SYNTHESIS OF BIODIESEL
FROM
VEGETABLE OIL

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE
IN
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BY

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ROURKELA

CERTIFICATE

This is to certify that the thesis entitled, "**Synthesis Of Biodiesel** " submitted by **Ms Smruti Rekha Dash** in partial fulfillment the requirements for the award of Master of Science Degree in chemistry with specialization in "**Environmental Chemistry**" at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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A C K N O W L E D G E M E N T

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To my

"parents"

WHO ARE ALWAYS THERE WITH THERE HELPING HAND ,CONSTANT SUPPORT AND ENCOURAGEMENT TO DO THIS WORK.

SYNOPSIS

My project deals with the synthesis of biodiesel from palm oil a cheaper vegetable oil of the market.

Palm oil is choosen as the raw material due to its high carbon content, kinetic viscosity & density. Alkali transesterification procedure is used for the conversion. After production the newly produced biodiesel is used for characterisation & it is found that it is a suitable alternate diesel at a relatively higher temperature due to high pour point & viscosity. It is found that 72-80% conversions make it cost effective alternate diesel fuel.

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CHAPTER-1

INTRODUCTION

INTRODUCTION

1.1 Introductory idea of biodiesel

India is a high energy importing nation where maximum percent of our energy is supplied by imported fuels since 2006. The diversification of kinds and sources of primary fuel is becoming vital energy issues in the country .

But the common fossil fuels are not so plentiful and there is a chance to run out eventually. If an alternative can be found that would convert. plant material to usable fuels it would demonstrate the green chemistry principle of using renewable starting materials such as substances derived from the growing plants rather than materials like fossil fuels that are irreplaceable in short term.

One such process is the manufacture of 'Bio diesel' an alternative to diesel fuel from vegetable. oil.

Dr. Ruddolf Diesel developed first engine to run on vegetable. oil in 1895 . He demonstrated his engine at world Estimation is 1900 using peanut as fuel. Before world war II bio diesel was introduced in south Africa to power heavy duty vehicles. Of late, environmental and economic concern has renewed the interest in biodiesel throughout the world, especially in Europe where it is in use from 20 years.

In this regard, biomass energy like biodiesel fuel from waste edible oil is thus becoming attractive due to the environmental and energy policies for promoting sustainable development and environmental pollution mitigation. Of the many energy productions from food wastes or food processing wastes, especially in waste edible oils, seem to be attractive based on bioresource sustainability, environmental protection and economic consideration. The energy obtained from waste edible oils is a from of renewable energy and in principle, utilizing this energy does not add carbon dioxide, which is one of the major green house gases to the atmospheric environment, in contrast to fossil fuels. Due to extremely low content of sulphure and nitrogen in the food waste its direct utilization as fuel in the combustion utilities (e.g internal combustion engine) generally generates less environmental pollution and health risk as compared to fossil fuels.

It is well known that the hydrocarbon in the diesel fuels includes a diversity of paraffins, olefins, napthenes and aromatics. Therefore carbon numbers of theses hydrocarbons present in the diesel fuels are mostly in the ranges of 12-22. Due to its high energy conversion and power output in diesel energy conversion and power output in diesel engines, diesel fuel has been extensively used in heavy trucks, city transport bus, electric generator farm equipment, etc on the otherhand, edible oil including vegetable oil and animal fats are principally glycerides (i.e triglycerides) formed from the glycerol and higher fatty acids(C12-C22) such as Lauric , myristic, palmitic , stearic , oleic, linolenic & linoleic acids. By way of transesterfication, the reaction of triglycerides with alcohol (e.g methanol) under the caustic catalyst (e.g potassium hydroxide) is processed to produce glycerol and monoalkyl esters which are known as biodiesel and can be potentially used as alternative diesel fuel in compression ignition (diesel) engines. Bio-diesel, one of green fuels and / or clean energies is compatible with traditional petroleum based diesel and both can be completely blended without any stratification. From the view point of its chemical composition and properties, bio-diesel fuels are biodegradable, low toxic and emit less air pollutants than hydrocarbon based diesel.. However the use of biodiesel shall face to its high cost relative to petroleum- based oils, and some problems related to decrease power output and torque force and to the increase in NO x emissions with increasing biodiesel content in the blends.

