"BIODIESEL PRODUCTION USING JATROPHA OIL"

A Major Project Report
Submitted In Partial Fulfillment of the Requirements
For The Degree Of

MASTER OF TECHNOLOGY
IN
CHEMICAL ENGINEERING
(ENVIRONMENTAL PROCESS DESIGN)

BY
SHUKLA. PURVI. H.
(05MCH005)

Department of Chemical Engineering

INSTITUTE OF TECHNOLOGY
NIRMA UNIVERSITY OF SCIENCE & TECHNOLOGY
AHMEDABAD 382 481
MAY 2007

CERTIFICATE

This is to certify that the Major Project entitled "Biodiesel Production Using Jatropha Oil" submitted by Ms. Shukla. Purvi H (05MCH005), towards the partial fulfillment of the requirements for the award of Degree of Master of Technology in Chemical Engineering (Environmental Process Design) of Nirma University of Science and Technology is the record of work carried out by her under my supervision and guidance. The work submitted has in my opinion reached a level required for being accepted for examination. The results embodied in this project work to the best of my knowledge have not been submitted to any other University or Institution for award of any degree or diploma.

Project Guide:	**Co-Guide:**
(Prof. A.P. Vyas)	**(Mrs. F. K. Patel)**
Head of Chemical Engg. Dept.	**Lecturer,**
Institute of Technology,	**Institute of Technology,**
Nirma University	**Nirma University**

(Prof. A.P. Vyas)	**(Prof. A. B. Patel)**
Head of Chemical Engg. Dept.	**Director**
Institute of Technology	**Institute of Technology**
Nirma University	**Nirma University**

Examiners:	**i.**	**ii.**
	(Name and Signature)	**(Name and Signature)**

ABSTRACT

The world is confronted with the twin crises of fossil fuel depletion and environmental degradation. Efforts are under way in many countries, including India, to search for suitable alternative diesel fuels that are environment friendly. The need to search for these fuels arises mainly from the standpoint of preserving the global environment and the concern about long-term supplies of conventional hydrocarbon-based fuels.

Biofuel is referred to as liquid or gaseous fuels for the transportation sector that are predominantly produced from biomass. Among the different possible sources, biodiesel, an alternative diesel fuel is derived from vegetable oil, animal fats, or waste vegetable oils, is obtained by reacting the oil or fat with an alcohol (transesterification) in the presence of a catalyst to give the corresponding mono alkyl esters. Biodiesel is a renewable replacement to petroleum based diesel.

Biodiesel fuels offer a potentially very interesting alternative to mineral diesel regarding harmful emissions in addition to engine wear, cost and availability. Its biodegradability and given that all the organic carbon present is photosynthetic in origin, it does not contribute to a rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect.

The present work reports transesterification via catalytic route which is the better option among all the routes using the jatropha oil as a raw material. The catalyst used is KOH. The main focus is on the production of the biodiesel at the laboratory scale. Quality checking of the prepared sample is covered. Overall kinetic study and performance of B20 and B40 on the diesel engine was also performed.

The results of the project show that the yield of the biodiesel using jatropha oil is upto 80 to 85 %. The emission of the air pollutant like SO2 and SPM is decreases with the different biodiesel blends with different proportion without major changes in the engine performance.

ACKNOWLEDGEMENT

It gives me immense pleasure in expressing thanks and profound gratitude to my project guide **Prof A.P.Vyas** , Head of Chemical Engineering Department, and my co guide **Mrs. F. K. Patel ,** Lecturer , Chemical Department, Institute of Technology, Nirma University, Ahmedabad for their valuable guidance and continual encouragement throughout the my project work. I am heartily thankful to them for their precious time, suggestions and sorting out the difficulties of my topic that helped me a lot during this study.

I am also thankful to **Prof. A. B. Patel**, Director, Institute of Technology for his kind support in all respect during my study. I am thankful to Mr. M. H. Joshipura for helping in the procurement of the project work. I am thankful to all faculty members Mr R.A.Soni, Mrs Archana Patel, Ms. U.K. Kachhela, etc of Chemical Engineering Department, Nirma University, Ahmedabad for their special attention and suggestions towards the project work.

I am very thankful to the Mechanical Engineering Department of Nirma Univesity for providing me the laboratory facility for the testing purpose. I would like thanks Mr. R.N.Patel, Lecturer, Mechanical Engineering Department Nirma University Ahmedabad for his kind support and valuable guidance. I would like to extend my thanks to Mr H.M.Patel, Lecturer, Mechanical Engineering Department, Nirma University Ahmedabad for his valuable guidance. I m really thankful to them for their precious time, valuable guidance and continues co operation during project work.

I express my sincere thanks to the entire Laboratory Assistants from Chemical Engineering Department; Mr. Dhavalbhai, Mr. Girishbhai, Mr. Manishbhai, Mr. Devendrabhai and Mr. Chetanbhai for assisting in my experimentation work by providing all the accessories, equipments and chemicals for experimentation. I would like to extend my thanks to Mr. Chiragbhai Laboratory Assistant of the Mechanical Engineering Department for his continuous support during the experimental work. I am thankful to Miss. Sunita Parmar for her kind support and cooperation for

departmental resources. I would like to thanks all who is directly or indirectly involved during my project work.

The blessings of God and my Parents make the way for completion of my project work. I am very much grateful to them. I am thankful to all those friends specially hostel friends and my class mates who always help, moral support and encourage me.

Shukla Purvi H

Roll No. 05MCH005

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE AND ABBREVIATIONS

- BD - biodiesel
- CN - Cetane Number
- CO - Carbon Monoxide
- HC - Hydrocarbon
- PP - Pour Point
- EPA - Environnemental Protection act
- B100 - Pure Biodiesel
- CO_2 - Carbon Dioxide
- B20 - 20 % blend of biodiesel with pure diesel
- B40 – 40 % blend of biodiesel with pure diesel
- NO_X - Oxides Of Nitrogen
- GHG - Green House Gas
- WVO - Waste Vegetable Oil
- TBO - Tree Bearing Oil
- FFA- Free Fatty Acids
- LCA - Life Cycle Assessment
- SVO - Straight Vegetable Oil
- SCM - Supercritical Methanol
- KOH - Potassium Hydroxide
- RPM - Revolution Per Minute
- SPM - Suspended Particulate Matter
- LPM - Liter Per Minute
- TG - Triglyceride
- DG - Di Glyceride
- MG - Monoglycerides
- E - Alkyl Ester
- r_A - Rate Of Reactant A
- C_A - Final Concentration of A
- k - Rate Constant
- SFC - Specific Fuel Consumption
- FC - Fuel Consumption

- BP - Brake Power
- N - Rotational Speed
- ASTM - American Society of Testing Material

CHAPTER 1

INTRODUCTION

1.1 Introduction

Diesel fuels have an essential function in the industrial economy of a country. These are used in heavy trucks, city trucks, city transport buses, locomotive, electric generators, farm equipment, underground mine equipment etc. compared to the rest of the world, India's demand for diesel fuels is roughly six times that of gasoline. The need to search for these fuels arises mainly from the standpoint of preserving the global environment and concern about long term supplies of conventional hydrocarbon based diesel fuels. Among the different possible resources, diesel fuels derived from triglyceride (vegetable oils/animal fats) present a promising alternative to substitute diesel fuels. Fatty acid methyl esters, known as biodiesel, derived from triglycerides by transesterification with methanol have received the most attention.

Variety of the feedstocks is used to produce biodiesel namely edible and non edible oils, waste vegetable oil, animal fats etc. Under Indian condition only such plant sources can be considered for biodiesel production which is not edible oil in appreciable quantity and which can be grown in large-scale on wastelands. The important potential tree species for bio-diesel in India are Neem, Karanja, Kusum, Pilu, Ratanjot, Mahua, Bhikal, Undi, Thumba, Sal Nahor, Jojoba, Kamala, Kokam etc. Considering all the options available among non-edible Tree Bearing Oil seeds, Jatropha Curcas has been identified as the most suitable seed. The resulting biodiesel using the transesterification method is quite similar to conventional diesel fuel in its main characteristics. Biodiesel is compatible with conventional diesel and the two can be blended in any proportion.

1.2 Objective of The Project

Objective of my project is divided into several individual parts

- Preparation of the biodiesel using jatropha oil
- Analysis of the prepared sample to check the quality of the prepared sample
- Effect of various parameters on the yield of biodiesel
- Overall kinetics study of the process

- Testing of the diesel, B20 and B40 on the four stroke single cylinder diesel engine
- Performance and Emission characteristics of diesel engine

1.3 Significance of Project

The world is confronted with the twin crises of fossil fuel depletion and degradation. The demand for petroleum is increasing with each passing day. In that case, it become etmost necessity to search for alternative fuels which are renewable and in that biodiesel emerges as a real solution. Biodiesel is a cleaner burning fuel than diesel and a suitable replacement. It is made from non toxic, biodegradable, renewable sources. Biodiesel fuels offer a potentially very interesting alternative to mineral diesel regarding harmful emissions in addition to engine wear, cost and availability. Additionally biodiesel does not contain carcinogens, such as poly aromatic hydrocarbons and nitrous poly aromatic hydrocarbons and therefore produces pollutants that are less detrimental to human health when burned. It has a significant potential for use as an alternative fuel in compression ignition diesel engines. It is technically competitive with conventional, petroleum derived diesel fuel and required no changes in the fuel distribution infrastructure. There are different routes available for the biodiesel production. From the several methods available the transesterification via alkali catalyst route is the widely used method for the biodiesel production.

1.4 Project Methodology

- Batch experiments for the production of the biodiesel were carried out in laboratory with small amount of the raw oil.
- After the preparation of the samples of the biodiesel the testing of the biodiesel was done to find out fuel properties of the sample. After that the result of the testing were compared with the ASTM standard.
- The kinetics study of the overall reaction was done by using the several data available.
- The testing of the sample was done on the diesel engine. The engine performance and exhaust emission parameters are the key parameters. The fuel consumption, break power, RPM etc was calculated to find out the engine

behavior using this blend. The emission measurement of the petrodiesel, B20 and B40 were also done on the same engine. The SPM, SO_2 and NOx are the main emission parameters which effect on the environment.

1.5 Preface of Project Report

This report of project contains mainly introduction, literature survey, jatropha, kinetics study, engine performance and exhaust emission, experimental procedure and set up, results and discussion and finally conclusion.

Chapter-1 Introduction consists of significance, Objective and methodology of project work. Chapter 2 literature surveys include the following: Introduction to biodiesel, different methods available for biodiesel production, different transesterification methods for biodiesel production, variables affecting the transesterification reaction characterization of biodiesel, biodiesel specification as per the ASTM standard, the advantages and limitations of it, feedstock for biodiesel. Chapter 3 is focusing on the jatropha. It describes the characterization of jatropha, use of jatropha, advantages and limitations of jatropha, comparison of properties of jatropha oil with diesel. Chapter 4 gives detail idea about the kinetic study of the reaction. It describes the possible reactions during biodiesel production, development of model, than it shows the overall kinetics study of the reaction and gives the overall rate equation for the reaction. Chapter 5 describes theoretical background of the performance and exhaust emission. It shows the detail about the engine used for the testing, emission measurement methods etc.

Chapter 6 contains the experimental procedure and set up for the experiments which were done into the laboratory. This mainly focus on the production process, then analysis of the sample into the laboratory, its property checking with standards available, than finally testing it on the engine. Chapter 7 results and discussion includes the results of production of the biodiesel, analysis results, diagram of the performance of the engine performance, pie chart for the comparison of emission between prepared samples.

At last the conclusion derived from the project work and future scope of work.

CHAPTER 2

LITERATURE SURVEY

2. LITERATURE SURVEY

2.1 General

2.1.1 Introduction to Biofuels

The term bio-fuel is referred to as liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. Bio-fuels are generally considered as offering many priorities, including sustainability, reduction of greenhouse gas emissions, regional development, social structure and agriculture, security of supply. [2]

Known petroleum reserves are estimated to be depleted in less than 50 years at the present rate of consumption. In developed countries there is a growing trend towards employing modern technologies and efficient bio-energy conversion using a range of biofuels, which are becoming cost-wise competitive with fossil fuels.[2]

Biomass appears to be an attractive feedstock for three main reasons. First, it is a renewable resource that could be sustainably developed in the future. Second, it appears to have formidably positive environmental properties resulting in no net releases of carbon dioxide (CO_2) and very low sulfur content. Third, it appears to have significant economic potential provided that fossil fuel prices increase in the future. [2]

Advantages of bio-fuels are the following:

- Bio-fuels are easily available from common biomass sources
- Bio-fuels have a considerable environment friendly potential
- They are biodegradable and contribute to sustainability
- It is renewable energy source
- CO_2 emission in the life cycle is less compare another fuels

Main Biomass Conversion Processes

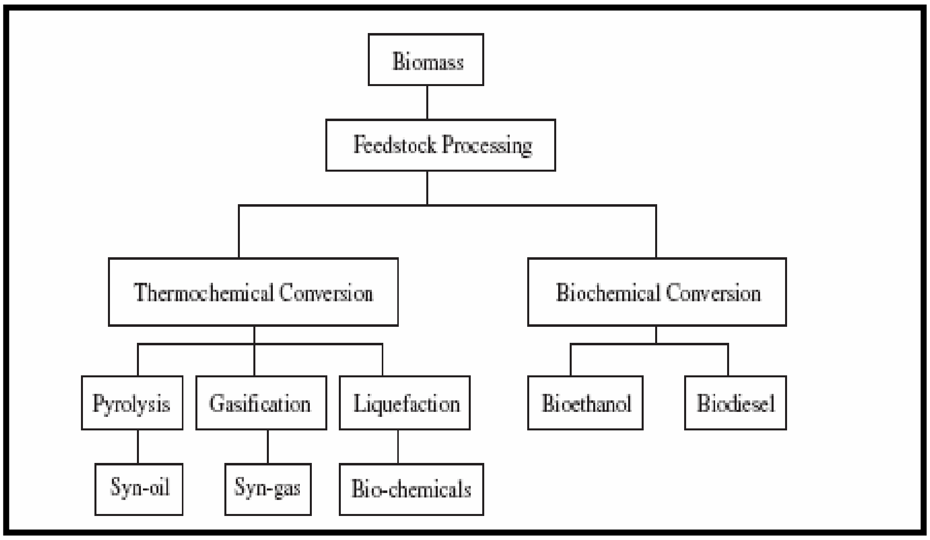


Figure 2.1 Main Biomass Conversion Processes [2]

Resources of Main Liquid Biofuels For Automotives

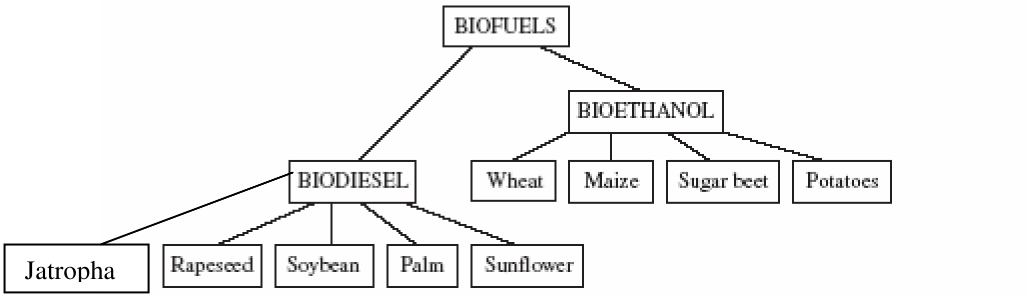


Figure 2.2 Resources of Main Liquid Biofuels for Automotives [2]

2.1.2 Historical Background [10, 13]

- Transesterification of a vegetable oil was conducted in early 1853, by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional.
- Rudolf Diesel's prime model, a single 10 ft (3 m) iron cylinder with a flywheel at its base, ran on its own power for the first time in Augsburg, Germany on August 10, 1893. In remembrance of this event, August 10 has been declared International Biodiesel Day.
- Diesel later demonstrated his engine and received the "Grand Prix" (highest prize) at the World Fair in Paris, France in 1900. This engine stood as an example of Diesel's vision because it was powered by peanut oil—a biofuel, though not strictly biodiesel, since it was not transesterified. He believed that the utilization

of a biomass fuel was the real future of his engine.

- In a 1912 speech, Rudolf Diesel said "the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time”.
- During the 1920s diesel engine manufacturers altered their engines to utilize the lower viscosity of the fossil fuel (petrodiesel) rather than vegetable oil, a biomass fuel. The petroleum industries were able to make inroads in fuel markets because their fuel was much cheaper to produce than the biomass alternatives. The result was, for many years, a near elimination of the biomass fuel production infrastructure. Only recently have environmental impact concerns and a decreasing cost differential made biomass fuels such as biodiesel a growing alternative.
- In 1970, scientists discovered that the viscosity of vegetable oils could be reduced by a simple chemical process and that it could perform as diesel fuel in modern engine. Since then the technical developments have come a long way and the plant oil today has been highly established as bio fuel, equivalent to diesel.
- Research into the use of trans-esterified sunflower oil and refining it to diesel fuel standard was initiated in South Africa in 1979.
- By 1983 the process to produce fuel quality engine-tested bio-diesel was completed and published internationally.
- An Austrian Company, Gaskoks, obtained the technology from the South African Agricultural Engineers, put up the first pilot plant for bio-diesel in November 1987 and the erection of the first industrial bio-diesel plant on 12 April 1989, with a capacity of 30 000 tons of rapeseed per annum projects.
- Throughout the 1990s, plants were opened in many European countries, including the Czech Republic, France, Germany, and Sweden. At the same time, nations in other parts of world also saw local production of biodiesel starting up and by 1998; the Austrian Biofuels Institute identified 21 countries with commercial biodiesel.
- In the 1990s, France launched the local production of biodiesel fuel obtained by the transesterification of rapeseed oil. It is mixed to the proportion of 5% into regular diesel fuel, and to the proportion of 30% into the diesel fuel used by some captive fleets (public transportation). Renault, Peugeot, and other manufacturers

have certified truck engines for use with up to this partial biodiesel level. Experiments with 50% biodiesel are under ways.
- In 1991, the European Community proposed a 90% tax reduction for the use of bio fuels, including biodiesel. Today 21 countries worldwide produce biodiesel.
- In September of 2005 Minnesota became the first state to require that all diesel fuel sold in that state contain part biodiesel. The Minnesota law requires at least 2% biodiesel in all diesel fuel sold.

2.1.3 Definition of - "Biodiesel"

General Definition of Biodiesel

Biodiesel is a renewable fuel for diesel engines derived from natural vegetable/animal oils, and which meets the standard specification.

Technical Definition for Biodiesel

Biodiesel is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animals fats, and meeting the requirements of standard specifications.

2.2 Methods for the Production of the Biodiesel

1. Direct Use and Blending
2. Pyrolysis
3. Microemulsifcation
4. Transesterification

1. Direct Use and Blending [1, 6]

It has been found that these neat vegetable oils can be used as diesel fuels in conventional diesel engines. Vegetable oils, such as palm, soya bean, sunflower, peanut, and olive oil, as can be used directly as an alternative fuels.

The advantages of vegetable oils as diesel fuel are,

- Liquid nature-portability
- Heat content (80% of diesel fuel)
- Ready availability and
- Renewability

The disadvantages are,

- Higher viscosity

- Lower volatility and
- 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;

- Coking and trumpet formation on the injectors to such an extent that fuel
- Atomization does not occur properly or is even prevented as a result of plugged orifices
- Carbon deposits
- Oil ring sticking
- Thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils

These limitations, coupled with the reactivity of unsaturated vegetable oils, do not allow the engine to operate trouble free for longer period of time. Direct use of vegetable oils and/or the use of blends of the oils have generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines.

These problems can be solved, if the vegetable oils are chemically modified to biodiesel, which is similar in characteristics to diesel.

2. Pyrolysis [1, 6]

Pyrolysis refers to the conversion of one substance into another by means of heat or by mean of a heat with catalysts in the presence of air or nitrogen purge. Thermal decomposition of triglycerides produces the compounds of classes including alkanes, alkenes, alkadienes, aromatics and carboxylic acids.

Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids.

Thermal decomposition of triglycerides produces the compounds of classes including alkanes, alkenes, alkadienes, aromatics and carboxylic acids

.

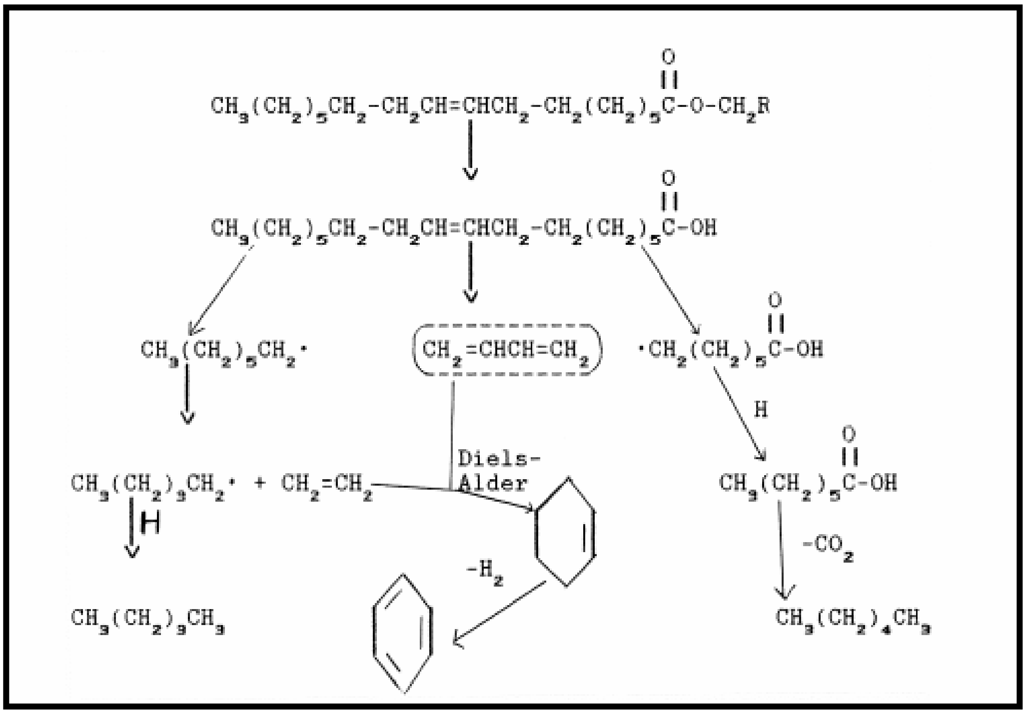


Figure 2.3 Thermal Decomposition Mechanisms [1]

Different types of vegetable oils produce large differences in the composition of the thermally decomposed oil. Figure outline a schematic that accounts for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids from pyrolysis of triglycerides. Mechanisms for the thermal decomposition of triglycerides are likely to be complex because of many structures and multiplicity of possible reactions of mixed triglycerides. Generally, thermal decomposition of these structures proceeds through either a free-radical or carbonium ion mechanism.

The liquid fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. There was no waste water or air pollution. The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived

3. Microemulsification [1, 6]

A microemulsion is defined as colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1±150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles.

Microemulsions are isotropic, clear, or translucent thermodynamically stable dispersions of oil, water, surfactant, and often a small amphiphilic molecule, called co surfactant. The droplet diameters in microemulsions range from 100 to 1000 A.

A microemulsion can be made of vegetable oils with an ester and dispersant (co solvent), or of vegetable oils, an alcohol and a surfactant, with or without diesel fuels. Microemulsions because of their alcohol content have lower volumetric heating values than diesel fuels, but the alcohols have high latent heat of vaporization and tend to cool the combustion chamber, which would reduce nozzle coking. A microemulsion of methanol with vegetable oils can perform nearly as well as diesel fuels.

4. Transesterification [1, 6]

Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except this alcohol is used instead of water. This process has been widely used to reduce the viscosity of triglycerides. The transesterification reaction is represented by the general equation:

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

Transesterification of Vegetable Oil

Biodiesel is made through a chemical process called **"Transesterification"** whereby the glycerin is removed from the fat or vegetable oil. Biodiesel is thus an ester.

Transesterification, also called alcoholysis, is the displacement of alcohol from ester by another alcohol in a process similar to hydrolysis. Methanol is most commonly used for the purpose since it is the cheapest alcohol available. If methanol is used in the production process it is a methyl ester; if ethanol is used it is an ethyl ester.

Ethanol and higher alcohols such as Iso Propanol, Butanol etc, can also be used for the esterification. Using higher molecular weight alcohols improves the cold flow properties of biodiesel reduces the efficiency of transesterification process.

Simple Transesterification Reaction

Transesterification of vegetable oils with simple alcohol has long been the preferred method for producing biodiesel. In general, there are two methods of transesterification.

One method simply uses a catalyst and the other is without a catalyst. The former method

has a long history of development and the biodiesel produced by this method is now available in North America, Japan and some western European countries.

Chemistry Of Transesterification Reaction

The overall transesterification reaction is given by three consecutive and reversible equations as below:

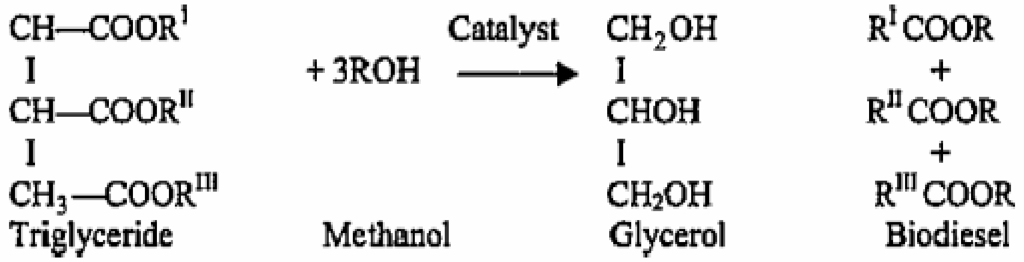
$$\text{Triglyceride} + \text{ROH} \overset{\text{catalyst}}{\Longleftrightarrow} \text{Diglyceride} + \text{R}^{\text{I}}\text{COOR}$$

$$\text{Diglyceride} + \text{ROH} \overset{\text{catalyst}}{\Longleftrightarrow} \text{Monoglyceride} + \text{R}^{\text{II}}\text{COOR}$$

$$\text{Monoglyceride} + \text{ROH} \overset{\text{catalyst}}{\Longleftrightarrow} \text{Glycerol} + \text{R}^{\text{III}}\text{COOR}$$

The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester molecule per mole of glyceride at each step.

