temperature inside combustion chamber at high loads. NOx emissions were observed to be increased with increase in blend content. This is because of high oxygen content in the biodiesel fuel. Nitrogen from air can easily mix with oxygen and produces the NO_x emissions. These emissions were observed to be increase with compression ratio due to lower ignition delay which increases the peak pressure and temperature. The NO_x emissions for diesel, B10, B15, B20 with load at CR16 and CR14 are illustrated in the following figures.

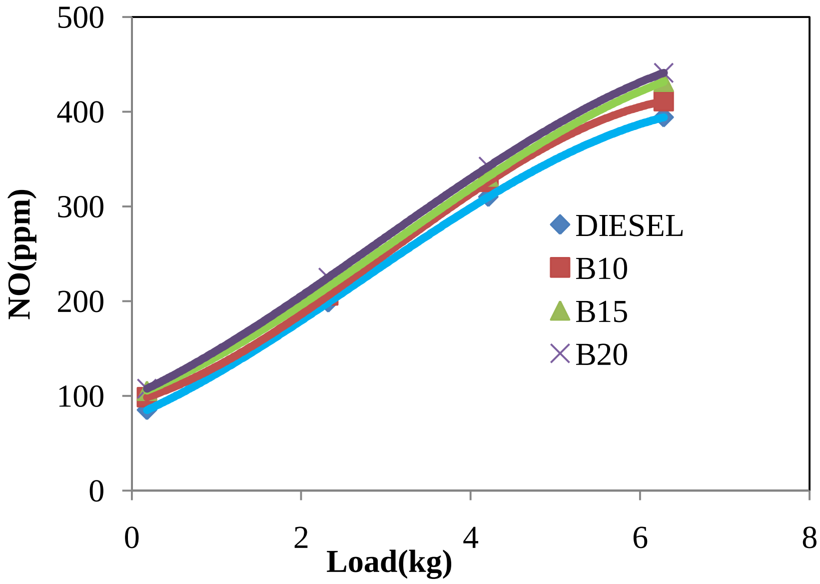


Fig 4.9 Variation of NOx emissions with load at CR16

It can be seen from the figures that NOx emissions for the diesel were lowest at both compression ratios. The NOx emissions of B20 blend were observed to be highest at all loads and both compression ratios.

4.4.4 CARBON DIOXIDE (CO_2) EMISSIONS

The CO_2 emissions for diesel, B10, B15, B20 with load at CR16 and CR14 were compared. It was observed that with increase in load the CO_2 emissions increases due to better combustion at high loads. The CO_2 emissions with diesel were highest .As the blend content increased, the CO_2 emissions were decreased. Carbon dioxide is formed on complete combustion of the fuel in oxygen. Here, carbon dioxide formation is less due to the fact that biodiesel in general is a low carbon fuel and has a lower elemental carbon to hydrogen ratio than diesel fuel. The CO_2 emissions were observed to be increased with the compression ratio this is due to the lower ignition delay that led to better combustion. The variation of CO_2 emissions with load at CR16 and CR14 are illustrated in the following figures.

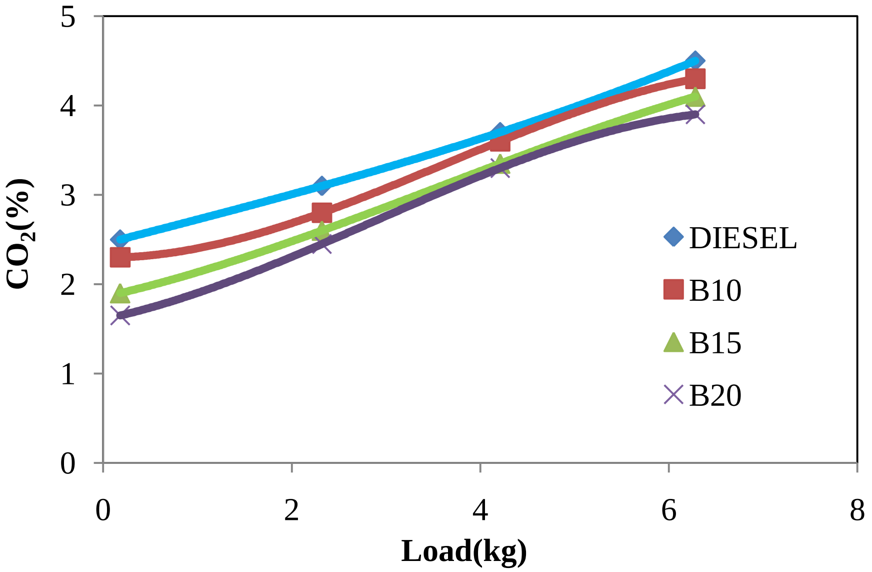


Fig4.10 Variation of CO_2 emissions with load at compression ratio16

It was observed that CO2 emissions were lowest for B20 blend at all loads for both compression ratios.

CHAPTER 5

CONCLUSION AND FUTURE SCOPE

CHAPTER 5

CONCLUSION AND FUTURE SCOPE

5.1 CONCLUSION

Present work is done to study the Standardization and optimization of biodiesel production from Tung oil using transestreification in order to design process parameter for production. The exhaust emission characteristics of Tung biodiesel blends B10, B15 and B20 were compared with diesel. Based on the results of the present work, following conclusion are drawn:

- The optimum conditions for maximum yield of biodiesel production were obtained at molar ratio of 5:1, reaction time 60 minutes and 1.5% KOH concentration. A maximum yield of 94% was determined.
- The fuel properties of optimized biodiesel were found to be comparable to diesel and were conforming to the latest biodiesel standards.
- The calorific value of optimized Tung seed biodiesel was 9100 Kcal/Kg which is lower than diesel fuel.
- The flash and fire point of Tung seed biodiesel were determined to be 180^{o}C and 194^{o}C respectively which are higher than diesel fuel.
- The cloud and pour point were also observed to be lower for biodiesel fuel.
- The emissions parameters of B10 blend such as CO, CO, and HC were nearly similar to diesel fuel. With increase in blend content these emissions were observed to be decreased. Among all blends, these emissions from B20 blend were observed to be lowest. The NOx emissions for B10 blend were observed to be lowest. The CO and HC emissions were lowered at higher compression ratio while NOx and CO2 emissions were higher at high compression ratio.

5.2 FUTURE SCOPE

Worldwide energy demands are increasing day-by-day. Major part of it is contributed by fossil fuels. Petroleum diesel being cheaper in cost has attracted the minds of people to use it as fuel in diesel engine which has increased the number of diesel fuelled vehicles. For a petroleum importing country like India it is a major concern. Due to this rapidly increasing demand of petroleum diesel biodiesel as an alternative fuel comes into consideration. Selection of inexpensive and available feedstock for biodiesel production within the country is the major concern. Tung oil is relatively an inexpensive and available raw material for biodiesel production.

- Attempts for making proper use of the unutilized Tung oil for the production of biodiesel should be undertaken by the government.
- Further studies can be carried out for making proper use of the by-products from Tung oil and prepared biodiesel.
- Long term stability study of the biodiesel and its blends in engine should be done.
- Additional investigation can be carried out for the production of ester of crude Tung oil from different alcoholic groups.
- Extensive Performance and exhaust emission of biodiesel can be done.

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