1.2 Role of oil to synthesize biodiesel

The catalytic conversion of waste edible oil by the transesterification process into biodiesel fuel has the advantage of both economic and environmental benefits. In this regard the biodiesel fuel has been demonstrated to be successfully produced from waste edible oils by an alkali- catalyzed transesterification process and can be considered as alternative fuels in diesel engines and other utilities. Because of increasing trend in crude oil, prices, limited resources in fossil fuels and environmental concern in ambient air quality, the objective of this paper will give a comprehensive review on the potential feasibility and regulatory incentives for promoting biodiesel production.

The main subjects covered in this paper are described in the following key elements.

Demonstration case : biodiesel production from waste edible oils.

Due to the increase in the price of the petroleum based oil and the environmental concerns about pollution coming from the car gases, biodiesel is becoming a developing area of high concern. There are different ways of production, with different kinds of raw materials: refine, crude or frying oils. Also there are different types of catalyst basic one such as sodium or potassium hydroxides, acids such as sulphuric acid, ion exchange resins, lipases and supercritical fluids.

One of the advantages of this fuel is that the raw materials used to produce it are natural and renewable. All these type of oils come from vegetables or animal fat, making it biodegradable and nontoxic.

Table -1(Properties of some common vegetable oils)

Vegetable oil	Kinematics viscosity (mm2/s)	Cetane no.	Cloud pt (0C)	Pour pt (0C)	Flash pt (0C)	Density(kg/l)	Lower heating value(MJ/kg)
Pea nut	4.9	54	5	-	176	0.883	33.6
Soyabean	4.5	45	1	-7	178	0.885	33.5
Babassu	3.6	63	4	-	127	0.875	31.8
Palm	5.7	62	13	-	164	0.880	33.5
Sunflower	4.6	49	1	-	183	0.860	33.5

Table –II (Oil composition)

Fattyacid	Palm oil(% mass)
Lauric	0.1
Myristic	1.0
Palmitic	42.8
Stearic	4.5
Oleic	40.5
Linoleic	10.1
linolenic	0.2

1.3 Flow Diagram for biodiesel production
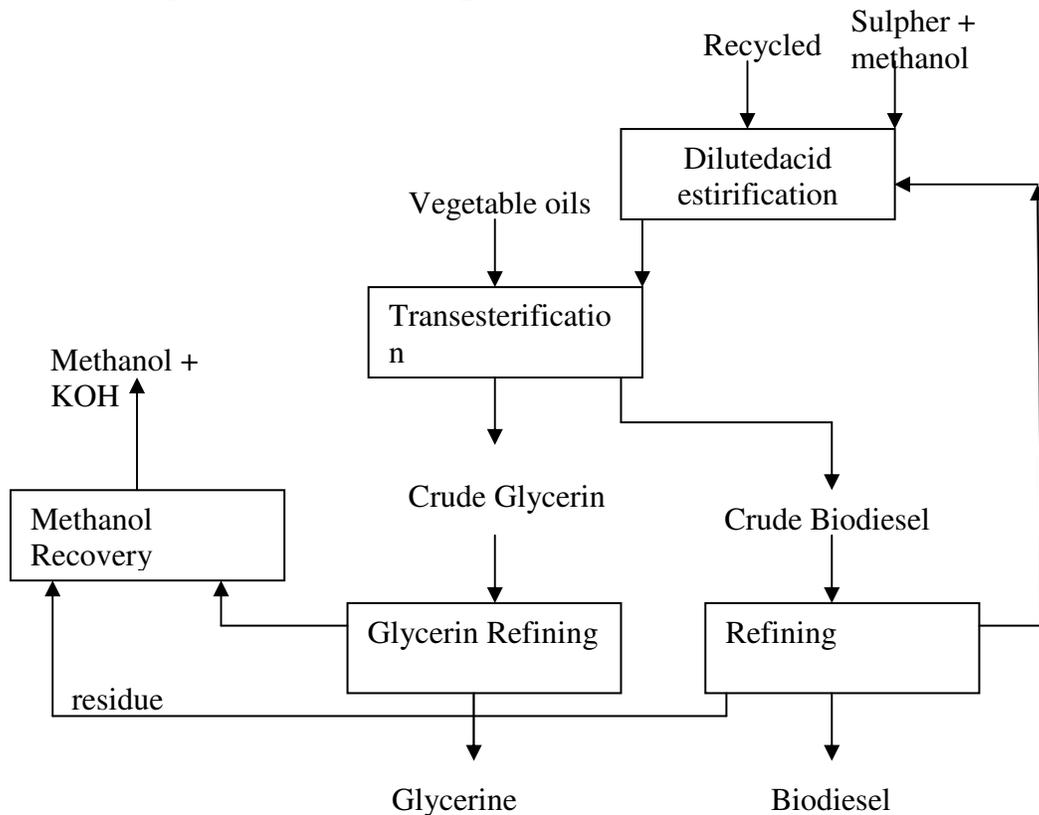
Biodiesel is manufactured from most vegetable oils of edible & non edible origin, animal fat & recycled grease through a process called tranesterification. It is the process of exchanging the alkoxy group of an ester compound by another alcohol. These reaction are catalyzed by an acid as base.