The overall chemical reaction of the transesterification process is:



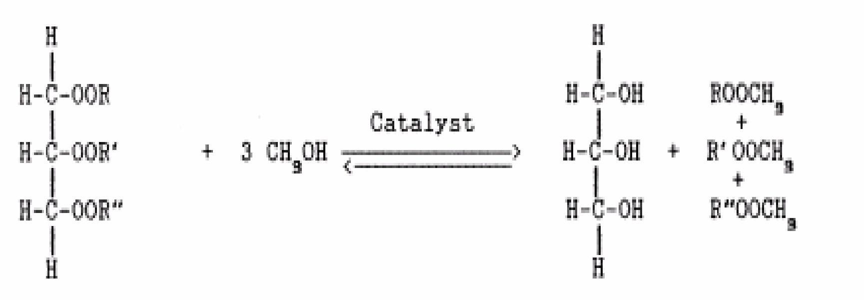
$$\begin{array}{cccc}
\text{CH—COOR}^{1} & & \text{CH}_2\text{OH} & \text{R}^{\text{I}}\text{COOR} \\
\text{I} & +3\text{ROH} \xrightarrow{\text{Catalyst}} & \text{I} & + \\
\text{CH—COOR}^{\text{II}} & & \text{CHOH} & \text{R}^{\text{II}}\text{COOR} \\
\text{I} & & \text{I} & + \\
\text{CH}_3\text{—COOR}^{\text{III}} & & \text{CH}_2\text{OH} & \text{R}^{\text{III}}\text{COOR} \\
\text{Triglyceride} & \text{Methanol} & \text{Glycerol} & \text{Biodiesel}
\end{array}$$

Where R^{I}, R^{II} and R^{III} are long-chain hydrocarbons which may be the same or different with $RZ–CH_3/C_2H_5$

As seen above, the transesterification is an equilibrium reaction in which excess alcohol is required to drive the reaction close to completion. Fortunately, the equilibrium constant favors the formation of methyl esters such that only a 5:1 molar ratio of methanol: triglyceride is sufficient for 95–98% yield of ester.

Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except than alcohol is used instead of water. This process has been widely used to reduce the viscosity of triglycerides.

If methanol is used in the above reaction, it is termed methanolysis. The reaction of triglyceride with methanol is represented by the general equation:



Triglyceride Methanol Glycerol Fatty Acid Methyl Esters

The fatty acid methyl esters (known as biodiesel) are attractive as alternative diesel fuels.

The detail of the biodiesel and its different production methods are given below. Here in this report I m going to discuss about the different transesterification method for the production of the biodiesel.

2.3 Transesterification Methods for Biodiesel Production

The process of converting the raw vegetable oil into biodiesel, which is fatty acid alkyl ester, is termed as transesterification. There are four routes as described below to biodiesel production from biolipids (biological oils and fats): [7, 9]

1. Alkali Catalysis Technology
2. Acid Catalysis Technology
3. Lipase Catalysis Technology
4. Super Critical Methanol Technology

1. Alkali Catalysis Technology

Different Alkali Catalysts [7, 8, 9]

- Sodium Hydroxide (NaOH)
- Potassium Hydroxide (KOH)
- Sodium Methoxide
- Potassium Methoxide
- Sodium Propoxide

- Sodium Bytoxide
- Sodium Ethoxide

For a basic catalyst, either sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be used with methanol or ethanol as well as any kind of oils, refine, crude or frying.

Mechanism of Base Catalyzed Reaction [15]

The reaction mechanism for alkali-catalyzed transesterification is formulated as three steps:

1. The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate, from which the alkyl ester and the corresponding anion of the diglyceride are formed.

In this process it is better to produce the Alcoxy before the reaction to obtain a better global efficiency. The alcoxi reaction is

$$R-CH_2OH+NaOH \rightarrow H_2O+R-CH_2ONa.$$

2. The latter deprotonates the catalyst can react with a second molecule of alcohol and starts another catalytic cycle.

3. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

Mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure:

Alkaline metal alkoxides (CH_3ONa) are the most active catalysts, since they give very high yields (O98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. Potassium carbonate, used in a concentration of 2 or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation.

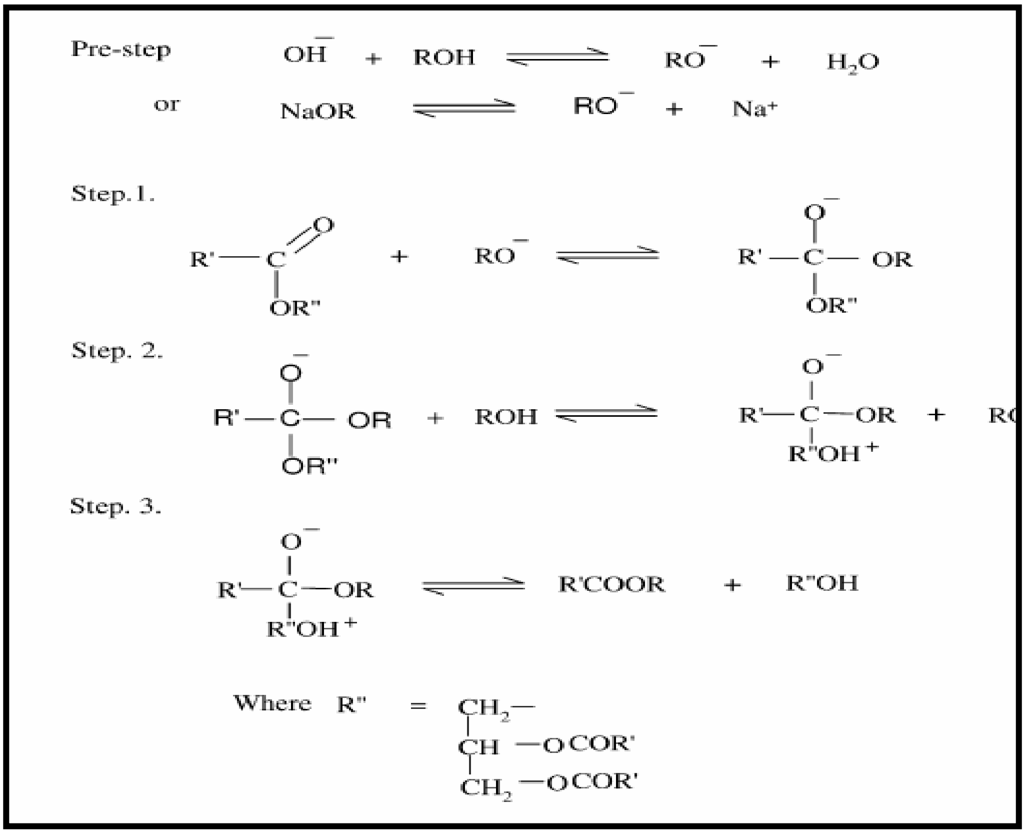


Figure 2.4 Mechanism of Base Catalyzed [9]

Effect of Different Variables on the Reaction [7, 8, 9]

1. Effect of Moisture and Free Fatty Acids

For alkali catalyzed transesterification, the glyceride and alcohols must be substantially anhydrous because water caused a partial reaction change to saponification, which produces soap. The soap consumes the catalyst and reduces the catalyst efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerol.

2. Effect of Molar Ratio

Another important variable affecting the ester yield is the molar ratio of alcohol to vegetable oil. The stoichiometric of the transesterification reaction requires 3 mol of alcohol per mol triglyceride to yield 3 mol of fatty esters and 1 mol of glycerol. Higher molar ratios results in greater ester conversion in a shorter time. The molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% on a weight basis.

3. Effect of Catalyst Type

Sodium methoxide has been found to be more effective than sodium hydroxide, presumably because a small amount of water is produced upon mixing NaOH and MeOH. However, sodium hydroxide and potassium hydroxide are also able to catalyze transesterification, and because of their cheapness, are widely used in industrial biodiesel production.

4. Effect of Reaction Temperature

Another important variable is the reaction temperature. The standard value for the reaction to take place is 60 ^{0}C, but depending on the type of catalyst different temperatures will give different degrees of conversion, and for that reason the temperature range should be from 25 to 120 ^{0}C.

Advantages and Limitations of This Technology [7, 8, 9]

Advantages

- The last one has fewer safety problems because it is less toxic.
- The reason why there is a great interest in the alkali process is it is more efficient and less corrosive than the acid process, making it a preferred catalyst to be used in industries.
- The reaction is fast and completed within few hours.

Limitations

- The limits of this technology are due to the sensitivity that this process has to purity of reactants, to the fatty acid, as well as to the water concentration of the sample.
- If you have too much water you run the risk of making some soap instead of the desired product.

2 Acid Catalysis Technologies

This way of production is the second conventional way of making the biodiesel. The idea

is to use the triglycerides with alcohol and instead of a base to use an acid—the most commonly used is sulfuric acid and some authors prefer sulfonic acid. This type of catalyst gives very high yield in esters but the reaction is very slow, requiring almost always more than one day finishing. [7, 8, 9]

Different Acid Catalysts [7, 8, 9]

1 Sulfuric Acid
2 Phosphoric Acid
3 Hydrochloric Acid
4 Organic Sulfonic Acid

Mechanism of Acid Catalyzed Material [9]

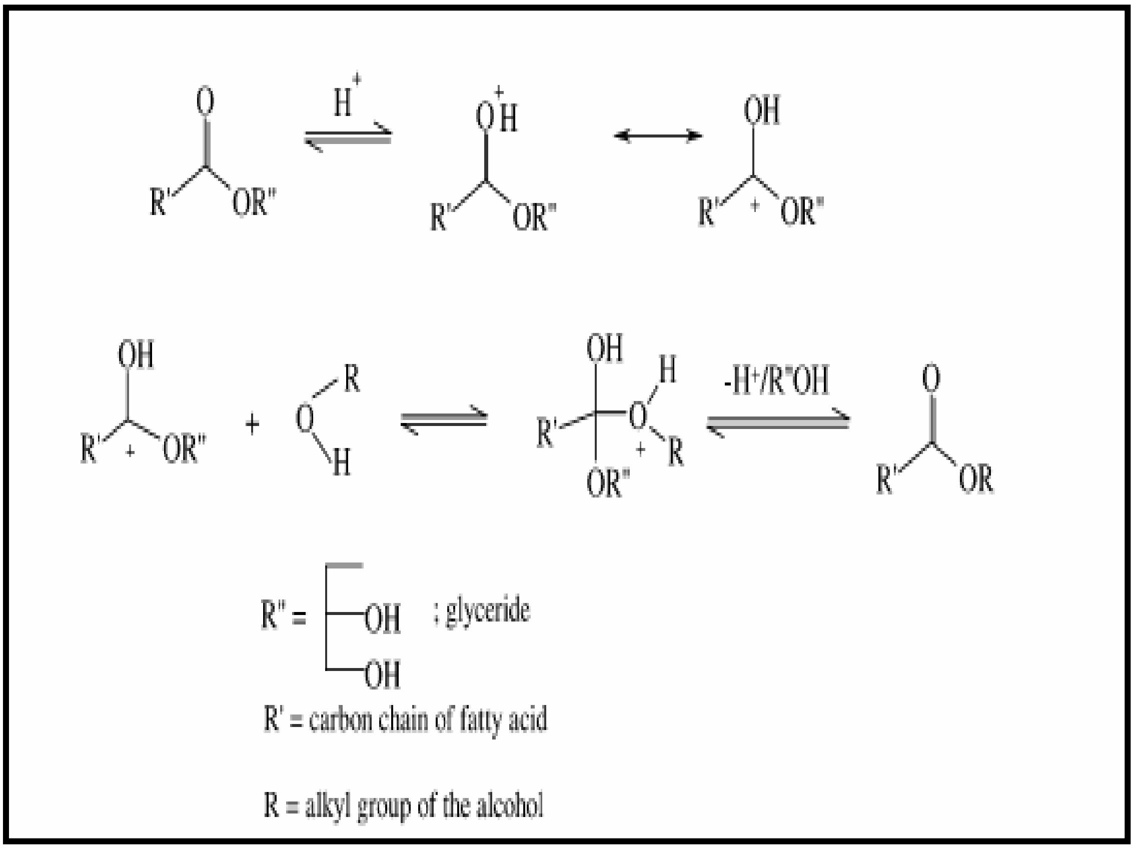


Figure 2.5 Mechanism of Acid Catalyzed Material [9]

Factors Affecting the Acid Catalyzed Transesterification Reaction [7, 8]

1. Effect of Temperature

The temperature range varies from 55 to 80 ^{0}C. desirable product with 1 mol% of sulfuric acid with a molar ratio of 30:1 at 65 ^{0}C and they get 99% of conversion in 50 h, while the butanolysis will need 117 ^{0}C and the ethanolysis 78 ^{0}C but the times should be 3 and 18 h, respectively.

2. Effect of Molar Ratio

The possible operation condition is, usually, molar ratio 30:1. The type of alcohol, as well as the oils, is the same as the one that can be used in alkali catalyst reaction.

3. Catalyst and Fatty Acids

The amount of catalyst supposed to be added to the reactor varies from 0.5 to 1 mol%.

The typical value is 1%, but some authors have used 3.5 mol%. The acid transesterification is a great way to make biodiesel if the sample has relatively high free fatty acid content. In general, a 1 mol% of sulfuric acid is a good amount for a final conversion of 99% in a time around 50 h.

Advantages and Limitations

Advantages

- It gives very high yields

Limitations

- Reaction is very slow, requiring almost more than one day to finish

3. Lipase Catalysis Technologies

Lipase esterification is a viable method for the production of alkyl esters from animal fat or vegetable oils**.** Lipases are enzymes used to catalyze some reaction such as hydrolysis of glycerol, alcoholysis and acidolysis, but it has been discovered that they can be used as catalyst for transesterification and esterification reactions too. [7, 8]

Biocompatibility, biodegradability and environmental acceptability of the biotechnical procedure are the desired properties in agricultural and medical applications. The extra cellular and the intracellular lipases are also able to catalyze the transesterification of triglycerides effectively. [7, 8]

Advantages

- No chemical additives are required.
- Possibility of regeneration and reuse of the immobilized residue, because it can be left in the reactor if you keep the reactive flow.
- Use of enzymes in reactors allows use of high concentration of them and that makes for a longer activation of the lipases.
- A bigger thermal stability of the enzyme due to the native state.
- Immobilization of lipase could protect it from the solvent that could be used in the reaction and that will prevent all the enzyme particles getting together.
- Separation of product will be easier using this catalyst.

Some Limitations

- You can lose some initial activity due to volume of the oil molecule.
- Number of support enzyme is not uniform.

- Biocatalyst is more expensive than the natural enzyme.
- The production cost of lipase catalyst is significantly higher than the alkaline catalyst.

4 Transesterification Using Supercritical Fluids

With the aim of developing a novel methanolysis process for oil without using any catalyst the scientists made a fundamental study of biodiesel production in supercritical methanol. [7, 8, 9]

The transesterification of triglycerides by supercritical methanol (SCM), ethanol, propanol and butanol, has proved to be the most promising process. A non-catalytic BD production route with supercritical methanol has been developed that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids. [7, 8, 9]

The basic idea of supercritical treatment is based on the effect of the relationship between pressure and temperature upon the thermo physical properties of the solvent, such as dielectric constant, viscosity, specific weight and polarity.

The transesterification of sunflower oil was investigated in SCM and supercritical ethanol at various temperatures (475–675 K). [7, 8, 9]

Factors Affecting SCM Method [7, 8, 9]

1 Increasing the reaction temperature, especially to supercritical temperatures, had a favorable influence on ester conversion
2 In the supercritical alcohol transesterification method, the yield of conversion increases to 50–95% in the first 10 min.
3 The presence of water affected positively the formation of methyl esters in our supercritical methanol method.

2.3.1 Comparison of Different Technologies

Comparison between the different technologies which are mainly available and developed process is given in the table:

Table 2.1 Comparison of Different Technologies [8]

Variable	Alkali Catalysis	Lipase Catalysis	Supercritical Alcohol	Acid Catalysis
Reaction Temperature (^{0}C)	60–70	30–40	239–385	55–80
Free Fatty Acid In Raw Materials	Saponified Products	Methyl Esters	Esters	Esters
Water In Raw Materials	Interference With Reaction	No Influence	-	Interference With Reaction
Yield Of Methyl Esters	Normal	Higher	Good	Normal
Recovery Of Glycerol	Difficult	Easy	-	Difficult
Purification Of Methyl Esters	Repeated Washing	None	-	Repeated Washing
Production Cost Of Catalyst	Cheap	Relatively Expensive	Medium	Cost

2.4 Variables Affecting the Transesterification Reaction

The process of transesterification is affected by various factors depending upon the reaction condition used. These factors and their effects are described below: [1, 4, 6, 9]

- Effect Of Free Fatty Acid And Moisture
- Effect Of Reaction Temperature
- Catalyst Type And Concentration
- Molar Ratio Of Alcohol To Oil And Type Of Alcohol
- Effect Of Reaction Time
- Mixing Intensity
- Effect Of Using Organic Co- Solvents
- Purity Of Reactants

1. Effect of Free Fatty Acid and Moisture

The free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. For the different vegetables oils the free fatty acid value is different. To carry the base catalyzed reaction to completion; a free fatty acid (FFA) value lower than 3% is needed. The higher the acidity of the oil, smaller is the conversion efficiency. Both, excess as well as insufficient amount of catalyst may cause soap formation. [1, 4, 6]

2. Effect of Reaction Temperature

The literature has revealed that the rate of reaction and yield of esters are strongly influenced by the reaction temperature. However, the reaction is conducted close to the boiling point of methanol (60–70 ^{0}C) at atmospheric pressure for a given time. Such mild reaction conditions require the removal of free fatty acids from the oil by refining or pre esterification. Therefore, degummed and de acidified oil is used as feedstock [2, 6, 8, 15]

Pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240 ^{0}C), where simultaneous esterification and transesterification take place with maximum yield obtained at temperatures ranging from 60 to 80 8C at a molar ratio of 6:1. Further increase in temperature is reported to have a negative effect on the conversion. The studies indicate that given enough time, transesterification can proceeds satisfactory at ambient temperatures in the case of alkaline catalyst. [1, 6, 8, 9]

3. Catalyst Type and Concentration

Catalysts are classified as alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed. Sodium alkoxides are the most efficient catalysts, although KOH and NaOH can also be used. Transmethylation occurs in the presence of both alkaline and acidic catalysts. However if a glyceride has a higher free fatty acid content and more water, acid-catalyzed transesterification is suitable.]. As they are less corrosive to industrial equipment, alkaline catalysts are preferred in industrial processes. A concentration in the range of 0.5–1% (w/w) has been found to yield 94–99% conversion to vegetable oil esters, and further increase in catalyst concentration does not affect the conversion but adds to extra cost, as the catalyst needs to be removed from the reaction mixture after completion of the reaction. [1, 6, 8, 9]

4. Molar Ratio of Alcohol to Oil and Type of Alcohol [1, 6, 8, 9]

- One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio of 6:1 should be used.
- The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters. However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium to back to the left, lowering the yield of esters.
- Mainly two alcohols are used for the production of biodiesel one is methanol and second one is ethanol. The base catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters. Specifically the formation of stable emulsion during ethanolysis is a problem. Methanol and ethanol are not miscible with triglycerides at ambient temperature, and the reaction mixtures are usually mechanically stirred to enhance mass transfer. During the course of reaction, emulsions usually form.
- In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters. The emulsions are caused in part by formation of the intermediates monoglycerides and diglycerides, which have both polar hydroxyl groups and non-polar hydrocarbon chains.

5. Effect of Reaction Time

The conversion rate increases with reaction time. Reaction time is the controlling factor in determining the yield of methyl esters. The studies indicate that given enough time, transesterification can proceeds satisfactory at ambient temperatures in the case of alkaline catalyst. [1, 6, 8, 9]

6. Effect of Mixing Intensity

In the transesterification reaction, the reactants initially form a two-phase liquid system. Mixing is very important in the transesterification reaction, as oils or fats are immiscible with sodium hydroxide–methanol solution. [1, 6, 8, 9]

The reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate. As methyl esters are formed, they act as a mutual solvent for the reactants and a single-phase system is formed. The mixing effect is most significant during the slow rate region of the reaction. As the single phase is established, mixing becomes insignificant. The understanding of the mixing effects on the kinetics of the transesterification process is a valuable tool in the process scale-up and design. [1, 6, 8, 9]

7. Effect of Using Organic Co- Solvents

In order to conduct the reaction in a single phase, co solvents like tetrahydrofuran, 1, 4 dioxane die ethyl ether etc are used. The processes comprise solubilizing oil or fat in methanol or ethanol by addition of a co solvent in order to form a one-phase reaction mixture, and adding an esterification catalyst. The processes proceed quickly, usually in less than 20 min, at ambient temperatures, atmospheric pressure and without agitation. The co-solvent increases the rate of reaction by making the oil soluble in methanol, thus increasing contact of the reactants. The lower alkyl fatty acid monoesters produced by the process can be used as biofuels and are suitable as diesel fuel replacements or additives [1, 6, 8, 9]

8. Purity of Reactants

Impurities in the oil affect the conversion level considerably. It is reported that about 65–84% conversion into esters using crude vegetable oils has been obtained as compared to 94–97% yields refined oil under the same reaction conditions. The free fatty acids in the crude oils have been found to interfere with the catalyst. This problem can be solved if the reaction is carried out under high temperature and pressure conditions. [1, 6, 8, 9]

2.5 Characteristics of Biodiesel

Biodiesel as automotive fuel has properties of close to those of Diesel fuels and as such can be directly used in existing diesel engines with no or minor modifications. It can be used alone or mixed in any ratio with petrodiesel. The most common blend is B20, a mix of 20% biodiesel with 80% petroleum diesel. Biodiesel has 11% oxygen by weight and essentially contains no sulphur or aromatics.

The biodiesel esters are characterized for their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion and volatility. Methyl and ethyl esters prepared from a particular vegetable oil had similar viscosities, cloud points and pour points, whereas methyl, ethyl, 2-propyl and butyl esters derived from a particular vegetable oil had similar gross heating values.

Biodiesel is non-flammable and non-toxic and reduces tailpipe emissions, visible smoke and noxious fumes and odors. Biodiesel is better than Diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability. [3, 9, 11, 12]

2.5.1 Fuel Properties of Biodiesel Oil

1. Viscosity [3]

Viscosity is a measure of the internal friction or resistance of an oil to flow. As the temperature of oil is increased, its viscosity decreases, and it is, therefore, able to flow more readily. Viscosity is measured on several different scales, including Redwood viscometer , Engler Degrees, Saybolt Seconds, etc., the number of seconds required for 50 ml. of oil to flow out of a standard Redwood viscosimeter at a definite temperature.

Viscosity is the most important property of biodiesel since it affects the operation of the fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Biodiesel has a viscosity close to that of diesel fuels. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors.

2. Density [3]

Density is another important property of biodiesel. It is the weight of a unit volume of fluid. Specific gravity is the ratio of the density of a liquid to the density of water. The specific gravity of biodiesel ranges between 0.87 and 0.89. 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.

3. Cetane Number [3]

Cetane number is indicative of its ignition characteristics. The cetane number measures how easily ignition occurs and the smoothness of combustion. Cetane number (CN) is based on two compounds, namely hexadecane with a cetane number of 100 and heptamethylnonane with a cetane number of 15. The CN scale also shows that straight chain, saturated hydrocarbons have higher CN compared to branched chain or aromatic compounds of similar molecular weight and number of carbon atoms. . Cetane number affects a number of engine performance parameters like combustion, stability, driveability, white smoke, noise and emissions of CO and HC.

Biodiesel has higher cetane number than conventional diesel fuel, which results in higher combustion efficiency The CN is a measure of the ignition quality of Diesel fuels, and high CN implies short ignition delay. The CN is one of the prime indicators of the quality of Diesel fuel. It relates to the ignition delay time of a fuel upon injection into the combustion chamber. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN will be. The CN of biodiesel from animal fats is higher than those from vegetable oils.

4. Cloud Point and Pour Point [3]

Two important parameters for low temperature applications of a fuel are cloud point (CP) and pour point (PP). The CP is the temperature at which wax first becomes visible when the fuel is cooled. The PP is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. Biodiesel has higher CP and PP compared to conventional Diesel.

5. Flash Point [9]

Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. The flash point of biodiesel is higher than the petrodiesel, which is safe for transport purpose

6. Neutralization Number [9]

Neutralization number is specified to ensure proper ageing properties of the fuel and/or a good manufacturing process. It reflects the presence of free fatty acids or acids used in manufacture of biodiesel and also the degradation of biodiesel due to thermal effects.

7. Carbon Residue [9]

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

2.5.2 Physical Properties

Some of the physical characteristics of biodiesel are given in Table-2.2:

Table 2.2 Physical Properties of Biodiesel [11]

Properties	Values
Specific Gravity	0.88
Viscosity @ 20 ^{0}Ċ (Centistokes)	7.5
Cetane Index	49
Cold Filter Plugging Point (Ċ)	-12
Net Heating Value (kilojoules/Liter)	33,300
Boiling Point	> 400 ^{0}F
Vapor Pressure (Mm Hg)	< 5mm Hg @ 72 ^{0} F
Flash Point	321 ^{0} F
Solubility In Water	Insoluble
Appearance	Light To Dark Yellow Clear Liquid
Odor	Light Musty Odor

2.5.3 Emission Characteristics [3]

Emission Impacts for Biodiesel Fuels

Biodiesel fuels have generally been found to be non-toxic and are biodegradable, which may promote their use in applications where biodegradability is desired. Neat biodiesel and biodiesel blends used in an unmodified Diesel engine reduce particulate matter (PM), hydrocarbons (HC) and carbon monoxide (CO) emissions and increase nitrogen oxides (NOx) emissions compared with petroleum based Diesel fuel.

