# Study of various methods of biodiesel production and properties of biodiesel prepared from waste cotton seed oil and waste mustard oil

**A thesis submitted in the partial fulfilment of the requirement for the**

**award of degree of**

**Master of Engineering**

**IN**

**Thermal engineering**

***Submitted By***

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# CERTIFICATE

I hereby declare that the work which is being presented in the dissertation work entitled **Study of various methods of biodiesel production and properties of biodiesel prepared waste cotton seed oil and waste mustard oil** in partial fulfilment of the requirements for the award of degree of Master of Engineering with specialization in THERMAL ENGINEERING submitted in the Mechanical Engineering Department of Thapar University, Patiala, is an authentic record of my own work carried out under the supervision and guidance of Mr Sumeet Sharma, Dr. K. Kundu and Dr. S.K. Mohapatra and refers other researchers works which are duly listed in the reference section.

The matter presented in this thesis has not been submitted in part or full to any other university or institute for the award of any degree.

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This is to certify that above declaration made by the student concerned is correct to the best of my knowledge & belief.

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# ABSTARCT

Biodiesel, an alternative fuel is derived from the fats of animals and plants. As energy demand increases and fossil fuels are limited, research is directed towards alternative renewable fuels. Besides exploring historical background of biodiesel production from vegetable oils, it also provides insight of different methodologies evolved for the conversion of vegetable oil in biodiesel. Properties of waste edible oil (cotton seed oil and mustard oil) have been compared with the properties of petro-diesel; showing a comparable regime for satisfactory optimized blend which is to be selected for the better performance of a C.I. engine with biodiesel. Biodiesel reportedly has number of technical advantage over petro-diesel especially on safety and environmental considerations. Cold starting, clogging and storage are some serious technological disadvantages associated with biodiesel. The work presented in this thesis is mainly divided into two main parts. In the first part study of different methods of production of biodiesel (direct blending, transesterification, pyrolysis and micro emulsion) from waste cooking oil is to be examined. The most commonly used method is transesterifcation of vegetable oils and animal fats. The transesterifcation reaction is affected by molar ratio of glycerides to alcohol, catalysts, reaction temperature, reaction time and free fatty acids and water content of oils or fats. The second part includes the study of characteristics of biodiesel prepared from vegetable oils (waste cotton seed oil and waste mustard oil).The characteristics of biodiesel are to be checked at different blends(B10, B15, B20) and select the optimum blend based on these characteristics. The characteristics include FFA value, density, viscosity, flash point and fire point, cloud point and pour point, carbon residue content and ash residue content.

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## NOMENCLATURE

| | |
|---|---|
| ICE | Internal combustion engine |
| D | Diesel |
| B100 | 100% biodiesel |
| B10 | 10% biodiesel + 90% petro diesel |
| B15 | 15% biodiesel + 85% petro diesel |
| B20 | 20% biodiesel + 80% petro diesel |
| FAME | Fatty acid methyl ester |
| ASTM | American Society of Testing and Materials |
| WCO | Waste cooking oil |
| CSME | Cotton seed methyl ester |
| MME | Mustard methyl ester |

# CHAPTER 1

# INTRODUCTION

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## Introduction

Bio-diesel is an alternative to petroleum-based fuels derived from vegetable oils, animal fats, and used waste cooking oil including triglycerides. Vegetable oils are widely available from various sources, and the glycerides present in the oils can be considered as a viable alternative for diesel fuel. They have good heating power and provide exhaust gas with almost no sulphur and aromatic polycyclic compounds. Vegetable oils are produced from plants, their burning leads to a complete recyclable carbon dioxide ($CO_2$). $CO_2$ associated with solar energy falling on earth gets converted in to the feedstock through photosynthesis. Vegetable oils available through this feedstock can be used to produce biodiesel. [1].

The use of vegetable oil for energy purposes is not new. It has been used world over as a source of energy for lighting and heating since time immemorial. As early as in 1900, a diesel-cycle engine was demonstrated to run wholly on groundnut oil at the Paris exposition. Even the technology of conversion of vegetable oil into biodiesel is not new and is well established. However the unprecedented rise in fuel prices recently has made it economically attractive. The present availability of vegetable oils in the world is more than enough to meet the edible oil requirements, and surplus quantity available can partially meet requirements of biodiesel production. However, there is a considerable potential to further enhance the oilseeds production in the world to meet the increasing demand for food and biodiesel.

## 1.1 Need for Biodiesel

Due to the increase in price of petroleum and environmental concern about pollution coming from automobile emission, biodiesel is an emerging as a developing area of high concern. The world is confronted with the twin crises of fossil fuel depletion and environmental degradation. Alternative fuels, promise to harmonize sustainable development, energy conversion, management, efficiency and environmental preservation. Vegetable oil is a promising alternative to petroleum products. The economic feasibility of biodiesel depends on the price of crude petroleum and the cost of transporting diesel over long distances to remote areas.

It is a fact that the cost of diesel will increase in future owing to increase in its demand and limited supply. A great deal of research and development on internal combustion engines has taken place not only in the design area but also in finding an appropriate fuel. Many researchers have concluded that biodiesel holds promise as an alternative fuel for diesel engines, since its properties are very close to diesel fuel. The fuel properties of biodiesel such as cetane number, heat of combustion, gravity, and viscosity influence the combustion and so the engine performance and emission characteristics because it has different physical and chemical properties than petroleum-based diesel fuel.

The consumption of diesel oil is several times higher than that of petrol. Due to the shortage of petroleum products and its increasing cost, efforts are on to develop alternative fuel especially for diesel oil for its partial replacement. It has been found that the vegetable oils are promising fuels because their properties are similar to that of diesel and are produced easily and renewably from the crops. Vegetable oils have comparable energy density, cetane number, heat of vaporization and stiochiometric air-fuel ratio with that of the diesel fuel. Vegetable oils are non-toxic, renewable sources of energy, which do not contribute to the global $CO_2$ build up. In terms of the economic benefits, vegetable fuels could be used as an emergency energy source in the event of another petroleum fuel shortage.

Vegetable oil from crops such as soybean, peanut, sunflower, rape, coconut, cotton, mustard, linseed and castor have been tried in many parts of the world, which lack of petroleum reserves as fuels for CI engines. The long chain hydrocarbon structure, vegetable oils have good ignition characteristics, however they cause serious problems such as carbon deposits build up, poor durability, high density, high viscosity, lower calorific value, more molecular weight and poor combustion. These problems lead to poor thermal efficiency, while using vegetable oil in the diesel engine. These problems can be rectified by different methods which are used to reduce the FFA value and viscosity of vegetable oils. These methods are: transesterification method, dilution method and cracking method. [1]

### 1.2 Why can vegetables oils be used as diesel fuels

The vegetable oils, animal fats, and their derivatives such as alkyl esters are suitable as diesel fuel because there must be some similarity to petro diesel fuel or at least to some of its components. The fuel property that best shows this suitability is called the cetane number. In addition to ignition quality as expressed by the cetane scale, several other properties are important for determining the suitability of biodiesel as a fuel. Heat of combustion, pour point, cloud point, (kinematic) viscosity, is among the most important of these properties. [2]

### 1.3 Background and Sources

Vegetable oils were used as emergency fuels and for other purposes during World War II. Concerns about the rising use of petroleum fuels and the possibility of resultant fuel shortages in the United States in the years after World War II played a role in inspiring a dual fuel project at The Ohio State University (Columbus, Ohio), during which cottonseed oil and corn oil, and blends with conventional diesel fuel, were investigated. Brazil prohibited the export of cottonseed oil in order to substitute it for imported diesel fuel. Reduced imports of liquid fuel were also reported in Argentina, necessitating the commercial exploitation of vegetable oils. China produced diesel fuel, lubricating oils, “gasoline,” and “kerosene,” the latter two by a cracking process, from Tung and other vegetable oils. The Japanese battleship Yamato reportedly used edible refined soybean oil as bunker fuel.[2]

In modern times, biodiesel is derived, has been derived from many different sources, including vegetable oils, animal fats, used frying oils, and even soap stock. Generally, factors such as geography, climate, and economics determine which vegetable oil is of most interest for potential use in biodiesel fuels. In the United States, soybean oil considered as a prime feedstock. In Europe, it is rapeseed (canola) oil; and in tropical countries, it is palm oil.

### 1.4 Development of Biodiesel in India

Biodiesel is a relatively new product in India. The use of vegetable oils for engine fuels may seem insignificant today. But such oil may in the course of time become as important as petroleum and the coal tar products of present time. Scientists discovered that the viscosity of vegetable oil could be reduced in a simple chemical process in 1970 and that it could work well as diesel fuel in modern engine. The fuel is called Biodiesel. It is alternative fuel that can be used in diesel engines and provides power similar to conventional diesel fuel. It reduces the countries dependence on foreign oil imports. As per its end use it is classified with petroleum products industry more particularly with diesel. Cost of petroleum products is directly proportional to the living cost of common man. Although biodiesel is new product but it is going to replace product of petroleum industry i.e. diesel in future.

The southern railway adopted a three pronged strategy of large scale processing of oil into biodiesel and making use of it for its large fleet of road vehicles and locomotives. Awareness in India is only now giving shape to projects. In Andhra Pradesh four companies viz. Southern Online Biotechnology (SBT), Tree Oils Ltrs (Zaheerabad) Natural Bio Energy and the GMR group have seriously entered into this project. Others include Vrideshwar SSK Ltd. (Ahmednagar, Maharashtra) the Simbhioly Sugar Mills (Ghaziabad, Uttar Pradesh), Mewar Sugar Mills (Jaipur) SM Dyechem (Thane, Maharashtra) R.S. Petrochemicals (Punjab) and Progressive Petroleum (Mumbai). The Aditya Birla group proposed a project in Malaysia, which did not come off. All of them feel that government should offer incentives to offset risk of a Greenfield area. [1]

### 1.5 Vegetable Oil acts as a C .I. Engine Fuel

Vegetable oil can be produced from plant sources, which are viable to produce on a mass scale or in local rural areas on many land conditions. The various edible vegetable oils like sunflower, soybean, peanut, cotton seed etc have been tested successfully in the diesel engine. Research in this direction with edible oils yielded encouraging results. Diesel is produced from crude oil, biodiesel is produced from vegetable oils and either edible or non edible oils can be used depending on their properties, using diesel derived from vegetable oils is not a new idea. When Rudolf Diesel invented the diesel engine he used peanut vegetable oil fuel in Paris as an alternative to diesel. Using straight vegetable oils as a fuel substitute an option but only with many modifications to be performed on the engine itself for continued satisfactory engine performance. In future more advanced engines may be designed to cope with these crude oils. However at the current time and for a transition period to a cleaner fuel system biodiesel is a viable option**.** To allow the use of vegetable oils as a fuel without modification of the engine, the fuel needs to be modified for compatibility with the engine. As the diesel engines are designed for diesel fuel any substitute needs to have similar properties for the engine to operate satisfactorily. Biodiesel is a viable opportunity that will not incur large costs for a new infrastructure as the storage and distribution will be the same as the diesel infrastructure.

### 1.6 Advantages and Disadvantages of Straight Vegetable Oil as C. I. Engine Fuel

The vegetable oil has found good application in diesel engine since its invention. Most of the oils are compatible with diesel fuel, hence blending of vegetable oil with diesel is one possible option and time consuming, and oil quality depending transesterification process can be eliminated. Crude vegetable oil has a high viscosity compared to diesel, which can give rise to many problems. If the oil is too viscous, in cold conditions the oil may solidify to such an extent that it will not flow into the engine correctly; also resulting in the injector is choking and ring sticking. Even if solidification is slight it will clog the fuel filter and nozzle, starving the engine of fuel. Viscous fuel will not disperse correctly in the cylinder once released from the nozzle and therefore will not mix with the compressed air, causing large quantities of unburnt HC emissions and low fuel efficiency. The high viscosity has been shown to cause problems if the engine is started in cold conditions. [1]

### 1.7 Technical Aspects

The kinematic viscosity of vegetable oils is about an order of magnitude greater than that of conventional, petroleum-derived diesel fuel. High viscosity causes poor atomization of the fuel in the engine's combustion chambers and ultimately results in operational problems, such as engine deposits. Since the renewal of interest during the late 1970s in vegetable oil derived fuels, four possible solutions to the problem of high viscosity have been investigated: transesterification, pyrolysis, dilution with conventional petroleum-derived diesel fuel, and micro emulsification. [2]

### 1.8 Alternative Fuels

#### A. Compressed Natural Gas (CNG)

Natural gas is a mixture of hydrocarbons-mainly methane and is produced either from gas wells or in conjunction with crude oil production. Due to its lower energy density for use as a vehicular fuel, it is compressed to a pressure of 20-25 MPa to facilitate storage in cylinders mounted in vehicle and so it is called Compressed Natural Gas. India's recoverable resources of more than 690 billion cubic meters make it a long-term substitute fuel for use in petrol & diesel engines. Low exhaust emissions, low noise, less maintenance, not prone to adulteration, driver's comfort etc are some of the attractive features of CNG as an automotive fuel. CNG is now established as a very successful alternative fuel for automobiles throughout the world. Infrastructure, onboard storage & issues on safety need proper attention for this fuel [7].

#### B. Liquefied Petroleum Gas (LPG)

LPG is a by-product of Natural Gas processing or product that comes from crude oil refining and is composed primarily of propane and butane with smaller amounts of propylene and butylenes. Since LPG is largely propane, the characteristics of propane sometimes are taken as a close approximation to those of LPG. Reduction in emissions, very less carbon build-up increases life of engine parts like spark plugs, little or no damage to soil or water if it is spilled, due to its rapid evaporation, higher octane number are some of the advantages of LPG fuel. In the initial stages of introduction of this fuel, issues like safety, storage and handling, extreme volatility of the fuel etc. needs proper attention.

### C. Methanol

Methyl alcohol - wood alcohol - may be obtained organically by the distillation of hardwoods at high pressure and a temperature of around 350°C itself a high energy consuming process. With a far higher cumulative toxicity rating than ethanol, the energy content is around 3.7 kWh per litre (about one third that of petrol), making it a less attractive alternative transport fuel. Trying to mix methanol with petrol brings problems - they are not entirely compatible, and the slightest amount of water absorbed by the fuel causes the alcohol to separate out in the bottom of the tank. Additives are commercially available, but this adds to the fuel cost. [1]

### D. Ethanol

Ethanol is a clear, colourless liquid with a characteristic, agreeable odour. In dilute aqueous solution, it has a somewhat sweet flavour, but in more concentrated solutions it has a burning taste. Ethanol has been made since ancient times by the fermentation of sugars. All beverages- ethanol and more than half of industrial ethanol is still made by this process. It can be made from raw materials such as sugarcane, sorghum, corn, barley, cassava, sugar beets etc using already improved and demonstrated technologies. Ethanol is used as an automotive fuel by itself and can be mixed with gasoline to form what has been called "gasohol" or can be mixed with diesel to form diesohol or E-diesel. Because the ethanol molecule contains oxygen, it allows the engine to more completely combust the fuel, resulting in fewer emissions.

## Selection of an Alternative Fuel

Some of the requirements of fuel which must be put under consideration while selecting Alternative fuels are as given below:

- It should be produced locally to cut transport cost and supply difficulty, to free foreign currency for other uses, and to reduce local under-employment.
- It should need only simple production plant to give low capital and cheap maintenance.
- It should require the minimum alteration to the engine to keep initial cost down and to

enable a return to diesel use if the alternative supply fails.

- It should have minimum harmful effect on the engine to ensure reliability and to reduce the need for skilled maintenance.

Selection of suitable renewable source of energy in place of petroleum fuels depends upon social, political, ecological, economical and technical factors. The fuels such as CNG, LPG, Propane, Hydrogen, Alcohols, Biogas, Producer gas, and derivatives of vegetable oils are receiving more & more attention. But as far as India is concerned because of its vast agro-forestry base, fuels of bio-origin can be considered to be ideal alternative renewable fuels to run the internal combustion engines. The bio-origin fuels could be Biogas, Biomass, Producer gas and derivatives of Vegetable Oils, which can be modified to bring their properties comparable to fossil fuels. Modern bio-energy options offer significant, cost-effective and perpetual opportunities toward meeting emission reduction targets while providing additional ancillary benefits arising from the wide occurrence of biomass materials. These include social benefits of employment in the growing, harvest and processing of biomass resources. [1]

### 1.7 Biodiesel

Biodiesel is an alternative fuel formulated exclusively for diesel engines. It is made from vegetable oil or animal fats or it is the name for a variety of ester based fuels generally defined as the mono alkyl esters made from vegetable oils through simple transesterification process.

Use of biodiesel in CI engine:

- It is recommended for use as a substitute for petroleum based diesel mainly because biodiesel is a renewable, domestic resource with an environmentally friendly emission profile and is readily biodegradable.
- Biodiesel is nontoxic, biodegradable. It reduces the emission of harmful pollutants from diesel engines (80% less $CO_2$ emissions, 100% less sulphur) but emissions of nitrogen oxides are increased.
- Biodiesel has a high cetane number. The high cetane numbers of biodiesel contribute to easy cold starting and low idle noise.
- The use of biodiesel can extend the life of diesel engines because it is more lubricating and furthermore, power output are relatively unaffected by biodiesel.

## 1.8 Likely impact of localized renewable energy generation using biodiesel in developing countries [5]

Likely important outcomes of localized energy generation using biodiesel in developing countries are as follows:

1) As fuel in stationary or mobile engines for water pumping (irrigation), grain milling, and transportation, lighting and heating and cooking.

2) Poverty reduction, especially that of women, by stimulating economic activities in rural areas by using the products of such plants for the manufacture of soap, medicines, lubricants, chemicals, fertilizers, insecticides.

3) Environment improvement through land reclamation, erosion control, enhanced soil fertility, a better microclimate and GHG mitigation i.e. expanded options for carbon dioxide abatement.

4) A reduced consumption of firewood and residues in rural areas hence a decrease in the deforestation rate.

5) An increase in the gross domestic product (GDP).

6) A reduction of expenditure of imported fuels for rural consumption.

7) The establishment of decentralized energy generation based on the use of plant oil.

## 1.9 Biodiesel Production Methods

**1. Direct use and Blending:** In this method, vegetable oils are directly mixed with the diesel.

The advantages of vegetable oils as diesel fuel are:

(1) Liquid nature-portability
(2) Heat content (80% of diesel fuel)
(3) Ready availability
(4) Renewability

The disadvantages are:

(1) Higher viscosity
(2) Lower volatility
(3) The reactivity of unsaturated hydrocarbon chains.

Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines.