$$R^{'}OH + R^{''}O - CO - R \rightarrow R''OH + R'O - CO - R$$
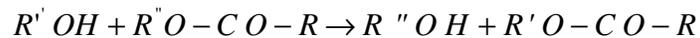
where R $^{/}$ & R $^{//}$ are alkyl groups.

In the transesterification of different types of oils, triglycerides react with an alcohol generally methanol or ethanol, to produce esters and glycerine. To make it possible a catalyst is added to the reaction.

$$CH_2-OOC-R_1 \qquad\qquad R_1-COO-R' \quad CH_2-OH$$
$$| \qquad\qquad\qquad\text{Catalyst} \qquad\qquad\qquad |$$
$$CH-OOC-R_2 + 3R'OH \quad\leftrightarrow\quad R_2-COO-R' + CH-OH$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CH_2-OOC-R_3 \qquad\qquad R_3-COO-R' \quad CH_2-OH$$

Glycerides   Esters   Glycerin
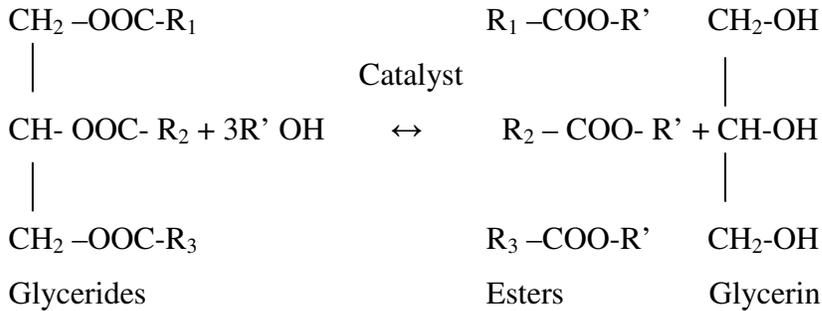
Where R_1, R_2, R_3 are alkyl groups .

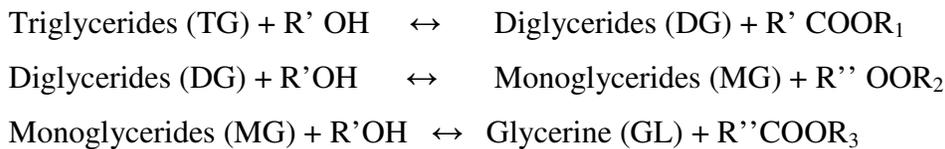The overall process is normally a sequence of three consecutive steps, which are reversible reaction. In the first step, from monoglyceride glycerine is obtained. In all these reactions esters are produced. The stocheometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product:

Triglycerides (TG) + R' OH $\quad\leftrightarrow\quad$ Diglycerides (DG) + R' $COOR_1$

Diglycerides (DG) + R'OH $\quad\leftrightarrow\quad$ Monoglycerides (MG) + R'' OOR_2

Monoglycerides (MG) + R'OH $\leftrightarrow$ Glycerine (GL) + R''$COOR_3$

Where R_1, R_2, R_3, $R^{/}$ are alkyl groups .