Biodiesel is the only alternative fuel to have a complete evaluation of emission results and potential health effects submitted to the U.S.EPA under the Clean Air Act Section 211(b). Emission results for pure biodiesel (B100) and mixed biodiesel (B20-20% biodiesel and 80% petrodiesel) compared to conventional diesel are given in Table.

Emissions of nitrogen dioxides are either slightly reduced or slightly increased depending on the duty cycle or testing methods.

Biodiesel decreases the solid carbon fraction of particulate matter (since the oxygen in the fuel enables more complete combustion to CO_2), eliminates the sulphur fraction (as there is no sulphur in the fuel), while the soluble or hydrogen fraction stays the same or is increased.

The life-cycle production and use of biodiesel produces approximately 80% less carbon dioxide and almost 100% less sulphur dioxide compared to conventional diesel

NOx increases with the increase in concentration of biodiesel in the mixture of biodiesel and petrodiesel. This increase in NO_X may be due to the high temperature generated in the fairly complete combustion process on account of adequate presence of oxygen in the fuel. This increase in NOx emissions may be neutralized by the efficient use of NOx control technologies, which fits better with almost nil sulphur biodiesel then conventional diesel containing sulphur.

Biodiesel Emissions Compared to Conventional Diesel

Table 2.3 Biodiesel Emissions Compared to Conventional Diesel [11]

Emissions	**B100**	**B20**
Regulated Emissions		
Total Unburned Hydrocarbons	-93%	-30%
Carbon Monoxide	-50%	-20%
Particulate Matter	-30%	-22%

NOx	+13%	+2%
Non-Regulated Emissions		
Sulphates	-100%	-20%*
Polyciclic Aromatic Hydrocarbons (PAH)**	-80%	-13%
NPAH (Nitrated PAHs)	-90%	-50%***
Ozone Potential of Speciated HC	-50%	-10%
Life-Cycle Emissions		
Carbon Dioxide (LCA)	-80%	
Sulphur Dioxide (LCA)	-100%	

2.5.4 Toxicity of Biodiesel [10]

Impacts on human health represent significant criteria as to the suitability of the fuel for commercial applications. Health effects can be measured in terms of fuel toxicity to the human body as well as health impacts due to exhaust emissions. Effects of biodiesel are given below

- Biodiesel is not a toxic and there is no hazards anticipated from ingestion
- Incidental to industrial exposure.
- Very mild human skin irritation.
- It is less than the irritation produced by 4% soap and water solution.
- It is biodegradable. It degrades at least 4 to 5 times faster then conventional diesel fuel.
- Biodiesel has a flash point of about 300 ^{0}F well above conventional diesel fuel.
- Spills of biodiesel can decolorize any painted surface if left for long.
- There is no tendency for the mutagenicity of exhaust gas to increase for a vehicle running on biodiesel.

2.5.5 Storage & Infrastructure [10]

In general, the standard storage and handling procedures used for petroleum diesel may be used for biodiesel. It is preferable to store the fuel in clean, dry and dark environment. Biodiesel may gel at low temperatures and care needs to be taken to avoid temperature extremes. Acceptable storage tank materials include mild steel, stainless steel, and fluorinated polyethylene and fluorinated polypropylene. Biodiesel has a solvent effect, which releases the deposits accumulated on tanks and pipes, which previously have been used for diesel. These deposits can be expected to clog filters initially and precautions should be taken for this.

2.5.6 Materials Compatibility [10]

Biodiesel over time will soften and degrade certain types of elastomers and natural rubber compounds. Materials like bronze, brass; copper, lead, tin and zinc may oxidize the diesel or biodiesel fuels and create sediments. Moreover, lead solders and zinc linings should be avoided, as should copper pipes, brass regulators and copper fittings. It is desirable to change all components, which are not biodiesel compatible to aluminum or stainless steel. The effect of B20 on vulnerable materials is diluted compared to higher blends. It may also be noted that most of the new generation vehicles can take biodiesel without any materials compatibility problems as they are already tuned to using low sulphur diesel, biodiesel etc.

2.5.7 Solvency of Biodiesel [10]

Biodiesel is a mild solvent. On prolonged contact with painted surfaces, it may deface some paints. Always wipe up spills and dispose of rags in a safe manner. Biodiesel soaked rags may self-combust if not handled properly. The most commonly encountered problem with solvency is biodiesel’s tendency to “clean out” storage tanks, including the vehicle fuel tanks and systems. Some type of diesel tends to form sediments that stick to and accumulate in storage tanks, forming layers of sludge or slime in the fuel systems. The older the system, and the poorer the maintenance, the thicker the accumulated sediments become. Biodiesel will dissolve these sediments and carry the dissolved solids into the fuel systems of the vehicles. Fuel filters will catch most of it, but in severe cases, the dissolved sediments have caused fuel injector failure. Few problems have been encountered with B20 in typical diesel storage situations. However, the solvency effect of the biodiesel in B20 is sufficiently diluted so that most problems encountered are minor and in general the problem goes away after the first few tanks of fuel.

2.5.8 Lubricity of Biodiesel [10]

Biodiesel blends offer superior lubricating properties, which may reduce engine wear and extend the life of fuel injection systems. Tests with two leading lubricity measuring systems-the BOCLE machine and the HFRR machine-show biodiesel blends offer better lubricating properties then conventional petroleum diesel.

Lubricity is especially important for rotary/distributor type fuel injection pumps in which parts are lubricated by the fuel itself and not by the engine oil.

2.6 Advantages of Biodiesel

1. Health Benefits

- Due to its less polluting combustion, biodiesel provides a 90% reduction in cancer risks and neonatal defects.
- Ozone layer - Reduces CO_2 emissions with~78% in comparison with fossil diesel, on life cycle base
- Fewer soot and particle emissions

2. Environmental Benefits

- Biodiesel is biodegradable and renewable by nature.
- Non-toxic and Biodegradable
- Biodiesel reduces emissions of carbon monoxide (CO) by approximately 50% and carbon dioxide by 78% on a net lifecycle
- Closed CO_2 cycle, thus reduces production of GHG
- As it produces substantially less carbon monoxide and 100% less sulfur dioxide emissions with no unburnt hydrocarbons and thus it is ideal fuel for heavily polluted cities.
- Biodiesel reduces serious air pollutants such as particulates and air toxicity.
- Biodiesel contains fewer aromatic hydrocarbons: benzofluoranthene: 56% reduction; Benzopyrenes: 71% reduction.
- Biodiesel can reduce by as much as 20% the direct (tailpipe) emission of particulates, small particles of solid combustion products, on vehicles with particulate filters, compared with low-sulfur (<50 ppm) diesel. Particulate emissions as the result of production are reduced by around 50%, compared with fossil-sourced diesel.
- Biodiesel has higher cetane rating than petrodiesel, which is insignificant in terms of emissions and performance.
- In the United States, biodiesel is the only alternative fuel to have successfully completed the Health Effects Testing requirements of the Clean Air Act.

3. Benefits for Engines

- Optimized viscosity and thus, reduction of engine wear

- Biodiesel extends the life of diesel engines.
- Needs no change in refueling infrastructures and spare part inventories.
- Maintains the payload capacity and range of conventional diesel engines

4. Macro-Economical Benefits

- Biodiesel could be cheaper than conventional diesel.
- Biodiesel has good potential for rural employment generation.
- Employment creation
- Increased security of energy supply
- Conservation of foreign exchange by reducing import quotas and improving country's balance of payments
- Diesel skilled mechanics can easily attend to biodiesel engines.
- 100% domestic fuel

2.7 Limitations of Biodiesel

- Slightly increase in the nitrous oxide emissions
- Quality of biodiesel depends on the blend thus quality can be tampered.
- Biodiesel has excellent solvent properties. Any deposits in the filters and in the delivery systems may be dissolved by biodiesel and result in need for replacement of the filters.
- There may be problems of winter operatibility.
- Spills of biodiesel can decolorize any painted surface if left for long.
- Neat biodiesel demands compatible elastomers (hoses, gaskets, etc.).
- High viscosity, low volatility, and poor cold flow these properties case several problems like,
    - Engine deposits
    - Injector coking
    - Piston ring sticking
- Although biodiesel cannot entirely replace petroleum-based diesel fuel
- It decreases, although will not eliminate, the country's dependence on imported petroleum.
- When added to regular diesel fuel in an amount equal to 1–2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel

fuel, into an acceptable fuel.

2.8 Biodiesel Feed Stocks

A variety of oils can be used to produce biodiesel. These include:

- Virgin oil feedstock; rapeseed and soybean oils are most commonly used, though other crops such as mustard, palm oil, hemp, jatropha, and even algae show promise (see List of vegetable oils for a more complete list)
- Waste vegetable oil (WVO)
- Animal fats including tallow, lard, yellow grease, and the by-products of the production of Omega-3 fatty acids from fish oil.
- Sewage. A company in New Zealand have successfully developed a system for using sewage waste as a substrate for algae and then producing bio-diesel

Thermal depolymerization is an important new process that reduces almost any hydrocarbon based feedstock, including non oil based feedstocks, into light crude oil.

2.8.1 Classification of Bio-diesel Resources [5]

Class-I: Bio-diesel From Oil Seeds

Class-II: Bio-diesel From Waste Oils

Class-I: Bio-diesel From Oil Seeds.

Category A – Conventional Cultivated Oil Yielding Crops

- Rape Seeds
- Ground Nut
- Sesame Seeds
- Rocket Seeds

Category B – Non Conventional Cultivated Oil Yielding Crops

- Sun flower
- Soybean
- Safflower

Category C – Industries Based Crops

- Linseed
- Castor beans
- Cotton seeds

Category D – Wild Plant Resources

- Pongame tree
- Olive tree
- Hemp oil
- Oat seeds
- Milk Thistle
- Carthamus seeds
- ***Jatropha***

Categories of Class-II Resources

- Straight Vegetable Oil (SVO)
- Waste Vegetable Oil (WVO)
- Animal Fats

2.8.2 Prospective Feedstock in India

Oil can be extracted from a variety of plants and oilseeds. Under Indian condition only such plant sources can be considered for biodiesel production which is not edible oil in appreciable quantity and which can be grown on large-scale on wastelands. Moreover, some plants and seeds in India have tremendous medicinal value, considering these plants for biodiesel production may not be a viable and wise option. Considering all the above options, probable biodiesel yielding trees in India are:

The important potential tree species for bio-diesel in India are as follows:

Table 2.4 Prospective Feedstock in India [15]

Name	Botanical Name	Oil Content (%)
Neem	Azadirachta indica	20
Karanja	Pongamia pinnata	27-39
Kusum	Schleichera	34
Pilu	Salvadora oleoides	33
Ratanjot	**Jatropha curces**	**30-40**
Mahua	Madhuca indica	35
Bhikal	Prinsepia utilis	37
Undi	C.inophyllum	50-73
Thumba	C.colocynthis	21
Sal	Shorea robusta	20

Nahor	Mesua ferrea	45
Jojoba	S.chinensies	-
Kamala	Mallotus phillipines	-
Kokam	Garcinia indica	-
Rubber Seed	Hevea Brasilensis	-

2.8.3 Selection of Species: Jatropha Curcas

From the all options available among non-edible Tree Bearing Oil (TBO) seeds, Jatropha Curcas has been identified as the most suitable seed. Jatropha is a genus of approximately 175 succulents, shrubs and trees from the family Euphorbiaceae. Jatropha Curcas is a widely occurring variety of TBO. It grows practically all over India under a variety of agro-climatic conditions. Thus it ensures a reasonable production of seeds with very little inputs. Different parts of the Jatropha plant have a different use. Whole the plant can be utilized for different purposes.

According to the Economic Survey (1995-96), Govt. of India, of the cultivable land area about 100-150 million hectares are classified as waste or degraded land

- Jatropha (*Jatropha curcas*, Ratanjyot, wild castor) thrives on any type of soil
- Needs minimal inputs or management; Propagation is easy
- Has no insect, pests & not browsed by cattle or sheep
- Can survive long periods of drought
- Yield from 3rd year onwards, continues for 25-30 years
- 25% oil from seeds by expelling, 30% by solvent extraction
- The meal after extraction an excellent organic manure

REFERENCES CHAPTER 2

1. Anjana Srivastava, Ram Prasad *"Triglycerides-Based Diesel Fuels"* Renewable & Sustainable Energy Reviews 4 (2000) 111-133 Received 20 May 1998; Received In Revised Form 1 June 1999; Accepted 7 July 1999
2. Ayhan Demirbas *"Progress And Recent Trends In Biofuels"* Progress In Energy And Combustion Science 33 (2007) 1–18, Received 28 March 2006; Accepted 28 June 2006
3. Ayhan Demirbas *"Biodiesel Production Via Non-Catalytic SCF Method And Biodiesel Fuel Characteristics",* Energy Conversion And Management 47 (2006) 2271–2282 Received 15 June 2005; Accepted 28 November 2005 Available Online 9 January 2006
4. B.K. Barnwal, M.P. Sharma *"Prospects Of Biodiesel Production From Vegetable Oils In India"* Renewable & Sustainable Energy Reviews 9 (2005) 363–378 Received 7 April 2004; Accepted 7 May 2004
5. Clean Power (Pvt.) Ltd. *"A Project Of Alternative Energy Development Board (Aedb) Government Of Pakistan"* Issue: 01 July, 2005
6. Fangrui Ma, Milford A. Hanna *"Biodiesel Production: A Review*" Bioresource Technology Bioresource Technology 70 (1999) 1- 15 , Received 24 March 1998; Revised 16 December 1998; Accepted 2 February 1999
7. Hideki Fukunda, Akihiko Konndo And Hideo Noda *"Biodiesel Production By Transesterification Of Oils"* Bioscience And Bioengineering Accepted September 2001, http://www.jstage.jst.go.jp/article/jbb/92/5/405/_pdf (25/9/06)
8. J.M. Marchetti, V.U. Miguel, A.F. Errazu *"Possible Methods For Biodiesel Production"* Renewable & Sustainable Energy Reviews (2005) 1-12 Received 18 July 2005; Accepted 24 August 2005
9. L.C. Meher, D. Vidya Sagar, S.N. Naik *"Technical Aspects Of Biodiesel Production By Transesterification - A Review"* Renewable & Sustainable Energy Reviews 10 (2006) 248–268, Received 17 February 2004; Accepted 15 September 2004
10. S Biswas, N Kaushik & G Srikanth *"Biodiesel: Technology & Business Opportunities – An Insight"* Technology Information, Forecasting and

Assessment Council (TIFAC) Department of Science & Technology, New Delhi,

11. http://www.techbizindia.com/Article1.pdf (9/8/06)
12. http://www.cpcb.nic.in/diesel/contents0902.htm(19/8/06)
13. http://www.feezol.com/astm.htm(16/10/06)
14. http://en.wikipedia.org/wiki/Biodiesel#Historical_background(9/8/06)
15. http://www.tifac.org.in/news/Bioenergy_1.htm(13/12/06)

CHAPTER 3

JATROPHA

3. JATROPHA

3.1 Introduction

The term “Jatropha” is usually used to refer to the species Jatropha Curcas, although there are approximately 170 known species of the plant. Jatropha is at present still wild plant – it is not cultivated through variety research. It belongs to the Euphorbia family.

The plant and its seeds are non edible (toxic) to animals and humans and therefore used worldwide as hedges (living fences) to protect agricultural fields.

There are 4 specific features of the Jatropha curcas plant that explain public interest,

- Low demand in terms of cultivation, water and soil quality with resulting suitability for degraded and unused lands and drought-prone zones
- Non edible leaves and fruits, which stop trespassing (if grown in hedges) and browsing by animals, but can be used as a nutrient rich fertilizer and as a windbreak thus conserving soil humidity
- A nut, whose oil can be used or processed for any energy purpose, lighting, soap and other uses (pharmaceutical, varnish, plant protection)
- Wooden parts, which can be used for reforestation, home of bee and bird, for charcoal or firewood.

3.2 Characteristics of Jatropha

3.2.1 Physical Description [2]

- It is a tall bush or small tree (up to 6 m height).
- The lifespan of this perennial bush is more than 50 years, and it can grow on marginal soils with low nutrient content.
- Jatropha Curcas, or “physic nut” has a straight trunk with thick branchlets
- It has green leaves with a length and width of 6 to 15 cm.
- The fruits have an “American Football” type of shape, of about 40 mm length and each contains 3 seeds (on average), which look like black beans with similar dimensions, of about 18 mm long (11-30) and 10 mm wide (7 – 11)

- The seed weight per 1000 seeds is about 750 grams, which is equivalent of 1333 seeds per kg on average.
- The seeds contain more than 30% of oil by weight.
- The branches contain whitish latex, which causes brown stains that are difficult to remove.
- Normally five roots are formed from seeds: one tap root and 4 lateral roots.
- Plants from cuttings do not develop the tap root, only the laterals.
- The appearance of the plants in a hedge can vary a lot. You may find plants with no leaves (dormant position) beside plants with green leaves. Both the availability of water and sunlight has influence on this effect.

3.2.2 Botanical Features [3]

It is a small tree or shrub with smooth gray bark, which exudes whitish colored, watery, latex when cut. Normally, it grows between three and five meters in height, but can attain a height of up to eight or ten meters under favorable conditions.

Leaves

It has large green to pale-green leaves, alternate to sub-opposite, three-to five-lobed with a spiral phyllotaxis.

Flowers

The petiole length ranges between 6-23 mm. The inflorescence is formed in the leaf axil. Flowers are formed terminally**,** individually, with female flowers usually slightly larger and occur in the hot seasons. In conditions where continuous growth occurs, an unbalance of pistillate or staminate flower production results in a higher number of female flowers.

Fruits

Fruits are produced in winter when the shrub is leafless, or it may produce several crops during the year if soil moisture is good and temperatures are sufficiently high. Each inflorescence yields a bunch of approximately 10 or more ovoid fruits.

Seeds

The seeds become mature when the capsule changes from green to yellow, after two to four months from fertilization. The blackish, thin shelled seeds are oblong and resemble small castor seeds. [3]

Moisture 6.20 %
Protein 18.00 %
Fat 38.00 %
Carbohydrates 17.00 %
Fiber 15.50 %
Ash 5.30 %

The oil content is 35 – 40% in the seeds and 50 – 60% in the kernel. The oil contains 21% saturated fatty acids and 79% unsaturated fatty acids. There are some chemical elements in the seed which are poisonous and render the oil not appropriate for human consumption.

3.2.3 Chemical Properties

The chemical analysis of Jatropha curcas oil is given in Table (3. 1).

Table 3.1 Chemical Analysis Of Jatropha Curcas Oil [3]

Parameter	**Value**
Acid value	38.2
Saponification value	195.0
Iodine value	101.7
Viscosity (31^{o}C) "Fatty acid"	40.4
Palmitic acid %	4.2
Stearic acid %	6.9
Oleic acid %	43.1
Linoleic acid %	34.3
Other acids %	1.4

3.2.4 Agronomy [2]

Germination of the Seeds

With good moisture conditions the germination of the seed takes 10 days the seed shell splits and the radicula emerges and four peripheral roots are formed soon after the development of the first leaves, the cotyledons wither and fall off.

Flowering

Flowering can commence even during the first year in 5 month after sowing, but this is only under extremely favorable conditions. Normally, flowering follows a longer period of vegetative development. Fruit development takes 90 days, from flowering until seed maturation.

In regions with a dry and a wet season, flower formation seems to be induced by the onset of the rainy season. It may flower again after having produced fruits, this second round of flowering may lead to another yield if conditions remain favorable for another 90 days. When conditions remain favorable after two generative cycles Jatropha does not respond by another round of flowering but grows vegatively. Reproduction will stop as soon as the dry season begins. In permanently humid regions flowering occurs during the whole year.

Development

Development corresponds to the rainy seasons: vegetative growth occurs during the rainy season, there is little increment or even leaf fall during the dry season. Plants can gain a height up to 5 m. and reach more than 50 years of age.

Propagation Methods

There are various methods of propagation of Jatropha, either generative or vegetative. Each method has a different labor intensity and risk for good establishment.

Intercropping

It should be noticed that some authors claim that the root system of cuttings, not having a pen root, but more lateral (side) roots, is less suitable than that of the seeded plants with pen roots in intercropping systems. The side roots make the plants use more space rather than depth. No systematic studies have been done on this feature.

Intercropping with Cassava is not recommended since the plants are both of the same Euphorbia family and Jatropha can be a host for noxious insects and diseases of Cassava.

Pests and Diseases

Jatropha currently seems to have little difficulty with diseases and pests. There might be a number of reasons for this, such as its inherent toxicity for many species, its variation in genetic material and its spread occurrence in the landscape.

3.3. Jatropha Cultivation: Yield and Productivity [4]

- Apart from planting the seeds, jatropha can also be propagated vegetatively from cuttings. Use of branch cutting for propagation results in rapid growth and the bush can be expected to bear fruit within one year.
- Seeds are best sown during mid-February to mid-March and the seedlings 60-75 cms. Tall can be transplanted to the field.
- In equatorial regions where moisture is not a limiting factor (i.e. continuously wet tropics or under irrigation), jatropha can bloom and produce fruit throughout the year. To withstand extreme drought conditions, jatropha plant sheds leaves to conserve moisture, which results in reduced growth.
- Although jatropha is adapted to soils with low fertility and alkalinity, better yields can be obtained on poor quality soils if fertilizers containing small amounts of nutrients viz. calcium, magnesium and sulfur are used for the first two years.
- Jatropha plant bears fruits from 2nd year of its plantation and the economic yield stabilizes from 4th or 5th year onwards. The plant has an average life with effective yield up to 50 years.
- Jatropha gives about 2 Kgs. of seed per plant.
    - In relatively poor soils such as in Kutch (Gujarat), the yields have been reported to be 1 Kg per plant
    - In lateritic soils of Nashik (Maharashtra), the seed yields have been reported as 0.75 - 1.00 Kg per plant.

- Thus the economic yield can be considered as 0.75-2.00 Kgs /plant and 4.00-6.00 MT per hectare per year depending on agro-climactic zone and agricultural practices.
- One hectare of plantation on average soil will give 1.6 MT oil. Plantation on poorer soils will give 0.9 MT of oil per hectare.
- 1 kg of fresh jatropha fruit would yield approximately 286-297 grams of seeds.
- It was found that 4 kg of seeds will yield 1 liter of oil using mechanical crusher
- While solvent extraction by hexane would yield 41% more oil.
- The cost of plantation has been estimated as Rs.20, 000/- per hectare, inclusive of plant material, maintenance for one year, training, overheads etc. It includes elements such as site preparation, digging of pits, fertilizers, irrigation, deseeding, and plant protection for one year i.e., the stage when it will start bearing fruits

Table 3.2 Comparison Of Extraction Method [3]

Extraction Method	**Yield Of Jatropha Oil, %**	**Efficiency, %**
Solvent Extraction With N-Hexane	39	100
Hydraulic Presses	30 - 35	76 - 90
Mechanical Expeller	25-30	64 – 77
Village Ghanis	25	64
Domestic Method By Boiling Water	22	56
Screw Press Oil Expeller (German Design)	32 - 34	82 - 87

3.4 Exploitation of Jatropha

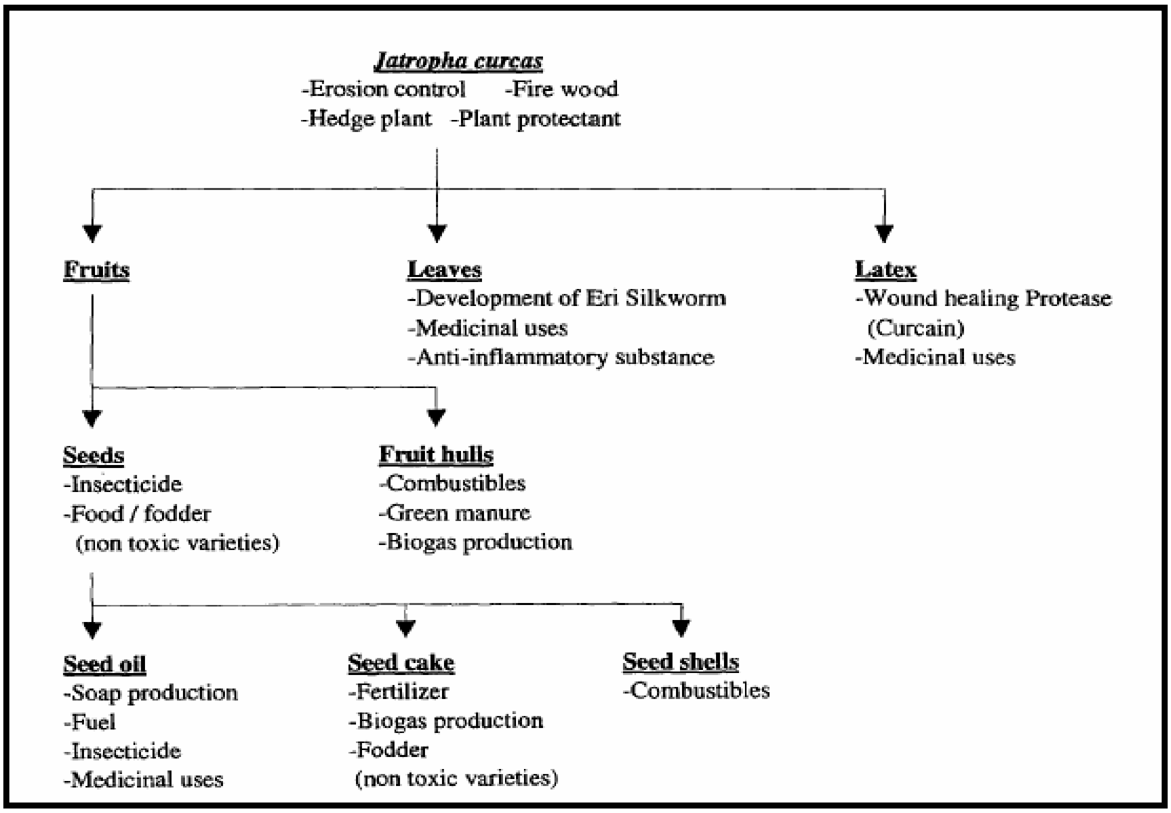


Figure 3.1 Exploitation of J. Curcas [1]

Different uses of different parts of Jatropha plant is described below:

Erosion Control as Hedge Plant [2]

In the tropics, the plant is widely used as a hedge in fields and settlements. It protects plants against wind erosion and keeps animals out. Jatropha is chosen for this purpose mainly because it can easily be propagated by cuttings, densely planted for this purpose, and because the species is not browsed by cattle. The roots also form a protection against water erosion, and can protect against soil erosion by runoff if planted with Vetiver grass or lemon grass.