The problems include:

(1) Fuel atomization does not occur properly

(2) Carbon deposits

(3) Oil ring sticking

(4) Thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils [4]

Known problems, probable cause and potential solutions for using straight vegetable oil in diesels show in below table 1.1[18]

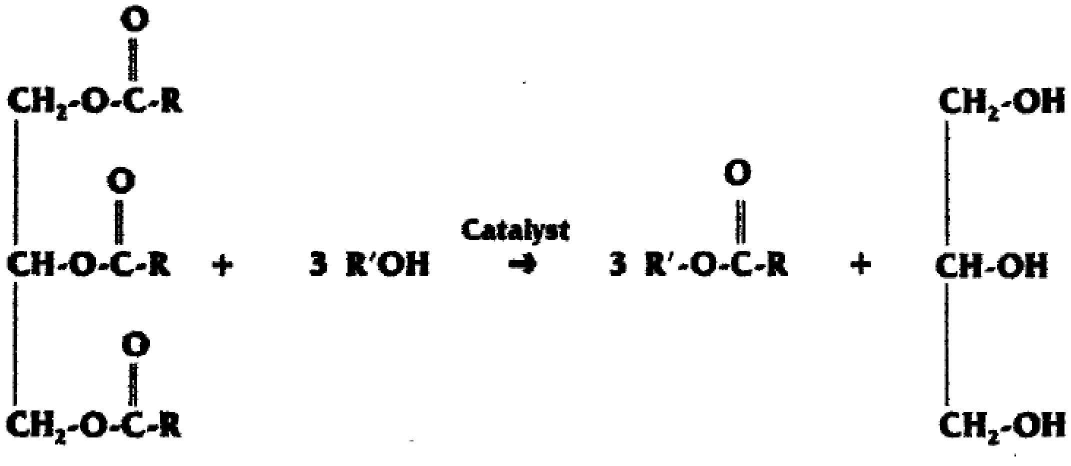
| Problem | Problem cause | Potential solution |
|---|---|---|
| Short-term | | |
| Cold weather starting | High viscosity and low flash point of Vegetable oils | Preheat fuel prior to injection |
| Plugging and gumming of filters, lines, injectors | Natural gums in vegetable oils, ash particles | Partially remove the oil to remove gums. |
| Engine knocking timing | Improper injection | Adjustinjection timing |
| Long-term | | |
| Carbon deposit on piston and head of engine | High viscosity of vegetable oils,incomplete combustion of fuel | Preheat fuel prior to injection |
| Excessive engine wear | Poor combustion at part load with vegetable oils,possibly free fatty acids in vegetable | Preheat fuel prior to injection, switch engine to diesel fuel operations at part load |

**2. Transesterification:** The majority of the methyl esters are produced using the base catalysed reaction because it is the most economic for several reasons [18]

- low temperature and pressure
- high yields and short reaction times
- direct conversion process
- simple in operation and environmentally benign

Transesterification can be defined as the process of reacting a triglyceride (oil) with an alcohol (e.g., methanol or ethanol) in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to chemically break the molecule of the oil into methyl or ethyl esters. Glycerine, also known as glycerol, is the by-product of this reaction. The process is similar to hydrolysis, except than alcohol is used instead of water. The general scheme of the transesterification reaction and the related process arrangement are shown in Schemes 2.1.

Biodiesel is produced through a process known as transesterification, as shown in the equation:



**Triacylglycerols (Vegetable oil)** **Alcohol** **Alkyl Ester (Biodiesel)** **Glycerol**

**Figure 1.1**

Where R is a long hydrocarbon chain, sometimes called fatty acid chains. [2]

**Flow chart of Transesterification process [18]**

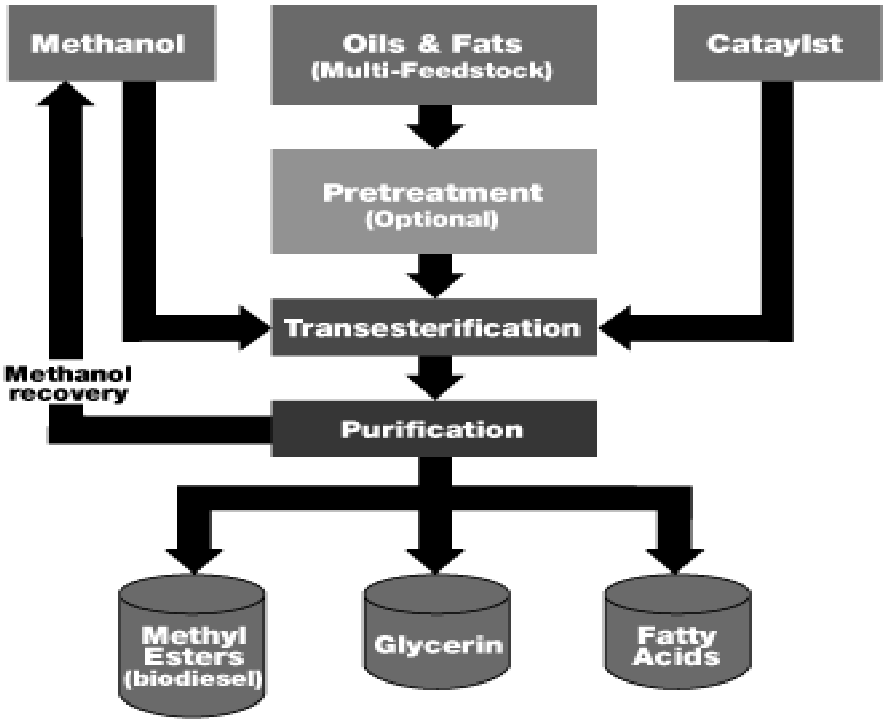


Figure: 1.2

A typical supply chain includes the production of vegetable oils or provision of other feedstock. The extracted and purified oils/fats than undergo the conversion to biodiesel in the production plant. The product, after purification steps is distributed to the end user.

**Feed Stock supply and biodiesel production and distribution [18]**

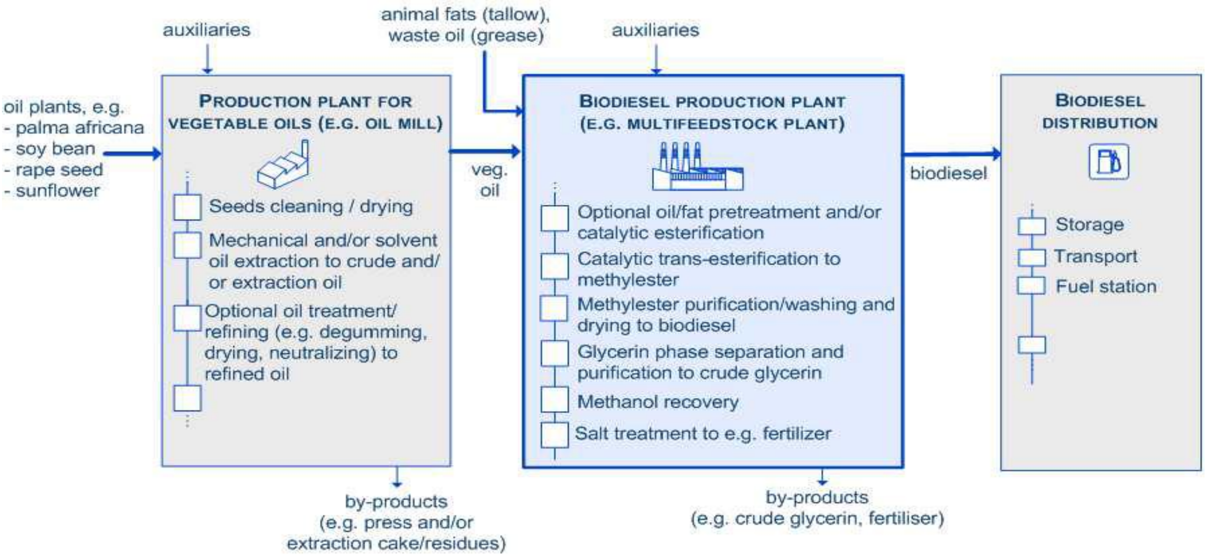


Figure: 1.3

Critical quality parameters in the process are:

- Complete reaction
- Removal of glycerol
- Removal of catalyst
- Removal of alcohol
- Absence of free fatty acids
- Low sulphur content

Methanol is used as the alcohol for producing biodiesel because it is the least expensive alcohol, although other alcohols such as ethanol may yield a biodiesel fuel with better fuel properties but it is expensive. Often the resulting products are also called fatty acid methyl esters (FAME) instead of biodiesel. The amount of alcohol used can be reduced by conducting the reaction in steps, where part of the alcohol and catalyst are added at the start of each step, and the glycerol is removed at the end of each step. Free fatty acids in the oils or fats can be converted to alkyl esters with an acid catalyst also. This can be followed by a standard alkali-catalysed transesterification to convert the triglycerides. Acid catalysts can be used for the transesterification of oils to alkyl esters, but they are much slower than alkali catalysts. [19]

**By-products issues**

An important aspect is that related with glycerol, the principal by-product of this process. It occurs in vegetable oils at a level of approximately 10 % by weight. Crude glycerol possesses very low value because of the impurities. However, as the demand and production of biodiesel grows, the quantity of crude glycerol generated will be considerable, and the utilization of it will become an urgent topic. Refining of the crude glycerol will depend on the economy of production scale and/or the availability of a glycerol purification facility. It is generally treated and refined through filtration, chemical additions and fractional vacuum distillation to yield various commercial grades. Small to moderate scale producers who cannot justify the high cost of purification find crude glycerol utilization or disposal to be a problem. Larger scale biodiesel producers refine their crude glycerol and move it markets in the food, pharmaceutical and cosmetic industries. There are a plenty of added value chemicals that can be obtained from glycerol.

**3. Pyrolysis (cracking):** Thermal cracking or pyrolysis is the process that causes the break of the molecules by heating at high temperatures that is, by the heating of the substance in the absence of air or oxygen in temperatures superior to 450°C, forming a mixture of chemical compounds with properties very similar to those of petro diesel. In some situations that process is supported by a catalyst for the break of the chemical connections, in order to generate smaller molecules. Differently of direct mixture, fats can be pyrolysis object for the production of smaller chain compounds. The pyrolysis of fats has been investigated for more than 100 years, especially in countries with small oil reserves. Typical catalysts to be used in the pyrolysis are the silicon oxide $SiO_2$ and aluminium oxide $Al_2O_3$.

The equipment for pyrolysis or thermal cracking is expensive. However, the products are chemically similar to diesel oil. The removal of the oxygen of the process reduces the benefits of an oxygenated fuel, reducing its environmental benefits and usually producing a fuel closer to gasoline than diesel. By the international nomenclature, the fuel produced by thermal cracking is not considered biodiesel, in spite of being a biofuel similar to the diesel oil. Cracking has great applicability in places that need smaller production volume and with smaller availability of qualified work.

The catalytic or thermal cracking produces a mixture of condensed hydrocarbons with output of around 80% in an organic phase. There is an aqueous phase, around 5% to 10% and the remaining are gases. Cracking has as strong point the absence of formation of aromatic compounds, of great pollutant potential. [3]

**4. Micro emulsion:** To solve the problem of the high viscosity of vegetable oils, micro emulsions with solvents such as methanol, ethanol and 1-butanol have been studied. A micro emulsion is defined as thermodynamically stable, isotropic liquid mixtures of oil, water and surfactant (compounds that lower the surface tension of a liquid, the interfacial tension between two liquids). They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles (an aggregate of surfactant molecules dispersed in a liquid colloid). [4]

### 1.12 Fuel Properties of selected fuels

The fuel characteristics include the physical and chemical properties of the fuel such as viscosity of fuel, pour and fire point of fuel, calorific value of fuel. The brief introduction regarding these properties is as follow:

#### A. Density

Bio-diesel is slightly heavier than conventional diesel fuel (specific gravity 0.88 compared to 0.84 for diesel fuel). This allows use of splash blending by adding bio-diesel on top of diesel fuel for making bio-diesel blends. Bio-diesel should always be blended at top of diesel fuel. If bio-diesel is first put at the bottom and then diesel fuel is added, it will not mix.

#### B. Kinematic viscosity

Viscosity is an important physical property of a diesel fuel. Improper viscosity leads to poor combustion, which results in loss of power and excessive exhaust smoke. Diesel fuels with extremely low viscosities may not provide sufficient lubrication for the closely fit pumps and Injector plungers. They can promote abnormal wear and cause injector and injector pump leakage and dribbling leading to loss of power as fuel delivered by the injector is reduced. Diesel fuel with higher viscosity is also not desirable as too viscous fuel increases pumping losses in injector pump and injectors, which reduces injection pressure resulting in poor atomization and inefficient mixing with air ultimately affecting the combustion process. [1]

#### C. Flash Point and fire Point

Flash point of a fuel is defined as the temperature at which it will ignite when exposed to a flame or spark. The flashpoint of bio-diesel is higher than the petroleum based diesel fuel. Flashpoint of bio-diesel blends is dependent on the flashpoint of the base diesel fuel used, and increase with percentage of bio-diesel in the blend. Thus in storage, biodiesel and its blends are safer than conventional diesel. The flashpoint of biodiesel is around 160, but it can reduce drastically if the alcohol used in manufacture of bio-diesel is not removed properly. Residual alcohol in the bio-diesel reduces its flashpoint drastically and is harmful to fuel pump, seals, elastomers etc. It also reduces the combustion quality.

#### D. Water content or Moisture content

Biodiesel and its blends are susceptible to growing microbes when water is present in fuel. The solvency properties of the biodiesel can cause microbial slime to detach and clog fuel filters**.** It affects on quality of biodiesel. High content of above property disturbs standard specification of biodiesel. It causes blockage of fuel filter and fuel lines.

### E. Cloud Point

Cloud point is the temperature at which a cloud or haze of crystals appear in the fuel under test conditions and thus becomes important for low temperature operations. Biodiesel generally has higher cloud point than diesel fuel.

### F. Pour Point

Normally either pour point or CFPP (Cold Filter Plugging Point) are specified. French and Italian bio-diesel specifications specify pour point whereas others specify CFPP. Since CFPP reflects more accurately the cold weather operation of fuel, it is proposed not to specify pour point for bio-diesel. Pour point depressants commonly used for diesel fuel do not work for biodiesel.

### G.FFA content

If the oil has a high water or free fatty acid (FFA) content the reaction will be unsuccessful due to saponification (saponification is defined as the reaction of an ester with a metallic base and water) commonly known as making soap, and make separation of the glycerol difficult at the end of the reaction. The FFA content of the raw oil will determine the quantity of biodiesel as the final product. A very low content of FFA (<0.2) can give a full 100% yield. [1]

### H. Calorific value

The total quantity of heat liberated by completely burning of one unit mass of fuel. The calorific value of a substance is the amount of energy released when the substance is burned completely to a final state and has released all of its energy.

### I. Ash content

It describes the amount of inorganic contaminants such as abrasive solids and catalyst residues and the concentration of soluble metal soaps contained in a fuel sample. These compounds are oxidized during the combustion process to form ash which is connected with engine deposits.

### J. Carbon residue content

It is correlates with respective amounts of glycerides, free fatty acids, soaps and catalyst residue. The parameter serves as a measure of the tendency of a fuel sample to produce deposits on injector tips and inside the combustion chamber. It is also influenced by high concentration of polyunsaturated fatty acid methyl esters and polymers. ［1］

### 1.13 Benefits of Biodiesel

Biodiesel is a domestically produced, clean-burning, renewable substitute for petroleum diesel. Using biodiesel as a vehicle fuel increases energy security, improves public health and the environment, and provides safety benefits.

#### A. Increasing Energy Security

The United States imports more than 60% of its petroleum, two-thirds of which is used to fuel vehicles in the form of gasoline and diesel. The demand for petroleum imports is increasing. With much of the worldwide petroleum reserves located in politically volatile countries, the United States is vulnerable to supply disruptions [5].

Biodiesel can be produced domestically and used in conventional diesel engines, directly substituting for or extending supplies of traditional petroleum diesel. It also has an excellent energy balance.

#### B. Protecting public health and the environment

Compared with using petroleum diesel, using biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons (HC), carbon monoxide (CO), sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter (PM). The reductions increase as the amount of biodiesel blended into diesel fuel increases. B100 provides the best emission reductions, but lower-level blends also provide benefits. B20 has been shown to reduce PM emissions 10%, CO 11%, and unburned HC 21%.

Using biodiesel also reduces greenhouse gas emissions because carbon dioxide released from biodiesel combustion is offset by the carbon dioxide sequestered while growing the soybeans or other feedstock. B100 use reduces carbon dioxide emissions by more than 75% compared with petroleum diesel. Using B20 reduces carbon dioxide emissions by 15%.

#### C. Biodiesel improves engine operation

Biodiesel improves fuel lubricity and raises the cetane number of the fuel. Diesel engines depend on the lubricity of the fuel to keep moving parts from wearing prematurely. Federal regulations reduced sulfur in diesel fuel to 15 ppm a few years ago, which resulted in reduced lubricity of petroleum diesel. Diesel specification ASTM D975 was modified to require lubricity; biodiesel provides adequate lubricity to meet this requirement at blends as low as 1%. [5]

### D. Providing safety benefits

Biodiesel is nontoxic, so it causes far less damage than petroleum diesel if spilled or otherwise released to the environment. It is also safer than petroleum diesel because it is less combustible. The flashpoint for biodiesel is higher than 150°C, compared with about 52°C for petroleum diesel. Biodiesel is safe to handle, store, and transport.

## 1.14 Advantages of biodiesel

1. Biodiesel is non toxic.
2. Biodiesel is biodegradable.
3. Biodiesel is safer to handle compared to standard diesel.
4. Biodiesel can be easily blended with standard diesel, and it can be used in most of today's vehicles even in form of pure biodiesel B100.
5. Biodiesel can help cut our reliance on fossil fuels, and improve our energy security and energy independence.
6. Biodiesel could be massively produced in many parts of the world; the US alone has the capacity to produce annually more than 50 million gallons of biodiesel.
7. Production and use of biodiesel accounts for significantly less emissions compared to standard diesel, approximately 78% less emissions compared to standard diesel. [2]
8. Biodiesel has very good lubricating properties, significantly better than standard diesel which can prolong engine's life.
9. Biodiesel has shorter ignition delay compared to standard diesel.
10. Biodiesel has no sulphur content, and so it doesn't contribute to acid rain formation.

## 1.15 Disadvantages of biodiesel

1. Biodiesel could lead to food shortages and increased food prices. The end result of this could be more hunger in the world.
2. Biodiesel is 20 times more susceptible to water contamination compared to standard diesel, and this could lead to corrosion, rotten filters, pitting in the pistons, etc
3. Pure biodiesel has significant problems with low temperatures. Biodiesel is significantly more expensive compared to standard diesel.
4. Biodiesel has significantly less energy content compared to standard diesel.
5. Biodiesel can release nitrogen oxide which can lead to the formation of smog [2].

### 1.16 Scope of work

In view of the large foreign exchange requirement for purchase of petroleum crude and the resulting unabated pollution, the government of India has set up a committee on development of bio-fuel in 2002-03. Utilization of used vegetable oils for production of biodiesel will prevent further wastage of already existing resources, and use of environmentally friendly fuel will create cleaner environment. The work presented in this thesis with respect to study of biodiesel from waste oil based on the availability of raw feedstock. As very less work has been done on deriving the biodiesel from waste cooking oils, so the goal of this work is to determine the usefulness of biodiesel. So our aim of study is mainly categorized in two parts:

1. Study of methods employed in extraction of biodiesel. The methods employed in extraction of biodiesel are: direct blending, transesterification, pyrolysis and micro emulsion.
2. Experimental work on properties of biodiesel and find the optimum blend based on these properties.