       Biodiesel monoalkyl ester is a cleaner burning diesel fuel made from natural, renewable sources such as vegetable oils. Biodiesel operates in compression ignition engines like petroleum diesel there by requiring no essential modification, monomer it can maintain the payload capacity and range of conventional diesel. Biodisel fuel can be made from new or used vegetable oils and animal fats.

1.4 Advantages of biofuel

The benefits of biodiesel are :

- The lifecycle production and use of biodiesel produces approximately 80% less carbon dioxide. Combustion of biodiesel alone produces over a 90% reductions in total unburned hydrocarbons and a 75-90% reduction in aromatic hydrocarbons. Biodiesel further provides significant reduction in particulates and carbon monoxide than conventional diesel fuel.
- Biodiesel is the only alternative fuel that runs in any conventional, unmodified diesel engine.
- Needs no change in refueling infrastructures and spare part inventories.
- Maintains the payload capacity and range of conventional diesel engines.
- Diesel skilled mechanics can easily attend to biodiesel engines,
- 100% domestic fuel.
- Neat biodiesel is non- toxic and biodegradable based on Ames mutagenicity tests, biodiesel provides or 90% reduction in cancer risk.
- Cetane number is significantly higher than that of conventional diesel fuel.
- Lubricity is improved over that of conventional diesel.
- Has a high flash pt of about $300^{0}F$ compared to that of conventional diesel, which has a flash pt of 125 F.

1.5 Disadvantages of biodiesel

Some of the disadvantages of biodiesel are :

- Quality of biodiesel depends on the the blend thus quality can be tempered.
- Biodiesel has excellent solvent production. Any deposits in the filters and in the delivery systems many be disolned by biodiesel and result in need for replacement of the filters.
- There may be problem of winter operability.
- Spills of biodiesel can decolourises any painted surface is left for long.
- Neat biodiesel demands compatible elastomers (hoses, guskets, etc).

CHAPTER-2

HISTORY OF BIODIESEL

HISTORY OF BIODIESEL

2.1 What is biodiesel?

- A substitute for or an additive to diesel fuel that is derived from the oils and fats of plants.

- An alternative fuel that requires no engine modifications and provides power similar to conventional diesel fuel.

- A biodegradable transportation fuel that contributes no net carbon dioxide or sulfur to the atmosphere, and is low in particulate emissions.

- A renewable, domestically produced liquid fuel that can help reduce . dependence on foreign oil imports.

2.2 HISTORY OF BIODIESEL

The concept of using vegetal oil as an engine fuel dates back to 1895 when **Rudolf Diesel** (1858-1913) developed the first engine to run on peanut oil, as he demonstrated at the World Exhibition in Paris in 1900. Unfortunately, R. Diesel died 1913 before his vision of a vegetable oil powered engine was fully realized.

Rudolph Diesel

"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 the petroleum and coal tar products of the present time" Rudolph Diesel, 1912

In 1900, Rudolf Diesel demonstrated his compression ignition engine at the World's Exhibition in Paris. In that prototype engine he used peanut oil, the first biodiesel. Vegetable oils were used until the 1920's when an alteration was made to the engine enabling it to use a residue of petroleum diesel. Although the diesel engine gained worldwide acceptance, biodiesel did not. With superior price, availability, and government subsidies, petroleum diesel quickly became the fuel of choice for the diesel engine.

In the mid 1970s, fuel shortages revived interest in developing biodiesel as an alternative to petroleum diesel. However, as the petroleum market was increasingly subsidized, biodiesel was again relegated to a minority "alternative" status. This political and economic struggle continues to limit the impact of the biodiesel industry today.