When grown from seeds, the plants are edible for the first 3 months, since the toxic material has not been developed yet. It should be protected from animals in these early stages. It can also be eaten safely, when steamed or stewed.

Medicinal Plant [2, 3, 5]

The name “Jatropha” refers to medicinal uses, from the Greek iatrós, meaning “doctor” and “trophè”, meaning “food”. Preparations of all parts of the plant, including seeds, leaves and bark, fresh or as a decoction, are used in traditional medicine and veterinary purposes

The latex of Jatropha contains an alkaloid known as "jatrophine" which is believed to have anti-cancerous properties. It is also used as an external application for skin diseases and rheumatism and for sores on domestic livestock. In addition, the tender twigs of the plant are used for cleaning teeth, while the juice of the leaf is used as an external application for piles. Finally, the roots are reported to be used as an antidote for snake-bites. The seed oil can be applied to treat eczema and skin diseases and to soothe rheumatic pain. The sap flowing from the stem is used to control the bleeding of wounds. The oil is use to soothe pain from rheumatism.

Raw Material for Dye [3]

The bark of Jatropha curcas yields a dark blue dye which is used for coloring cloth, fishing nets and lines.

Viruses [2]

Unfortunately the physic nut is a host for viruses that attack also cassava, since they belong to the same family of plants (such as the cassava superelongation disease). Therefore physic nut should not be used to fence in cassava fields.

For some countries it should be investigated if it does not contain viruses for major crops.

Insecticide/ Pesticide [3, 5]

The oil and aqueous extract from oil has potential as an insecticide. For instance, it has been used in the control of insect pests of cotton including cotton bollworm, and on pests of pulses, potato and corn.

The seeds are considered anthelimintic in Brazil, and the leaves are used for fumigating houses against bed-bugs. Also, the ether extract shows antibiotic activity against Styphylococcus aureus and Escherichia coli. Methanol extracts of Jatropha seed (which contains biodegradable toxins) are being tested in Germany for control of bilharzia-carrying water snails.

Seed Cake Uses

Manure [2]

A good application for the seed cake is to use it as organic manure, replacing chemical fertilizer. It has nitrogen content similar to that from cake of castor bean or chicken manure. The nitrogen content ranges from 3.2 to 3.8 %.

Input For Biogas Production [2]

The seed cake still contains oil. Hence the seed cake still contains much energy. The cake can in principle be converted into bio-gas by digestion in bio-gas tanks, together with other input materials, such as dung, leaves etc. The biogas can be used for cooking and lighting. The residue can still be used as organic fertilizer, as it retains all of its minerals and nutrients.

Input For Combustion or Charcoal Production [2]

Seed cake can be processed into pellets using screw-type presses. These pellets can be used for direct combustion, or they can be converted into charcoal where there is sufficient demand for charcoal, such as in the neighbourhood of large cities where there is a deforestation problem.

Seed Oil Uses

The seed oil can be used for production of soap, directly as fuel in oil lamps or stoves, or as PPO for diesel engines.

Soap Production [5]

The glycerin that is a by-product of biodiesel can be used to make soap, and soap can be produced from Jatropha oil itself. It will produce a soft, durable soap, and the rather simple soap making process is well adapted to household or small-scale industrial activity

Oil For Lighting And Cooking [5]

Jatropha nuts can be strung on grass and burned like candlenuts, and the oil to make candles. Although many researchers have described Jatropha as a potential domestic fuel for cooking and lighting, with properties similar to kerosene, it cannot be used directly in conventional kerosene stoves or lamps.

High ignition temperatures and viscosity (75.7 10^{-6} m^2/s) as compared to kerosene (50-55 C, and 2.2 $10^{-6} m^2/s$ respectively) mean that Jatropha oil will not burn as well, and would clog up all the tubes and nozzles in a conventional stove or lamp. Approaches to circumventing these problems are being tried. A low intensity lamp with a wick has been developed. The oil lamp requires a very short wick so that the flame is very close to the oil surface.

Alternative to Diesel [3]

It is significant to point out that, the non-edible vegetable oil of Jatropha curcas has the requisite potential of providing a promising and commercially viable alternative to diesel oil since it has desirable physicochemical and performance characteristics comparable to diesel. Cars could be run with Jatropha curcas without requiring much change in design.

3.5 Advantages of Jatropha oil [4]

- Jatropha can be grown in arid zones (20 cm rainfall) as well as in higher rainfall zones and even on land with thin soil cover.
- It is quick yielding specie even in adverse land situations viz. degraded and barren lands under forest and non-forest use, dry and drought prone areas, marginal lands, even on alkaline soils and also as agro-forestry crops. Jatropha can be a good plantation material for eco-restoration in all types of wasteland.
- Jatropha grows readily from plant cuttings or seeds up to the height of 3 - 5 m.
- Jatropha is not considered good forage material.
- The plant is highly pest and disease resistant.
- Various parts of the plant are of medicinal value, its bark contains tannin,
- The flowers attract bees and thus the plant is honey production potential.

- Jatropha removes carbon from the atmosphere, stores it in the woody tissues and assists in the build up of soil carbon.

3.6 Limitations [4]

- The jatropha also suffers from certain limiting factors, which need to be kept in mind while dealing with the specie. These are as follows:
- Jatropha cannot be grown on waterlogged lands and slopes exceeding 30o.
- The ideal climatic conditions for jatropha can be summarized as annual rainfall not exceeding 600 mm in moderate climatic conditions, 1200 mm in hot climatic zones and soil pH less than 9. The atmospheric temperature should not fall below 0 ^{0}C as the plants are sensitive to ground frost that may occur in winters.
- Jatropha seeds are hard and possess toxicity
- The golden flea beetle can harm particularly on young plants.
- Jatropha is also host to the fungus "frogeye", common in tobacco

3.7 Comparison of Properties Of Jatropha With Standard Of Diesel Oil

The comparison of properties of *Jatropha* oil and standard specifications of diesel oil are shown in Table 3.3:

Table 3.3 Comparison Of Properties Of Jatropha Oil And Standard Specifications Of Diesel Oil [31]

Specification	Standard specification of Jatropha oil	Standard specification of Diesel
Specific gravity	0.9186	0.82/0.84
Flash point	240/110 °C	50 °C
Carbon residue	0.64	0.15 or less
Cetane value	51.0	50.0 up
Distillation point	295 °C	350 °C

Kinematics Viscosity	50.73 cs	2.7 cs up
Sulpher %	0.13 %	1.2 % or less
Calorific value	9 470 kcal/kg	10 170kcal/kg
Pour point	8 °C	10 °C
Colour	4.0	4 or less

The seeds were imported from India five years ago, and were cultivated in the southern part of Egypt and irrigated by treated sewage water. It is worth mentioning that the cultivation has been very successful. It is now producing seeds, and the next step consists in studying the best means of making use and of its oil product.

REFERENCES CHAPTER 3

1. G.M. Giibitz , M. Mittelbach B, M. Trabi "*Exploitation Of The Tropical Oil Seed Plant Jatropha Curcas L*" Bioresource Technology 67 (1999) 73-82 Received 20 February 1998; Accepted 12 March 1998
2. *"Jatropha Handbook First Draft"* Handbook on Jatropha Curcas, Fact Foundation, www.factfuels. org/images/jatropha%20handbook%20march%202006.pdf (12/10/06)
3. http://www.pcra-biofuels.org/jatropha.htm(5/10/06)
4. http://www.tifac.org.in/news/Bioenergy_1.htm(13/12/06)
5. http://www.google.co.in/search?q=use+of+jatropha+oil+for+the+soap+production&hl=en&lr=&as_qdr=all&start=20&sa=N(12/12/06)

CHAPTER 4

EXPERIMENTAL PROCEDURE

&

SET UP

4. EXPERIMENTAL PROCEDURE AND SET UP

The experimental work was carried out in Chemical Process Industries Laboratory, Chemical Engineering Department, Nirma University, Ahmedabad. The process is batch process. The raw material was taken for the production of the biodiesel. Small amount of batch was taken for this purpose. After the preparation of the biodiesel the testing of the sample was done in the PRPC Laboratory, Nirma University, Ahmedabad. After that the result of that was compared with the ASTM standard. The testing on the engine was carried out at the Thermal Engineering Laboratory, Mechanical Engineering Department, Nirma University, Ahmedabad.

4.1 Experimental Set Up for Production of Biodiesel

4.1.1 Ingredients Used For the Experiments

Reaction Raw Materials

- Jatropha Oil
- Methanol (CH3OH) 99%+ pure
- Potassium Hydroxide

Materials for Titration

- Isopropyl alcohol 99%+ pure
- Distilled water
- Phenolphthalein solution

Materials for Washing

- Acetic acid (vinegar)
- Water

4.1.2 Instruments Required At the Experimental Work

For Experiment Purpose

Hot plate with temperature regulator, propeller coupled with electric motor for the stirring and for heating purpose

For Testing Of Sample

Redwood viscometer for viscosity measurement, smoke point apparatus, aniline point apparatus, cloud point apparatus, pour point apparatus

4.1.3 Apparatus Required At Experimental Work

Beaker, burette, measuring flask, thermometer, condenser, round bottom flask

4.2 Biodiesel Production Process

4.2.1 Schematic Diagram of the Production Process

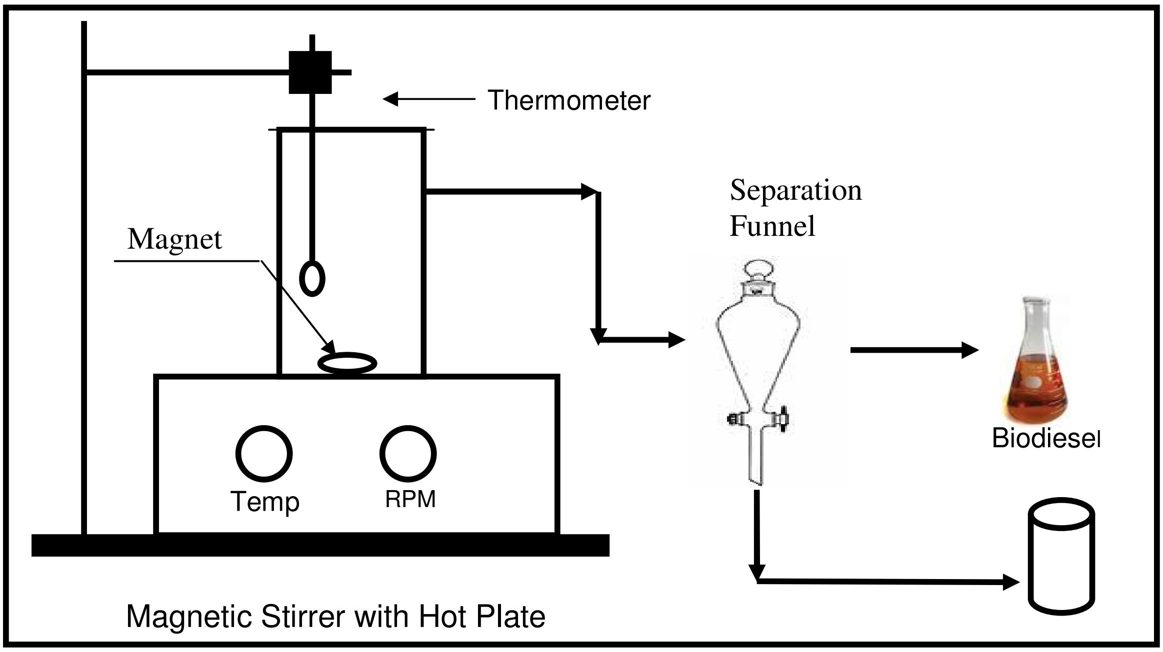


Figure 4.1 Schematic of Biodiesel Production Without Methanol Recovery

4.2.2 Experimental Procedure

Production Method

Take known quantity of jatropha oil (250 ml) into a 500 ml beaker. Preheat oil up to 50 to 60 ^{0}C. Preheating is used to remove unwanted moisture present in the oil. The transesterification is carried out in basic medium, and to achieve it KOH is used as a catalyst. Titration is done to calculate the amount of KOH required for the process. The procedure of the titration is given into the Appendix A.

Known quantity of the catalyst is dissolved into the 50 ml of methanol. Add the potassium methoxide (mixture of methanol and KOH) to the oil. A full speed propeller coupled to a electric motor is used for the stirring purpose. The reaction temperature is maintained up to 65 to 70 ^{0}C. Maintain the stirring and equilibrium temperature of 70 ^{0}C for an hour.

Figure 4.2 Experimental Set Up at Laboratory

Once the reaction is over the products are put into the separating funnel. Allow the solution to settle and cool for at least 8 hour, preferably longer. Two phases (having different density) are formed as a result of trans-esterification. Separation is done using a separating funnel. Upper layer consists of bio-diesel, alcohol, and some soap (formed as a result of side reaction saponification - free fatty acids get converted to soap). Lower layer consists of glycerin, excess alcohol, catalyst, impurities, and traces of unreacted oil. Purification of upper layer (to obtain bio-diesel) is done in two steps.

- Removal of alcohol – by keeping mixture at elevated temperature ~80 ºC.
- Removal of saponified products – by washing with warm water. Water is immiscible with bio-diesel, hence can be easily separated from bio-diesel.

2. Recovery of Methanol

Put the solution into the round bottom flask. The solution contains mainly biodiesel, glycerol and methanol. The condenser is provided horizontally. Heating is provided with the use of heating mental.

At the boiling point of the methanol it is get vaporized. The vapor of the methanol is condensed and the liquid methanol is collected on the other end of the condenser. The methanol is recovered back. After the methanol recovery, the separating of both the layer is done as per the first experiment.

Schematic of Recover of Methanol

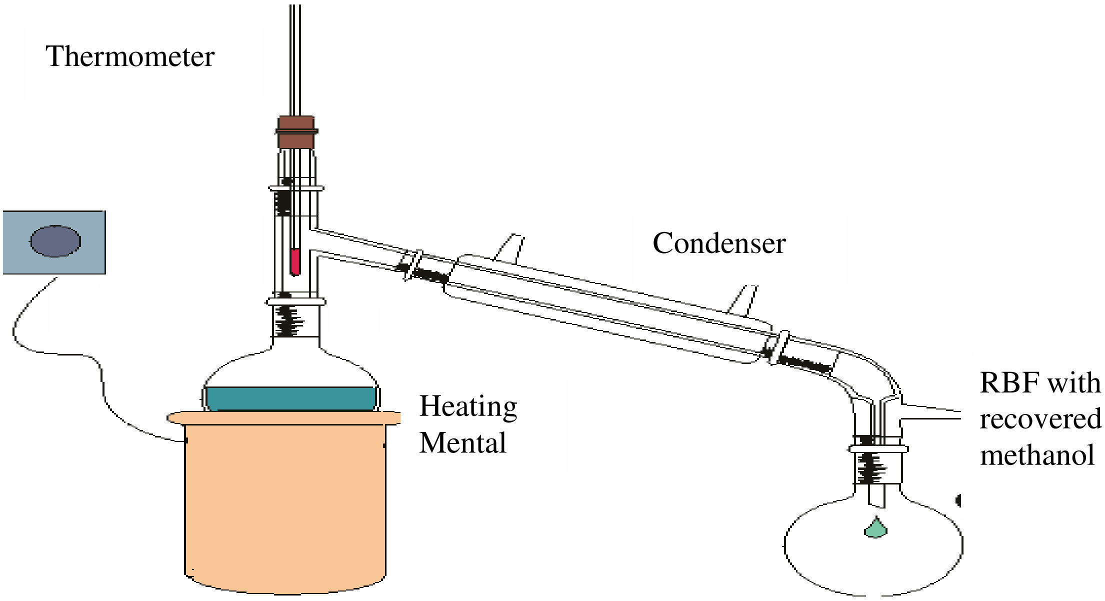


Figure 4.3 Methanol Recoveries from the Sample

Experimental Set Up At Laboratory

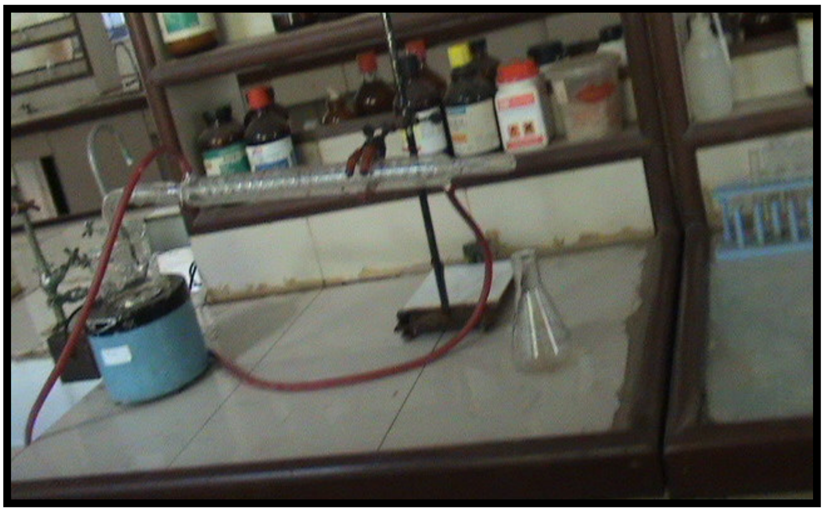


Figure 4.4 Experimental Set Up at Nirma Laboratory

4.3 Testing of Biodiesel Samples

The testing of the biodiesel sample was carried out in the Petroleum refining and Petrochemicals laboratory, Nirma university, Ahmedabad.

Figure 4.5 Biodiesel Sample Prepared at Laboratory

Testing of the following was done in the laboratory to find out recommended testing properties of biodiesel sample

- Flash and Fire point
- Pour Point
- Cloud Point
- Viscosity
- Aniline Point
- Smoke Point

For these purpose standard methods were used. For the viscosity measurement redwood viscometer was used. The flash and fire point of the samples were measured into the open cup apparatus. For the aniline point aniline point apparatus was used. For the smoke point smoke point apparatus was used.

4.4 Testing On The Diesel Engine

The testing was done in the thermal engineering laboratory at the mechanical engineering department Nirma University Ahmedabad. The testing of pure diesel, then B20 and B40 was done on the engine. The specifications of the engine are given in the chapter 6. The analysis of the sample properties are also given into chapter 6.

The schematic figure shows the arrangement of the equipments during the testing on the diesel engine.

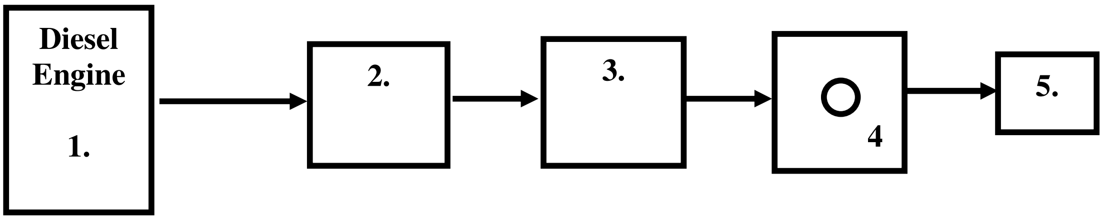


Figure 4.6 Schematic of the Sampling Train During Experiment

1. Diesel Engine
2. Particulate Matter Collector
3. Gas Collector
4. Rotameter
5. Vacuum Pump

This figure shows the gas monitoring kit. It shows the arrangement of the impinger tubes for the collection o the sample.

Experimental Procedure

1. **Petrodiesel**

- The first run was carried out with the neat diesel fuel. The fuel tank was filled with the diesel fuel. The different loads were applied to the engine. The run was taken with the no dead load and no spring load condition. To know the performance of the diesel engine the RPM of the engine, the time for the consumption of the 10 ml of the diesel fuel, exhaust air temperature etc were measured.
- To calculate the emission parameters like SPM, SO_2 and NO_X the sampling of the exhaust gas is necessary. Here in this experiment the exhaust gas sampling the gas sampler is used. In the gas sampler the impinger tubes are placed. In the impinger tubes are filled with the absorbing solutions respectively for SO_2 and NO_X.

Experimental set-up at laboratory is shown into the figure.

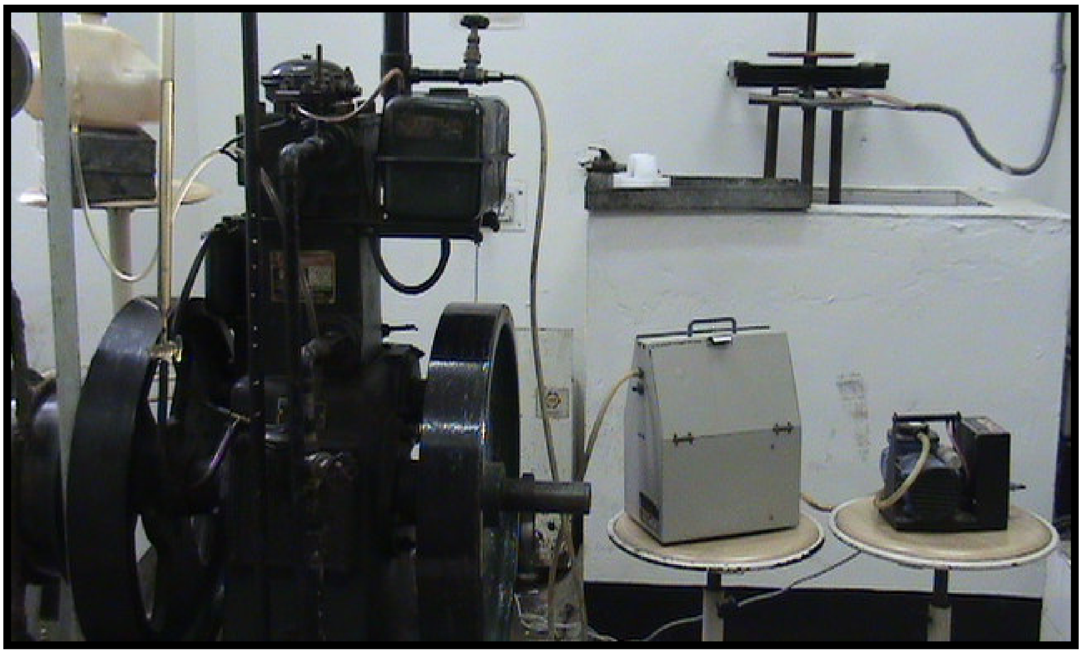


Figure 4.7 Experimental Set Up For Testing Performance Of Diesel

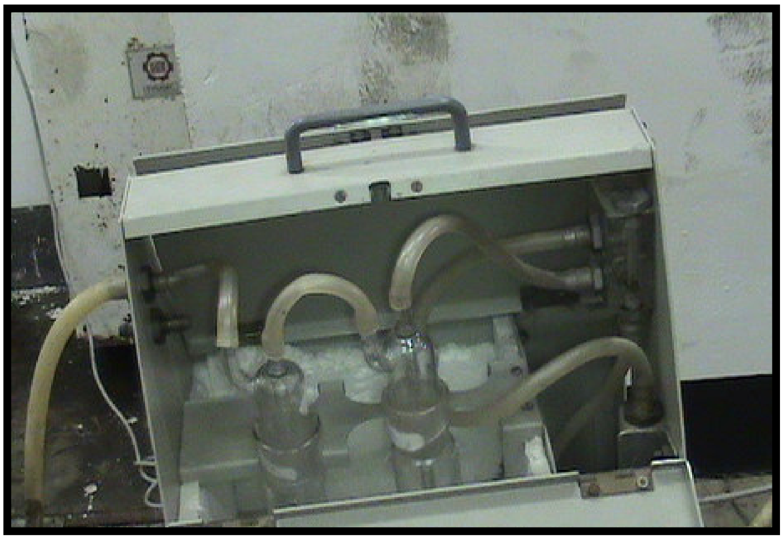


Figure 4.8 Gas Monitoring Kit

- During the sampling the order of the impinger for the collection is exhaust of the engine → SPM collector →impinger tube filled with SO_2 absorbing medium → impinger tube filled with NO_X absorbing medium →Vacuum Pump. This order of the collection device must follow during the sampling.

- The flow the exhaust gas was regulated with the nob given into the diesel engine. The rotameter is used as a flow meter which gives the flow into liter per minute. During all the experiment the flow rate of the exhaust gas was maintained 0.5 LPM.
- The sampling time for the gas was taken 15 min. After 15 min the samples into the gas sampler and wattman filter paper which was used to collect the SPM was taken to the laboratory for the analysis purpose.
- Before the sampling the weight of the wattman filter paper was done. After the sampling measure the weight of the filter paper. From this difference into the weight the SPM can be calculated. The detail calculation step for the SPM calculation is given into the Appendix.
- Similarly the absorbing solutions which are filled into the impinger tube were taken into the laboratory for the analysis purpose. The analysis procedure is given into the Appendix 3. The calibration curve for both the SO_2 and NO_X is also given into the appendix 3. The spectrophotometer is use for the analysis of the samples.
- The analysis of all the samples was done into the Chemical reaction Engineering Laboratory, Nirma University, Ahmedabad (Gujarat).
- The same procedure was repeated for the different load. At the different load the all the parameters were measured. 4 loads listed below were applied to the engine during testing.

Sample B20

B20 is the mixture of 20% biodiesel and 80% of petrodiesel. The 5 liter of total sample of B20 was prepared into the laboratory. This prepared B20 sample was tested on the same engine. The recommended properties for the diesel engine were tested for the B20 sample. This property and its method are given into the 5.2.