### 1.17 Organization of thesis

The division of dissertation divided into mainly five parts. The experimental work based on biodiesel production by transesterification method and properties of biodiesel, including the preparation of different blends (B 10, B15 and B20) of cotton seed methyl ester and mustard methyl ester with diesel and find the optimum blend based on these properties are presented in this thesis.

#### Chapter I

This chapter is related to alternative fuels and selection of alternative fuel for diesel engine. It describes the different methods employed in biodiesel production and fuel properties of biodiesel. It presents biodiesel demand, biodiesel requirement, advantages and disadvantages. It is experimentally measured that biodiesel, vegetable oil act as a fuel which provides good results in compression ignition engine. The origin, historical and economical aspects of biodiesel is also described in this chapter. According to market value, cost assessments of selected biodiesels are to be evaluated.

**Chapter II**

It is related to literature review and problem formulation. Extensive literature on production of biodiesel (transesterification), and properties of biodiesel are reviewed. Later in this chapter objectives and problem formulation are described. An overview of research work in the field of biodiesel with relation to preparation method and fuel properties is presented in the chapter.

**Chapter III**

This chapter deals with problem formulation. The problem formulation is mainly categorized in two parts:

1. Study of methods employed in extraction of biodiesel. The methods employed in extraction of biodiesel are: direct blending, transesterification, pyrolysis and micro emulsion.

2. Study on properties of different blends of biodiesel derived from waste cotton seed oil and waste mustard oil and optimum blend is to be selected based on these properties.

**Chapter IV**

This chapter describes the methodology used for standardization of methyl transesterification process parameters for waste cotton seed oil and waste mustard oil. It describes the characteristic fuel properties and experimental procedure adopted to calculate the properties of six different fuel blends and select the optimum blend based on these properties. The experiments were conducted in MERADO (Mechanical Engineering Research and Development Organization) Ludhiana. The parameters studied and methodologies adopted are discussed in this chapter..

**Chapter V**

This chapter deals with calculations and is categorized into two parts:

**First part includes the following work:**

- ❖ To optimize transesterification to produce biodiesel by varying the composition of catalyst.
- ❖ To determine fuel properties of biodiesel i.e. Viscosity and FFA value.

**Second part includes the following work:**

- To determine the properties of different blends of biodiesel with diesel derived from waste cotton seed oil and waste mustard oil and optimum blend is to be selected based on these properties.

**Chapter VI**

This chapter deals with results and discussions. Results and discussions regarding transesterification process and fuel characterization of selected biodiesel are narrated in this chapter.

**Chapter VII**

This chapter deals with conclusions.Conclusions regarding transesterification process and fuel characterization of selected biodiesel are narrated in this chapter.

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# CHAPTER 2

# LITERATURE REVIEW

## 2.1 INTRODUCTION

A large work has been done on different aspects of biodiesel. This chapter covers the literature on biodiesel production by different methods from waste vegetable oils and characteristics of biodiesel.

## 2.2 CATEGORIZATION OF LITERATURE

Literature is divided into following two main categories:

1. Biodiesel production methods.
2. Characteristics of biodiesel

### 2.2.1 Biodiesel production methods

**Fangrui Ma [6]** have described, biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. The cost of biodiesel, however, is the main hurdle to commercialization of the product. The used cooking oils are used as raw material, for the production of biodiesel and the adaption of continuous transesterification process and recovery of high quality glycerol from biodiesel by-product (glycerol) are primary options to be considered to lower the cost of biodiesel. Four different methods were examined for the production of biodiesel from waste cooking oils. These methods were direct use and blending, micro emulsions, thermal cracking (pyrolysis) and transesterifcation. The purpose of these methods is to lower the viscosity of the oil or fat. From the different methods available for producing biodiesel, transesterifcation of natural oils and fats is currently the method of choice, because transesterifcation is basically a sequential reaction. Triglycerides are first reduced to diglycerides.The diglycerides are subsequently reduced to monoglycerides. The monoglycerides are finally reduced to fatty acid esters. The order of the reaction changes with the reaction conditions. The foundations of this process are a shorter reaction time and greater production capacity. The recovery of high quality glycerol is another way to lower production cost. Because little water is present in the system, the biodiesel glycerol is more concentrated. Unlike the traditional soap glycerol recovery process, the energy required to recover biodiesel glycerol is low due to the elimination of the evaporation process. In addition, the process also is simpler than soap glycerol recovery since there is a negligible amount of soap in biodiesel glycerol. This implies that the cost of recovering high quality glycerol from biodiesel glycerol is lower than that of soap glycerol and that the cost of biodiesel fuel can be lowered if a biodiesel plant has its own glycerol recovery facility. Although blending of oils and other solvents and micro emulsions of vegetable oils lowers the viscosity, engine performance problems, such as carbon deposit and lubricating oil contamination, still exist. Pyrolysis produces more biogasoline than biodiesel fuel and an expensive process.

**Jon Van Gerpen [6]** have described biodiesel is an alternative diesel fuel produced from vegetable oils and animal fats. It consists of the monoalkyl esters formed by a catalysed reaction of the triglycerides in the oil or fat with a simple monohydric alcohol. But process complexity originates from contaminants in the feedstock, such as water and free fatty acids, or impurities in the final product, such as methanol, free glycerol, and soap. Processes have been developed to produce biodiesel from high free fatty acid feedstock, such as recycled restaurant grease, animal fats, and soap stock. Conventional processing involves an alkali catalysed process, but this is unsatisfactory for lower cost high free fatty acid feedstock due to soap formation. Pre-treatment processes using strong acid catalysts provide good conversion yields and high-quality final products.

**Knothe [6]** have investigated how ethyl esters were proposed as diesel fuel substitutes as early as 1937 in the Belgian Congo. Widespread investigation of these esters did not occur until the late 1970s and early 1980s when high petroleum prices inspired extensive research into alternative fuels. Vegetable oils were proposed as diesel fuels but were found to be problematic due mostly to their greater viscosity. Problems were found with piston and injector deposits and crankcase oil dilution and resultant oil thickening. Conversion of the oils to their alkyl esters reduced the viscosity to near diesel fuel levels and produced a fuel with properties that were similar to petroleum based diesel fuel and which could be used in existing engines without modifications.

**Freedman et al. [6]** have experimentally evaluated the results of a parametric study of the transesterification reaction variables that included temperature, molar ratio of alcohol to oil, type of catalyst, and the degree of refinement of the oil. They observed that the reaction proceeded to completion in 1 h at 60$^{o}$C but took 4 h at 32$^{o}$C. From this it is observed how the degree of reaction depends on the alcohol-to-oil ratio. Significant amounts of partially reacted mono and diglycerides will be present when the alcohol-to oil ratio is too low. From the experimental investigation it was examined an alcohol-to-oil ratio of 6:1 is necessary for a complete single-step reaction. Mono and diglycerides of saturated fatty acids crystallize easily from the biodiesel fuel and can cause fuel filter plugging and other performance problem.

**Van Gerpen and Dvorak [6]** have studied all commercial biodiesel producers use an alkali catalysed process for the transesterification process; but other approaches have also been proposed, including acid catalysis and enzymes. The use of acid catalysts has been found to be useful for preheating high free fatty acid feedstock to convert the FFAs to esters but the reaction rates for converting triglycerides to methyl esters are too slow. Enzymes have shown good tolerance for the free fatty acid level of the feedstock, but the enzymes are expensive and unable to provide the degree of reaction completion required to meet the ASTM fuel specification. Immobilization of the enzyme and use of multiple enzymes in sequence may provide future opportunities in this area.

**Saka and Kusiana [6]** have showed that it is possible to react the oil and methanol without a catalyst, which eliminates the need for the water washing step. However, temperatures of $300^oC$–$350^oC$ and methanol to oil molar ratios of 42:1 are required. While the reaction only requires 120 s, the purity of the final product needs to be fully characterized, and formation of non methyl ester compounds in significant amounts is possible.

**Boocock et al. [6]** developed a novel technique for accelerating the transesterification reaction rate. During its early stages, the transesterification reaction is limited by the low solubility of the alcohol, especially methanol, in the oil. Boocock proposed the addition of a cosolvent to create a single phase, and this greatly accelerates the reaction so that it reaches substantial completion in a few minutes. The technique is applicable for use with other alcohols and for acid-catalysed pre-treatment of high free fatty acid feed stocks. The primary concerns with this method are the additional complexity of recovering and recycling the co solvent although this can be simplified by choosing a co solvent with a boiling point near that of the alcohol being used. Additional concerns have been raised about the hazard level associated with the co solvents most commonly proposed, tetrahydrofuran and methyl tertiary butyl ether.

**S Saka [7]** have studied transesterification reaction of rapeseed oil in supercritical methanol was investigated without using any catalyst. An experiment has been carried out in the batch-type reaction vessel preheated at 350 and 400°C and at a pressure of 45–65 MPa, and with a molar ratio of 1:42 of the rapeseed oil to methanol. It was consequently demonstrated that, in a preheating temperature of 350°C, 240 s of supercritical treatment of methanol was sufficient to convert the rapeseed oil to methyl esters and that, the prepared methyl esters were basically the same as those of the common method with a basic catalyst, the yield of methyl esters by the former was found to be higher than that by the latter. In addition, it was found that this new supercritical methanol process requires the shorter reaction time and simpler purification procedure because of the unused catalyst.

**Gemma Vicente [8]** have evaluated the different basic catalysts (sodium meth oxide, potassium meth oxide, sodium hydroxide and potassium hydroxide) for methanolysis of sunflower oil. All the reactions were carried out under the same experimental conditions in a batch stirred reactor and the subsequent separation and purification stages in a decanter. When the four catalysts were used, the methyl ester concentrations were near 100 wt. %. High biodiesel purities are important for biodiesel applications since residual monoglyceride, diglyceride and triglyceride can cause serious problems in diesel engines. Biodiesel yields after the separation and purification steps were higher than 98 wt. % for the methoxide catalysts, because the yields losses due to triglyceride saponification and methyl ester dissolution in glycerol were negligible. However, these catalysts are more expensive and also more difficult to manipulate since they are very hygroscopic. The biodiesel yields for the sodium and potassium hydroxide were lower, 85.9 and 91.67 wt. %, respectively, because the yield losses were more substantial. The transesterification reaction using sodium hydroxide was the fastest, achieving nearly 100 wt. % methyl ester concentration in the biodiesel phase at 30 min. However, the reaction rates should be the essentially the same, when equivalent amounts of the catalysts are used.

**Y. Zhang [9]** has studied different continuous processes for biodiesel production from virgin vegetable oil or waste cooking oil under alkaline or acidic conditions. Detailed operating conditions and equipment designs for each process were obtained. A technological assessment of these processes was carried out to evaluate their technical benefits and limitations. Analysis showed that the alkali-catalysed process using virgin vegetable oil as the raw material required the fewest and smallest process equipment units but at a higher raw material cost than the other processes. The use of waste cooking oil to produce biodiesel reduced the raw material cost. The acid-catalysed process using waste cooking oil proved to be technically feasible with less complexity than the alkali-catalysed process using waste cooking oil, thereby making it a competitive alternative to commercial biodiesel production by the alkali-catalysed process.

**Fengxian Qiu [10]** have described biodiesel (fatty acid methyl esters, FAME) was prepared by transesterification of the mixed oil (soybean oil and rapeseed oil) with sodium hydroxide (NaOH) as catalyst. The effects of mole ratio of methanol to oil, reaction temperature, catalyst amount and reaction time on the yield were studied. In order to decrease the operational temperature, a co-solvent (hexane) was added into the reactants and the conversion efficiency of the reaction was improved. The optimal reaction conditions were obtained by this experiment: methanol/oil mole ratio 5.0:1, reaction temperature $55^0$C, catalyst amount 0.8 wt. % and reaction time 2.0 h. Under the optimum conditions, a 94% yield of methyl esters was reached. The properties of obtained biodiesel from mixed oil are close to commercial diesel fuel and is rated as a realistic fuel as an alternative to diesel.

**Weiliang Cao [11]** has showed transesterification of soybean oil in supercritical methanol has been carried out in the absence of catalyst. A co-solvent was added to the reaction mixture in order to decrease the operating temperature, pressure and molar ratio of alcohol to vegetable oil. With propane as co solvent in the reaction system, there was a significant decrease in the severity of the conditions required for supercritical reaction, which makes the production of biodiesel using supercritical methanol viable as an industrial process. A high yield of methyl esters (biodiesel) was observed and the production process is environmentally friendly. Furthermore the co-solvent can be reused after suitable pre-treatment.

**Nobutake Nakatani [12]** have reviewed that the transesterification of soybean oil catalysed by combusted oyster shell, which is waste material from shellfish farms. Powdered oyster shell combusted at a temperature above $700^o$C, at which point the calcium carbonate of oyster shell transformed to calcium oxide, acted as a catalyst in the transesterification of soybean oil. The reaction conditions of catalyst concentration and reaction time were optimized in terms of the fatty acid methyl ester concentration expressed as biodiesel purity. Under the optimized reaction conditions of a catalyst concentration and reaction time of 25wt. %. and 5 h, respectively, the biodiesel yield, expressed relative to the amount of soybean oil poured into the reaction, was more than 70% with high biodiesel purity. These results indicate oyster shell waste combusted at high temperature can be reused in biodiesel production as a catalyst.

**Xuejun Liu [13]** has showed transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. The reaction mechanism was proposed and the separate effects of the molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and water content were investigated. The experimental results showed that a 12:1 molar ratio of methanol to oil, addition of 8% CaO catalyst, $65^0$C reaction temperature and 2.03% water content in methanol gave the best results, and the biodiesel yield exceeded 95% at 3 h. The catalyst lifetime was longer than that of calcined K2CO3 catalysts. CaO maintained sustained activity even after being repeatedly used for 20 cycles and the biodiesel yield at 1.5 h was not affected much in the repeated experiments.

### 2.2.2 Characteristics of Biodiesel

**Osmano Souza Valente [14]** studied the physical–chemical properties of fuel blends of waste cooking oil biodiesel or castor oil biodiesel with diesel oil. The properties evaluated were fuel density, kinematic viscosity and sulphur content measured according to standard test methods. The results were analysed based on present specifications for biodiesel fuel in Brazil, Europe, and USA. Fuel density and viscosity were increased with increasing biodiesel concentration, while fuel sulphur content was reduced. The possible effects of fuel property variation with biodiesel concentration on engine performance and exhaust emissions and observed that maximum biodiesel concentration in diesel oil meets the required characteristics for internal combustion engine. Fuel blends with up to 20% waste cooking oil biodiesel or 35% castor oil biodiesel concentration in diesel fuel will meet present specifications for biodiesel density, kinematic viscosity in Brazil, Europe, and USA. The use of waste cooking oil biodiesel or castor oil biodiesel blended to diesel fuel can substantially reduce the fuel sulphur content at an equivalent rate for a given concentration. The fuel blends containing over 83% waste cooking oil biodiesel or soybean biodiesel in diesel fuel reduced the fuel sulphur content below 50 ppm.

**David Y. Z. Chang [15]** have studied about the methyl esters of soybean oil, known as biodiesel, are receiving increasing attention as renewable fuels for diesel engines. Biodiesel has a high cetane number, and offers the potential of emission reduction. The properties of biodiesel vary depending on its composition, and this may affect engine performance and emissions. Biodiesel fuels were prepared from feedstock's with modified compositions including the methyl esters of a low palmitic soybean oil, a partially transesterified soybean oil, a synthetic blend of saturated esters, and a commonly used methyl soy ate. These esters were blended with diesel fuel in 20% and 50% concentrations. The blended fuels were then tested in a diesel engine to investigate the effect of biodiesel composition on performance, combustion characteristics, and emissions. The results show that the engine performance and combustion process of all the blends were similar to diesel fuel with a slightly higher fuel consumption, a shorter ignition delay, and a lower premixed burning rate, with the exception of the blend of 20% partially transesterified fuel. All of the blends except the 20% partially transterified soybean oil demonstrated reductions in CO, HC, total particulate, and soot. The $NO_x$ emissions increased for all of the fuel blends. The blends with saturated esters provided a faster burning rate and a better emission reduction than the other fuels. These blends also showed the smallest increase in $NO_x$ emissions among the fuels tested.

**Gerhard Knothe [16]** defined the mono-alkyl esters of vegetable oils and animal fats were an alternative diesel fuel that is steadily gaining attention and significance. One of the most important fuel properties of biodiesel and conventional diesel fuel derived from petroleum is viscosity, which is also an important property of lubricants. Ranges of acceptable kinematic viscosity are specified in various biodiesel and petro diesel standards. The kinematic viscosity of numerous fatty compounds as well as components of petro diesel were determined at 40 °C (ASTM D445) as this is the temperature prescribed in biodiesel and petro diesel standards. Kinematic viscosity increases with chain length of either the fatty acid or alcohol moiety in a fatty ester or in an aliphatic hydrocarbon. The increase in kinematic viscosity over a certain number of carbons is smaller in aliphatic hydrocarbons than in fatty compounds. The kinematic viscosity of unsaturated fatty compounds strongly depends on the nature and number of double bonds with double bond position affecting viscosity less. Terminal double bonds in aliphatic hydrocarbons have comparatively small viscosity-reducing effect. Free fatty acids or compounds with hydroxyl groups possess significantly higher viscosity. The viscosity range of fatty compounds is greater than that of various hydrocarbons comprising petro diesel.

**Narayan Khatr [17]** have studied the properties of biodiesel and vegetable oils .Bio diesel having the higher heating values almost similar to diesel but differs in physical properties i.e. viscosity, density, bulk modulus, flash point and fire point. Viscosity is related with fluidity as it is measure of internal friction between the layers of fluid. Higher viscosity values of biodiesel affects the operation of fuel injection equipment, particularly at low temperatures and leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The viscosity values of vegetable oil methyl esters are between 2.8 and 5.1 $mm^2/s$. The viscosity values of vegetable oils are higher as compared to diesel even after transestrification process. Density is another important property of biodiesel that influences the mass flow rate of fuel is to be injected to cylinder for combustion. Specific gravity of biodiesels ranges between 848 and 885 g/L. Fuel injection equipment operates on a volume metering system, hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel. An increase in density from 848 to 885 g/L for biodiesels increases the viscosity from 2.8 to 5.1 CST.

# CHAPTER 3

# PROBLEM FORMULATION

The problem formulation is mainly categorized in two parts:

1. Study of methods employed in extraction of biodiesel. The methods employed in extraction of biodiesel are: direct blending, transesterification, pyrolysis and micro emulsion.

2. Study on properties of different blends of biodiesel derived from waste cotton seed oil and waste mustard oil and selection of optimum blend.