Now, increasing concerns about the potential of global climate change, declining air and water quality, and serious human health concerns are inspiring the development of biodiesel, as a renewable, cleaner burning diesel alternative. Biodiesel is made from recycled vegetable oil and various feedstock (i.e.- soy beans). As part of an active carbon cycle biodiesel feedstock production reduces the buildup of greenhouse gases, and in turn, global warming.

Biodiesel was introduced in South Africa before World War II to power heavy-duty vehicles. Recent environmental and domestic economic concerns have prompted a resurgence in the use of biodiesel throughout the world. In 1991, The European Community (EC) proposed a 90% tax deduction for the use of biofuels, including biodiesel. Biodiesel plants are now being built by several companies in Europe; each of these plants will produce up to 5.7 million liters (1.5 million gallons) of fuel per year.

In the United States, biodiesel is also being commercialized. Procter & Gamble Co. is currently the only U.S. manufacturer of biodiesel (primarily made from soybean oils); several U.S. demonstration programs, however, use biodiesel to fuel more than 200 vehicles, including buses, trucks, construction/maintenance equipment, and motor boats.

CHAPTER-3

LITERATURE SURVEY

Literature survey

As biodiesel is gaining considerable global attention & market. Standard are vital for its commercialization & market introduction.

Biodiesel is a fuel which is made from the organic oils. So, different group of scientists tried their best to synthesize the biodiesel from different sources like rape seed oil, soybean oil, fractionated lard & restaurant grease, waste palm oil, waste cooking oil, used frying oil, olive oil, sunflower oil, recycled cooking oil. Not only the variation in raw materials but optimization of process parameters can also be done by a host of scientists. Otara concentrated on transesterification from triglycerides when Klass et. al & krawezyk reported the transesterification of biomass from renewable energy sources. Fukuda, et.al & Grabosky, et al pointed the esterification of triglyceride by alkali metal used when alcohol transesterification was doe by Demirbas, et al.

Beside them analysis of fuel contents and properties of biodisel also attain the site of other group of scientist like Lin,et al ,Barnwal, et al, Tsai,et al, Chow, et al.

CHAPTER-4

OBJECTIVE

OBJECTIVE

4.1 IMPORTANCE OF BIODIESEL

Synthesis of biodiesel from vegetable oil is gaining considerable global attention & market. The quality of biodiesel is an inherent property coming out form the raw materials for example from vegetable oil or animal fat or namely the contents of ester, partial glycerides, total glycerol etc.

Different types of vegetable oils are used by previous researchers. literature survey reveals that palm oil contains better fuel properties yet very little literature survey have been revealed on this field. Moreover according to the market price crude palm oil is the cheapest example of vegetable oil which can be used as a source of biodiesel.And India is the second largest producer of palm oil.

Table –3

	Oil/ fat	Methyl ester	Iodine no	Cetane no
Palm kernel oil	20-26	8	12-18	70
Palm	20-38	14	44-58	65
Palm oleine	20-25	5	85-95	65
Palm stearic	35-40	21	20-45	85

4.2 Reasons for choosing palm oil

- Table 3 shows it containes fatty manily range from C12 to C22 which is optimum per production of biodiesel.
- High cetane no, flash point , cloud point, kinetic viscosity and relative density.
- Very easy to handle it.
- Relatively cheaper in market.
- Literature survey reveals very little information about it.