For the testing of the B20 use the same load which were used during the petrodiesel. This is necessary to compare the results with each other. Procedure was same as discussed above for the petrodiesel. The method of analysis was also same as shown into the appendix 3.

Sample B40

B20 is the mixture of 40% biodiesel and 60% of petrodiesel. The 5 liter of total sample of B40 was prepared into the laboratory. This prepared B20 sample was tested on the same engine.

For the testing of the B40 use the same load which were used during the petrodiesel. This is necessary to compare the results with each other. Procedure was same as discussed above for the petrodiesel. The method of analysis was also same as shown into the appendix B and C.

CHAPTER 5

KINETIC STUDY

5.1. Chemical Foundations of Biodiesel-Making

Biodiesel is fuel made from fat. It can be produced from vegetable oil or animal fat. Either virgin vegetable oil or waste vegetable oil (WVO) can be used to make quality fuel. Fats are converted to biodiesel through a chemical reaction involving alcohol and a catalyst.

5.1.1. Chemical Building Blocks

Fatty acids are a component of both vegetable oil and biodiesel. In chemical terms, they are carboxylic acids of the form:

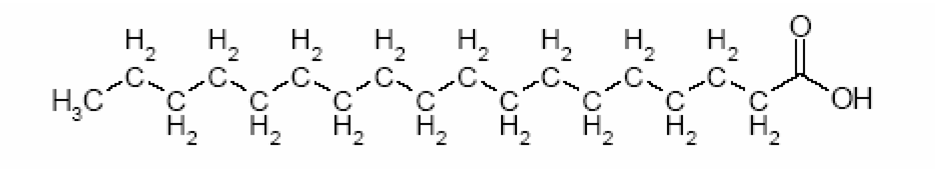


Figure 5. 1 Molecular Structure of an Idealized Fatty Acid [7]

Fatty acids which are not bound to some other molecule are known as free fatty acids.

When reacted with a base, a fatty acid loses a hydrogen atom to form soap.

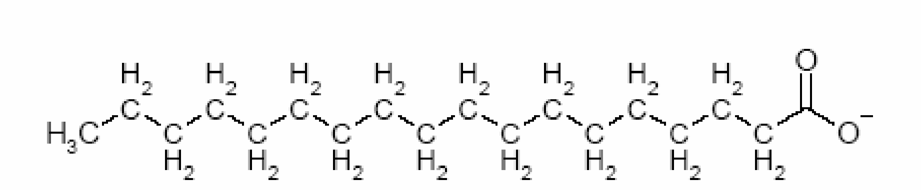
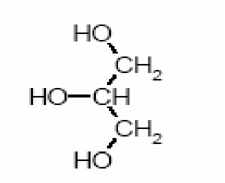


Figure 5.2 Molecular Structure of Soap [7]

Chemically, soap is the salt of a fatty acid.

The structures of fatty acids shown in this section are highly idealized. Real fatty acids vary in the number of carbon atoms, and in the number of double bonds. Glycerol, a component of vegetable oil and a by-product of biodiesel production, has the following form: [7]



Alcohols are organic compounds of the form *R-OH*, where *R* is a hydrocarbon. Typical alcohols used in biodiesel-making are methanol, ethanol, 1-propanol, and 1-butanol:.

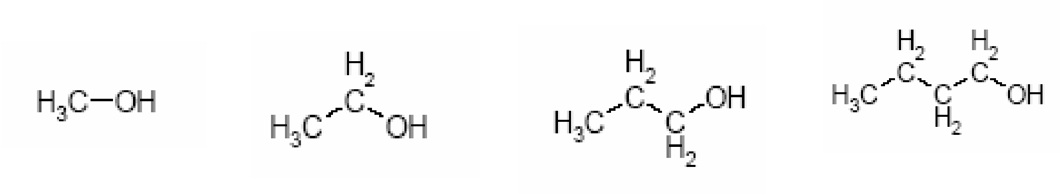


**Figure 5.3 Molecular Structure of Methanol, Ethanol,
1-Propanol and 1-Butanol. [7]**

Of these, methanol is the most commonly used to make biodiesel. Since ethanol is easily obtained from plant sugars, while methanol is commonly produced from natural gas, using ethanol makes for a more sustainable fuel. Ethanol is harder to use because it forms emulsions easily, making the separation of end products more difficult. This is especially true if the oil source is WVO.

Transesterification is sometimes called alcoholysis or if by a specific alcohol, by corresponding names such as methanolysis or ethanolysis.

Chemically, biodiesel is a fatty acid alkyl ester:

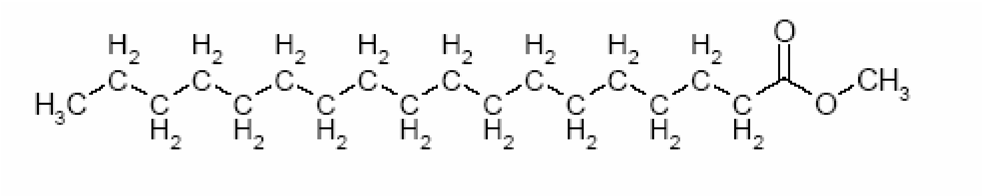


Figure 5.4 Biodiesel Molecules - Methyl Ester [7]

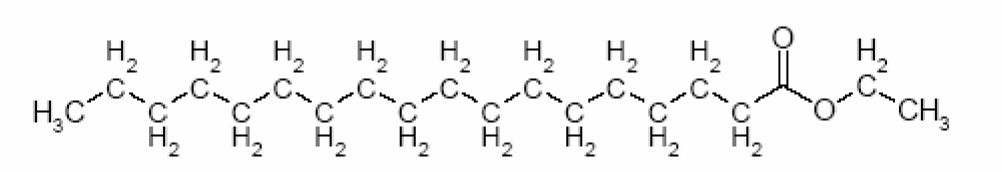


Figure 5.5 Biodiesel Molecules - Ethyl Ester [7]

An ester is a compound of the form:

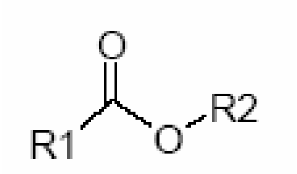


Figure 5.6 Form Of The Ester Compound. [7]

The biodiesel ester contains a fatty acid chain on one side, and a hydrocarbon called an alkane on the other. Thus, biodiesel is a fatty acid alkyl ester. Usually, the form of the alkane is specified, as in "methyl ester" or "ethyl ester".

Vegetable oil is a mixture of many compounds, primarily triglycerides and free fatty acids. A triglyceride is a tri-ester of glycerol and three fatty acids

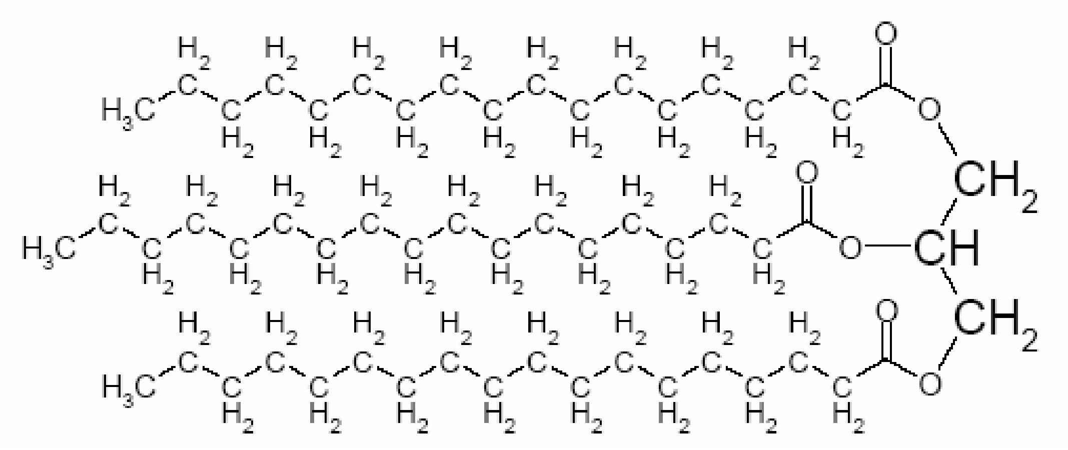


Figure 5.7 Molecular Structure Of Triglyceride. [7]

Petroleum diesel and biodiesel are both mixtures of organic compounds. The idealized petroleum molecule is cetane, pure paraffin. Compared to cetane, alkyl esters are somewhat longer, and more importantly, contain two oxygen atoms.

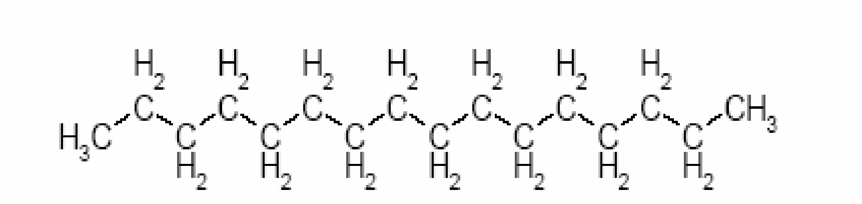


Figure 5.8 Cetane Molecule [7]

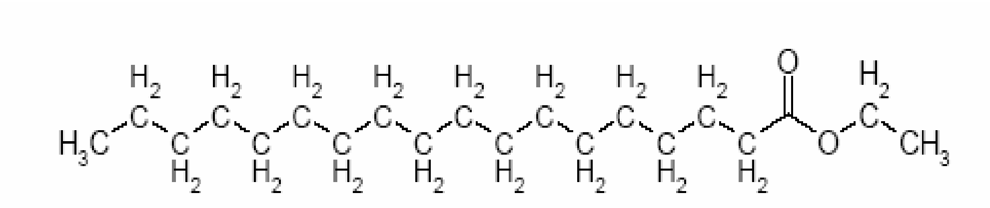


Figure 5.9 Ethyl Ester Molecule [7]

A rate expression characterizes the rate of reaction, and its form may either be suggested by theoritical considerations or simply be the result of an empirical curve fitting procedure. In any case the result of the constants of the equation can only be found by experiment.

The determination of the rate equation is usually a two step procedure; first the consideration dependency is found at fixed temperature and then the temperature dependency of the rate constant is found, yielding the complete rate equation.

The principal ways of making biodiesel are by transesterification of triglycerides and esterification of free fatty acids.

The transesterification reaction of triglycerides is as follows:

$$Triglyceride + 3Alcohol \xrightarrow{Catalyst} 3Biodiesel + Glycerol$$

5.2 Development of Kinetic Model [4, 7]

The overall reaction for transesterification can be written symbolically as:

$$\mathrm{TG} + 3\mathrm{ROH} \xrightarrow{\mathrm{KOH}} \mathrm{G} + 3\mathrm{E} \qquad 1.$$

This reaction occurs in three steps:

$$TG + ROH \Leftrightarrow DG + E$$
$$DG + ROH \Leftrightarrow MG + E$$
$$MG + ROH \Leftrightarrow G + E$$

Where

TG means triglycerides,

DG means diglycerides,

MG means monoglycerides,

G means glycerol,

E means alkyl esters, or biodiesel.

The catalyst is usually either potassium hydroxide (KOH), or sodium hydroxide (NaOH), also known as lye. When the catalyst dissolves in the alcohol, it forms an ionic solution, in which the K^+ or Na^+ ions and the OH^- ions are not directly bound to each other. The active ingredient is the hydroxide ion, OH^-. When describing chemical reactions and rate equations, the K^+ or Na^+ ions are never written out explicitly. [4, 7]

Hydroxide ion is the catalyst for base-catalyzed transesterification. It is also a reactant in the competing saponification reactions, in which it is consumed. Thus, saponification robs the transesterification reaction not only of reactants that could be made into biodiesel, but also of the catalyst needed for the reaction to proceed.

5.2.1 Development of the Rate Equation [4, 7]

1. Proposed Simplification [4, 7]

The development of the kinetic model begins with simplifying assumptions:

1. The concentration of free fatty acids is negligible.
2. Of all the theoretically possible reactions only two proceed to form products: the alcoholysis of glycerides (TG, DG, MG) and the saponification of TG, DG, MG, or alkyl esters (E).
3. All of the isomers of TG, DG, MG, and E proceed at the same rate, with the same mechanism.
4. Alcoholysis is catalyzed by OH^- or RO^- (alkoxides) ions. Concentrations of OH^- and RO^- ions are much smaller than those of TG and ROH.

2. Possible Reactions [4, 7]

The possible reactions are then

.1. Formation of alkoxide:

$$ROH + OH^- \underset{k_{1_r}}{\overset{k_1}{\Leftrightarrow}} RO^- + H_2O$$

2.

2. Alcoholysis

$$TG + RO^- \underset{k_{2_r}}{\overset{k_2}{\Leftrightarrow}} DG^- + E$$

3.

$$DG^- + ROH \underset{k_{3_r}}{\overset{k_3}{\Leftrightarrow}} DG + RO^-$$

4.

$$DG + RO^- \underset{k_{4r}}{\overset{k_4}{\Leftrightarrow}} MG^- + E \qquad 5.$$

$$MG^- + ROH \underset{k_{5r}}{\overset{k_5}{\Leftrightarrow}} MG + RO^- \qquad 6.$$

$$MG + RO^- \underset{k_{6r}}{\overset{k_6}{\Leftrightarrow}} G^- + E \qquad 7.$$

$$G^- + ROH \underset{k_{7r}}{\overset{k_7}{\Leftrightarrow}} G + RO^- \qquad 8.$$

Saponification

$$E + OH^- \overset{k_8}{\rightarrow} ROH + A \qquad 9.$$

$$TG + OH^- \overset{k_9}{\rightarrow} DG + A \qquad 10.$$

$$DG + OH^- \overset{k_{10}}{\rightarrow} MG + A \qquad 11.$$

$$MG + OH^- \overset{k_{11}}{\rightarrow} G + A \qquad 12.$$

Where, A is the soap of the corresponding fatty acid chain [4, 7]

Whereas = depicts an equilibrium (reversible) reaction, → indicates an irreversible (only one way) step and k_i or k_{ir} are the reaction rate constants of the direct or reverse steps of the given reaction. In the reversible reaction the ratio k_i/k_{ir} defines the equilibrium constant of the given reaction K_i. The irreversible step is the reaction with $K_i \rightarrow \infty$, *i*.e. $k_i >> k_{ir}$ (at a given pressure and temperature). Its final state is characterized by the practically full exhaustion of the reactant with lower initial concentration.

However, it is known that in such complicated reaction schemes rarely all reaction steps influence the real reaction rate to the same extent. Generally some of them are dominant with respect to their great or small velocity in comparison with the other steps. We assume the same in the proposed scheme for following reasons. [4, 7]

1) The alkaline-catalyzed methanolysis of the rapeseed oil takes from several tens of minutes to several hours (according to ratios n and p) at room temperature till it reaches equilibrium. On the other hand the formation of methanolate X, *i*.e. the exchange of proton between M and OH by reaction (2) is a matter of seconds. Therefore,

$dW/dt = 0$ ḍW $\approx$const.

2. Similarly we suppose that also all other exchanges of protons between anions DG–, MG–, G– ,X and the neutral molecules M, DG, MG, G, *i.e.* reactions (4), (6) and (8), are in both steps much faster than the reversible transformations of TG, DG, MG by X to E and DG, MG, G, *i*.e. reactions (3), (5) and (7), and much faster than all the irreversible saponification (9-12). In other words, we presume that [4, 7]

$$
\begin{aligned}
&k_2, k_{2r} << k_3, k_{3r}\\
&k_4, k_{4r} << k_5, k_{5r}\\
&k_6, k_{6r} << k_7, k_{7r}\\
&k_3, k_{3r}, k_5, k_{5r}, k_7, k_{7r} > k_8, k_9, k_{10}, k_{11}
\end{aligned}
\qquad 13.
$$

3. On this basis the stationary state for following reaction components is valid [4, 7]

$$d\,[DG^-]/dt = d[MG^-]/dt = d[G^-]/dt = d[RO^-]/\,dt = d[H_2O]/dt = 0 \qquad 14.$$

Application of these steady states leads to following expressions:

$$DG^- = X.(k_2.TG + k_{3r}.DG)/(k_{2r}.E + k_3.M)$$
$$MG^- = X.(k_4.DG + k_{5r}.MG)/(k_{4r}.E + k_5.M)$$
$$G^- = X.(k_6.MG + k_{7r}.G)/(k_{6r}.E + k_7.M)$$
$$X = (k_1/k_{1r}).M.OH/W = K_1.M.OH/W$$

4. With respect to inequalities (15) and because relative concentrations of all compounds are mostly in the interval (0.01; 1), following inequalities can be further presumed: [4]

$k_{3r}.\ DG >> k_2.\ TG$

$k_3.\ M >> k_{2r}\ .\ E$

$k_{5r}\ .\ MG >> k_4.\ DG$

$k_5\ .\ M >> k_{4r}.\ E\ ;\ k_{7r}\ .$

$G >> k_6\ .\ MG$

$k_7\ .\ M >> k_{6r}\ .\ E$

5. Eliminating small terms and substituting the equilibrium relations into the rate equations for the corresponding species, we obtain by normalizes the remaining species by the initial concentrations of triglyceride and alcohol, as follows: [4, 7]

$$\begin{array}{cc} TG=[TG]/a, & \\ a=[TG]_0 & OH=[OH^-]/a \\ DG=[DG]/a & W=[H_2O]/a \\ MG=[MG]/a & ROH=[ROH]/b, \\ G=[G]/a & b=[ROH]_0 \\ A=[A]/a & E=[E]/b \end{array} \qquad 15.$$

6. Using the simplifying conditions 1), 2) and 3) in the complete reaction scheme (2)-(12) we obtain a simpler reaction scheme: [4]

TG + M + OH = DG + E + OH
DG + M + OH = MG + E + OH
MG+ M + OH = G + E + OH
E + OH = A + M
TG + OH = A + DG
DG + OH = A + MG
MG + OH = A + G

3. Steps to Derive First Differential Equation [4, 7]

Equations used for the derivation of first differential equations are,

$$ROH + OH^- \underset{k_{1r}}{\overset{k_1}{\Leftrightarrow}} RO^- + H_2O$$

$$TG + RO^- \underset{k_{2r}}{\overset{k_2}{\Leftrightarrow}} DG^- + E$$

$$DG^- + ROH \underset{k_{3r}}{\overset{k_3}{\Leftrightarrow}} DG + RO^-$$

This really involves six elementary reactions. These elementary reactions are,

$$ROH + OH^- \xrightarrow{k_1} RO^- + H_2O \tag{A.}$$

$$RO^- + H_2O \xrightarrow{k_1} ROH + OH^- \tag{B.}$$

$$TG + RO^- \xrightarrow{k_2} DG^- + E$$ C.

$$E + DG^- \xrightarrow{k_3} TG + RO^-$$ D.

$$DG^- + ROH \xrightarrow{k_3} DG + RO^-$$ E.

$$DG + RO^- \xrightarrow{k_{3R}} DG^- + ROH$$ F.

$$TG + OH^- \xrightarrow{k_9} DG + A$$ G.

Assumptions are

$[TG_0] = 0$

$[DG_0] = 0$

Rate of TG

$$-r_{TG} = k_2 * [TG] * [RO^-]$$
$$-r_{TG} = -k_{2r} * [E] * [DG^-]$$
$$-r_{TG} = k_9 * [TG] * [OH^-]$$

The rate of the TG can be written as

$$-r_{TG} = k_2 * [TG] * \left[RO^- \right] - k_{2r} * [E] * \left[DG^- \right] + k_9 * [TG] * \left[OH^- \right]$$

Rate of RO^-

$$-r_{RO^-} = -k_1 * [ROH] * \left[OH^- \right]$$
$$-r_{RO^-} = k_{1r} * [RO^-] * [H_2O]$$
$$-r_{RO^-} = k_2 * [TG] * \left[RO^- \right]$$
$$-r_{RO^-} = -k_{2r} * [E] * \left[DG^- \right]$$

Therefore, the rate of RO$^-$ can be written as,

$$-r_{RO^-} = -k_1 * [ROH] * \left[OH^-\right] + k_{1r} * [RO^-] * [H_2O] + k_2 * [TG] * \left[RO^-\right] - k_{2r} * [E] * \left[DG^-\right]$$

<u>For the rate of DG$^-$</u>

$$-r_{DG^-} = -k_2 * [TG] * \left[RO^-\right]$$

$$-r_{DG^-} = k_{2r} * [E] * [DG^-]$$

$$-r_{DG^-} = k_3 * [DG^-] * [ROH]$$

$$-r_{DG^-} = -k_{2r} * [DG] * \left[RO^-\right]$$

Therefore the resulting differential equation for rate of DG$^-$ is,

$$-r_{DG^-} = -k_2 * [TG] * \left[RO^-\right] + k_{2r} * [E] * [DG^-] + k_3 * [DG^-] * [ROH] - k_{2r} * [DG] * \left[RO^-\right]$$

For intermediates rate of formation = rate of disappearance. This can be applied for both RO$^-$ and DG$^-$, so the concentration of both can be written as,

$$\left[RO^-\right] = \frac{k_1}{k_{1r}} \frac{[ROH] * \left[OH^-\right]}{[H_2O]}$$

Similarly for [DG$^-$],

$$\left[DG^-\right] = \frac{k_{3r}}{k_3} \frac{[DG] * \left[RO^-\right]}{[ROH]}$$

The final form of [DG$^-$] is

$$\left[DG^-\right] = \frac{K_1}{K_3} \frac{[DG] * \left[OH^-\right]}{[H_2O]}$$

From the above discussed theory we know that,

$d[DG^-]/dt = d[MG^-]/dt = d[G^-]/dt = d[RO^-]/dt = d[H_2O]/dt = 0$

And

$$\begin{gathered} TG = [TG]/a, \\ a = [TG]_0 \\ DG = [DG]/a \\ MG = [MG]/a \\ G = [G]/a \\ A = [A]/a \end{gathered}$$

$$\begin{gathered} OH = [OH^-]/a \\ W = [H_2O]/a \\ ROH = [ROH]/b, \\ b = [ROH]_0 \\ E = [E]/b \end{gathered}$$

3. The value of the equilibrium constants are,

$$K_1 = \frac{k_1}{k_{1r}} = \frac{[RO^-][H_2O]}{[ROH][OH^-]}$$

$$K_3 = \frac{k_3}{k_{3r}} = \frac{[DG][RO^-]}{[DG^-][ROH]}$$

By putting the value of both $[RO^-]$ and $[DG^-]$ into the rate equation for TG we get, the rate equation in the following form.

$$-\frac{dTG}{dt} = b \cdot OH \cdot (k_2' \cdot TG \cdot ROH - k_{2r}' \cdot DG \cdot E) + a \cdot OH \cdot k_9 \cdot TG$$

Where

$$k_2' = \frac{k_2 K_1}{W} \qquad k_{2r}' = \frac{k_{2r} K_1}{K_3 W}$$

Similarly we can derive all differential equations. The resulting differential equations are, [4, 7]

$$-\frac{dTG}{dt} = b \cdot OH \cdot (k_2' \cdot TG \cdot ROH - k_{2r}' \cdot DG \cdot E) + a \cdot OH \cdot k_9 \cdot TG$$

$$-\frac{dDG}{dt} = b \cdot OH \cdot (-k_2' \cdot TG \cdot ROH + k_{2r}' \cdot DG \cdot E + k_4' \cdot DG \cdot ROH - k_{4r}' \cdot MG \cdot E) \\ + a \cdot OH \cdot (-k_9 \cdot TG + k_{10} \cdot DG)$$

$$-\frac{dMG}{dt} = b \cdot OH \cdot (-k_4' \cdot DG \cdot ROH + k_{4r}' \cdot MG \cdot E + k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E) \\ + a \cdot OH \cdot (-k_{10} \cdot DG + k_{11} \cdot MG)$$

$$\frac{dG}{dt} = b \cdot OH \cdot (k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E) + a \cdot OH \cdot k_{11} \cdot MG$$

$$-\frac{dOH}{dt} = \frac{dA}{dt} = b \cdot OH \cdot k_8 \cdot E + a \cdot OH \cdot (k_9 \cdot TG + k_{10} \cdot DG + k_{11} \cdot MG)$$

$$-\frac{dROH}{dt} = \frac{dE}{dt} = b \cdot OH \cdot (k_2' \cdot TG \cdot ROH - k_{2r}' \cdot DG \cdot E + k_4' \cdot DG \cdot ROH - k_{4r}' \cdot MG \cdot E \\ + k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E - k_8 \cdot E)$$

Where

$$k'_2 = \frac{k_2 K_1}{W} \qquad k'_4 = \frac{k_4 K_1}{W} \qquad k'_6 = \frac{k_6 K_1}{W}$$

$$k'_{2r} = \frac{k_{2r} K_1}{K_3 W} \qquad k'_{4r} = \frac{k_{4r} K_1}{K_5 W} \qquad k'_{6r} = \frac{k_{6r} K_1}{K_7 W} \qquad 17.$$

And

$$K_1 = \frac{k_1}{k_{1r}} = \frac{[RO^-][H_2O]}{[ROH][OH^-]} \qquad K_3 = \frac{k_3}{k_{3r}} = \frac{[DG][RO^-]}{[DG^-][ROH]}$$

$$K_5 = \frac{k_5}{k_{5r}} = \frac{[MG][RO^-]}{[MG^-][ROH]} \qquad K_7 = \frac{k_7}{k_{7r}} = \frac{[G][RO^-]}{[G^-][ROH]} \qquad 18.$$

5.2.2 Balance Equations [4, 7]

The following balance equations also apply:

$$\begin{aligned}
&TG + DG + MG + G = 1\\
&ROH + E = 1\\
&OH + A = p,\\
&p = \frac{[OH^-]_0}{[TG]_0}\\
&nE + 3TG + 2DG + MG + A = 3,\\
&n = \frac{[ROH]_0}{[TG]_0}
\end{aligned} \qquad 19.$$

In the overall reaction, the alcohol molecules are only consumed to make alkyl esters. Thus, the second balance equation states that the sum of the alcohol molecules and the ester molecules must equal the original quantity of alcohol molecules. Similarly, the hydroxide ions are only consumed in the production of soap. Therefore, the number of hydroxide ions plus the number of soap molecules must equal the original amount of hydroxide ions, as indicated in the third balance equation. Finally, since fatty acid chains are not destroyed either, their total number is also constant, equal to three times the initial amount of triglyceride. The fourth balance equation enforces this condition. The ester variable, E, is multiplied by the initial molar ratio of alcohol to triglycerides in order place each non dimensional variable on the same scale.