During the course of this work, a study of different methods employed in production of biodiesel was observed. The four methods investigated were direct blending, pyrolysis, micro emulsion and transestreification. Although all these methods are used for production of biodiesel but each method have their own drawbacks. The drawbacks of these methods are given below:

**1. Direct Mixing**: In this method, vegetable oils are directly mixed with diesel.

The disadvantages of vegetable oils as diesel fuel are:

1. Higher viscosity
2. Lower volatility
3. The reactivity of unsaturated hydrocarbon chains.

Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines. The problems include:

1. Fuel atomization does not occur properly
2. Carbon deposits
3. Oil ring sticking
4. Thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils. [4]

**2. Pyrolysis (Thermal cracking)**: Thermal cracking or pyrolysis is the process that causes the break of the molecules by heating at high temperatures that is, by the heating of the substance in the absence of air or oxygen in temperatures superior to 450°C, forming a mixture of chemical compounds with properties very similar to those of petro diesel.

The disadvantages of this method are:

1. The equipment for pyrolysis or thermal cracking is expensive.
2. The removal of the oxygen of the process reduces the benefits of an oxygenated fuel, reducing its environmental benefits and usually producing a fuel closer to gasoline than diesel.
3. By the international nomenclature, the fuel produced by thermal cracking is not considered as biodiesel, in spite of being a biofuel similar to the diesel oil.
4. Cracking has great applicability in places that need smaller production volume and with smaller availability of qualified work.
5. Not accepted from the points of view of ash content, carbon residues and pouring point.

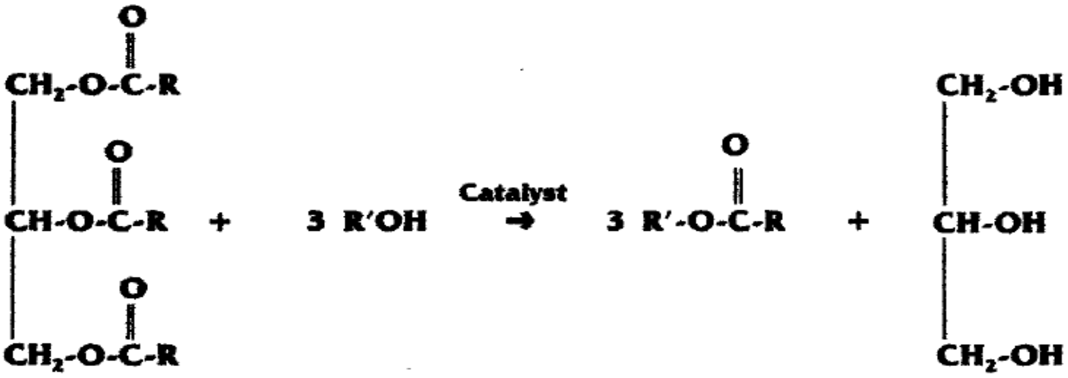
**3. Micro emulsion:** Micro emulsification, practiced also to increase the cetane number and reduce the viscosity. Diesel fuel, vegetable oil, alcohol, surfactant and additive for increasing of cetane number are mixed in suitable proportions and the mixture transformed, under vigorous stirring, into a micro emulsion with lower viscosity [18]. Alcohols as methanol, ethanol and propenol are used as additives for reducing of viscosity, higher ones as surfactants and alkyl nitrates as cetane number improvers.

The disadvantages of this method are:

Laboratory tests for motors operating on fuels created by micro emulsion show carbon deposits due to incomplete combustion, injector needle sticking and an increase in the viscosity of the lubricating oil. [18]

**4. Transesterification**: In this method, the vegetable oil is subjected to a chemical reaction. In that reaction, the vegetable oil is reacted in the presence of a catalyst (usually a base) with an alcohol (usually methanol) to give the corresponding alkyl esters of the FA mixture that is found in the vegetable oil.

Biodiesel is produced through a process known as transesterification, as shown in the equation:



**Triacylglycerols (Vegetable oil)** **Alcohol** **Alkyl Ester (Biodiesel)** **Glycerol**

Where R is a long hydrocarbon chain, sometimes called fatty acid chains. [2]

**Note: - From discussion of above four methods it was concluded that biodiesel was extracted from different methods i.e. micro emulsion, pyrolysis and transesterification, but each method has their own drawbacks. Transesterification is reliable method for the extraction of biodiesel as compare to pyrolysis, direct blending and micro emulsion because of the following reasons:**

1. Low temperature and pressure
2. High yield and short reaction time
3. Direct conversion process
4. Simple in operation
5. Easy availability
6. Less viscosity
7. Less cost
8. Simple methodology

## 3.2 Objectives of work

**This work has been carried out with following aims and objectives:**

**1. To optimize transesterification to produce biodiesel by varying the composition of catalyst.**

**2. To prepare biodiesel from waste cotton seed and waste mustard oils.**

**3. To determine fuel properties of selected edible oils and its biodiesels.**

**4. To determine the properties of different blends of biodiesel derived from waste cotton seed oil and waste mustard oil and optimum blend is to be selected based on these properties.**

**5. To compare properties of different blends prepared from cotton seed and mustard methyl ester with diesel fuel.**

**The properties were checked in MERADO (Mechanical Engineering Research and Development Organization) Ludhiana (Punjab)**

- **The selected properties are:**
- FFA value
- Density
- Viscosity
- Flash point and fire point
- Cloud point and pour point
- Carbon residue content
- Ash residue content

# CHAPTER 4

# MATERIALS AND METHODS

This chapter describes the methodology used for standardization of methyl transesterification process parameters for waste cotton seed oil and waste mustard oil. It describes the characteristic fuel properties and experimental procedure adopted to calculate the properties of six different fuel blends and select the optimum blend based on these properties. The experiments were conducted in MERADO (Mechanical Engineering Research and Development Organization) Ludhiana. The parameters studied and methodologies adopted are discussed in this chapter.

## 4.1. Materials

The waste cotton seed oil and waste mustard oil used in this present study was obtained from different resources i.e. college canteen, sweet shops and confectionaries. The commercial diesel fuel was purchased from petrol pump which is nearer to Guru Nanak Dev Engineering College, Ludhiana (Punjab). All chemicals (Methanol, KOH Catalyst, and Silica gel) were provided by MERADO lab. Water bath shaker is used for transesterification of waste cotton seed oil and waste mustard oil. The fuel properties have been determined by using equipments such as hydrometer, Redwood viscometer, closed cup flash and fire apparatus, cloud and pour point apparatus and bomb calorimeter.

## 4.2. Standardization of Transesterification Process

### 4.2.1 Single stage process

1. A known quantity of oil (previously filtered up to 53 micron thickness sieve) was taken.
2. The above filtered oil i.e., triglyceride molecule was taken in biodiesel reactor vessel.
3. Neutralizing the free fatty acids using sodium or potassium meth oxide (known quantity of methanol) was used because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol) with known amount of alkali NaOH of KOH as a catalyst
4. Creating an alcohol ester under desired temperature with suitable speed. Stir for agitating the mixture.
5. Within a process period of 1 hr, biodiesel was formed along with the glycerine with clear phase separation.

**The methyl transesterification of waste cotton seed were carried out as per the steps described in Fig. 4.1**

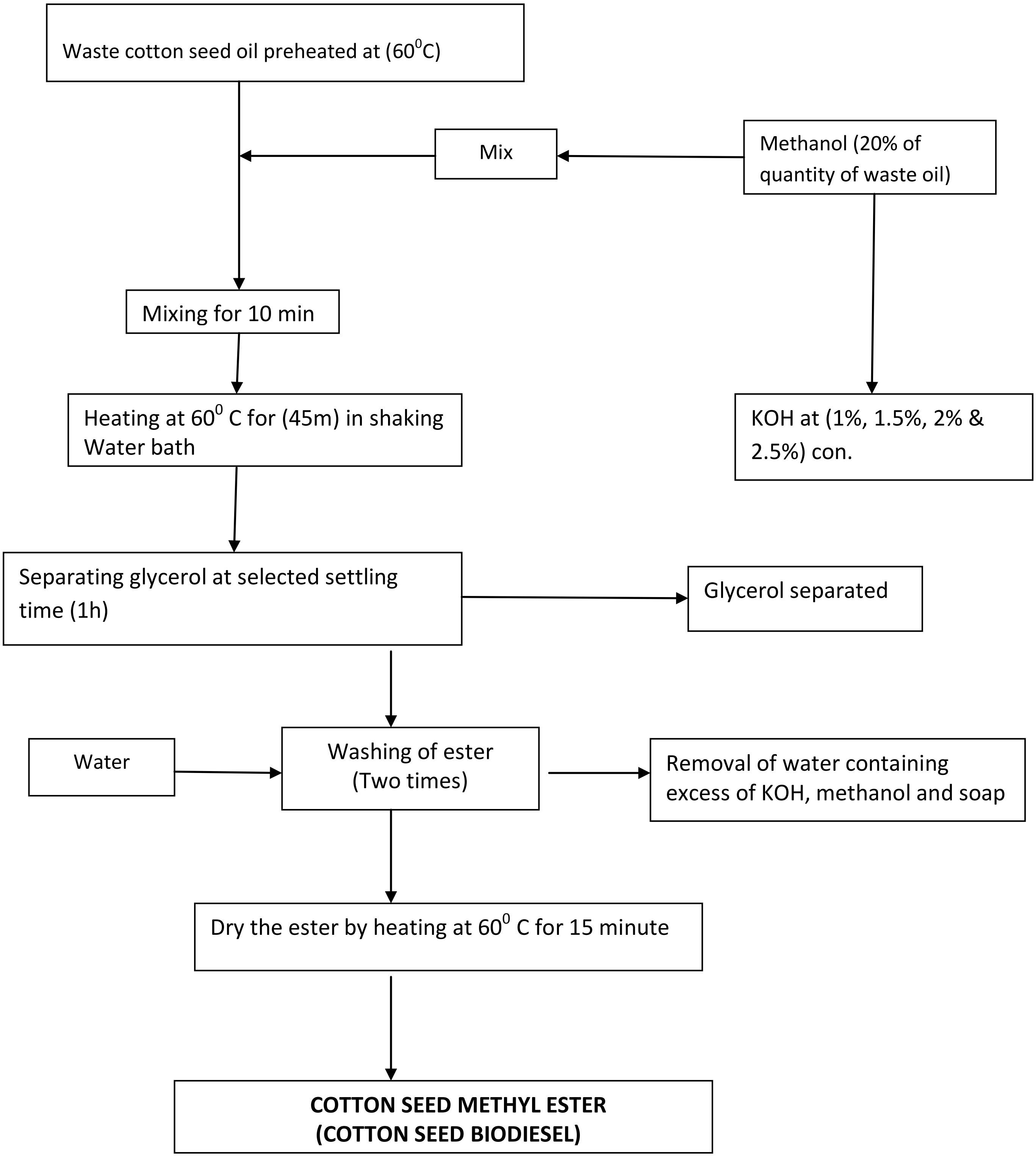


Fig. 4.1 Schematic diagram of simple procedure developed for the production of cotton seed methyl ester

**The methyl transesterification of waste mustard oil were carried out as per the steps described in Fig. 4.2**

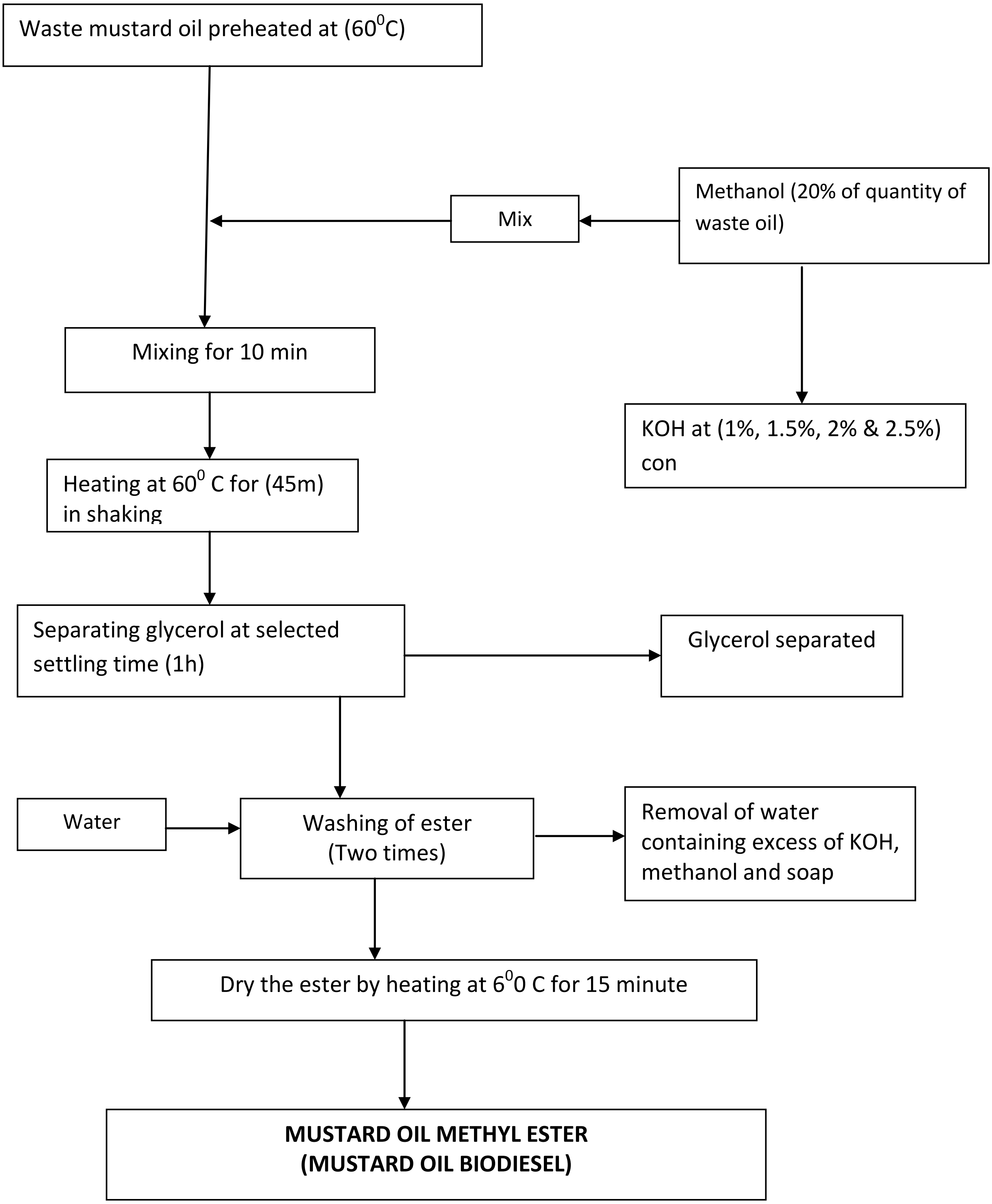


Fig. 4.2 Schematic diagram of simple procedure developed for the production of Waste mustard methyl ester.

## 4.3. Standardization of methyl transesterification process parameters:

Transesterification process is defined as the process in which chemically reacting triglycerides such as one of the vegetable oil react 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 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 three 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.

The following parameters affect the level of ester recovery:

- Molar ratio of vegetable oil- alcohol mixture
- Preheating time
- Preheating temperature
- Reaction time
- Reaction temperature
- Type of catalyst
- Concentration of catalyst

The effect of process parameters shown in Table 4.1 were studied to standardize the transesterification process for estimating recovery of ester as well as recovering ester of lowest possible viscosity. In order to standardize the process parameters, four levels of catalyst (KOH) concentration (1%, 1.5% 2%, and 2.5%) were set. The transesterification was done at 5:1 molar ratio and then allowed to settle for 1 hour in order to obtain maximum recovery of ester with lowest possible kinematic viscosity as reported by past researchers. Total 8 ester samples were prepared to study the effect of the four levels of catalyst concentration on ester recovery and subsequent measure of their kinematic viscosity. The water bath shaker used for transesterification which is shown in plate 4.3.

**Fig:** 4.3 Water bath shaker for transesterification

Table 4.1 Process parameters selected for standardization of transesterification process (waste cotton seed oil and waste mustard oil).

| **Optimizing parameter** | **Level selected** |
|---|---|
| Preheating temperature ($^0$C) | 60$^o$C |
| Molar ratio | 5:1 |
| Catalyst concentration | 1%, 1.5%, 2%, 2.5% |
| Reaction time (Minutes) | 60 minutes |
| Reaction temperature ($^0$C) | 60$^0$C |
| Settling time | 1hr |

## 4.4 PROCEDURE OF MAKING BIODIESEL:-

The vegetable oils and fats are made up mainly of triglycerides. When, these triglycerides react chemically with alcohols in presence of a catalyst (base/acid) result in fatty acid esters. These esters show striking similarity to petroleum derived diesel and are called "Biodiesel". Biodiesel is produced by transesterification of oil obtains from the seeds. A short detail for making biodiesel is given below:

1. Oil was taken in a flask.
2. Methanol (by weight) and a potassium hydroxide (by weight) were taken into a flask according to the composition which we want to prepare.
3. The mixture was stirred until the KOH is fully dissolved in a methanol.
4. The mixture was heated on a heater up to 60°C.
5. The mixture was placed in a water bath shaker and stirred for one hour.
6. The mixture was allowed to sit until the waste glycerine settles to the bottom.
7. The mixture was pour into a separator (for 1 hour) for settle the glycerine in to the bottom.
8. Drain out the waste glycerine.
9. The liquid remaining was raw biodiesel Ester.
10. Wash the raw biodiesel using regular tap water to remove impurities.
11. The washing process was repeated as required 2 to 4 more times or until water was mostly clears.
12. Biodiesel was allowed to settle until remaining water drops to the bottom.
13. Polish the biodiesel using either heat or air drying.
14. Pump through a filter into a storage container.
15. Now we have clean dry biodiesel which were safely use to fill up in vehicle.

# CHAPTER 5

# CALCULATIONS

This chapter is categorized into two parts:

**First part includes the following work:**

- To optimize transesterification to produce biodiesel by varying the composition of catalyst.
- To determine fuel properties of biodiesel i.e. viscosity and FFA value.

**Second part includes the following work:**

- To determine the properties of different blends of biodiesel with diesel derived from waste cotton seed oil and waste mustard oil and optimum blend is to be selected based on these properties.

**The selected properties are:**

- FFA value
- Density
- Viscosity
- Flash point and fire point
- Cloud point and pour point
- Carbon residue content
- Ash residue content

The properties were checked in MERADO (Mechanical Engineering Research and Development Organization) Ludhiana (Punjab)

## (A) FIRST PART OF CALCULATION:

**5.1 Effect of catalyst on the yield of biodiesel: -** The effect of KOH concentration was studied in the range of 1-2.5% (weight of KOH/weight of oil).The reaction temperature was kept constant at $60^0$C. It was found that the ester recovery increases as the amount of catalyst decreased from 2.5-1%. Ester recovery decreases drastically as KOH concentration increases above 2.5% whereas ester recovery increase as KOH concentration reduces to almost 1%. This lesser recovery at high KOH concentration may possibly be due to high soap formation. It also shows that the lowest molar ratio of alcohol to oil, lesser amount of KOH can be used.