Table –4

Fuel properties of palm oil

Property	Unit	value
Ester-content	% mass	98.5 to 99.5
Density at 15^0C	kg/l	0.873-0.86
Viscosity at 40^0C	mm^2/sec	4.415-3.5
Flash point	^{0}C	182-120
Cloud point	^{0}C	15.2-18
Pour point	^{0}C	15
Sulphur content	% mass	<0.001
Carbon residue	% mass	0.02-0.03
Acid value	mg KOH/g	58.3 –59
Monoglyceride content	% mass	<0.4
Diglyceride content	% mass	<0.2
Triglyceride content	% mass	<0.1
Total glycerol content	% mass	<0.01

CHAPTER-5

EXPERIMENTAL DETAILS

EXPERIMENTAL DETAILS

5.1 METHODOLOGY

For a basic catalyst, either sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be used with methanol or ethanol and with any kind of oils like refine, crude or frying. In this process it is better to produce the Alkoxy group before the reaction to obtain a better globlal efficiency. The reaction is

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

The alcohol oil molar ratio that should be used varies from N = 1:1 – 6:1. However N = 6:1 is that most used ratio giving an important conversion for the alkali catalyst without using a great amount of alcohol. The types of alcohol are usually methanol and ethanol. The last one has fewer safety problem because it is less toxic.

The oils used could come from any vegetable e.g. corn, canola, peanut sun flower, soy bean, olive, palm, palm kernel. The amount of catalyst that should be added to the reactant varies from 0.5% to 1% w/w, but the prefered value lies between 0.005% and 0.35% w/w .

The last but not least important variable is the reaction temperature. The standard value for the reaction to take place is 60^0c but depending on the type of catalyst different temperature will give different degrees of conversion and for that reason the temperature range should be from 25 to 120^0c .

5.1TRANSESTERIFICATION

It is the process of exchanging the alkoxy group of an ester compound by another alcohol. These reactions are catalysted by the addition of an acid or base.

Alcohol + ester → different ester+ different alchol

In the transesterification process of converting vegetable oils to biodiesel the "R" groups are the fatty acids, which are usually 12 to 22 carbons in length. The large vegetable oil molecule is reduced to about 1/3 its original size, lowering the viscosity making it similar to diesel fuel. The resulting fuel operates similar to diesel fuel in an engine. The reaction produces three molecules of an ester fuel from one molecule of vegetable oil.

Transesterification of vegetable oils.
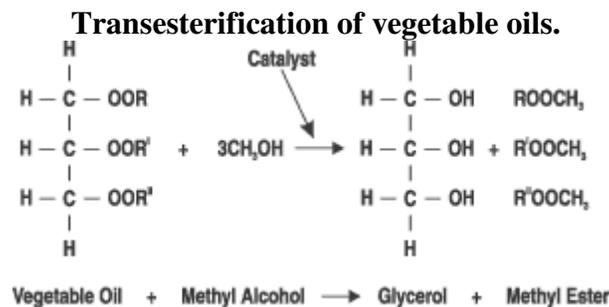
Acids can catalyse the reaction by donating a H^+ to the carboxyl group, thus making it more reactive, while bases can catalyse the reaction by removing H^+ from the alcohol, thus making it more reactive.

5.3 Neutralisation /water washing system

Due to incomplete separation achieved by the first decanting process the purpose of the neutralization step was to neutralize the residual alkali catalyst in the crude fatty acid methyle ester(FAME) by using a weak acid (i.e acetic acid) solution . Then the stream was further washed with saturated saline water and clean water and thereafter poured into another decanting funnel, where the FAME in the crude oil was further separated from the glycerol, methanol And residual salts for 30 mins at room temperature.

5.4 Distillation (purification) system

In order to produce a high quality of biodiesel fuel similar to the specifications of diesel fuel , the distillation was applied to purify FAME in the upper ester layer of second

decanting funnel. A partial condenser was used to provided simple separation of the FAME from trace amounts of water and methanol in the column over head. On the other hand, the unreacted oil remained at the bottom of distillation column. The bottom residue can be transferred to the transesterification unit or reused as liquid fuel.

The properties of biodiesel fuel make complete similarity to those of petroleum-based diesel fuel.