The initial conditions are [4, 7]

$$\begin{aligned} &TG_0 = 1 \\ &ROH_0 = 1 \\ &OH_0 = p \\ &DG_0 = MG_0 = G_0 = E_0 = A_0 = 0 \end{aligned} \qquad 20.$$

Assuming that all reactions have reached equilibrium, we have the additional equilibrium equations:

$$\begin{aligned} K_2 &= \frac{k_2}{k_{2r}} = \frac{[DG^-][E]}{[TG][RO^-]} \\ K_4 &= \frac{k_4}{k_{4r}} = \frac{[MG^-][E]}{[DG][RO^-]} \\ K_6 &= \frac{k_6}{k_{6r}} = \frac{[G^-][E]}{[MG][RO^-]} \end{aligned} \qquad 21.$$

Combining with the equations the new rate constants can be defined

$$\begin{aligned} K_2' &= K_2 K_3 = \frac{[DG][E]}{[TG][ROH]} = \frac{DG \cdot E}{TG \cdot ROH} = \frac{k_2'}{k_{2r}'} \\ K_4' &= K_4 K_5 = \frac{[MG][E]}{[DG][ROH]} = \frac{MG \cdot E}{DG \cdot ROH} = \frac{k_4'}{k_{4r}'} \\ K_6' &= K_6 K_7 = \frac{[G][E]}{[MG][ROH]} = \frac{G \cdot E}{MG \cdot ROH} = \frac{k_6'}{k_{6r}'} \end{aligned} \qquad 22.$$

This leads directly to

$$\begin{aligned} DG &= K_2' \frac{1-E}{E} TG \\ MG &= K_4' \frac{1-E}{E} DG = K_2' K_4' \left(\frac{1-E}{E}\right)^2 TG \\ G &= K_6' \frac{1-E}{E} MG = K_2' K_4' K_6' \left(\frac{1-E}{E}\right)^3 TG \end{aligned} \qquad 23.$$

Substituting (2-22) into the molecule balance for glycerol backbone (2-19) provides

$$TG = \frac{1}{1 + K_2'\left(\frac{1-E}{E}\right) + K_2' K_4' \left(\frac{1-E}{E}\right)^2 + K_2' K_4' K_6' \left(1 + K_6' \frac{1-E}{E}\right)^3} \qquad 24.$$

Finally, substituting (2-22) and (2-23) into the fatty acid molecule balance (2-18) gives the desired result:

$$n = \frac{1}{E}\left\{3 - \frac{3 + 2K_2'\left(\frac{1-E}{E}\right) + K_2' K_4' \left(\frac{1-E}{E}\right)^2}{1 + K_2'\left(\frac{1-E}{E}\right) + K_2' K_4' \left(\frac{1-E}{E}\right)^2 + K_2' K_4' K_6' \left(1 + K_6' \frac{1-E}{E}\right)^3} - p\right\} \qquad 25.$$

For any choice of E and p, the evaluation of (2-24) establishes the amount of alcohol that is needed.

Kinetics Study For Overall Transesterification Reaction

To find out the rate constant values at the intermediate steps is very lengthy process. Here in this report we carried out the kinetics of overall reaction. The reaction is reversible reaction. In this reaction total six variables are there.

The overall reaction for transesterification can be written symbolically as:

$$\mathrm{TG} + 3\mathrm{ROH} \xrightarrow{\mathrm{KOH}} \mathrm{G} + 3\mathrm{E}$$

5.2.2 Method to Analyze Kinetic Data [5]

There are two procedures for analyzing kinetic data.

- Integral method of analysis
- Differential method of analysis

Integral Method of Analysis:

In this method we guess a particular form of rate equation and, after appropriate integration and mathematical manipulation predict that the plot of a certain concentration versus time should yield a straight line. The data are plotted, and if a reasonably good straight line is obtained, then the rate equation is said to satisfactory fit the data.

Differential Method of Analysis

In this method we test the fit of the rate expression to the data directly and without any integration.

Here in this report the differential method of analysis is used to find out the overall rate of the reaction. The procedure of the method is given below.

The procedure is as follows: [5]

1. Plot the C_A versus t data, and then by eye carefully draw a smooth curve to represent the data. This curve most likely will not pass through all the experimental points.

2. Determine the slope of this curve at suitably selected concentration values. These slopes $dC_A/dt = r_A$ are the rates of reaction at these compositions.

3. Now search the for a rate expression to represent this r_A vs C_A data, either by.

(a) Picking the testing a particular rate form $r_A = k\,f(C_A)$ or

(b) Testing an nth order form $-r_A = k\ C_A^n$ by taking logarithms of the rate equation.

5.3 Rate Equation For The Overall Transesterification Reaction

Table 5.1 Data for the Overall Reaction

Sr. No	Time (T) Minutes	Concentration C_A (mol/ml)	Conversion	Slope From The Graph (dC_A/dt)	Log($-dC_A/dt$)	$Log_{10}C_A$
1	0	5.97	0	-	-	0.79
2	15	5.074	0	-	-	0.79
3	30	4.2	21	-0.1	-1	0.623
4	45	2.25	53	-0.06933	-1.15	0.3521
5	60	1.253	79	-0.040625	-1.391	0.097
6	75	0.9552	84	-0.02360	-1.627	-0.1135
7	90	0.7761	86	0		

Intercept of the graph: -1.55 = log k

Slope = 0.9447 = n

There fore the rate equation is

$$-r_A = 0.02818 C_A^{0.9447} \frac{mol}{ml * \min}.$$

REFERENCES CHAPTER 5

1. Anton A. Kiss, Alexandre C. Dimian, Gadi Rothenberg *"Linking Experiments To Modeling In Biodiesel Production",* [http://www.nt.ntnu.no/users/skoge/prost/proceedings/escape16-pse2006/Part%20A/Volume%2021A/N52257-Topic2/Topic2-%20Oral/1144.pdf]
2. Bruno Wenzel, Maicon Tait, Aparecido Módenes, Alexander Kroumov, *"Modelling Chemical Kinetics of Soybean Oil Transesterification Process for Biodiesel Production: An Analysis of Molar Ratio between Alcohol and Soybean Oil Temperature Changes on the Process Conversion Rate",* Bioautomation, 2006, 5, 13-22 [http://www.clbme.bas.bg/bioautomation/5_1.2.pdf] (7/3)
3. Egle Sendzikienea, Violeta Makarevicienea, Prutenis Janulisa, Saulius Kitrysb *"Kinetics of free fatty acids esterification with methanol in the production of biodiesel fuel", Eur. J. Lipid Sci. Technol.* 106 (2004) 831–836
4. Karel Komers, Franti¡sek Skopal, Radek Stloukal, Jaroslav Machek *"Kinetics and mechanism of the KOH –catalyzed methanolysis of rapeseed oil for Biodiesel production", Eur. J. Lipid Sci. Technol.* 104 (2002) 728–737
5. Octave Levenspiel, " *Chemical Reaction Engineering*", Published By John Willey & Sons, Third Edition
6. Pankaj Tiwari, Rajeev Kumar, Sanjeev Garg "*Transesterification, Modeling and Simulation of Batch Kinetics of Non- Edible Vegetable Oils for Biodiesel Production*",[http://www.nt.ntnu.no/users/skoge/prost/proceedings/aiche-2006/data/papers/P73677.pdf] (5/3)
7. Timothy Lawrence Turner, *"Modeling and Simulation of Reaction Kinetics for Biodiesel Production"* http://www.lib.ncsu.edu/theses/available/etd-08102005- 000319/unrestricted/etd.pdf (26/2)

CHAPTER 6

PERFORMANCE & EXHAUST EMISSION OF BIODIESEL ENGINE

6. PERFORMANCE AND EXHAUST EMISSION OF BIODIESEL ENGINE

6.1 Introduction

Internal combustion engines, particularly diesel engines, are widely used as prime movers in the transport industry, power generation and also used in agricultural applications. Diesel engines operate at a relatively higher efficiency compared to their counterparts. Current and future legislation on emissions require engine developers to produce cleaner and more efficient power plant systems.

The diesel engine is an internal combustion engine that uses compression ignition, in which fuel ignites as it is injected into air in the combustion chamber that has been compressed to temperatures high enough to cause ignition.

6.2 Fuel Properties of Biodiesel

Since most modern diesel engines have direct injection fuel systems, and these engines are more sensitive to fuel spray quality than indirect injection engines, a fuel with properties that are closer to diesel fuel is needed. Therefore, most recent studies have focused on fuel-grade biodiesel production which meets the standards. [2]

- Viscosity
- Density
- Cetane Number
- Cloud Point and Pour Point
- Flash Point
- Neutralization Number
- Carbon Residue

The fuel properties are discussed in chapter 2.

Comparison of Selected Fuel Properties for Petrodiesel & Biodiesel is given in the appendix D.

6.3 Parameters of The Test Engine

6.3.1 Single Cylinder Four Stroke Diesel Engine (IS – 11170)

- Engine No : CM387283
- Type : FM – II – TRB
- Kw / bhp : 5.9 / 8
- RPM : 850
- S.F.C. : 265 g / Kwh
- Fuel oil : LDO / HSD
- Lobe Oil : SAE – 30
- Governing : Class B
- Mfg By : Field Marshal, P. M. Diesel Limited, Rajkot

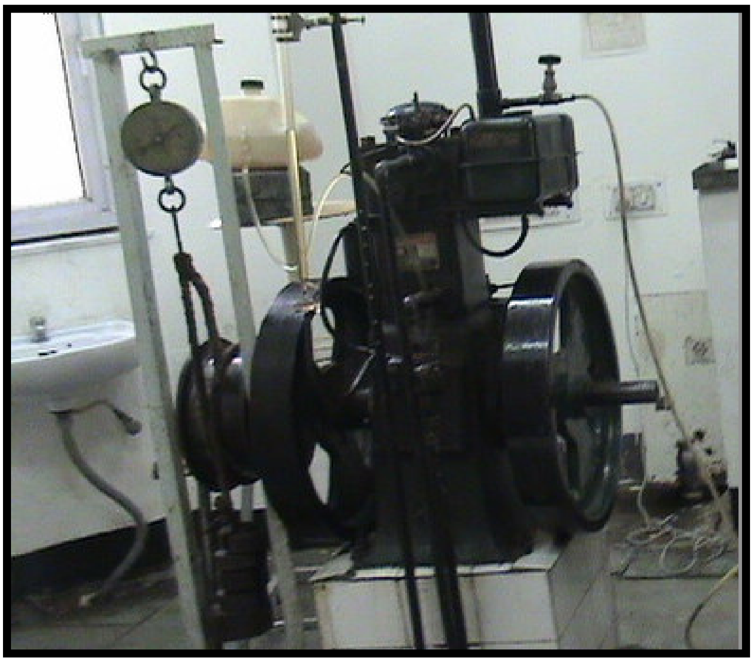


Figure: 6.1 Four Stroke Single Cylinder Test Engine At Nirma Laboratory

6.3.2 Test Fuels

Three test fuels were used for the testing purpose. The fuels are neat diesel fuel, and a blend of 20 percent biodiesel by volume in the diesel fuel and a blend of 40 percent biodiesel by volume in the diesel fuel.

The neat diesel fuel was collected from the thermal engineering laboratory at Nirma University Ahmedabad Gujarat.

The biodiesel which was used for the testing was prepared into the laboratory during the project. That prepared biodiesel was used for the testing.

The 5 liter of the sample of B20 was prepared at the laboratory. The required fuel properties are shown into the table.

6.3.3 Engine Performance Test

The experimental installation used in this work presented here, consists of single-cylinder four stroke engines. This is a water -cooled, direct-injection, four-stroke diesel engine. A dynamometer was used to load the engine at increments of 2 kg to a maximum load of 10 kg. The reaction force and the torque were measured by means of a 100×0.5 N spring balance attached to the dynamometer arrangement. At each loading, the speed of the shaft was measured using a hand held tachometer. The fuel was fed to the injector pump under gravity Thermometer was used to measure the temperature of the exhaust gas. The diesel/B20/B40 fuel blends were tested successfully in the unmodified diesel engine.

6.4 Engine Performance Parameters

1. Fuel consumption

Fuel consumption is "how much fuel the engine burns each hour." **Specific Fuel Consumption”**, often shortened to **SFC**, is an engineering term that is used to describe the fuel efficiency of an engine design w/ a mechanical output. It measures the mass of fuel needed to provide a given power for a given period. The common unit of measure is lb/hp·h - that is, pounds of fuel consumed for every horsepower generated during one hour of operation or kg/kW·h in metric units. Therefore a *lower* number indicates better efficiency. [8,9]

SFC is dependent on engine design, but differences in the SFC between different engines using the same underlying technology tend to be quite small. Generally, SFC within a particular class of engine will decrease when the compression ratio is increased. Increasing overall pressure ratio on jet engines also tends to decrease SFC. Diesel engines have better SFC than gasoline, largely because they have much higher compression ratios and therefore they can convert more of the heat produced into power. [8, 9]

Fuel consumption can be calculated using the following formula:

$$F.C = \frac{m_f}{time} \times \rho$$

Where

m_f = ml of fuel

ρ = density of the fuel

Brake Specific Fuel Consumption (**BSFC**) is a measure of an engine's efficiency. It is the rate of fuel consumption divided by the rate of power production. BSFC is specific for the piston engine known as the reciprocating engine. The general term is specific fuel consumption (SFC). [8, 9]

To calculate BSFC, use the formula

BSFC = Fuel rate / Power

Where:

Fuel rate is the fuel consumption in grams per hour (g/hr)
Power is the power produced in Kilowatts where **kW = w * Tq / 9549.27**
w is the engine speed in rpm
Tq is the engine torque in newton meters (N·m)

2. Fuel Power (F.P.)

Fuel power is the thermal power released by burning fuel inside the engine.

F.P. = mass of fuel burned per second x calorific value of the fuel.

F.P. = mf x C.V.

All engines burn fuel to produce heat that is then partially converted into mechanical power. The chemistry of combustion is not dealt with here.

Calorific Value

This is the heat released by burning 1 kg of fuel. There is a higher and lower value for fuels containing hydrogen. The lower value is normally used because water vapor formed during combustion passes out of the system and takes with it the latent energy. We can now define the fuel power.

Fuel Power = Mass of fuel/s x Calorific Value

3. Brake Power

Brake power is the output power of an engine measured by developing the power into a brake dynamometer on the output shaft. Dynamometers measure the speed and the torque of the shaft. The Brake Power is calculated with the formula

$$B.P = \frac{2\pi NT}{60000}$$

$$B.P(KW) = \frac{2\pi N(W-S)g \times R_{effective}}{60000}$$

Where,

$$R_{effective} = \frac{D+d}{2}$$

T is the torque in N m

In all cases the torque is **T = net brake force x radius**

4. Brake Thermal Efficiency

This tells us how much of the fuel power is converted into brake power.

ηBTh = B.P./F.P.

Conversion to other units

For different units of power, torque, or angular speed, a conversion factor must be inserted into the equation. Also, if rotational speed (revolutions per time) is used in place of angular speed (radians per time), a conversion factor of 2π must be added because there are 2π radians in a revolution [10]:

$$\text{Power} = \text{torque} \times 2\pi \times \text{rotational speed}$$

Where rotational speed is in revolutions per unit time

Useful formula in SI units:

$$\text{Power (kW)} = \frac{\text{torque (Nm)} \times \pi \times \text{rotational speed (rpm)}}{30000}$$

Some people (e.g. American automotive engineers) use horsepower (imperial mechanical) for power, foot-pounds (lbf·ft) for torque and rpm's (revolutions per minute) for angular speed. This results in the formula changing to:

$$\text{Power (hp)} \approx \frac{\text{torque(lbf} \cdot \text{ft)} \times \text{rotational speed (rpm)}}{5252}$$

6.5 Emission Parameters Measurement Methods

Main emission parameters to be measured are,

- **SPM**
- **SO_2**
- **NO_X**

Air Sampling [4]

The most important objective of any air sampling exercise is to obtain a genuine and representative sample. In addition, the sampling should be carried out long enough and at a rate that allows collection of an analytically measurable sample.

A typical air sampling system consists of a sample collector, a flow meter to measure the airflow through the collector, and a vacuum pump to draw the air sample through the system. Figure shows a typical arrangement of air sampling equipment. The flow meter can be placed either upstream or down stream from the sample collector if the pressure drop across the collector is low, but when this is not the case the flow meter must be placed upstream of the sample.

Here in this case the flow of the exhaust gas coming from the engine is low. It is in the range of 0.4 to 0.6 LPM. So in this case we can put the flow meter downstream from the sample collector.

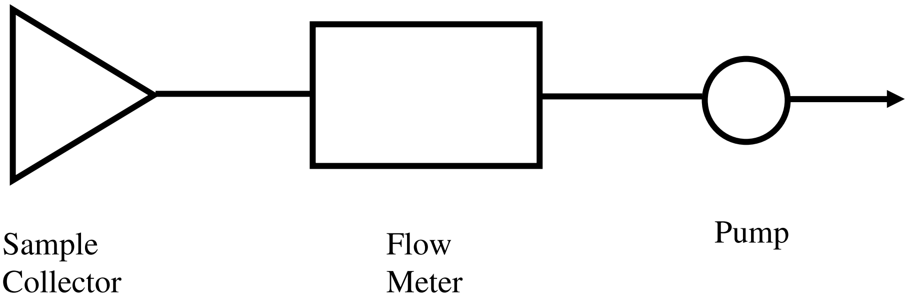


Figure 6.2 Typical Air Sampling Systems [4]

The function of a sample collector is to retain the desired pollutant either alone or as a mixture. The pollutant thus collected is analyzed at a later stage. The choice of collector to be used for collecting the sample is governed by the nature of the pollutant and the method of analysis to be employed. Individual sample collectors are generally grouped into two categories: those that can be used to collect gaseous pollutants and those used for particulate pollutants.

Collection of Gaseous air pollutants

Several methods are available for collection of gaseous air pollutants. The common ones are

- The grab sampling
- Absorption in liquid
- Absorption on a solid material
- Freeze out sampling

Here, in this thesis work for the collection of the gaseous sample we use the absorption into a liquid medium. The SPM is measured using the small filter in which the filtering media is wattman filter paper.

Absorption In The Liquid

Absorption of gaseous pollutants into a liquid medium is probably the most commonly employed method of collecting the sample. Absorption separates the desired pollutant from air either through directly solubility in the absorbing medium or by chemical reaction. Many different types of collectors are in use ranging from simple bubbles to complex devices which provide high degree of gas liquid contact. [4]

In this project work we use the impinger tube as a collector for gas sampling. It is the most widely used collector. In the impinger the gas stream is impinged at high velocity onto a flat surface thus providing good contact between the gas and the liquid. The flat surface can be the bottom of the collector or a specially designed plate. This device can handle the flow rate up to 30 LPM. Impinger can collect gases with efficiencies often approaching those of fritted glass collectors and unlike the latter they are easy to clean and maintain.

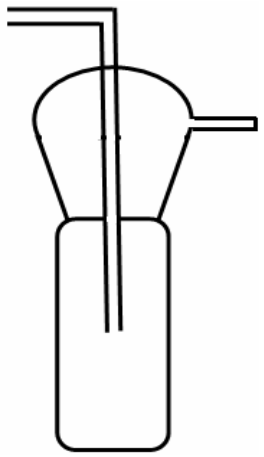


Figure 6.3 Simple Bubbler [4]

REFERENCES CHAPTER 6

---

1. Ayhan Demirbas *"Biodiesel Production Via Non-Catalytic SCF Method And Biodiesel Fuel Characteristics",* Energy Conversion And Management 47 (2006) 2271–2282 Received 15 June 2005; Accepted 28 November 2005 Available Online 9 January 2006

2. B.K.Bhaskara Rao, *"Modern Petroleum Refining Processes*", Fourth Edition, Oxford & IBH Publishing Co. Pvt. Ltd, New Delhi

3. Christopher A. Sharp *"Exhaust Emissions And Performance Of Diesel Engines With Biodiesel Fuels"* Southwest Research Institute

4. C.S.Rao, "*Environmental Pollution Control Engineering*" new age international (P)Limited Publishers New delhi

5. F.K. Forson , E.K. Oduro, E. Hammond-Donkoh *"Performance Of Jatropha Oil Blends In A Diesel Engine*" Renewable Energy 29 (2004) 1135–1145, Received 31 October 2002; accepted 7 November 2003 (15/3/07)

6. L.C. Meher, D. Vidya Sagar, S.N. Naik **"***Technical Aspects Of Biodiesel Production By Transesterification - A Review"* Renewable & Sustainable Energy Reviews 10 (2006) 248–268, Received 17 February 2004; Accepted 15 September 2004

7. http://www.cpcb.nic.in/diesel/contents0902.htm(19/8/06)

8. www.freestudy.co.uk/thermodynamics/t4201.pdf (21/3/07)

9. http://www.motorhomeadvice.com/articles/index.php?page=answer&id=15 (21/3/07)

10. http://en.wikipedia.org/wiki/Torque (21/3/07)

CHAPTER 7

RESULTS & DISCUSSION

7. RESULTS AND DISCUSSION

Various experiments were done to produce the biodiesel from the jatropha oil. The experimental procedures were given in the chapter 5. Experiments are divided mainly into following type:

1. Preparation of the biodiesel
2. Property analysis of the prepared sample
    - Smoke point
    - Aniline point
    - Cloud point
    - Pour point
    - Viscosity
3. Testing of the B20 on the four stroke diesel engine
4. Emission characteristics of B20 and B40
5. Comparison of Emission of Petrodiesel , B20 and B40
6. Kinetics study of overall reaction

7.1 Result of Production of Biodiesel

Jatropha oil which is used for the raw material gives the yield of the biodiesel up to 80 % which is good. The table 7.1 shows the results of the experiments. The 34 % of the methanol can be recovered after the production process.

7.1.1 Condition of the experiment

- Temperature: 55 to 60 ^{0}C
- Equipment: Magnetic Stirrer with Hot plate
- Preheating Of The Jatropha Oil: 30 to 35 ^{0}C
- RPM: 700 to 750
- Catalyst Quantity : 2.85 gm / 250ml of jatropha oil *
- Methanol Quantity Taken: 20 % of jatropha oil quantity

[* The catalyst quantity has been calculated using the titration method described into the Appendix A]

Table 7.1 Production of Biodiesel

Jatropha Oil Taken	Biodiesel	Glycerol	KOH Quantity Required	Methanol recovered
1.5 liter	1100 ml	235 ml	11.4 gm/1lit of jatropha oil	130 ml/300ml

7.1.1 Comparison of Results with ASTM Standards

Table 6.2 shows the comparison of the fuel properties of the laboratory prepared biodiesel with the ASTM standard. The results show that the results of the prepared sample are in the range of the ASTM standard. The prepared sample is good by quality.

Table 7.2 Comparison of Results with ASTM Standards

	Results of Prepared Sample of biodiesel	ASTM Standard for Biodiesel
Specific Gravity (kg/liter)	0.852	0.86
Flash Point (^{0}C)	110	130
Kinematic Viscosity	0.347(stokes)	1.9-6.0 mm^2/s
Cetane Number (min)	53.98	50.0 up
Pour Point (^{0}C)	-10	-8
Cloud Point (^{0}C)	0 ^{0}C	-1 ^{0}C

7.2 Fuel Property Analysis of Samples

This table 6.2 shows the different properties of diesel, pure biodiesel and blending of 20 % of the prepared biodiesel with the 80% of the diesel fuel. Result shows the fuel property of the B20 is coming between the range of biodiesel and diesel. The flash and fire point is coming little high compare to diesel fuel. Cetane number is also high compare to diesel fuel which is good for the proper burning.

Table 7.3 Fuel Property Analysis of Samples

Sr No	Fuel Properties	Diesel	Biodiesel	B20
1	Flash Point	51 ^{0}C	110	87
2	Fire Point	63 ^{0}C	123	102
3	Density (gm/ml)	0.840	0.853	0.76
4	Kinematic Viscosity (stokes)	0.31	0.331	0.52
5	Aniline Point (^{0}C)	86	88	91
7	Cetane Number (min)	50	53.74	72
8	Pour Point (^{0}C)	-5	-10	-7
9	Cloud Point (^{0}C)	-15	0 ^{0}C	-1^{0}C

7.2.1 ASTM Distillation Data for B20

ASTM data gives the boiling range of the prepared sample. Here for the B20 sample the boiling range is high. This high boiling range is good for the fuel.