**5.2 Method to calculate the yield of biodiesel from waste cotton seed oil:-**First calculates the density of waste cotton seed oil. The procedure to calculate the density of waste cotton seed is given below:-

Weight of empty cylindrical flask (150 ml) = 174.421 gm

Volume of waste cotton seed oil taken in a cylindrical flask = 100 ml

Weight of cylindrical flask with waste cotton seed oil = 265.598 gm

Weight of waste cotton seed oil alone = 265.588-174.421 = 91.199 gm

We know,

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{91.199\text{ gm}}{100\text{ ml}} = 0.91\text{ gm/ml}^3$$

From above calculations, the amount of biodiesel taken in each sample was 91 gm.

Now calculate the yield of cotton seed biodiesel by varying the composition of KOH catalyst. The concentration of KOH was varying from 1% to 2.5 %.

**CASE 1:**- Amount of waste cotton seed oil taken = 91 gm

Amount of methanol = 20 % i.e. 20 % of 91 gm = 18.2 gm

Amount of KOH concentration = 1% = 0.91 gm

Weight of empty cylindrical flask = 135.992 gm

Weight of cylindrical flask with waste cotton seed oil (91 gm) = 213.115 gm

Now transesterification process was done to convert the waste cotton seed oil into biodiesel. After transesterification process, the yield obtained was 77.123 gm. So amount of yield of biodiesel obtained was 77.123 gm from 91 gm of waste cotton seed oil.

**CASE 2:**- Amount of waste cotton seed oil taken = 91 gm

Amount of methanol = 20 % i.e. 20 % of 91 gm = 18.2 gm

Amount of KOH concentration = 1.5 % =1.365 gm

Weight of empty cylindrical flask = 138.688 gm

Weight of cylindrical flask with waste cotton seed oil (91 gm) = 210.508 gm

Now transesterification process was done to convert the waste cotton seed oil into biodiesel. After transesterification process, the yield obtained was 71.82 gm. So amount of yield of biodiesel obtained was 71.82 gm from 91 gm of waste cotton seed oil.

**CASE 3:-** Amount of waste cotton seed oil taken = 91 gm

Amount of methanol = 20 % i.e. 20 % of 91 gm = 18.2 gm

Amount of KOH concentration = 2% = 1.82 gm

Weight of empty cylindrical flask = 132.54 gm

Weight of cylindrical flask with waste cotton seed oil (91 gm) = 196.72 gm

Now transesterification process was done to convert the waste cotton seed oil into biodiesel. After transesterification process, yield obtained was 64.186 gm. So amount of yield of biodiesel obtained was 64.186 gm from 91 gm of waste cotton seed oil.

**CASE 4:-** Amount of waste cotton seed oil taken = 91 gm

Amount of methanol = 20 % i.e. 20 % of 91 gm = 18.2 gm

Amount of KOH concentration = 2.5 % = 2.275 gm

Weight of empty cylindrical flask = 134.56 gm

Weight of cylindrical flask with waste cotton seed oil (91 gm) = 191.54 gm

Now transesterification process was done to convert the waste cotton seed oil into biodiesel. After transesterification process, yield obtained was 56.98 gm. So amount of yield of biodiesel obtained was 56.98 gm from 91 gm of waste cotton seed oil.

**The effect of composition of KOH on the yield of biodiesel prepared from waste cotton seed oil is shown in table 5.1**

Yield of Biodiesel obtained from waste cotton seed oil

| Amount of oil (gms) | conc. of KOH | Methanol (gms) | Amount of Yield (gms) |
|---|---|---|---|
| 91 | 1% (0.91 g) | 18.2 | 77.12 |
| 91 | 1.5% (1.365 g) | 18.2 | 71.82 |
| 91 | 2% (1.82 g) | 18.2 | 64.18 |
| 91 | 2.5% (2.275 g) | 18.2 | 53.94 |

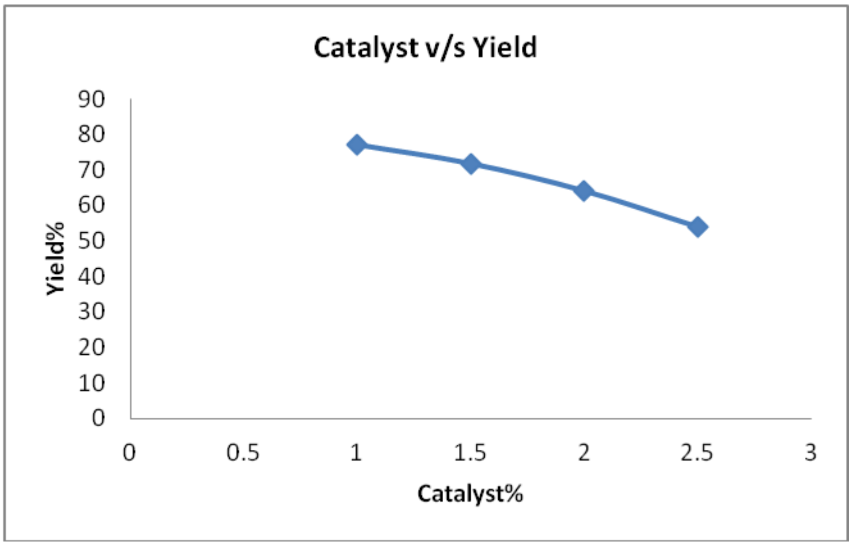


**Fig: 5.1 Yield of cotton seed methyl ester varies with respect to catalyst**

The effect of KOH concentration was studied in the range of 1-2.5% (weight of KOH/weight of oil). It was found that the ester recovery increases as the amount of catalyst decreased from 2.5-1%. Ester recovery decreases drastically as KOH concentration increases above 2.5% whereas ester recovery increase as KOH concentration reduces to almost 1%. This lesser recovery at high KOH concentration may possibly be due to high soap formation.

**5.3 Method to calculate yield of biodiesel from waste mustard oil:-**First calculates the density of waste mustard oil. The procedure to calculate the density of waste mustard oil is given below:-

Weight of empty cylindrical flask (250 ml) = 271.033 gm

Volume of waste mustard oil taken in a cylindrical flask = 100 ml

Weight of cylindrical flask with waste mustard oil = 358.28 gm

Weight of waste mustard oil alone = 358.28 - 271.033 = 87.247 gm

We know,

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{87.247\text{ gm}}{100\text{ ml}} = 0.87\text{ gm/ml}^3$$

From above calculations, the amount of biodiesel taken in each sample was 87 gm.

Now calculate the yield of mustard oil by varying the composition of KOH concentration. The concentration of KOH was varying from 1% to 2.5 %.

**CASE 1**:- Amount of waste mustard oil taken = 87 gm

Amount of methanol = 20 % i.e. 20 % of 87 gm = 17.4 gm

Amount of KOH concentration = 1 % = 0.87 gm

Weight of empty cylindrical flask = 136.029 gm

Weight of cylindrical flask with waste mustard oil (87 gm) = 219.260 gm

Now transesterification process was done to convert the waste mustard oil into biodiesel. After transesterification process, the yield obtained was 83.231 gm. So amount of yield of biodiesel obtained 83.231 gm from 87 gm of waste mustard oil.

**CASE 2:**- Amount of waste mustard oil taken = 87 gm

Amount of methanol = 20 % i.e. 20 % of 87 gm = 17.4 gm

Amount of KOH concentration = 1.5 % =1.305 gm

Weight of empty cylindrical flask = 138.711 gm

Weight of cylindrical flask with waste mustard oil (91 gm) = 215.201 gm

Now transesterification process was done to convert the waste mustard oil into biodiesel. After transesterification process, yield obtained was 76.49 gm. So amount of yield of biodiesel obtained was 76.49 gm from 87 gm of waste mustard oil.

**CASE 3**:- Amount of waste mustard oil taken = 87 gm

Amount of methanol = 20 % i.e. 20 % of 87 gm = 17.4 gm

Amount of KOH concentration = 2 % =1.74 gm

Weight of empty cylindrical flask = 135.57 gm

Weight of cylindrical flask with waste mustard oil (87 gm) = 201.11 gm

Now transesterification process was done to convert the waste mustard oil into biodiesel. After transesterification process, yield obtained was 65.54 gm. So amount of yield of biodiesel obtained was 65.54 gm from 87 gm of waste mustard oil.

**CASE 4:**- Amount of waste cotton mustard oil taken = 87 gm

Amount of methanol = 20 % i.e. 20 % of 87 gm = 17.4 gm

Amount of KOH concentration = 2.5 % =2.175 gm

Weight of empty cylindrical flask = 137.53 gm

Weight of cylindrical flask with waste mustard oil (87 gm) = 196.78 gm

Now transesterification process was done to convert the waste mustard oil into biodiesel. After transesterification process, yield obtained was 59.25 gm. So amount of yield of biodiesel obtained was 59.25 gm from 87 gm of waste mustard oil.

**The effect of composition of KOH on the yield of biodiesel prepared from waste mustard oil is shown in table 5.2**

Yield of Biodiesel obtained from waste mustard oil

| Amount of oil (gms) | Conc. Of KOH | Methanol (gms) | Amount of yield (gms) |
|---|---|---|---|
| 87 | 1% (0.87 g) | 17.4 | 83.23 |
| 87 | 1.5% (1.305 g) | 17.4 | 76.49 |
| 87 | 2% (1.74 g) | 17.4 | 65.54 |
| 87 | 2.5% (2.175 g) | 17.4 | 58.82 |

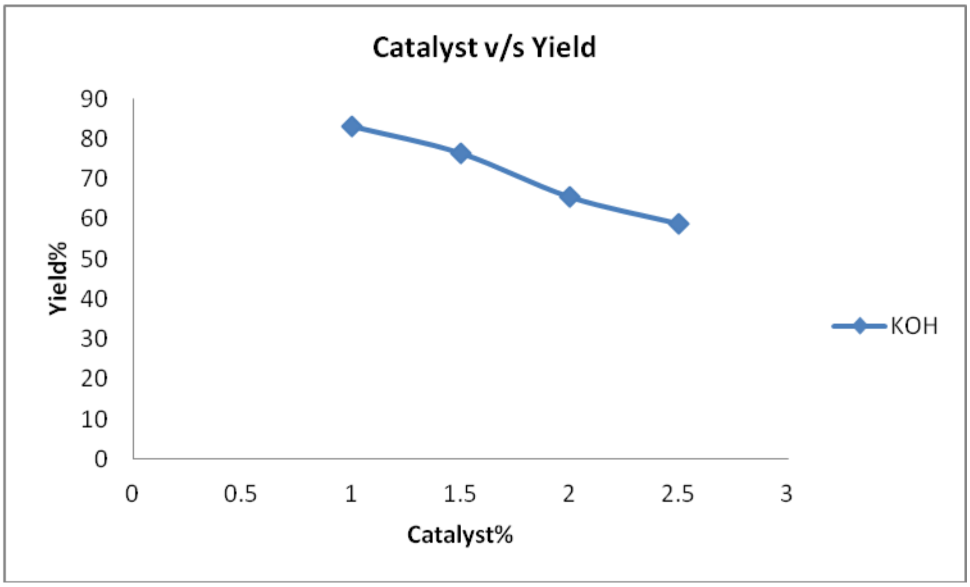


**Fig: 5.2 Yield of mustard methyl ester varies with respect to catalyst**

The effect of KOH concentration was studied in the range of 1-2.5% (weight of KOH/weight of oil). It was found that the ester recovery increases as the amount of catalyst decreased from 2.5-1%. Ester recovery decreases drastically as KOH concentration increases above 2.5% whereas ester recovery increase as KOH concentration reduces to almost 1%. This lesser recovery at high KOH concentration may possibly be due to high soap formation.

**5.4 Effect of catalyst on the properties of biodiesel: -** The varying concentration of KOH affects the yield of biodiesel. When the biodiesel was prepared from oil by the transesterification process, generally two properties were checked. These properties were FFA Value (Free Fatty Acid) and Viscosity. Viscosity is an important property of a bio diesel. Improper viscosity leads to poor combustion, which results in loss of power and excessive exhaust smoke. With extremely low viscosities may not provide sufficient lubrication for the pumps and Injector plungers. They can promote abnormal wear and cause injector and injector pump leakage. Higher viscosity is also not desirable as too viscous fuel increases pumping losses in injector pump and injectors, which reduces injection pressure resulting in poor atomization and inefficient mixing with air ultimately affecting the combustion process. [1].So the viscosity is an important property to check because it was neither to low nor too high.

The second property which we checked was FFA Value. If the oil has a high water or free fatty acid (FFA) content the reaction will be unsuccessful due to saponification (saponification is defined as the reaction of an ester with a metallic base and water) commonly known as making soap, and make separation of the glycerol difficult at the end of the reaction. The FFA content of the raw oil will determine the quantity of biodiesel as the final product. A very low content of FFA (<0.2) can give a full 100% yield [1]. So these two properties were important to check when biodiesel is extract from oil.

### 5.5 Procedure for calculating the FFA Value:-

As FFA can cause saponification instead of biodiesel production it is important to know the FFA content within an oil batch and whether it is necessary to take steps to reduce the content for success in the transesterification process. FFA content can be acquired from the use of a titration.

The method for FFA estimation is described below:

1. Take 50 ml spirit in a conical flask with the addition of the indicator phenolphthalein
2. 10 ml of base oil is added to the conical flask
3. Heat contents until first bubbling occurs (approx 70°C)
4. Phenolphthalein will indicate end of reaction as a red/pink colour when NaOH is used as titrate (0.1N)
5. When quantities are know the FFA content can be calculated.

Weight of sample = Volume × density

$(28.2 \times V \times N)/ (\text{weight of sample})$

Where V = volume of NaOH consumed in the titration

N = Normality of NaOH

### 5.6 FFA Value of cotton seed biodiesel at different concentration of KOH is as follows:-

**CASE 1:-** When concentration of KOH is 1 %:-

FFA Value = $(28.2 \times 0.1 \times 0.5)/ 10 = 0.139$

**CASE 2:-** When concentration of KOH is 1.5 %:-

FFA Value = $(28.2 \times 0.1 \times 0.4)/ 10 = 0.1128$

**CASE 3:-** When concentration of KOH is 2 %:-

FFA Value = (28.2×0.1×0.32)/ 10 = 0.090

**CASE 4:-** When concentration of KOH is 2.5 %:-

FFA Value = (28.2×0.1×0.2)/ 10 = 0.0564

### 5.7 FFA Value of mustard biodiesel at different concentration of KOH is as follows:-

**CASE 1:-** When concentration of KOH is 1 %:-

FFA Value = (28.2×0.1×0.45)/ 10 = 0.1296

**CASE 2:-** When concentration of KOH is 1.5 %:-

FFA Value = (28.2×0.1×0.4)/ 10 = 0.126

**CASE 3:-** When concentration of KOH is 2 %:-

FFA Value = (28.2×0.1×0.25)/ 10 = 0.0705

**CASE 4:-** When concentration of KOH is 2.5 %:-

FFA Value = (28.2×0.1×0.1)/ 10 = 0.0282

### 5.8 Procedure for calculating the viscosity:-

Viscosity can be defined as the resistance to flow of liquid due the internal friction between the liquid and surface. 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 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 and fuel delivery rates.

A Redwood viscometer was used for measurement of kinematic viscosity of selected fuel samples. The instrument measures the time of gravity flow in seconds of a fixed volume of the fluid (50 ml) through specified orifice made in a 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 agate jet at the bottom up to a specified level indicated in a cup. The cup was surrounded by water jacket having an immersion heater. The heater was heated to $38^0$C by regulating the rate of heating using a voltage regulator of the instrument. A simple 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 samples. Each test was replicated thrice. Kinematic viscosity in centistokes was then calculated from time units by using the relationships:-

$$V_k = 0.26\ t - 179/t \qquad (I)$$

When 34 < t < 100 and

$$V_k = 0.24\ t - 50/t \qquad (ii)$$

When t > 100

$V_k$ = Kinematic viscosity in centistokes, cSt

t = Time for flow of 50 ml sample,

**Fig: 5.1 Redwood viscometer**

### 5.9 Viscosity of cotton seed biodiesel at different concentration of KOH is as follows:-

**CASE 1**:- **When concentration of KOH is 1 %:-**

| Sr. No. | Temperature ($^0$c) | Time (seconds) |
|---|---|---|
| 1. | 40 | 38.7 |
| 2. | 40 | 37.6 |
| 3. | 40 | 37 |

Calculate the mean of time i.e. (38.7+37.6+37)/ 3 = 113.3 / 3 = 37.76 seconds

The time (t) in seconds lies within the range 34 < t < 100

Put the value in formula, $v_k = 0.24\ t - 179 / t$

$$V_k = 0.24 \times 37.76 - (179 / 37.76)$$

$$= 9.0624 - 4.740$$

$$= 4.32 \text{ cSt}$$

**CASE 2**:- **When concentration of KOH is 1 %:-**

| Sr. No. | Temperature ($^0$c) | Time (seconds) |
|---|---|---|
| 1. | 40 | 36.2 |
| 2. | 40 | 35.7 |
| 3. | 40 | 35.6 |

Calculate the mean of time i.e. (36.2+35.5+35.6)/ 3 = 107.5 / 3 = 35.8 seconds

The time (t) in seconds lies within the range 34 < t < 100

Put the value in formula, $v_k = 0.24\ t - 179 / t$

$$V_k = 0.24 \times 35.8 - (179 / 35.8)$$

$$= 8.6 - 5.0$$

$$= 3.6 \text{ cSt}$$

**CASE 3**:- **When concentration of KOH is 2 %:-**

| Sr. No. | Temperature ($^0$c) | Time (seconds) |
|---|---|---|
| 1. | 40 | 34.3 |
| 2. | 40 | 34 |
| 3. | 40 | 33.9 |

Calculate the mean of time i.e. (34.3+34+33.9)/ 3 = 102.2 / 3 = 34.06 seconds

The time (t) in seconds lies within the range $34 < t < 100$

Put the value in formula, $v_k = 0.24\ t - 179 / t$

$$V_k = 0.24 \times 34.06 - (179 / 34.06)$$

$$= 8.176 - 5.255$$

$$= 2.9\ \text{cSt}$$

**CASE 4**:- **When concentration of KOH is 2.5 %:-**

| Sr. No. | Temperature ($^0$c) | Time (seconds) |
|---|---|---|
| 1. | 40 | 32.6 |
| 2. | 40 | 32.2 |
| 3. | 40 | 31.8 |

Calculate the mean of time i.e. (32.6+32.2+31.8)/ 3 = 96.6 / 3 = 32.2 seconds

The time (t) in seconds lies within the range $34 < t < 100$

Put the value in formula, $v_k = 0.24\ t - 179 / t$

$$V_k = 0.24 \times 32.2 - (179 / 32.2)$$

= 7.728 – 5.559

= 2.1 cSt

**5.10 Viscosity of mustard biodiesel at different concentration of KOH is as follows**:-

**CASE 1**:- **When concentration of KOH is 1 %:-**

| Sr. No. | Temperature ($^0$c) | Time (seconds) |
|---|---|---|
| 1. | 40 | 38.8 |
| 2. | 40 | 38.2 |
| 3. | 40 | 37.9 |