5.5 Procedure for alkali catalysed method :-

1. 2-3 pellets of sodium hydroxide are added to 21ml of methanol and dissolved by continuous mixing.
2. The charged mixture is taken in a 250ml beaker and 100 ml vegetable oil is added to it.
3. Vigorously shaken for 3-4 hours.
4. It is transferred to a separating funnel and allowed to settle for 24 hrs.
5. Lower layer is run off & discarded because it contains only glycerol.
6. The crude product is mixed with 10 ml distilled water and shaken well for 20 mins at room temperature. Again it is put in separating funnel & allowed to settle for 24 hrs. The lower layer is discarded.
7. About 0.5 mg of sodium sulphate is added & stirred for about 20 mins. Unreacted sodium thiosulphate will settle down. The upper layer which is the biodiesel is decanted .

5.6 Kinetics of the reactions

The reason why there is a great interest in the alkali process is that it is more efficient and less corrosive then the acid process, making it a preferred catalyst to be used in the industries.

Kinetic studies have been made by Freedman, Noureddini and Zho and Darnako and Cheryan.

The general form of the governing set of differential equation characterizing the stepwise reaction involved in the transesterification of triglycerides is the following.

$$\frac{d[TG]}{dt} = -K_1[TG][A] + K_2[DG][A] - K_7[TG][A]^3 + K_8[A][GL]^3$$

$$\frac{d[DG]}{dt} = K_1[TG][A] - K_2[DG][E] - K_3[DG][A] + K_4[MG][E]$$

$$\frac{d[MG]}{dt} = K_3[DG][A] - K_4[MG][E] - K_5[MG][A] + K_6[E][GL]$$

$$\frac{d[TG]}{dt} = K_1[TG][A] - K_2[DG][E] + K_3[DG][A] - K_4[MG][E] + K_5[MG][A]$$
$$- K_6[GL][E] + K_7[TG][A]^3 - K_8[E]^3[GL]$$

$$\frac{d[A]}{dt} = -\frac{d[E]}{dt}$$

A is alcohol conc. and E denotes ester conc.. Kinetics parameter was estimated using the equation

$K(T) = AT^n \exp{-E/RT}$

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.

Table -5 Values of kinetic parameter

kinetic parameter	value
K_1	0.049
K_2	0.102
K_3	0.218
K_4	1.280
K_5	0.239
K_6	0.007
K_7	7.84E-5
K_8	1.58E-5

5.7 TEST PROCEDURES

5.7.1 MOISTURE CONTENT

A known weight of sample oil in a porcelain crucible is heated in an air oven at 100-110 ^{0}c till all the moisture is removed (1 hrs).

OBSERVATION & CALCULATION:

Weight of empty crucible   = W1 gms

Weight of crucible + sample   = W2 gms (before heating)

Weight of crucible + sample   = W3 gms (after heating)

% Moisture in the sample $= \dfrac{weight \text{ of moisture}}{\text{weight of sample}} \times 100$

$$= \dfrac{W2 - W3}{W2 - W1} \times 100$$

5.7.2 ASH CONTENT:

A known weight of the sample in a porcelain crucible is heated over the burner till combustion is complete leaving behind ash as residue . (1 hrs)

OBSERVATION & CALCULATION:

Weight of empty crucible   = W1 gms

Weight of crucible + sample   = W2 gms (before heating)

Weight of crucible + ash   = W3 gms (after heating)

% moisture in coal $= \dfrac{weight \text{ of ash}}{\text{weight of sample}} \times 100$

$$= \dfrac{W3 - W1}{W2 - W1} \times 100$$

5.7.3 CARBON RESIDUE OF AN OIL BY CONRADSONS APPARATUS :

THEORY:

Carbon residue is expressed in terms of percentage of carbon and determines the amount of carbon left behind on evaporating an oil sample under specified conditions in a given

apparatus. The result gives information about relative carbon forming property of an oil which is useful for its use as a lubricant, fuel oil or gas manufacture.

PROCEDURE

The oil is taken in a porcelain or silica crucible of about 30 ml capacity with one or two glass beads to prevent bumping during heating. The crucible is placed in a skidmore iron crucible of capacity 65-82 ml containing sand so that the level of the two crucibles are same. The skidmore crucible is placed in a bigger iron crucible containing sand so that the level of all the crucible are same. The entire arrangement is placed on a sand and covered with a hood with a chimney. The heating is done with a meker type burner.