Table 7.4 ASTM Distillation Data For B20

Volume (ml)	**Temperature (^{0}C)**	**Time (Sec)**
10	72	1320
10	203	794
10	212	280
10	212	289
10	228	169
10	237	146
10	240	83
10	248	80
10	250	104

7.3 Kinetics Study of Overall Reaction

Table 7.5 Data for the kinetic study

Sr. No	Time (T) Minutes	Concentration C_A (mol/ml)	Conversion	Slope From The Graph (dC_A/dt)	Log($-dC_A/dt$)	$Log_{10}C_A$
1	0	5.97	0	-	-	0.79
2	15	5.074	0	-	-	0.79
3	30	4.2	21	-0.1	-1	0.623
4	45	2.25	53	-0.06933	-1.15	0.3521
5	60	1.253	79	-0.040625	-1.391	0.097
6	75	0.9552	84	-0.02360	-1.627	-0.1135
7	90	0.7761	86	0		

Intercept of the graph: -1.55 = log k

Slope = 0.9447 = n

There fore the rate equation is

$$-r_A = 0.02818 C_A^{0.9447} \frac{\text{mol}}{\text{ml} * \text{min.}}$$

This is the rate equation for the overall reaction

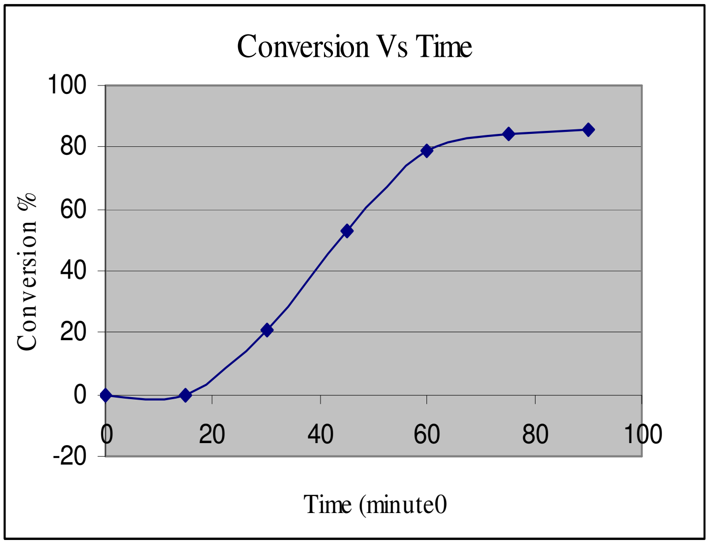


Figure 7.1 Conversion Vs time plot

As the time increases the conversion of the reaction also increases up to some extent. Above figure shows the conversion vs. time chart.

7.4 Testing Of the Samples on the Diesel Engine

The following engine performance parameters were computed using standard equations provided in:

- Brake power
- Fuel Consumption
- Brake specific fuel consumption
- Torque
- Brake thermal efficiency

The steps of calculation of all this parameters are discussed into the chapter 5. The formula used to calculate all this parameters are also given into the chapter 5.

Table 7.7 Performance Data Of The Diesel Engine

FOR PURE DIESEL

Sr. No	W (kg)	S (kg)	M_f (ml)	t (second)	Nrpm	Texhaust (^{0}C)
1	0	0	10	52	850	50
2	1	11	10	46	850	96
3	4	21	10	38.59	840	165
4	10	34	10	31.72	830	210
5	13	41	10	27.21	825	240

For B20

Sr. No	W (kg)	S (kg)	M_f (ml)	t (second)	Nrpm	Texhaust (^{0}C)
1	0	0	10	47.9	850	60
2	1	9	10	28.93	850	85
3	4	17	10	26.25	850	110
4	11	34	10	17.19	845	145
5	15	42	10	14.26	840	220

For B40

Sr. No	W (kg)	S (kg)	M_f (ml)	t (second)	Nrpm	Texhaust (^{0}C)
1	0	0	10	43.01	850	58
2	1	9	10	25.8	850	80
3	4	17	10	19.25	840	103
4	11	34	10	15.1	845	139
5	15	42	10	11.1	830	223

Table 7.8 Engine Performance Test Results

FOR PURE DIESEL

W (kg)	S (kg)	B.P (KW)	F.C (kg/sec)	B.S.F.C (gm/KW-hr)	Torque (N-m)	Nrpm
0	0	0	1.62 x 10^{-4}	576	0	850
1	11	1.3608	1.82x 10^{-4}	655.2	15.28	850
4	21	2.2861	2.17 x 10^{-4}	781.2	25.98	840
10	34	3.1891	2.64 x 10^{-4}	950.4	36.69	830
13	41	3.6982	3.08x 10^{-4}	1111.32	42.80	825

For B20

W (kg)	S (kg)	B.P (KW)	F.C (kg/sec)	B.S.F.C (gm/KW-hr)	Torque (N-m)	Nrpm
0	0	0	1.78 x 10^{-4}	0	0	850
1	9	1.0886	2.90x 10^{-4}	960.022	12.23	850
4	17	1.768	3.2 x 10^{-4}	654.54	19.87	850
11	34	3.0928	4.88x 10^{-4}	568.02	35.16	845
15	42	3.65	5.88x 10^{-4}	579.94	41.27	840

For B40

W (kg)	S (kg)	B.P (KW)	F.C (kg/sec)	B.S.F.C (gm/KW-hr)	Torque (N-m)	Nrpm
0	0	0	1.95 x 10^{-4}	0	0	850
1	9	1.0822	3.25 x 10^{-4}	1081.13	12.23	850
4	17	1.747	4.3 x 10^{-4}	886.09	19.87	840
11	34	3.0928	5.56 x 10^{-4}	647.18	35.16	845
15	42	3.6086	7.56 x 10^{-4}	754.19	41.27	830

7.4.1 Effect of break power (B.P) on brake specific fuel consumption (B. S.F.C)

Figure compares the specific fuel consumption of diesel and various blends of biodiesel and diesel oil at varying brake loads in the range of 1 kg to 15 kg. it was observed that the specific fuel consumption of the oils as well as the blends were increasing as per increasing the load. Though the blends maintained a similar trend to that of diesel, the SFC in the case of the blends was higher compared to diesel oil in the entire load range. This is mainly due to the combined effect of the relative fuel density, viscosity and heating value of the blends.

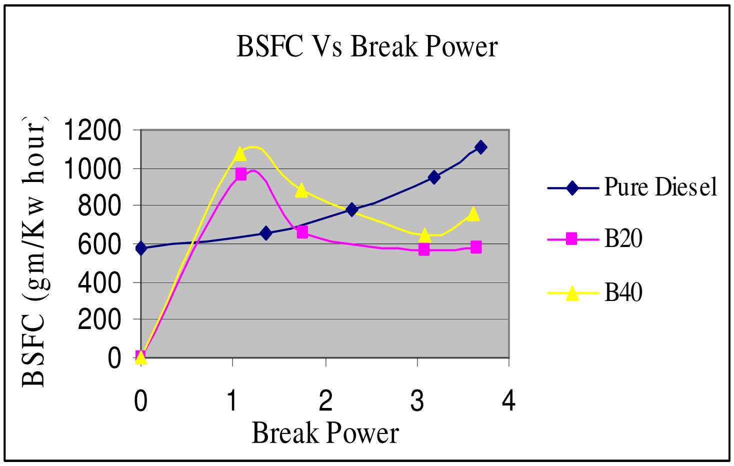


Figure 7.1 Plot of S.F.C vs. Break power

7.4.2 Effect of Break Power on Exhaust Gas Temperature

Figure compares the specific fuel consumption of diesel and various blends of biodiesel and diesel oil at varying brake loads in the range of 1 kg to 15 kg. it was observed that the

Exhaust gas temperature increased with increase in the break power in all the case. But compare to the diesel fuel the exhaust temperature of the B20 and B40 blend is relatively low.

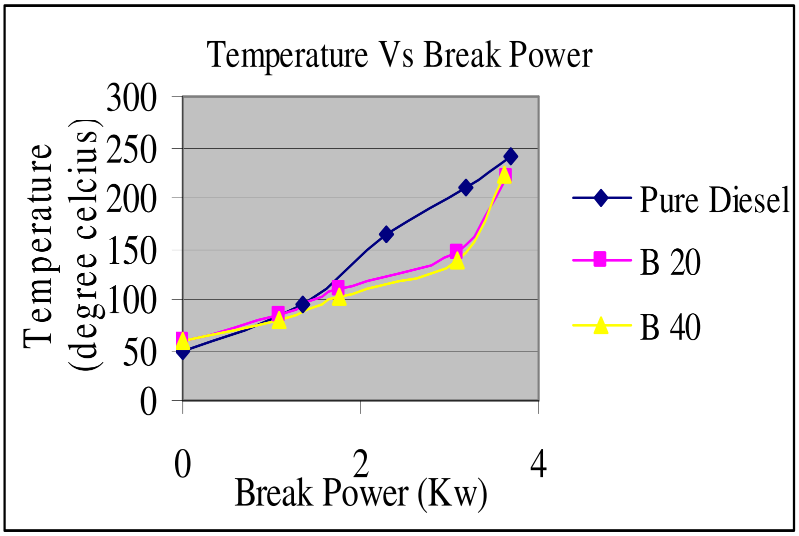


Figure 7.2 Plot of Exhaust Temperature vs. Break Power

7.4.3 Effect of Torque on the Break Power

Figure shows the variation of brake power with increasing torque on the engine. There is no more change on the brake power against torque. The performance of the engine is nearly same for B20 and B40 blend.

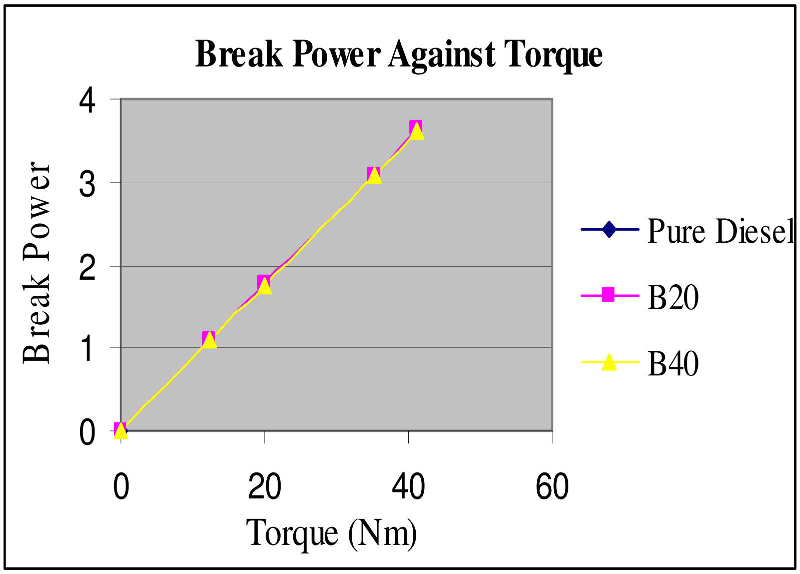


Figure 7.2 Plot of Break Power vs. Torque

7.5 Emission Parameters

The results of emission of the main three parameters namely SPM, SO_2 and NO_X are given below. The main aim of using this bio fuels is to reduce the emission of such kind of the pollutants which are harmful to the environment directly or indirectly. The SPM emission of the B20 and B40 is less compare to the diesel fuel. The emission of SPM for B40 is less than B20.

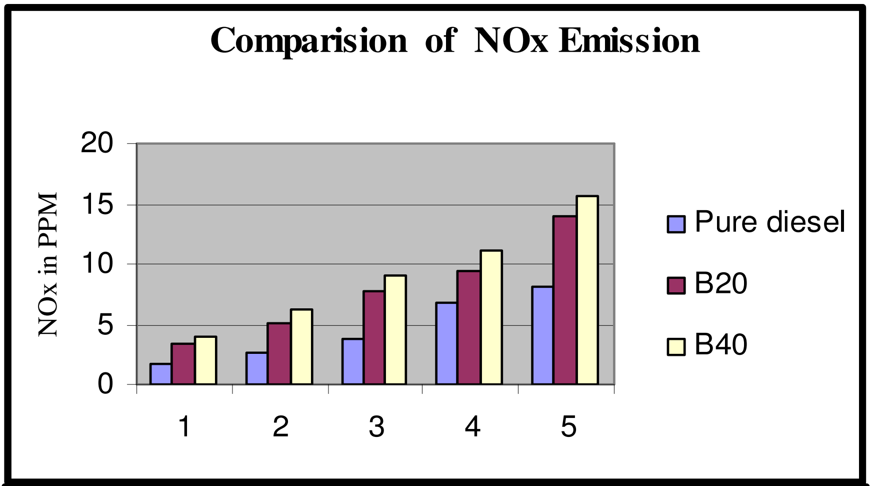
Similarly the SO_2 emission is also decreases for both B20 and B40 compare to diesel fuel. This shows that the sulphur content in the B20 and B40 is very less compare to diesel fuel. But the NOx emission is increases compare to the diesel fuel. This is one drawback of it. For B40 the emission of NOx is high compare to both the diesel fuel and B20. But although biodiesel is more environmental friendly as it can reduce the emission of the SPM and SO_2 from which SPM is the measure problem in vehicles. This is very harmful to the human health.

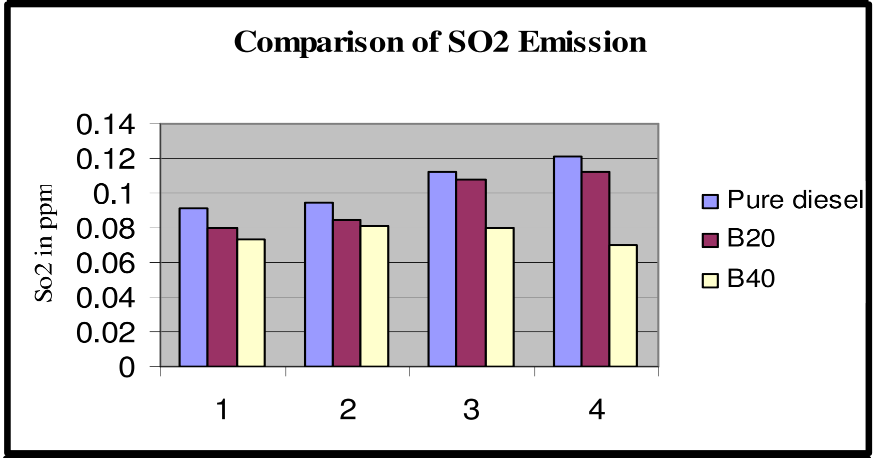
7.5.1 Comparison Table

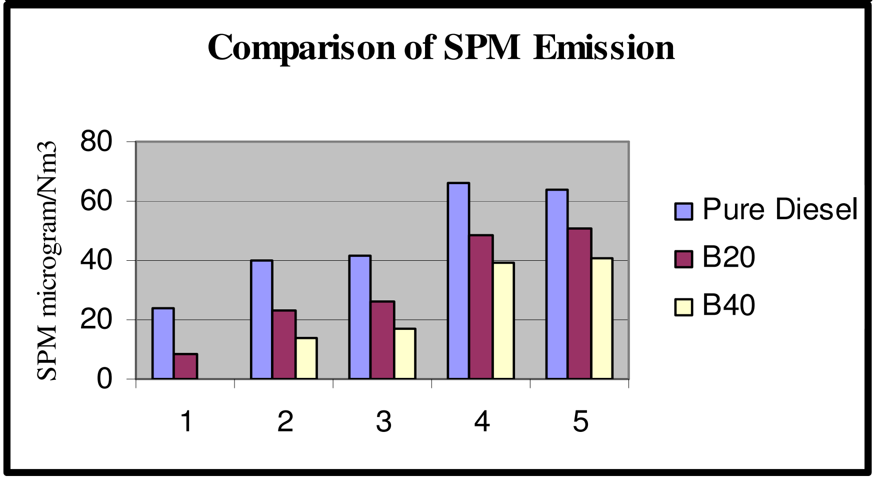
Table 7.9 Emission Parameters of Pure Diesel, B20 and B40

FOR PURE DIESEL				
Sr. No	Dead Load (Kg)	NO_X (ppm)	SO_2 (ppm)	SPM (mg/Nm^3)
1	0	1.69	BDL	23.69
2	1	2.73	0.091	39.87
3	4	3.85	0.095	41.59
4	11	6.72	0.1127	65.91
5	13	8.108	0.1215	63.73
For B20 Blend				
Sr. No	Dead Load (Kg)	NO_X (ppm)	SO_2 (ppm)	SPM (mg/Nm^3)
1	0	3.43	BDL	8.19
2	1	5.17	0.08036	23.37
3	4	7.83	0.08470	26.09
4	11	9.37	0.1082	48.2
5	13	13.90	0.1121	50.4
For B 40 blend				
Sr. No	Dead Load (Kg)	NO_X (ppm)	SO_2 (ppm)	SPM (mg/Nm^3)
1	0	3.97	BDL	-
2	1	6.25	0.0735	14.07
3	4	9.11	0.0810	16.79
4	11	11.2	0.891	39.6
5	13	15.7	0.987	41.11

7.5.2 Comparison Chart For Emission Parameters Of Pure Diesel, B20 And B40







[Note: In the above graph 1, 2, 3, 4, 5 indicates different dead load conditions shown in the table 7.8]

CHAPTER 8

CONCLUSION

8. CONCLUSION

The production of the biodiesel using the jatropha oil was tried at the laboratory of the Nirma University Ahmedabad. The batch experiment was carried out to produce the biodiesel using the Jatropha oil and alkali catalyst. KOH was used as a catalyst for the entire experiments. The amount of the catalyst used per 1 litre of the jatropha oil was 11.4 gm. The temperature condition maintained was 55 to 60 ^{0}C. The yield of the biodiesel was coming in the range of 78 to 82 % which is good.

The fuel property analysis was done to check whether the prepared biodiesel meets with the ASTM standard for biodiesel or not. The results of the experiments show that the quality of the produced biodiesel is nearer to the ASTM standard available. From this we can conclude that the jatropha oil biodiesel is good by quality.

The testing on the four stroke single cylinder diesel engine shows the positive results in most of the aspects. The B20 and B40 samples were tested on the diesel engine and performance and emission parameters were measured.

The temperature of the exhaust gas was increases as the load on the engine increases. But by comparing the results of diesel, B20 and B40 it is observed that the exhaust gas temperature in case of both B20 and b40 was lower than the diesel. There is not much effect of the torque on the break power while using B20 and B40 blends. In case of B20 and B40 the fuel consumption is slightly increases compare to diesel in both the case.

The emission of the SPM decreases while using both B20 and B40 blends compare to the diesel fuel. The SO_2 emission is also reduces with B20 and B40 blends. But slightly increase in the NOx was observed during the experiments.

From all this points discussed above we can conclude that though some limitations the jatropha biodiesel is good for the engine.

CHAPTER 9

SCOPE OF FURTHER WORK

9. SCOPE OF FURTHER WORK

In the present work the production of the biodiesel using the jatropha oil as a raw material using alkali catalyst was done. The property analysis and its performance and exhaust emission on the diesel engine was done. The kinetic study of overall reaction was done. Here in this report the kinetic model for the kinetics study was discussed in detail.

The detail study in the kinetic side of the reaction can be done. Here this thesis only shows the overall kinetics of the reaction. There are intermediate steps during the transesterification reaction. Using the HPLC or gas chromatography methods the concentration of the intermediates can be obtained. This is the most interesting part to carry extent this project work.

Using different catalyst like acid catalyst and lipase catalyst with the same raw material the production can be done. By the comparison of the results the catalyst which gives the most efficient product can be found out.

Design of the pilot plant for the production of the biodiesel can be done which is very helpful for the scale up of the plant.

REFERENCES

1. A.K.Gupta, S.V.A.R.Sastry ***"Developing The Rate-Equation For Biodiesel Production Reaction"*** Department Of Chemical Engineering, Indian Institute Of Technology, New Delhi
2. Anjana Srivastava, Ram Prasad ***"Triglycerides-Based Diesel Fuels"*** Renewable & Sustainable Energy Reviews 4 (2000) 111-133 Received 20 May 1998; Received In Revised Form 1 June 1999; Accepted 7 July 1999
3. Ayhan Demirbas, ***"Biodiesel Production From Vegetable Oils Via Catalytic And Non-Catalytic Supercritical Methanol Transesterification Methods"*** Progress In Energy And Combustion Science 31 (2005) 466–487 Received 18 April 2005; Accepted 23 September 2005
4. Ayhan Demirbas *"**Biodiesel Production Via Non-Catalytic SCF Method And Biodiesel Fuel Characteristics**"*, Energy Conversion And Management 47 (2006) 2271–2282 Received 15 June 2005; Accepted 28 November 2005 Available Online 9 January 2006
5. Ayhan Demirbas ***" Progress And Recent Trends In Biofuels"*** Progress In Energy And Combustion Science 33 (2007) 1–18, Received 28 March 2006; Accepted 28 June 2006
6. B.K. Barnwal, M.P. Sharma ***"Prospects Of Biodiesel Production From Vegetable Oils In India"*** Renewable & Sustainable Energy Reviews 9 (2005) 363–378 Received 7 April 2004; Accepted 7 May 2004
7. B.K.Bhaskara Rao, ***" Modern Petroleum Refining Processes"*** Fourth Edition, Oxford & IBH Publishing Co. Pvt. Ltd (Book)
8. C.S.Rao, ***"Environmental Pollution Control Engineering"*** New Age International (P)Limited Publishers New delhi
9. F.K. Forson , E.K. Oduro, E. Hammond-Donkoh "***Performance of jatropha oil blends in a diesel Engine"*** Renewable Energy 29 (2004) 1135–1145, Received 31 October 2002; accepted 7 November 2003 (15/3/07)

10. Fangrui Ma, Milford A. Hanna ***"Biodiesel Production: A Review*"** Bioresource Technology Bioresource Technology 70 (1999) 1- 15 , Received 24 March 1998; Revised 16 December 1998; Accepted 2 February 1999
11. "*Feasibility Report Small Scale Biodiesel Production*" Waste Management And Research Centre,http://www.wmrc.uiuc.edu/main_sections/tech_assist/small-scale-biodiesel.pdf (15/9/06)
12. G.M. Giibitz , M. Mittelbach B, M. Trabi ***"Exploitation Of The Tropical Oil Seed Plant Jatropha Curcas L"*** Bioresource Technology 67 (1999) 73-82 Received 20 February 1998; Accepted 12 March 1998
13. Hideki Fukunda, Akihiko Konndo And Hideo Noda *"**Biodiesel Production By Transesterification Of Oils"*** Bioscience And Bioengineering Accepted 4 September 2001, http://www.jstage.jst.go.jp/article/jbb/92/5/405/_pdf (25/9/06)
14. ***"Jatropha Handbook First Draft"*** Handbook on Jatropha Curcas, Fact Foundation, www.fact-fuels.org/images/jatropha%20handbook%20march%202006.pdf (12/10/06)
15. J.M. Marchetti, V.U. Miguel, A.F. Errazu ***"Possible Methods For Biodiesel Production"*** Renewable & Sustainable Energy Reviews (2005) 1-12 Received 18 July 2005; Accepted 24 August 2005
16. Jon Van Gerpen ***"Biodiesel Processing And Production"*** Fuel Processing Technology 86 (2005) 1097– 1107
17. L.C. Meher, D. Vidya Sagar, S.N. Naik ***"Technical Aspects Of Biodiesel Production By Transesterification - A Review"*** Renewable & Sustainable Energy Reviews 10 (2006) 248–268, Received 17 February 2004; Accepted 15 September 2004
18. Manuel Frondel_, Jorg Peters ***"Biodiesel: A New Oildorado?"*** Energy Policy, Volume 35, Issue 3, March 2007, 1675-1684
19. S.K.Maiti***, "Handbook of Methods in Environmental Studies (Air ,Noise, Soil and Overburden Analysis) Volume II"***ABD Publication Jaipur 2003 (Book)
20. Stephan Friedrich ***"A World Wide Review Of The Commercial Production Of Biodiesel – A Technological, Economic And Ecological Investigation Based On***

Case Studies”
itnp.wuwien.ac.at/archiv_doc/BAND41_FRIEDRICH.PDF(10/12/06)

21. S Biswas, N Kaushik & G Srikanth *“**Biodiesel: Technology & Business Opportunities – An Insight”*** Technology Information, Forecasting and Assessment Council (TIFAC) Department of Science & Technology, New Delhi, http://www.techbizindia.com/Article1.pdf (9/8/06)
22. Clean Power (Pvt.) Ltd. ***“A Project Of Alternative Energy Development Board (Aedb) Government Of Pakistan”*** Issue: 01 July, 2005
23. http://www.biodiesel.org/resources/reportsdatabase/viewall.asp
24. www.freestudy.co.uk/thermodynamics/t4201.pdf (21/3/07)
25. http://www.motorhomeadvice.com/articles/index.php?page=answer&id=15 (21/3/07)
26. http://en.wikipedia.org/wiki/Torque (21/3/07)
27. http://www.nrl.co.in/faq.htm(6/12/06)
28. http://www.pcra-biofuels.org/jatropha.htm(5/10/06)
29. http://en.wikipedia.org/wiki/Biodiesel#Historical_background(9/8/06)
30. http://www.tifac.org.in/news/Bioenergy_1.htm(13/12/06)
31. http://www.tnau.ac.in/tech/swc/jatropha.pdf(11/11/06)
32. http://www.underutilized species.org/Documents/PUBLICATIONS/jatropha_curcas_india.pdf (1/10/06)
33. http://www.biodieselmagazine.com/article.jsp?article_id=1250
34. http://paniit.iitd.ac.in/~chemcon/paper/DevelopmentRateequaltionSVARSASTRY.pdf -26/9/06
35. http://www.cpcb.nic.in/diesel/contents0902.htm(19/8/06)
36. http://www.fact-fuels.org/images/jatropha%20handbook%20march%202006.pdf(
37. http://www.fao.org/docrep/x5402e/x5402e11.htm#top(22/12/06)
38. http://www.feezol.com/biodiesel.htm(16/10/06)
39. http://www.feezol.com/astm.htm(16/10/06)
40. http://www.echotech.org/mambo/index.php?option=com_docman&task=doc_view&gid=178&Itemid=68(25/11/06)

41. http://www.google.co.in/search?q=use+of+jatropha+oil+for+the+soap+production&hl=en&lr=&as_qdr=all&start=20&sa=N(12/12/06)
42. http://www.mymesra.com.my/index.php?ch=lubricants&pg=lub_general&ac=glossary(10/12/06)

APPENDIX: A

TITRATION METHOD TO CALCULATE CATALYST QUANTITY

APPENDIX A

Titration Method to Calculate the Quantity of the Catalyst:

- Dissolve 1 gram of KOH in 1 liter of distilled or de-ionized water (0.1% KOH solution). Use phenolphthalein solution to get end point.
- In a smaller beaker, dissolve 1 ml of dewatered oil in 10 ml of pure isopropyl alcohol.
- Warm the beaker gently by standing it in some hot water, stir until all the oil dissolves in the alcohol and the mixture turns clear.
- Add 2 drops of phenolphthalein solution. Using a burette, add 0.1% KOH solution drop by drop to the oil alcohol phenolphthalein solution, stirring all the time, until the solution stays pink (magenta) for 10 seconds.
- Take the number of mls of 0.1% KOH solution used to get the end point and add 5.0. This is the number of grams of KOH will need per liter of oil.