Calculate the mean of time i.e. (38.8+38.2+37.9)/ 3 = 114.9 / 3 = 38.3 seconds

The time (t) in seconds lies within the range 34 < t < 100

Put the value in formula, $v_k = 0.24\ t – 179 / t$

$V_k = 0.24 \times 38.3 – (179 / 38.3)$

= 9.192 – 4.673

= 4.5 cSt

**CASE 2**:- **When concentration of KOH is 1.5 %:-**

| Sr. No. | Temperature ($^0$c) | Time (seconds) |
|---|---|---|
| 1. | 40 | 36.4 |
| 2. | 40 | 36 |
| 3. | 40 | 35.9 |

Calculate the mean of time i.e. (36.4+36+35.9)/ 3 = 108.3 / 3 = 36.1 seconds

The time (t) in seconds lies within the range $34 < t < 100$

Put the value in formula, $v_k = 0.24\ t - 179 / t$

$$V_k = 0.24 \times 36.1 - (179 / 36.1)$$

$$= 8.664 - 4.95$$

$$= 3.7 \text{ cSt}$$

**CASE 3**:- **When concentration of KOH is 2 %:-**

| Sr. No. | Temperature ($^0$c) | Time (seconds) |
|---|---|---|
| 1. | 40 | 34.8 |
| 2. | 40 | 35.4 |
| 3. | 40 | 34 |

Calculate the mean of time i.e. (34.8+35.4+34)/ 3 = 104.2 / 3 = 34.73 seconds

The time (t) in seconds lies within the range $34 < t < 100$

Put the value in formula, $v_k = 0.24\ t - 179 / t$

$$V_k = 0.24 \times 37.76 - (179 / 34.73)$$

$$= 8.336 - 5.154$$

$$= 3.1 \text{ cSt}$$

**CASE 4:- When concentration of KOH is 2.5 %:-**

| Sr. No. | Temperature ($^0$c) | Time (seconds) |
|---|---|---|
| 1. | 40 | 33.6 |
| 2. | 40 | 33.1 |
| 3. | 40 | 32.7 |

Calculate the mean of time i.e. (33.6+33.1+32.7)/ 3 = 99.4 / 3 = 33.13 seconds

The time (t) in seconds lies within the range $34 < t < 100$

Put the value in formula, $v_k = 0.24\ t – 179 / t$

$$V_k = 0.24 \times 33.13 – (179 / 33.13)$$

$$= 7.952 – 5.40$$

$$= 2.5 \text{ cSt}$$

**The effect of KOH concentration on FFA value and Viscosity of cotton seed biodiesel is shown in table 5.3**

**Properties of cotton seed biodiesel**

| Amount of yield (gms) | conc. of KOH | FFA value | Viscosity (CS) |
|---|---|---|---|
| 77.12 | 1% | 0.141 | 4.2 |
| 71.82 | 1.5% | 0.112 | 3.6 |
| 64.1 | 2% | 0.090 | 3 |
| 53.94 | 2.5% | 0.0564 | 2.5 |

**The effect of KOH concentration on FFA value and Viscosity of mustard oil biodiesel is shown in table 5.4.**

**Properties of mustard biodiesel**

| Amount of yield (gms) | Conc. Of KOH | FFA Value | Viscosity |
|---|---|---|---|
| 83.23 | 1% | 0.129 | 4.9 |
| 76.49 | 1.5% | 0.0126 | 3.7 |
| 65.54 | 2% | 0.0705 | 3.2 |
| 58.82 | 2.5% | 0.0282 | 2.5 |

## SECOND PART OF CALCULATION:

The second part of calculation describes fuel properties and experimental procedure adopted to calculate the properties of six different fuel blends and select the optimum blend based on these properties. The experiments were conducted in MERADO (Mechanical Engineering Research and Development Organization) Ludhiana

Following fuel properties of selected oils at different blends (B10, B15, B20) are to be determined to select the optimum blend.

- FFA value
- Density
- Viscosity
- Flash point and fire point
- Cloud point and pour point
- Carbon residue content
- Ash residue content

The equipments which were used to determine the fuel properties of cotton seed and mustard biodiesel were determined according to the relevant specifications from the biodiesel standards ASTM D6751. Most of these parameters comply with the limits prescribed in the ASTM D6751. The characteristic fuel properties of esters-diesel blends in the proportions of 10:90, 15:85 and 20:80 on volume basis were determined in accordance with standards of Bureau of Indian Standards, New Delhi and the Institute of Petroleum, London.

Table 5.5: Standard methods for calculating the properties [1]

| Properties | Method used |
|---|---|
| Kinematic Viscosity | IS: 1448[P: 25]:1976 |
| Flash point and fire point | IS: 1448[P: 32]:1992 |
| Cloud point and pour point | IS: 1448[P: 10]:1970 |
| Ash Content (%) | ASTM D482 |
| Carbon residue content (%) | ASTM D189 |
| Calorific value (KJ/Kg) | IS: 1448[P: 6]:1984 |
| FFA content (%) | Titration with 0.1N NaOH |

Table 5.6: Apparatus used for calculating the properties [1]

| Properties | Apparatus used |
|---|---|
| Density | Weighing balance |
| Kinematic viscosity | Redwood Viscometer |
| Flash point and fire point | Flash and fire point apparatus |
| Ash content | Muffle furnace |
| Cloud point and pour point | Cloud and pour point apparatus |
| Carbon residues | Carbon residue apparatus |

**5.11 Blends of cotton seed methyl ester and mustard methyl ester with petro diesel were prepared. The blends were prepared at B 10, B15. B20. The procedure for making blends is given below:-**

1. Take a cylindrical flask of 200 ml.
2. The blends were prepared of 150 ml amount.
3. The blend B10 was prepared by taking 10 ml of biodiesel and 140 ml of petro diesel.
4. The blend B20 was prepared by taking 15 ml of biodiesel and 135 ml of petro diesel.
5. The blend B30 was prepared by taking 20 ml of biodiesel and 130 ml of petro diesel.
6. The blends were prepared by volume.
7. Bio-diesel is slightly heavier than conventional diesel fuel (specific gravity 0.88 compared to 0.84 for diesel fuel). This allows use of splash blending by adding bio-diesel on top of diesel fuel for making bio-diesel blends. Bio-diesel should always be blended at top of diesel fuel. If bio-diesel is first put at the bottom and then diesel fuel is added, it will not mix.
8. After the blends were prepared, they were put in different bottles.

The properties of B10, B15 and B20 blend (cotton seed biodiesel with petro diesel) and then properties of B1O, B15 and B20 (mustard biodiesel with petro diesel) were checked. The properties were checked at MERADO (Mechanical Engineering Research and Development Organization) Ludhiana are discussed one by one:-

**1**. **DENSITY: -** Bio-diesel is slightly heavier than conventional diesel fuel (specific gravity 0.88 compared to 0.84 for diesel fuel). This allows use of splash blending by adding bio-diesel on top of diesel fuel for making bio-diesel blends. Bio-diesel should always be blended at top of diesel fuel. If bio-diesel is first put at the bottom and then diesel fuel is added, it will not mix.

**5.12 Density of different blends i.e., B10, B15, and B20 (cotton seed biodiesel with petro diesel) and B100 (cotton seed biodiesel) is given below:**

**CASE 1:- B10 BLEND (cotton seed biodiesel with petro diesel)**

The procedure of calculate the density of B10 blend is given below:-

Weight of empty cylindrical flask (100 ml) = 130.042 gm

Volume of B10 blend taken in a cylindrical flask = 50 ml

Weight of cylindrical flask with B10 blend = 171.942 g

Weight of B10 blend alone = 171.942 – 130.042 = 41.9 gm

We know,
$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{41.9\text{ gm}}{50\text{ ml}} = 0.815\text{ gm/ml}^3$$

**CASE 2:- B15 BLEND (cotton seed biodiesel with petro diesel)**

The procedure of calculate the density of B15 blend is given below:-

Weight of empty cylindrical flask (100 ml) = 129.951 gm

Volume of B15 blend taken in a cylindrical flask = 50 ml

Weight of cylindrical flask with B15 blend = 172.051 gm

Weight of B15 blend alone = 172.051 – 129.951 = 42.10 gm

We know,
$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{42.10\text{ gm}}{50\text{ ml}} = 0.842\text{gm/ml}^3$$

**CASE 3:- B20 BLEND (cotton seed biodiesel with petro diesel)**

The procedure of calculate the density of B20 blend is given below:-

Weight of empty cylindrical flask (100 ml) = 129.751 gm

Volume of B20 blend taken in a cylindrical flask = 50 ml

Weight of cylindrical flask with B20 blend = 172.490 gm

Weight of B20 blend alone = 172.051 – 129.751 = 42.30 gm

We know,
$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{42.30\text{ gm}}{50\text{ ml}} = 0.846\text{ gm/ml}^3$$

**CASE 4:- B100 (cotton seed biodiesel)**

The procedure of calculate the density of B100 blend is given below:-

Weight of empty cylindrical flask (100 ml) = 129.29 gm

Volume of B100 blend taken in a cylindrical flask = 50 ml

Weight of cylindrical flask with B100 blend = 174.790 gm

Weight of B100 blend alone = 174.790 – 129.29= 45.50 gm

We know,

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{45.50\ \text{gm}}{50\ \text{ml}} = 0.91\ \text{gm/ml}^3$$

### 5.13 Density of different blends i.e., B10, B15, and B20 (mustard biodiesel with petro diesel) and B100 (mustard biodiesel) is given below:

**CASE 1:- B10 BLEND (mustard biodiesel with petro diesel)**

The procedure of calculate the density of B10 blend is given below:-

Weight of empty cylindrical flask (100 ml) = 129.858 gm

Volume of B10 blend taken in a cylindrical flask = 50 ml

Weight of cylindrical flask with B10 blend = 171.558 gm

Weight of B10 blend alone = 171.558 – 129.858 = 41.70 gm

We know,

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{41.70\ \text{gm}}{50\ \text{ml}} = 0.834\ \text{gm/ml}^3$$

**CASE 2:- B15 BLEND (mustard biodiesel with petro diesel)**

The procedure of calculate the density of B15 blend is given below:-

Weight of empty cylindrical flask (100 ml) = 129.81 gm

Volume of B15 blend taken in a cylindrical flask = 50 ml

Weight of cylindrical flask with B15 blend = 171.610 gm

Weight of B15 blend alone = 171.610 – 129.81 = 41.80 gm

We know,

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{41.80\ \text{gm}}{50\ \text{ml}} = 0.836\ \text{gm/ml}^3$$

**CASE 3:- B20 BLEND (mustard biodiesel with petro diesel)**

The procedure of calculate the density of B20 blend is given below:-

Weight of empty cylindrical flask (100 ml) = 130.105 gm

Volume of B20 blend taken in a cylindrical flask = 50 ml

Weight of cylindrical flask with B20 blend = 172.005 gm

Weight of B20 blend alone = 172.005 – 130.105 = 41.90 gm

We know, $$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{41.90\text{ gm}}{50\text{ ml}} = 0.838\text{ gm/ml}^3$$

**CASE 4:- B100 (mustard biodiesel)**

The procedure of calculate the density of B20 blend is given below:-

Weight of empty cylindrical flask (100 ml) = 129.005 gm

Volume of B100 blend taken in a cylindrical flask = 50 ml

Weight of cylindrical flask with B100 blend = 172.558 gm

Weight of B100 blend alone = 172.505 – 129.005 = 43.50 gm

We know, $$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{43.50\text{ gm}}{50\text{ ml}} = 0.87\text{ gm/ml}^3$$

**2. FFA VALUE:-** If the oil has a high water or free fatty acid (FFA) content the reaction will be unsuccessful due to saponification (saponification is defined as the reaction of an ester with a metallic base and water) commonly known as making soap, and make separation of the glycerol difficult at the end of the reaction. The FFA content of the raw oil will determine the quantity of biodiesel as the final product. A very low content of FFA (<0.2) can give a full 100% yield.

The procedure of calculate the FFA Value is given below:-

1. Take 50 ml of Neutralise spirit in a conical flask with the addition of the indicator phenolphthalein
2. 10 ml of base oil is added to the conical flask
3. Heat contents until first bubbling occurs (approx 70°C)
4. Phenolphthalein will indicate end of reaction as a red/pink colour when NaOH is used as titrate (0.1N)
5. When quantities are know the FFA content can be calculated.

$$\text{Weight of sample} = \text{Volume} \times \text{density}$$

$$(28.2 \times V \times N)/\ (\text{weight of sample})$$

Where,

$V$ = volume of NaOH consumed in the titration

$N$ = Normality of NaOH

**5.14 FFA value of different blends i.e., B10, B15, and B20 (cotton seed biodiesel with petro diesel) is given below:**

**CASE 1:- B10 BLEND (cotton seed biodiesel with petro diesel)**

FFA Value = (28.2×0.1×0.31)/ 10 = 0.090

**CASE 2:- B15 BLEND (cotton seed biodiesel with petro diesel)**

FFA Value = (28.2×0.1×0.35)/ 10 = 0.10

**CASE 3:- B20 BLEND (cotton seed biodiesel with petro diesel)**

FFA Value = (28.2×0.1×0.4)/ 10 = 0.109

**5.15 FFA value of different blends i.e., B10, B15, and B20 (mustard biodiesel with petro diesel) and is given below:**

**CASE 1:- B10 BLEND (mustard biodiesel with petro diesel)**

FFA Value = (28.2×0.1×0.25)/ 10 = 0.072

**CASE 2:- B15 BLEND (mustard biodiesel with petro diesel)**

FFA Value = (28.2×0.1×0.3)/ 10 = 0.084

**CASE 3:- B20 BLEND (mustard biodiesel with petro diesel)**

FFA Value = (28.2×0.1×0.35)/ 10 = 0.095

**3. VISCOSITY: -** Viscosity is an important property of a diesel. Improper viscosity leads to poor combustion, which results in loss of power and excessive exhaust smoke. Diesel fuels with extremely low viscosities may not provide sufficient lubrication for the closely fit pumps and Injector plungers. They can promote abnormal wear and cause injector and injector pump leakage and dribbling leading to loss of power as fuel delivered by the injector is reduced. Diesel fuel with higher viscosity is also not desirable as too viscous fuel increases pumping losses in injector pump and injectors, which reduces injection pressure resulting in poor atomization and inefficient mixing with air ultimately affecting the combustion process. The procedure of calculate the kinematic viscosity is given below:-

A Redwood Viscometer was used for measurement of kinematic viscosity of selected fuel samples. The instrument measures the time of gravity flow in seconds of a fixed volume of the fluid (50 ml) through specified orifice made in a 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 agate jet at the bottom up to a specified level indicated in a cup. The cup was surrounded by water jacket having an immersion heater. The heater was heated to $38^0$C by regulating the rate of heating using a voltage regulator of the instrument. A simple 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 samples. Each test was replicated thrice. Kinematic viscosity in centistokes was then calculated from time units by using the relationships:-

$$V_k = 0.26\,t - 179/t \qquad \text{(i)}$$

When 34 < t < 100 and

$$V_k = 0.24\,t - 50/t \qquad \text{(ii)}$$

When t > 100

$V_k$ = Kinematic viscosity in centistokes, cSt

t = Time for flow of 50 ml sample,

**5.16 Viscosity of different blends i.e., B10, B15, and B20 (cotton seed biodiesel with petro diesel) and is given below:**

**CASE 1:- B10 BLEND (cotton seed biodiesel with petro diesel)**

| Sr. No. | Temperature ($^0$C) | Time (seconds) |
|---|---|---|
| 1. | 40 | 32.8 |
| 2. | 40 | 31.6 |
| 3. | 40 | 32.4 |

Calculate the mean of time i.e. (32.8+31.6+32.4)/ 3 = 96.8 / 3 = 32.26 seconds

The time (t) in seconds lies within the range 34 < t < 100

Put the value in formula, $v_k = 0.24\,t - 179 / t$

$$V_k = 0.24 \times 32.26 - (179 / 32.26)$$

$$= 7.744 - 5.548$$

$$= 2.19 \text{ cSt}$$

**CASE 2:- B15 BLEND (cotton seed biodiesel with petro diesel)**

| Sr. No. | Temperature ($^0$C) | Time (seconds) |
|---|---|---|
| 1. | 40 | 33.2 |
| 2. | 40 | 32.0 |
| 3. | 40 | 33.0 |

Calculate the mean of time i.e. (33.2+32.0+33.0)/ 3 = 98.2 / 3 = 32.73 seconds

The time (t) in seconds lies within the range $34 < t < 100$

Put the value in formula, $v_k = 0.24\ t – 179 / t$

$$V_k = 0.24 \times 32.73 – (179 / 32.73)$$

$$= 7.856 – 5.468$$

$$= 2.38 \text{ cSt}$$

**CASE 3:- B20 BLEND (cotton seed biodiesel with petro diesel)**

| Sr. No. | Temperature ($^0$C) | Time (seconds) |
|---|---|---|
| 1. | 40 | 33.9 |
| 2. | 40 | 33.6 |
| 3. | 40 | 34.0 |

Calculate the mean of time i.e. (33.9+33.6+34.0)/ 3 = 101.5 / 3 = 33.83 seconds

The time (t) in seconds lies within the range $34 < t < 100$

Put the value in formula, $v_k = 0.24\ t – 179 / t$

$$V_k = 0.24 \times 35.8 – (179 / 33.83)$$

= 8.592 – 5.29

= 2.82 cSt

**5.17 Viscosity of different blends i.e., B10, B15, and B20 (mustard biodiesel with petro diesel) and is given below:**

**CASE 1:- B10 BLEND (mustard biodiesel with petro diesel)**

| Sr. No. | Temperature ($^0$C) | Time (seconds) |
|---|---|---|
| 1. | 40 | 33.4 |
| 2. | 40 | 32.6 |
| 3. | 40 | 32.0 |

Calculate the mean of time i.e. (323.4+32.6+32.0)/ 3 = 98 / 3 = 32.66 seconds

The time (t) in seconds lies within the range 34 < t < 100

Put the value in formula, $v_k = 0.24\ t – 179 / t$

$V_k = 0.24 \times 32.66 – (179 / 32.66)$

= 7.84 – 5.4807

= 2.35 cSt

**CASE 2:- B15 BLEND (mustard biodiesel with petro diesel)**

| Sr. No. | Temperature ($^0$C) | Time (seconds) |
|---|---|---|
| 1. | 40 | 33.5 |
| 2. | 40 | 32.9 |
| 3. | 40 | 33.0 |

Calculate the mean of time i.e. (33.5+32.9+33.0)/ 3 = 99.4 / 3 = 33.13 seconds

The time (t) in seconds lies within the range 34 < t < 100

Put the value in formula, $v_k = 0.24\ t - 179 / t$

$$V_k = 0.24 \times 33.13 - (179 / 33.13)$$

$$= 7.952 - 5.402$$

$$= 2.54 \text{ cSt}$$

**CASE 3:- B20 BLEND (mustard biodiesel with petro diesel)**

| Sr. No. | Temperature ($^0$C) | Time (seconds) |
|---|---|---|
| 1. | 40 | 33.9 |
| 2. | 40 | 34.6 |
| 3. | 40 | 34.0 |

Calculate the mean of time i.e. (33.9+34.6+34.0)/ 3 = 102.5 / 3 = 34.16 seconds

The time (t) in seconds lies within the range $34 < t < 100$

Put the value in formula, $v_k = 0.24\ t - 179 / t$

$$V_k = 0.24 \times 34.16 - (179 / 34.16)$$

$$= 8.20 - 5.24$$

$$= 2.95 \text{ cSt}$$

**4. FLASH AND FIRE POINT: -** The temperature, at which material gives so many vapors, when mixed with air, forms an ignitable mixture and gives a momentary flash on application of a small pilot flame. 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 sufficient 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$^0$C. The flash and fire point of the fuel samples was determined as per **IS: 1448 [P: 32]: 1992**.

A Pensky Martin Flash Point (closed) apparatus as shown in fig 3.6 was used for measuring the flash and fire point of the fuel samples.

The procedure to calculate the Flash point is given below:-

1. 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.
2. 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 $5^0$C per min.
3. The temperature was measured with the help of a thermometer of -10 to $400^0$C range.
4. At every $1^0$C temperature rise, flame was introduced for a moment with the help of a shutter.
5. The temperature at which a flash appeared in the form of sound and light was recorded as flash point.
6. The fire point was recorded as the temperature at which fuel vapor catches fire and stays for minimum of five seconds.

**Fig 5.2: Pensky Marten apparatus used for measurement of flash and fire point**

### 5.18 The Flash point and Fire point of Blends B10, B15, B20 (cotton seed biodiesel with petro diesel) is given below: - Table: 5.7

| Sr.No | Blends | Flash Point($^0$C) | Fire Point($^0$C) |
|---|---|---|---|
| 1. | B 10 | 65 | 70 |
| 2. | B15 | 70 | 75 |
| 3. | B20 | 70 | 75 |
| 4. | B100 | 160 | 165 |

### 5.19 The Flash point and Fire point of Blends B10, B15, B20 (mustard biodiesel with petro diesel) is given below: - Table: 5.8

| Sr.No | Blends | Flash Point($^0$C) | Fire Point($^0$C) |
|---|---|---|---|
| 1. | B 10 | 70 | 75 |
| 2. | B15 | 75 | 80 |
| 3. | B20 | 65 | 70 |
| 4. | B100 | 145 | 150 |

**5. CLOUD AND POUR POINT: -**The Cloud and Pour point is 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 fig 3.5.

The procedure of calculate the cloud point is given below:-

1. The apparatus mainly consists of 12 cm high glass tubes of 3 cm diameter.
2. These tubes are enclosed in an air jacket, which is filled with a freezing mixture of crushed ice and sodium chloride crystals.
3. 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.

4. 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 were 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 flow ability. 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.

### 5.20 The Cloud point and Pour point of Blends B10, B15, B20 (cotton seed biodiesel with petro diesel) is given below: - Table: 5.9

| Sr. No | Blends | Cloud Point ($^{0}$C) | Pour Point ($^{0}$C) |
|---|---|---|---|
| 1. | B 10 | -3 | -8 |
| 2. | B15 | -9 | -14 |
| 3. | B20 | -7 | -12 |
| 4. | B100 | -4 | -9 |

**Fig 5.3: Cloud and pour point apparatus**

**5.21 The Cloud point and Pour point of Blends B10, B15, B20 (mustard biodiesel with petro diesel) is given below**: - **Table: 5.10**

| Sr. No | Blends | Cloud Point ($^0$C) | Pour Point ($^0$C) |
|---|---|---|---|
| 1. | B 10 | -9 | -14 |
| 2. | B15 | -5 | -10 |
| 3. | B20 | -2 | -7 |
| 4. | B100 | 4 | -12 |

5. **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, cotton seed and mustard oil were measured as per the standard **ASTM D482-IP 4** of Institute of Petroleum, USA. An electric muffle furnace of was used in the experiment as shown in fig. The procedure for calculate the value of Ash content is given below:-

1. First, sample was taken in a silica dish.
2. The dish was first weighed empty and then with the fuel sample (14-15 gm).
3. The sample weight was obtained from the difference between the initial and final weight of the dish.
4. The sample was then placed in the muffle furnace and heated at 500$^0$C for 20 minutes. The ash content was obtained using the equation given below:-

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

Where, $A_C$ = Ash content, percent

**Table below shows the values of different blends (cotton seed biodiesel with petro diesel) which are used to calculate the ash content: - Table: 5.11**

| Blends<br>Steps | B 10 | B15 | B20 | B100 |
|---|---|---|---|---|
| Wt. of empty disc (gm) | 31.523 | 32.662 | 38.886 | 37.611 |
| Add biodiesel (14-15 gm) | 14.278 | 14.124 | 14.335 | 14.120 |
| Wt. of disc after exp.(gm) | 31.524 | 32.663 | 38.787 | 37.613 |

**Fig 5.4: - MUFFLE FURNACE**

**5.22 Ash content of different blends i.e., B10, B15, and B20 (cotton seed biodiesel with petro diesel) and is given below:**

**CASE 1:- Calculation of ash content for B10 blend**

$$A_C = \frac{\text{(Wt. of dish after exp. - Wt. of dish)}}{\quad} \times 100$$

$$(\text{Wt. of sample})$$

$$= \frac{(31.524 - 31.523)}{14.278} \times 100$$

$$= 0.010\ \%$$

**CASE 2:- Calculation of ash content for B15 blend**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(32.663 - 32.662)}{14.124} \times 100$$

$$= 0.0122\ \%$$

**CASE 3:- Calculation of ash content for B20 blend**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(31.787 - 31.785)}{14.335} \times 100$$

$$= 0.014\ \%$$

**CASE 4:- Calculation of ash content for B100 (cotton seed biodiesel)**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(37.613 - 37.611)}{14.120} \times 100$$

$$= 0.018\ \%$$

**Table below shows the values of different blends (mustard biodiesel with petro diesel) which are used to calculate the ash content: - Table: 5.12**

| Blends<br>Steps | B 10 | B15 | B20 | B100 |
|---|---|---|---|---|
| Wt. of empty disc (gm) | 35.952 | 29.772 | 39.730 | 38.730 |
| Add biodiesel (14-15 gm) | 14.250 | 14.270 | 14.160 | 14.739 |
| Wt. of disc after exp.(gm) | 32.9521 | 29.773 | 39.732 | 38.732 |

**5.23 Ash content of different blends i.e., B10, B15, and B20 (mustard biodiesel with petro diesel) and is given below**

**CASE 1:- Calculation of ash content for B10 blend**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(32.95214 - 32.9520)}{14.250} \times 100$$

$$= 0.0105\ \%$$

**CASE 2:- Calculation of ash content for B15 blend**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(29.773 - 29.772)}{14.270} \times 100$$

$$= 0.0128\ \%$$

**CASE 3:- Calculation of ash content for B20 blend**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(39.7321 - 39.730)}{14.160} \times 100$$

$$= 0.0149\ \%$$

**CASE 4:- Calculation of ash content for B100 (cotton seed biodiesel)**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(38.732 - 38.730)}{14.739} \times 100$$

$$= 0.0189\ \%$$

**6. CARBON RESIDUE: -** Carbon residue was determined for different fuels by using a carbon residue apparatus. The measurement was made in accordance with the **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.

The procedure for calculate the value of Ash content is given below:-

1. First, the bulb was weighed empty and then with the fuel sample (4-5 gm).

2. Add 4-5 gm fuel in a bulb and weighed gain.

3 The sample weight was obtained from the difference between the initial and final weight of the bulb.

4. The sample was then placed in the carbon residue measurement content and heated at 500$^0$C for 20 minutes. The carbon residue content was obtained using the equation given below:-

$$C_r = \frac{WC}{W_S} \times 100$$

Where,

Cr = Carbon residue, %

Wc = Weight of carbon residue, g

Ws = Weight of the sample, g

**Fig 5.5: Carbon Residue Content Apparatus**

**The table below shows the values of different blends (cotton seed biodiesel with petro diesel) which are used to calculate the carbon residue content:-Table: 5.13**

| Blends / Steps | B 10 | B15 | B20 | B100 |
|---|---|---|---|---|
| Wt. of empty bulb (gm) | 10.550 | 9.250 | 8.965 | 10.920 |
| Add sample (4-5 gm) | 4.460 | 4.740 | 4.370 | 4.230 |
| Wt. of bulb after exp.(gm) | 10.5509 | 9.2509 | 8.9655 | 10.9204 |

**5.24 Carbon residue content of different blends i.e., B10, B15, and B20 (cotton seed biodiesel with petro diesel) and is given below:**

**CASE 1:- Calculation of carbon residue content for B10 blend**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(10.5509 - 10.550)}{4.460} \times 100$$

$$= 0.02038\ \%$$

**CASE 2:- Calculation of carbon residue content for B15 blend**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(9.2509 - 9.250)}{4.740} \times 100$$

$$= 0.0198\ \%$$

**CASE 3:- Calculation of carbon residue content for B20 blend**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(8.9655 - 8.965)}{4.370} \times 100$$

$$= 0.01324\ \%$$

**CASE 4:- Calculation of carbon residue content for B100 (cotton seed biodiesel)**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(10.9204 - 10.920)}{4.230} \times 100$$

$$= 0.0112\ \%$$

**The table below shows the values of different blends (mustard biodiesel with petro diesel) which are used to calculate the carbon residue content: - Table: 5.14**

| Blends<br>Steps | B 10 | B15 | B20 | B100 |
|---|---|---|---|---|
| Wt. of empty bulb (gm) | 10.565 | 10.120 | 9.962 | 10.957 |
| Add sample (4-5 gm) | 4.448 | 4.556 | 4.546 | 4.298 |
| Wt. of bulb after exp.(gm) | 10.5659 | 10.1209 | 9.96290 | 10.9575 |

**5.25 Carbon residue content of different blends i.e., B10, B15, and B20 (mustard biodiesel with petro diesel) and is given below**

**CASE 1:- Calculation of carbon residue content for B10 blend**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(10.5659 - 10.565)}{4.556} \times 100$$

$$= 0.02064\ \%$$

**CASE 2:- Calculation of carbon residue content for B15 blend**

$$A_C = \frac{(\text{Wt. of dish after exp. - Wt. of dish})}{(\text{Wt. of sample})} \times 100$$

$$= \frac{(10.1209 - 10.120)}{4.740} \times 100$$

$$= 0.02026\ \%$$

**CASE 3:- Calculation of carbon residue content for B20 blend**

$$A_C = \frac{\text{(Wt. of dish after exp. - Wt. of dish)}}{\text{(Wt. of sample)}} \times 100$$

$$= \frac{(9.9629 - 9.962)}{4.546} \times 100$$

$$= 0.0198\ \%$$

**CASE 4:- Calculation of carbon residue content for B100 (cotton seed biodiesel)**

$$A_C = \frac{\text{(Wt. of dish after exp. - Wt. of dish)}}{\text{(Wt. of sample)}} \times 100$$

$$= \frac{(10.9575 - 10.957)}{4.298} \times 100$$

$$= 0.0138\ \%$$

**7. CALORIFIC VALUE: -** The heat of combustion or calorific value of a fuel is an important measure since it is the heat produced by the fuel within the engine that enables the engine to do the useful work. The gross heat of combustion of fuel samples was determined as per **IS: 1448 [P: 6]: 1984** with the help of a Widson Scientific Works make Isothermal Bomb Calorimeter (Plate 3.9). A fuel sample of 1 ml 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.

The gross 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

$\Delta T$ = Rise in Temperature, $^0$C

$M_S$ = Mass of sample burnt, g

**Fig 5.7: Bomb Calorimeter used for measurement of Calorific value**

**Table below shows the calorific value of B10, B15, B20 blends (cotton seed biodiesel with petro diesel) and B100 (cotton seed biodiesel):- Table: 5.15**

| Blends | B 10 | B 15 | B 20 | B 100 |
|---|---|---|---|---|
| Calorific value kJ/kg | 42700 | 42550 | 42400 | 40000 |

**Table below shows the calorific value of B10, B15, B20 blends (mustard biodiesel with petro diesel) and B100 (mustard biodiesel):- Table: 5.16**

| Blends | B 10 | B 15 | B 20 | B 100 |
|---|---|---|---|---|
| Calorific value kJ/kg | 41754.3 | 41631.45 | 41508.6 | 39542.98 |

# CHAPTER 6

# RESULTS AND DISCUSSIONS

Worldwide, biodiesel is largely produced by methyl transesterification of edible and non edible oils. The concept of methyl transesterification is gaining attention as ethanol is derived from renewable biomass sources. The studies were, therefore, conducted on standardizing methyl transesterification process parameters for waste cotton seed oil and waste mustard oil, characteristic fuel properties of diesel, waste cotton seed oil and waste mustard oil, methyl esters of cotton seed biodiesel and mustard biodiesel and their 10%, 15% and 20% blends with diesel.

The recovery of ester as well as its kinematic viscosity is affected by the transesterification process parameters such as catalyst concentration, reaction temperature and reaction time, molar ratio used. The above parameters were standardized to obtain methyl ester of waste cotton seed and mustard oil with lowest possible kinematic viscosity and highest level of recovery. The fuel properties such as kinematic viscosity, relative density, cloud and pour point, flash and fire point, ash content and carbon diesel, waste cotton seed oil, mustard oil and methyl ester of cotton seed and mustard oil as well as their blends with diesel were compared. The results of parameters measured and their analytical interpretation with discussion are presented in this chapter.

## 6.1 Standardization of Transesterification Process Parameters regarding cotton seed methyl ester and mustard methyl ester

Transesterification of vegetable oils is done to significantly reduce its viscosity by separating glycerol content from it. The separation of glycerol is influenced by the parameters such as molar ratio, catalyst type, catalyst concentration, reaction time, reaction and temperature, etc. The recovery of ester and reduction in kinematic viscosity of a vegetable oil due to separation of glycerol largely depend on selecting the appropriate process parameters as mentioned below. Table 6.1 and 6.2 revealed ester recovery, FFA Value and its kinematic viscosity regarding CME with different catalyst concentration (1%, 1.5%, 2% and 2.5%).

Table 6.1 Ester recovery and its respective kinematic viscosity regarding cotton seed methyl ester

(Catalyst concentration=1%, 1.5%, 2%, 2.5%)

| Reaction Temperature $^0C$ | Reaction Time Min | Catalyst Con. % | Methanol Quantity gm | Oil Taken gm | Settling Time hr | Ester Recovery gm | Kinematic Viscosity cSt | FFA Value |
|---|---|---|---|---|---|---|---|---|
| 60 | 60 | 1 | 18.2 | 91 | 1 | 77.12 | 4.32 | 0.139 |
| 60 | 60 | 1.5 | 18.2 | 91 | 1 | 71.82 | 3.6 | 0.112 |
| 60 | 60 | 2 | 18.2 | 91 | 1 | 64.10 | 2.9 | 0.090 |
| 60 | 60 | 2.5 | 18.2 | 91 | 1 | 53.94 | 2.1 | 0.0564 |

Table 6.2 Ester recovery and its respective kinematic viscosity regarding mustard methyl ester

(Catalyst concentration=1%, 1.5%, 2%, 2.5%)

| Reaction Temperature $^0C$ | Reaction Time Min | Catalyst Con. % | Methanol Quantity gm | Oil Taken gm | Settling Time hr | Ester Recovery gm | Kinematic Viscosity cSt | FFA Value |
|---|---|---|---|---|---|---|---|---|
| 60 | 60 | 1 | 17.4 | 87 | 1 | 83.23 | 4.5 | 0.143 |
| 60 | 60 | 1.5 | 17.4 | 87 | 1 | 76.49 | 3.7 | 0.126 |
| 60 | 60 | 2 | 17.4 | 87 | 1 | 65.54 | 3.1 | 0.0835 |
| 60 | 60 | 2.5 | 17.4 | 87 | 1 | 58.82 | 2.5 | 0.0423 |

## 6.2 Effect of ester recovery (cotton seed methyl ester)

Table 6.1 shows the methyl ester recovered by transesterification process carried out at different quantity of catalyst concentration. It is evident from the table that the recovery of cotton seed methyl esters observed at different catalyst concentration varied between 53.94 to 77.12 gram. It is, therefore, seen that highest recovery of 77.12 of methyl ester was obtained at 91 gm when raw cotton seed oil was reacted with 20% of methanol at $60^0$ C for 45 minute in presence of 1 percent KOH and then allowed to settle for 1 hr. After the reaction is over within the specified time period the mixture is poured in to a separating flask and kept 1 hour for settling. The upper layer is methyl ester (biodiesel) and lower dark layer is glycerol. Now the pure biodiesel is ready for using in diesel engine. Although the ester recovery is higher at 1% concentration of catalyst, but at these percentage the value of Viscosity and FFA Value was also higher. At 1.5 % concentration of catalyst the ester recovery was less but the value of Viscosity and FFA was lie with in the range. Further addition of catalyst was decreasing the ester recovery and also the values of viscosity and FFA decreasing.

Table 6.3 Optimized process parameters for maximum yield of ester regarding cotton seed methyl ester

| Reaction Temperature $^0$C | Reaction Time Min | Catalyst Con. % | Methanol Quantity gm | Oil Taken gm | Settling Time hr | Ester Recovery gm | Kinematic Viscosity cSt | FFA Value |
|---|---|---|---|---|---|---|---|---|
| 60 | 60 | 1.5 | 18.2 | 91 | 1 | 71.82 | 3.6 | 0.112 |

## 6.3 Effect of ester recovery (mustard methyl ester)

Table 6.2 shows the methyl ester recovered by transesterification process carried out at different quantity of catalyst concentration. It is evident from the table that the recovery of mustard methyl esters observed at different catalyst concentration varied between 58.82 to 83.23 gram. It is, therefore, seen that highest recovery of 83.23 gm of methyl ester was obtained from 87 gm when raw cotton seed oil was reacted with 20% of methanol at $60^0$ C for 45 minute in presence of 1 percent KOH and then allowed to settle for 1 hr. After the reaction is over within the specified time period the mixture is poured in to a separating flask and kept 1 hour for settling. The upper layer is methyl ester (biodiesel) and lower dark layer is glycerol. Now the pure biodiesel is ready for using in diesel engine. Although the ester recovery is higher at 1% concentration of catalyst, but at these percentage the value of Viscosity and FFA Value was also higher. At 1.5 % concentration of catalyst the ester recovery was less but the value of Viscosity and FFA was lie with in the range. Further addition of catalyst was decreasing the ester recovery and also the values of viscosity and FFA decreasing.