Reference:

http://www.svlele.com/biodiesel_process.htm

APPENDIX: B

FUEL PROPERTY ANALYSIS

ENGINE PERFORMANCE CALCULATION

APPENDIX B

B.1 Diesel Property Analysis

❖ Aniline Point

Aniline point apparatus

By using this method we get the aniline point in the ^{0}C. This aniline point is useful to calculate the cetane number.

❖ Diesel Index Calculation

- Diesel Index = [0.018 A.P ^{0}C + 0.32] API
- Specific Gravity = Sample Density (60 ^{0}F) / Water Density (60 ^{0}F)
- Degree API = [141.5/Specific Gravity] – 131.5

❖ Cetane Number Calculation

- Cetane Number =0.72* Diesel Index +10

❖ Viscosity

- Apparatus : Redwood viscometer
- Time of flow from experiment for sample 1 =
- In case of Redwood Viscometer, the Kinematic viscosity (n) of liquid and the time (t) required to pass 50cc of liquid are correlated by the expression

$$n = 0.0026t - 1.175/t$$

Where,

n - Kinematic Viscosity in stokes
t - Time in seconds to collect 50 cc of oil.

❖ Flash and Fire Point

Equipment: Open cup apparatus

❖ Smoke Point

Apparatus: Smoke point apparatus

In the sample no smoke generated.

- Cloud and pour Point

  Apparatus: pour point apparatus (using laboratory scale apparatus)

B.2 Engine Performance Calculation

Fuel Consumption

$$F.C = \frac{m_f}{time} \times \rho$$

Where

m_f = ml of fuel

ρ = density of the fuel

Brake Specific Fuel Consumption (BSFC)

BSFC = Fuel_rate / Power

Where:

Fuel_rate is the fuel consumption in grams per hour (g/hr)

Power is the power produced in Kilowatts where kW = w * Tq / 9549.27

w is the engine speed in rpm

Tq is the engine torque in newton meters (N·m)

Brake Power

$$B.P = \frac{2\pi NT}{60000}$$

$$B.P(KW) = \frac{2\pi N(W - S)g \times R_{effective}}{60000}$$

Where,

$$R_{effective} = \frac{D + d}{2}$$

D = 300 mm

d = 12.7 mm

T is the torque in N m

In all cases the torque is **T = net brake force x radius**

❖ Torque

$$\text{Power (kW)} = \frac{\text{torque (Nm)} \times \pi \times \text{rotational speed (rpm)}}{30000}$$

References:

1. B.K.Bhaskara Rao, "Modern Petroleum Refining Processes", Fourth Edition, Oxford & IBH Publishing Co. Pvt. Ltd, New Delhi
2. www.freestudy.co.uk/thermodynamics/t4201.pdf (21/3/07)
3. http://www.motorhomeadvice.com/articles/index.php?page=answer&id=15 (21/3/07)
   http://en.wikipedia.org/wiki/Torque (21/3/07)

APPENDIX: C

EMISSION CHARACTERISTICS OF FUEL

- Method to Measure NO_X
- Method to measure SO_2
- Calibration Curve for NO_X
- Calibration Curve for SO_2

APPENDIX C

C 1 Method to Measure NO_X

Modified Jacobs – Hochheiser Method or Arsenite Method for Oxides of Nitrogen

Principle of Method

The collection and fixation of Nitrogen dioxide (NO_2) in air is done by scrubbing a known volume of air through a solution of basic sodium arsenite. The nitrite ion thus formed is reacted with sulfanilamide and n- (1 naphthyl) ethylenediamine (NEDA) in phosphoric acid to form the highly flammable azo dye. The method is standardized by using $NaNO_2$ standards. Standardization is based upon the empirical observation that 0.74 moles of $NaNO_2$ produces same colour as 1 mole of NO_2. The absorbance of the highly coloured azo dye is measured on a spectrophotometer at a wavelength of 540 nm.

Apparatus and Glassware

1. Spectrophotometer
2. Volumetric flasks : 50, 100, 250, 500 and 1000 ml
3. Graduated cylinder 1000 ml
4. Pipettes: 1, 2, 5, 10, 15 ml
5. Test tubes

Chemicals and Reagents

Chemicals

1. NaOH
2. Sulfanilamide
3. Sodium Arsenite
4. N- (1 Naphthyl) Ethylenediamine (NEDA)
5. H_2O_2 (30 %)
6. $NaNO_2$
7. Phosphoric acid (85%)

Reagents

1. Absorbing reagent: Dissolve 4 g of NaOH in distilled water then add 1 g of sodium arsenite and dilute to 1L with distilled water.
2. Sulfanilamide: Dissolve 20 g of sulfanilamide in 700 ml of distilled water. Add, with mixing 50 ml of conc. Phosphoric acid (85%) and dilute to 1L. the solution is stable for one month if refrigerated.
3. NEDA Solution: Dissolve 0.5 g of N- (1 Naphthyl) Ethylenediamine (NEDA) in water to form 500 ml of solution. This solution is stable for one month if refrigerated and protected from light.
4. Hydrogen Peroxide: Dilute 0.2 ml of H_2O_2 (30 %) to 250 ml with distilled water. The solution may be used for one month if refrigerated and protected from light.
5. Standard Sodium Nitrite Solution: Dissolve sufficiently desiccated 1.5 g of $NaNO_2$ (97 % purity) in distilled water and dilute to 1 L. this solution contains 1000 µg NO2/ml. the amount of $NaNO_2$ to use is calculated as follows.

$$G = (1.5/ A) \times 100$$

Where,

G = amount of $NaNO_2$ in g

A = assay, %

1.5 = gravimetric factor is converting NO_2 into $NaNO_2$

Preparation Of Calibration Curve

- Dilute 5.0 ml of 1000 µg NO_2 / ml solution to 200 ml with absorbing reagent. This solution contains 25 µg NO2/ml.
- Pipette 1, 2, 3 and 4 ml of 25 µg NO_2 / ml solution into 50 – ml volumetric flask and dilute to the mark with absorbing reagent. The solution is now contains 0.50, 1.0, 1.5 and 2.0 µg NO_2 / ml respectively.
- Pipette out exactly 10 ml from each dilution. To it, add 1 ml H_2O_2, 10 ml of sulfanilamide and 1.4 ml of NEDA solution with through mixing after the addition of each reagent.

- Prepare a blank in same manner with the addition of 10 ml of absorbing solution.
- Wait for 10 min for color development. Measure the absorbance at 540 nm wavelength against the blank. Plot the absorbance versus µg NO_2/ml

Method For The Analysis Of The Sample

- After the sampling add distilled water to make up the volume if there is an evaporation loss during sampling
- Pipette out 10 ml of the exposed absorbing solution into a 50 ml flask
- Add 1 ml of H_2O_2 solution to oxidize any absorbance SO_2 to sulfate
- Then add, with thorough mixing, 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution
- Treat 10 ml of unexposed absorbing solution in the same way to be used as a blank
- Allow 10 min for optimum colour development and measure the absorbance at 540 nm against the blank. Using a standard curve, read the number of µg NO_2 / ml

Calculations

<u>Step 1</u>

Calculate the volume of air sampled, m^3

$$V = (F1 + F2) \times T \times 10^{-6} / 2$$

Where,

V = volume of air sampled, m^3

F1 = measured flow rate before sampling ml / min

F2 = measured flow rate before sampling, ml/ min

T = time of sampling, min

10^{-6} conversions of ml to m^3

<u>Step 2</u> :

The ambient level of NO_2 is determined as

$$\mu g\ NO_2 / m^3 = \frac{\mu g\ NO_2 / ml\ (measured)\ X\ Volume\ of\ Absorbing\ Reagent}{0.85\ X\ V}$$

Where,

V = volume of air sampled, m^3

0.85 = empirical collection efficiency

Step 3:

If desired, concentration of nitrogen oxide may be calculated in ppm NO_2 as follows;

$$NO_2 \text{ in ppm} = (\mu g\ NO^2 / m^3) \times 5.32 \times 10^{-4}$$

C.2 Method to Measure SO_2

PRA Method or Colorimetric Method (Improved West and Gaeke method) for Sulphur Dioxide (SO_2)

Principle

When SO_2 from the air stream is absorbed in a sodium tetra chloromercurate solution, it forms a stable di chloro sulphito mercurate complex $(HgCl_2SO_3)^{-2}$, which then behaves effectively as fixed SO_3^{-2} in solution. The amount of SO_2 is then estimated by the color produced when p – rasoniline – hysrochloride and formaldehyde is added to the solution. The red violet color is shown strong absorbance at 560 nm.

Chemical and Reagents

Chemicals

1. Sodium chloride, NaCl
2. Mercury chloride, $HgCl_2$
3. Para – rasoniline hydrochloride $c_{19}h_{18}cln_2$
4. Sodium metabisulphite, $Na_2S_2O_5$
5. Formaldehyde solution, 40 %
6. Starch powder (soluble)
7. Iodine solution
8. Conc. HCl

9. Di sodium salt of EDTA
10. Sulphuric Acid

Reagents

1. Absorbing Solution: Dissolve 27.2 g (0.1 moles) mercuric chloride ($HgCl_2$) and 11.7g (0.2 moles) sodium chloride NaCl in 1L of distilled water. (Caution: Highly poisonous if spilled on skin flush off with water immediately). Add 0.066 g of sodium salt of EDTA per liter of absorbing solution to remove the interference of iron and other heavy metals. The pH of this solution should be checked which is approximately 4.0 and the solution is rejected if pH of this solution is above 5.2. This solution may be stored at room temperature for several months (maximum 6 months), but it should be discarded if formation of precipitate is noticed.
2. Para Rasoniline Hydrochloride, (0.04 % w / v): acid bleached analytical grade chemical should be used. The PRA dye should have an assay greater than 95% and an absorbance maximum at 543 or 544 mµ. Dissolve 0.20 g of p – rosaniline hydrochloride in 100 ml of distilled water and filter the solution after 48 hours. This solution is stable for at least 3 months if stored in the dark and kept cool. Pipette out 20 ml of this solution into a 100 ml volumetric flask/ to it, add 6 ml of conc. Hydrochloride acid. Allow to stand for 5 minutes, then dilute to the mark up to 100 ml with distilled water. This solution should be pale yellow with a green tint. It may be stored at room temperature in an amber bottle for a week or about 2 week if refrigerated.
3. Formaldehyde (HCHO) solution 0.2 % (v/v): dilute 5 ml of 40 % formaldehyde solution to 1 L with distilled water. Prepare fresh solution daily. Solution remains stable for approximately 1 to 2 days.
4. Sodium Sulfite Solution: dissolve 640 mg of sodium metabisulphide ($Na_2S_2O_5$ assay 65.5 % as SO_2) in 1L of distilled water. This yields a solution of approximately of 0.40 mg/ml as SO_2 or 400 µg SO_2/ml. the actual concentration of the solution is determined by titration with standard 0.01 N iodine with starch an indicator and should be adjusted to 0.0123 N. then, 1 ml is equivalent to 150 µl of SO_2 (25 0C, 760 mm Hg) prepare the solution freshly and standardize.

Standardization of $Na_2S_2O_6$ Solution

- Take 10 ml of 0.01 N I2 solution in 100 ml conical flask
- Add 2 drops of starch indicator solution
- Titrate against $Na_2S_2O_5$ solution
- Starch solution: Make a thin paste of 1.25 g of soluble starch in cold water and pour into 500 ml of boiling water while stirring. Boil for few minutes. Keep in glass stoppered bottle.
- Stock iodine solution (0.1 N): Place 12.7 g of I2 in a 250 ml beaker, add 40 g potassium iodide (KI) and 25 ml water, stir until dissolved, and make up to 1 L with distilled water.
- Iodine solution (0.01N): Prepare approximately 0.01 N iodine solutions by diluting 50 ml of stock solution to 500 ml with distilled water.
- Sulfamic acid (0.6 % 0: Dissolve 0.6 g sulfamic acid in 100 ml of distilled water. Prepare freshly before use. Stable for few days if protected from atmospheric oxidation.

Preparation Of Calibration Curve For SO_2

- Immediately after standardization of sulphite solution, pipette out exactly 2.16 ml of standard solution (0.0123N) and dilute to 100 ml with absorbing solution. this final solution contains 3.0 µL of SO_2/ ml. this solution is stable for 30 days, if stored at 5 ^{0}C
- Pipette out 0.5, 1.0, 1.5, and 2 ml portions of the diluted standard sulfite solution to a series of 10 ml volumetric flask and dilute to the mark with absorbing reagent.
- To each of these 10 ml volumetric flask, add 1 ml para – rasoniline and 1 ml formaldehyde solution and mix well.
- Blank: take 10 ml portion of unexposed absorbing solution (fresh) and add 1 ml of para – rasoniline hydrochloride and 1 ml of formaldehyde.
- Wait for 20 minutes for colour development
- After 20 minutes read the absorbance at 560 nm in a spectrophotometer with the blank as reference.

Method For The Analysis Of The Sample

- Set up the sampling train.
- The gaseous sampling device is available along with the high volume sampler (HVS).
- Pipette out exactly 30 ml of absorbing reagent into the impinger tube.
- In the beginning note the initial flow rate by rotameter, preferably at 0.2 to 2.5 liters / min within this range, efficiency of sampling should be greater than 98 %.
- Sample of sufficient time to give between 0.5 to 3 µg SO_2 /ml of absorbing solution.
- At the end of sampling, note the final flow rate by rotameter.
- Transfer the exposed absorbing solution into a lebelled plastic container and bring to the laboratory for analysis of SO_2
- Shield the solution from direct sunlight during sampling and storage
- Leave the solution for 20 minutes to allow any O_2 present to decay.
- Check, if Hg is precipitated, remove it by filtration or centrifugation. Make up the clear sample to 30 ml with ditilled water to compensate for evaporation losses.
- Pipette exactly, 10 ml of exposed absorbing solution for analysis
- Add 1 ml of Para rasoniline followed by 1 ml formaldehyde solution and mix well. Run a blank preparation also. Wait for 20 minutes and measure the absorbance in spectrophotometer at 560 nm.

Calculation

Step 1:

Calculation of volume of air sampled

$$V = \frac{(F1 + F2) \times T}{2}$$

Where,

V= volume of air sampled, l

F1 = measured flow rate before sampling, L/min

F2 = measured flow rate after sampling. L / min

T = time of sampling, min

<u>Step 2:</u>

Calculation of Concentration of SO_2

In calibration graph, concentration of SO_2 put as µL / ml, therefore, concentration will be derived as ppm. Next, the unit of ppm is converted to µg/ m^3. For conversion of SO_2 concentration in ppm to µg/ m3 at25 ^{0}C and 760 Hg pressure, following formula is used,

$$\mu g/\ m^3 \text{ of } SO_2 = \text{ppm by volume x } 64 \text{ x } 10^6 / 24470$$

SO_2 (ppm) by volume = µL of SO_2 / ml (from calibration curve) / Volume of air sampled, L

C.3 Calibration Curve For NO_X

Absorbance Data for the Curve

Table C .1 Absorbance Data For NOx

Sr. No.	Conc. Of NO_X	Absorbance (In 540 nm)
1	0	0
2	0.5	0.319
3	1	0.662
4	1.5	0.921
5	2	1.222

Calibration Curve

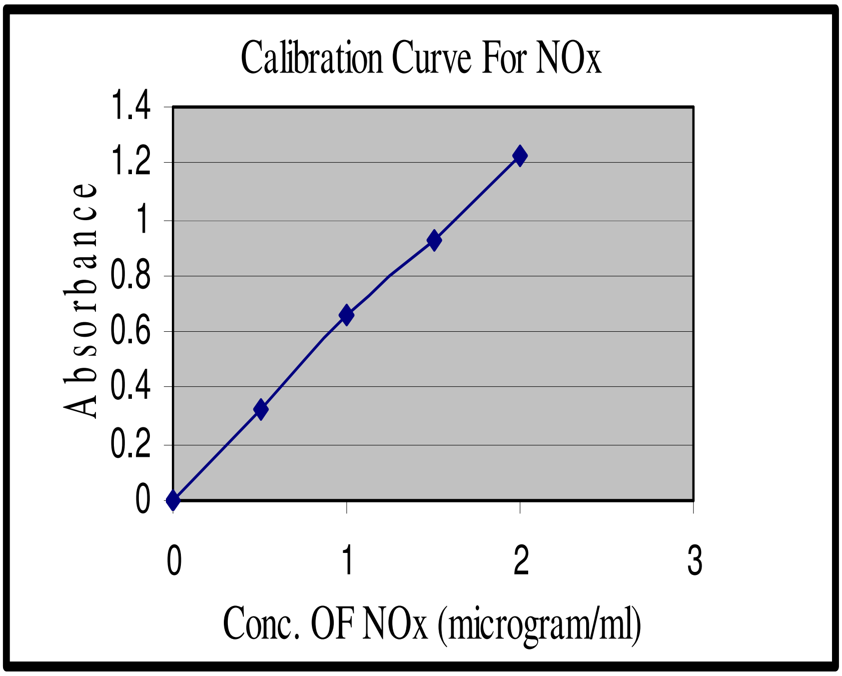


Figure C.1 Calibration Curve For NOx

C.4 Calibration Curve For SO_2

Absorbance Data for the Curve

Table C .1 Absorbance Data for NOx

Sr. No.	Conc. Of SO_2 in µL/ml	Absorbance (in 560 nm)
1	0.15	0.105
2	0.30	0.201
3	0.45	0.352
4	0.60	0.468

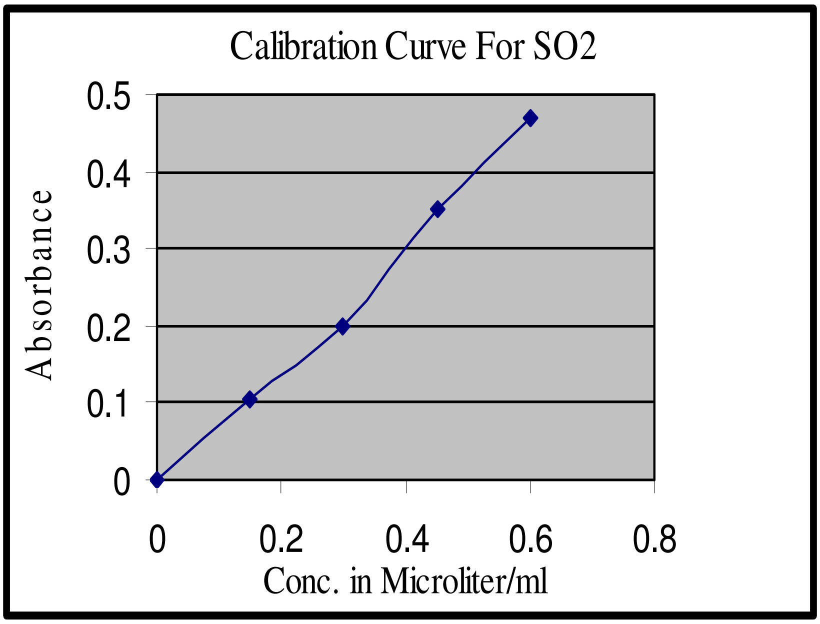


Figure C. 2 Calibration Curve for SO_2

Reference:

- S.K.Maiti, ***"Handbook of Methods in Environmental Studies (Air ,Noise, Soil and Overburden Analysis) Volume II",***ABD Publication Jaipur 2003 (Book)

APPENDIX: D

ASTM STANDARDS

- Biodiesel Specifications
- Biodiesel Standards of Different Countries
- Specifications for B20

APPENDIX D

D.1 Biodiesel Specifications

ASTM D-6751 Standards for Biodiesel

Flash point (closed cup)	130°C min. (150°C average)
Water and sediment	0.050% by vol., max.
Kinematic viscosity at 40°C	1.9-6.0 mm2/s
Ramsbottom carbon residue, % mass	0.10
Sulfated ash	0.020% by mass, max.
Sulfur	0.05% by mass, max.
Copper strip corrosion	No. 3 max
Cetane	47 min.
Carbon residue	0.050% by mass, max.
Acid number -- mg KOH/g	0.80 max.
Free glycerin	0.020 % mass
Total glycerine (free glycerine and unconverted glycerides combined)	0.240% by mass, max.
Phosphorus content	0.001 max. % mass
Distillation	90% @ 360°C

Table D.1 ASTM D-6751 Standards For Biodiesel

[http://www.feezol.com/astm.htm(16/10/06)]

D. 2 Biodiesel Standards of Different Countries

Specifications	Units	Australia	France	Germany	Italy	Sweden	USA	Draft EU
Standard/Specification		ONC1191	-	DINE51606	UNI10635	SS155436	ASTMD6751	EN14214
Introduction Date		Jly 1997	Spt1997	Spt1997	Apr1997	Nov1996	Dec2001	2001

Density @15ċ	g/cm^3	0.85-0.89	0.87-.89	.875-0.90	0.86-0.90	0.87-0.90	-	0.86-0.90
Viscosity@40ċ	mm^2/s	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	1.9-6.0	3.5-5.0
Flash Point	ċ	≥100	≥100	≥110	≥100	≥100	≥130	≥130
CFPP	ċ	0/-15	-	0-10/-20	-	-5	-	0/-15
Pour Point	ċ	-	-10	-	0/-15	-	-	-
Sulphur	%max	0.02	0.02	0.01	0.01	0.01	0.05	0.01
CCR 100%max		0.05	-	0.05	-	-	0.05	-
10%disti.residue	%max	-	0.3	-	0.5	-	-	0.3
SulphatedAshx	%max	0.02	-	0.03	-	-	0.02	0.01
(Oxid).Ash ,mx	%mass	-	-	-	0.01	0.01	-	-
Water max.	mg/kg	-	200	300	700	300	≤0.05	500
TotalContaminants	mg/kg	-	-	20	-	20	-	-
Cu Corrosion	3h/50ċ	-	-	1	-	-	NO.3	1
Cetane No.		≥49	≥49	≥49	-	≥48	≥47	≤≥49
Neutral No.		≤0.8	≤0.5	≤0.5	≤0.5	≤0.6	≤0.8	≤0.02
Methanol	%mass	≤0.20	≤0.01	≤0.3	≤0.02	≤0.02	-	≤0.02
Ester Content	%mass	-	≥96.5	-	≥98	≥98	-	≥96.5
Monoglyceride	%mass	-	≤0.8	≤0.8	≤0.8	≤0.8	-	≤0.8
Diglyceride	%mass	-	≤0.2	≤0.4	≤0.2	≤0.1	-	≤0.20
Triglyceride	%mass	-	≤0.2	≤0.4	≤0.1	≤0.1	-	≤0.03
Free Glycerol	%mass	≤0.02	≤0.02	≤0.02	≤0.05	≤0.02	≤0.02	0.25
Total Glycerol	%mass	0.24	0.25	0.25	-	-	0.24	≤115
Iodine No.		≤120	≤115	≤115	-	≤125	-	-
C18:3 & higher acids		≤15	-	-	-	-	-	10

Phosphorous	ppm	≤20	≤10	≤10	≤10	≤10	≤10	10
Alkaline Matter	(Na,K)	-	≤5	≤5	≤10	≤10	-	≤360
Distillation 95%	ċ	-	≤360	-	-	-	≤360	*
IBP min.	ċ	-	-	-	-		-	*
Bound Glycerin		-	-	-	-		-	Max 0.8
Oxidation Stability	Hrs.	-	-	-	-		-	6 min.
Sediment		-	-	-	-		-	≤0.05
Cloud Point		-	-	-	-		*	-

Table D.2 Biodiesel Standards of Different Countries

http://www.cpcb.nic.in/diesel/contents0902.htm(19/8/06)

D. 3 Comparison of Selected Fuel Properties for Petrodiesel & Biodiesel

Fuel Property	Petrodiesel	Biodiesel
Fuel Standard	ASTM D975	ASTM PS121
Fuel Composition	C10-C21 HC	C12-C22 FAME
Lower Heating Value, Btu/gal	131,295	117,093
Kin. Viscosity, @40 C	1.3-4.1	1.9-6.0
Specific Gravity, kg/l @ 60 F	0.85	0.88
Density, lb/gal @ 15 C	7.079	7.328
Water, ppm by wt.	161	0.05% max.
Carbon, wt%	87	77
Hydrogen, wt%	13	12
Oxygen by dif. Wt%	0	11
Sulphur, wt%	0.05 max.	0.00-0.0024
Boiling Point, Degrees C	188-343	182-338

Flash Point, Degrees C	60-80	100-170
Cloud Point, Degrees C	-15 to 5	-3 to 12
Pour Point, Degrees C	-35 to -15	-15 to 10
Cetane Number	40-55	48-65
Stoichiometric Air/Fuel Ratio	15	13.8
BOCLE Scuff, gm	3,600	>7,000
HFRR, microns	685	314

Table D.3 Comparison of Selected Fuel Properties for Petrodiesel & Biodiesel

[http://www.cpcb.nic.in/diesel/contents0902.htm(19/8/06)]

D.4 ASTM PS 121 Biodiesel for B20

PROPERTY	ASTM METHOD	LIMITS	UNITS
Flash point	D93	100.0 min	Degree C
Water & Sediment	D2709	0.050 max	% vol.
Kinematic Viscosity, 40 ^{0}C	D445	1.9 – 6.0	Mm^2/sec
Sulfated Ash	D874	0.020 max	% mass
Sulfur	D5453	0.0015 max	% mass
Copper Strip Corrosion	D130	No. 3 Max	
Cetane Number	D613	46 min	
Cloud Point	D2500	Report to custmer	^{0} C
Carbon Residue 100 % Sample	D4530	0.050	% mass
Carbon Residue ramsbottom	D524	0.090	% mass

Acid Number	D664	0.80	mg KOH/gm
Free glycerin	D6584	0.020	% mass
Total glycerin	D6584	0.240	% mass

Figure D.4 ASTM PS 121 Biodiesel for B20

References:

http://www.feezol.com/astm.htm(16/10/06)

http://www.cpcb.nic.in/diesel/contents0902.htm(19/8/06)]

http://www.cpcb.nic.in/diesel/contents0902.htm(19/8/06)