Table 6.4 Optimized process parameters for maximum yield of ester regarding mustard methyl ester

| Reaction Temperature $^0$C | Reaction Time Min | Catalyst Con. % | Methanol Quantity gm | Oil Taken gm | Settling Time hr | Ester Recovery gm | Kinematic Viscosity cSt | FFA Value |
|---|---|---|---|---|---|---|---|---|
| 60 | 60 | 1.5 | 17.4 | 87 | 1 | 76.49 | 3.7 | 0.126 |

- **Fuel Characterization**

## 6.4 Characterization of blends of cotton seed methyl ester

### 6.4.1. Density

The relative density of B10, B15, B20 blends and cotton seed methyl ester were observed 8.5, 8.0, 7.0 and 9.6 percent higher than that of diesel respectively. The experimental results indicated that the relative density of cotton seed methyl ester is higher to that of diesel.

### 6.4.2. Free Fatty Acid content

The FFA content of B10, B15, B20 blends and cotton seed methyl ester were observed 0.090%, 0.10%, 0.109% and 0.112%.

### 6.4.3. Kinematic viscosity

The kinematic viscosity of of B10, B15, B20 blends and cotton seed methyl ester were found as 2.19, 2.38, 2.28 and 3.6 centistokes at $40^0$C. Cotton seed methyl ester had the kinematic viscosity 7.692 percent less than that of diesel. The results indicated that the blend B 20 was observed the kinematic viscosity decreases as compared to blend B 10 and blend B 15 due to experimental error.

### 6.4.4. Flash and fire point

The blends B10, B15, B20 have higher flash and fire point as compare to diesel. The flash and fire point of cotton seed methyl ester was found higher than that of diesel respectively. The results indicated that the blend B 15 was observed the flash and fire point 16.66 percent higher than that of diesel.

### 6.4.5. Cloud and pour point

The blends B10, B15, B20 have higher cloud and pour point as compare to diesel. The cloud and pour point of cotton seed methyl ester was also higher as compared of diesel respectively. The results indicated that the blend B 10 was observed the cloud point nearly to that of diesel.

### 6.4.6. Ash content

It is clear from the results that the blends and cotton seed methyl ester increased the ash content to great extent with diesel respectively.

### 6.4.7. Carbon residue content

The ester of cotton seed and and their blends were found to have carbon residue content lower than that of diesel which is better for engine performance and it also prevents carbon deposition inside the combustion chamber. The blend B 20 has lowest carbon residue content as compare to B 10 and B 15.

### 6.4.8. Calorific value

The calorific value of diesel, cotton seed methyl ester and blend B 10 were found as 43,000, 40,000 and 40,300 KJ/Kg respectively. The calorific value of blend B 10 is decreased by 6.27% than that of diesel whereas the calorific value of cotton seed methyl ester is decreased by 6.97% than that of diesel. The result shows that the calorific value of B10 blend is lower than diesel fuel.

**Table 6.5 Fuel properties of cotton seed methyl ester and their blends compared to diesel**

| Sr.No | Properties | Units | B100 CSE | B10 | B15 | B20 | Diesel | ASTM D6751 |
|---|---|---|---|---|---|---|---|---|
| 1. | Density | Kg/m$^3$ | 910 | 838 | 842 | 846 | 0.830 | 0.84-0.92 |
| 2. | FFA value | % | 0.112 | 0.090 | 0.10 | 0.109 | - | <0.2 |
| 3. | Viscosity | cSt | 3.6 | 2.19 | 2.38 | 2.28 | 3.9 | 1.9-6.0 |
| 4. | Flash point | $^0$C | 160 | 65 | 70 | 70 | 60 | >130 |
| 5. | Fire point | $^0$C | 165 | 70 | 75 | 75 | 65 | - |
| 6. | Cloud point | $^0$C | -3 | -9 | -7 | -4 | -12 | -10 |
| 7. | Pour point | $^0$C | -8 | -14 | -12 | -9 | -16 | -15 |
| 8. | Ash content | % | 0.0180 | 0.010 | 0.012 | 0.014 | <0.02 | <0.02 |
| 9. | Carbon Residue | % | 0.0112 | 0.02038 | 0.0198 | 0.01324 | - | 0.05 max |
| 10 | Calorific value | KJ/Kg | 40000 | 42700 | 42550 | 42400 | 43000 | - |

## 6.5. Characterization of blends of mustard methyl ester

### 6.5.1. Density

The relative density of B10, B15, B20 blends and mustard methyl ester were observed 4.3, 4.0, 3.8 and 4.8 percent higher than that of diesel respectively. The experimental results indicated that the relative density of mustard methyl ester is slightly increased to that of diesel.

### 6.5.2. Free Fatty Acid content

The FFA content of B10, B15, B20 blends and mustard methyl ester were observed 0.072%, 0.084%, 0.095% and 0.126%.

### 6.5.3. Kinematic viscosity

The kinematic viscosity of of B10, B15, B20 blends and mustard methyl ester were found as 2.35, 2.54, 2.95 and 3.7 centistokes at $40^0$C. Mustard methyl ester had the kinematic viscosity 5.12 percent less than that of diesel. The results indicated that the blend B 10 was observed the kinematic viscosity 40.05 percent less than that of diesel.

### 6.5.4. Flash and fire point

The blends B10, B15 have higher flash and fire point as compare to diesel. The flash and fire point of mustard methyl ester was found higher than that of diesel respectively. The results indicated that the blend B 20 was observed the lower flash and fire point as compare to blend B10 and B 15. The flash and fire point of blend B 20 was lower due to experimental error.

### 6.5.5. Cloud and pour point

The blends B10, B15, B20 have higher cloud and pour point as compare to diesel. The cloud and pour point of mustard methyl ester was also higher as compared of diesel respectively. The results indicated that the blend B 10 was observed the cloud point nearly to that of diesel.

### 6.5.6. Ash content

It is clear from the results that the mustard methyl ester and their blends increased the ash content to great extent with diesel respectively.

### 6.5.7. Carbon residue content

The ester of mustard and and their blends were found to have carbon residue content lower than that of diesel which is better for engine performance and it also prevents carbon deposition inside the combustion chamber. The blend B 20 has lowest carbon residue content as compare to B 10 and B 15.

### 6.5.8. Calorific value

The calorific value of diesel, mustard methyl ester and blend B 20 were found as 43,000, 39,542 and 41,508 KJ/Kg respectively. The calorific value of blend B 20 is decreased by 3.46% than that of diesel whereas the calorific value of mustard methyl ester is decreased by 8.86% than that of diesel. The result shows that the calorific value of B10 blend is lower than diesel fuel.

**Table 6.6 Fuel properties of mustard methyl ester and their blends compared to diesel**

| Sr.No | Properties | Units | B100 ME | B10 | B15 | B20 | Diesel | ASTM D6751 |
|---|---|---|---|---|---|---|---|---|
| 1. | Density | Kg/m$^3$ | 870 | 834 | 836 | 838 | 0.830 | 0.84-0.92 |
| 2. | FFA value | % | 0.126 | 0.072 | 0.084 | 0.095 | - | <0.2 |
| 3. | Viscosity | cSt | 3.7 | 2.35 | 2.54 | 2.95 | 3.9 | 1.9-6.0 |
| 4. | Flash point | $^0$C | 145 | 70 | 75 | 65 | 60 | >130 |
| 5. | Fire point | $^0$C | 150 | 75 | 80 | 70 | 65 | - |
| 6. | Cloud point | $^0$C | 4 | -9 | -5 | -2 | -12 | -10 |
| 7. | Pour point | $^0$C | -12 | -14 | -10 | -7 | -16 | -15 |
| 8. | Ash content | % | 0.0189 | 0.0105 | 0.0128 | 0.0149 | <0.02 | <0.02 |
| 9. | Carbon Residue | % | 0.0138 | 0.02064 | 0.02026 | 0.0198 | - | 0.05 max |
| 10. | Calorific value | KJ/Kg | 39542.98 | 41754 | 41631 | 41508 | 43000 | - |

## 6.6. Comparison of blends of cotton seed methyl ester and mustard methyl ester

Comparison of different blends of cotton seed methyl ester and mustard methyl ester based on properties are given below:

### 6.6.1. Density

The relative densities of B10 blends of cotton seed and mustard methyl ester were observed less as compared to blends B 15 and B 20 of both esters. The experimental results indicated that the relative density of B 10 blend of mustard methyl ester is slightly less to that of diesel.

### 6.6.2. Free Fatty Acid content

The FFA content of B10, B15, B20 blends of mustard methyl ester were observed less than the blends of cotton seed methyl esters.

### 6.6.3. Kinematic viscosity

The kinematic viscosity of of B10, B15, B20 blends of cotton seed methyl ester were found as 2.19, 2.38, 2.28 centistokes at $40^0$C. Mustard methyl ester blends have higher kinematic viscosity as compared to cotton seed ester. The results indicated that viscosity of B 20 blend of cotton seed methyl ester was observed less as compared to viscosity B 15 blend of cotton seed methyl ester, which was incorrect due to experimental error.

### 6.6.4. Flash and fire point

The blend B15 of cotton seed methyl ester and mustard methyl ester have higher flash and fire point as compare to blends B 10 and B 15 of both the esters. The flash and fire point of blend B 20 of mustard methyl ester was lower as compared to B10 and B15 blend of mustard ester due to experimental error.

### 6.6.5. Cloud and pour point

The B10 blend of both esters has lower cloud and pour point as compare to B 15 and B 20 blends of both esters.

### 6.6.6. Ash content

It is clear from the results that blends of mustard methyl ester has higher ash content as compared to blends of cotton seed methyl ester.

### 6.6.7. Carbon residue content

The blends B 10, B 15 and B 20 of cotton seed methyl were found to have carbon residue content lower than that of blends of mustard methyl ester which is better for engine performance and it also prevents carbon deposition inside the combustion chamber. The blend B 20 has lowest carbon residue content as compare to B 10 and B 15 of both the esters.

### 6.6.8. Calorific value

The blends B 10, B 15 and B 20 of cotton seed methyl were found to have higher calorific value than that of blends of mustard methyl ester. The blend B 20 of both esters has lowest calorific value as compared to B 10 and B 15 blends of both esters.

**Table: 6.7 Comparison of properties of different blends**

| Sr.No | Properties | Units | BLENDS (cotton seed methyl ester with diesel) | | | BLENDS (mustard methyl ester with diesel) | | |
|---|---|---|---|---|---|---|---|---|
| | | | B10 | B15 | B20 | B10 | B15 | B20 |
| 1. | Density | Kg/m$^3$ | 838 | 842 | 846 | 834 | 836 | 838 |
| 2. | FFA value | % | 0.084 | 0.107 | 0.118 | 0.072 | 0.084 | 0.095 |
| 3. | Viscosity | cSt | 2.19 | 2.38 | 2.28 | 2.35 | 2.54 | 2.95 |
| 4. | Flash point | $^0$C | 65 | 70 | 70 | 70 | 75 | 65 |
| 5. | Fire point | $^0$C | 70 | 75 | 75 | 75 | 70 | 65 |
| 6. | Cloud point | $^0$C | -9 | -7 | -4 | -9 | -5 | -2 |
| 7. | Pour point | $^0$C | -14 | -12 | -9 | -14 | -10 | -7 |
| 8 | Ash content | % | 0.010 | 0.012 | 0.014 | 0.0105 | 0.0128 | 0.0149 |
| 9. | Carbon Residue | % | 0.02038 | 0.0198 | 0.01324 | 0.02064 | 0.02026 | 0.0198 |
| 10. | Calorific value | KJ/Kg | 42700 | 42550 | 42400 | 41754 | 41631 | 41508 |

## CHAPTER 7

## CONCLUSIONS

The overall studies based on the production of biodiesel from waste cotton seed oil and waste mustard oil, fuel characterization of cotton seed and mustard methyl esters were carried out.

The following conclusions can be drawn:

**1**. The recovery of esters by transesterification of waste cotton seed oil and waste mustard oil with methanol are affected by varying the composition of catalyst.

The recovery of cotton seed methyl ester at lowest kinematic viscosity (3.6 cSt) was 71.82 gram from 91 gram is possible at the following standardized concentration of catalyst.

a) Molar ratio: - 5:1

b) Reaction time: - 60 minutes

c) Catalyst concentration:-1.5%

d) Reaction temperature:-$60^0$C

e) Settling time: - 1 hour

The recovery of mustard methyl ester at lowest kinematic viscosity (3.7 cSt) was 76.49 gram from 87 gram is possible at the following standardized concentration of catalyst.

a) Molar ratio: - 5:1

b) Reaction time:-60 minutes

c) Catalyst concentration: - 1.5%

d) Reaction temperature: - $60^0$C

e) Settling time: - 1 hour.

**2.** The relative density of B10 blends of cotton seed and mustard methyl ester were observed less as compared to blends B 15 and B 20 of both esters. The experimental results indicated that the relative density of B 10 blend of mustard methyl ester is slightly less to that of B 10 blend of cotton seed methyl ester. The relative density of cotton seed methyl ester and its B10 blend were observed 9.6 and 8.5 percent higher than that of diesel respectively. The relative density of mustard methyl ester and its B10 blend were observed 4.8 and 4.3 percent higher than that of diesel respectively. So B 10 blend was more suitable as compared to B 15 and B 20 blends of both the esters. Bio-diesel should always be blended at top of diesel fuel. If bio-diesel is first put at the bottom and then diesel fuel is added, it will not mix.

**3.** The FFA content of B10, B15, B20 blends of mustard methyl ester were observed less than the blends of cotton seed methyl esters. The FFA content of B 10 blends of both esters were less as compared to B 15 and B 20 blends of both esters. So B 10 blend was more optimized as compared to B 15 and B 20 blends of both the esters. If the oil has a high water or free fatty acid (FFA) content the reaction will be unsuccessful due to saponification (saponification is defined as the reaction of an ester with a metallic base and water) commonly known as making soap, and make separation of the glycerol difficult at the end of the reaction. The FFA content of the raw oil will determine the quantity of biodiesel as the final product. A very low content of FFA (<0.2) can give a full 100% yield.

**4.** The kinematic viscosity of of B10, B15, B20 blends of cotton seed methyl ester were found as 2.19, 2.38, 2.82 centistokes at $40^0$C. Mustard methyl ester blends have higher kinematic viscosity as compared to cotton seed ester. Mustard methyl ester had the kinematic viscosity 5.12 percent less than that of diesel and cotton seed methyl ester had the kinematic viscosity 7.692 percent less than that of diesel. The results indicated that the B 10 blends of both the esters were observed the kinematic viscosity 40.05 and 43.8 percent less than that of diesel. So B 10 blend was more optimized as compared to B 15 and B 20 blends of both the esters. Viscosity 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 injection pumps and power loss due to pump leakage whereas high viscosity may results in excessive pump resistance, filter blockage, high pressure and coarse atomization and fuel delivery rates.

**5.** The blends B10, B15, B20 of cotton seed and mustard methyl esters have higher flash and fire point as compare to diesel. The flash and fire point of cotton seed methyl ester and mustard methyl ester was found higher than that of diesel respectively. The results indicated that the blend B 15 of cotton seed methyl ester was observed the flash and fire point 16.66 percent higher than that of diesel. The blend B 20 of mustard methyl ester was observed the lower flash and fire point as compare to blend B10 and B 15. The flash and fire point of blend B 20 was lower due to experimental error. The blend B15 of cotton seed methyl ester and mustard methyl ester have higher flash and fire point as compare to blends B 10 and B 20 of both the esters. So B 15 blend was more optimized as compared to B 10 and B 20 blends of both the esters. Flashpoint of bio-diesel blends is dependent on the flashpoint of the base diesel fuel used, and increase with percentage of bio-diesel in the blend. Thus in storage, biodiesel and its blends are safer than conventional diesel. The flashpoint of biodiesel is around 160, but it can reduce drastically if the alcohol used in manufacture of bio-diesel is not removed properly. Residual alcohol in the bio-diesel reduces its flashpoint drastically and is harmful to fuel pump, seals, elastomers etc. It also reduces the combustion quality.

**6.** The blends B10, B15, B20 of cotton seed and mustard methyl esters have higher cloud and pour point as compare to diesel. The cloud and pour point of cotton seed methyl ester and mustard methyl ester was also higher as compared of diesel respectively. The results indicated that the blend B 10 of both the ester was observed the cloud point nearly to that of diesel. The B10 blend of both esters has lower cloud and pour point as compare to B 15 and B 20 blends of both the esters. At low operating temperature fuel may thicken and not flow properly affecting the performance of fuel lines, fuel pumps and injectors. Therefore B 10 blend was reliable to use in cold weather.

**7.** It is clear from the results that ash content increases as we increase the amount of biodiesel in petro diesel. The blends B10, B15 and B20 of cotton seed and mustard methyl ester have higher ash content as compared to diesel. B 10 blend was more optimized as compared to B 15 and B 20 blends of both the esters because it has lower ash content as compared to B15 and B 20 blends of both the esters. Ash content describes the amount of inorganic contaminants such as abrasive solids and catalyst residues and the concentration of soluble metal soaps contained in a fuel sample. These compounds are oxidized during the combustion process to form ash which is connected with engine deposits.

**8.** The esters of cotton seed and mustard were found to have carbon residue content lower than that of diesel which is better for engine performance and it also prevents carbon deposition inside the combustion chamber. The blend B 20 of both the esters has lowest carbon residue content as compare to B 10 and B 15. The blends B 10, B 15 and B 20 of cotton seed methyl were found to have carbon residue content lower than that of blends of mustard methyl ester. Therefore, on the basis of carbon residue content it was determined that cotton seed ester was better as compared to mustard ester.

**9.** The calorific value of a substance is the amount of energy released when the substance is burned completely to a final state and has released all of its energy. The calorific value of diesel, cotton seed methyl ester and mustard methyl ester were found as 43,000, 40,000 and 39542 KJ/Kg respectively. The calorific value of blend B 10 of cotton seed methyl ester was decreased by 6.27% than that of diesel whereas the calorific value of cotton seed methyl ester is decreased by 6.97% than that of diesel. The calorific value of blend B 20 of mustard methyl ester was decreased by 3.46% than that of diesel whereas the calorific value of mustard methyl ester was decreased by 8.86% than that of diesel. The blends B 10, B 15 and B 20 of cotton seed methyl were found to have higher calorific value than that of blends of mustard methyl ester. The blend B 20 of both esters has lowest calorific value as compared to B 10 and B 15 blends of both esters. So B 10 blend was more optimized as compared to B 15 and B 20 blends of both the esters.

**10.** The results indicates that characteristics of B10 blend of cotton seed methyl ester and mustard methyl ester was more optimized as compare to B15 and B20 blends.

**11.** Use of 10% blend of CSME and MME as partial diesel substitutes can go a long way in conservation measure, boosting economy, reducing uncertainty of fuel availability and making more self-reliant.

**12.** CSME and MME are non-toxic, biodegradable, environment-friendly, renewable fuels and do not add to global warming.

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