Initially, it is heated strongly so that ignition starts within 10+1 minutes marking the pre ignition period. When smoke appears over the chimney the burner is tilted so that the sides of the crucible are heated and the vapours burn. The flame is so adjusted that the vapours burn uniformly and the burning period is 13+ minutes. When vapour cease to burn and no more blue smoke is observed the burner is readjusted to heat at the bottom as in the beginning and heating is continued to red hot for exactly 7 minutes. Thus, the total heating period is 30+2 minutes. After heating, the arrangement is allowed to cool until no smoke appears. The hood is then removed and the porcelain crucible is cooled in a dessicator and weighted.

OBSERVATION & CALCULATION: (Carbon residue)

Weight of crucible + bead = W1 g

Weight of crucible + bead + oil = W2 g (before heating)

Weight of crucible + bead + carbon residue = W3 g (after heating)

$$\% \text{ carbon residue} = \frac{weight \text{ of carbon residue}}{\text{weight of oil}} \times 100$$

$$= \frac{W3 - W1}{W2 - W1} \times 100$$

5.7.4 FLASH POINT OF AN OIL BY PENSKY – MARTEINS CLOSED CUP FLASH POINT APPARATUS.

THEORY:

The flash point of an oil is defined as the minimum temperature at which it gives sufficient vapours, which when mixed with air forms an inflammable mixture and gives rise to a momentary flash of light on the application of a pilot flame.

This gives information regarding the volatility of the oil necessary to prevent fire hazards

PROCEDURE:

The oil is placed in the cup provided in the apparatus. The cup is then closed with the cover and the thermometer placed in its position. The electrical heating system is adjusted so that the rise in temperature is about 1^0C in two minutes. The pilot flame is then kept burning. The heating is continued with constant stirring with the increase in temperature. Readings are taken at every 5^0C interval to obtain the approximate flash point value. Once the flash occurs the temperature is allowed to rise about 5^0c more and the heating is then discontinued. Then it is allowed to cool with constant stirring and readings are taken with every 10^0c fall to temperature till no flash occurs. Then minimum temp. at which the flash occurs gives the flash point of the oil.

OBSERVATION

Temp.	Remark	Temp.	Remark
40^0c	No flash	60^0c	Flash
45^0c	No flash	65^0c	Flash
50^0c	No flash	64^0c	Flash
55^0c	No flash	63^0c	Flash
		62^0c	Flash
		61^0c	Flash
		60^0c	Flash
		59^0c	Flash
		58^0c	Flash
		57^0c	No flash

RESULT: The flash point of the oil is $58^0c = 134.4^0f$

5.7.5 VISCOSITY OF AN OIL BY REDWOOD VISCOMETER:

THEORY: Absolute and kinematic viscosities of a fluid can be determined by Redwood viscometer according to the formula.

Absolute viscosity = (Apt – Bp/t)

And kinematic viscosity = Absolute viscosity/p = (At –B/t)

Where A & B are instrument constants, t = time of flow in seconds for 50ml of the oil and p the density of the oil. The values of A & B are :

Time of flow in seconds for 50 ml	A	B
34-100	0.00260	1.79
Over 100	0.00247	0.50

The value are calculated in centistokes. The coefficient of viscosity is given by the formula ; $\mu = \pi p^4 t/8vl$.

Where 't' is the time of flow in seconds for vml of the oil through a capillary of length '1' and radius 'r', 'p' being the pressure causing the flow. It the same experimental arrangement is used for two different oils then we have at any given temperature.

PROCEDURE:

The cup which can be electrically heated is filled up to the proper level with the oil. Every time a reading is to be taken. The total pressure on the system, thus remains constant. The oil is then heated gradually and the time of flow for 50 ml of the sample at different temperature are recorded.

OBERVATION AND CALCULATION

Temp.0c			Time in seconds	kinematic viscosity in centistokes
Initial	Final	Mean		
35.0	36.0	35.5	600	1.48

reading must be taken at intervals of atleast 10^0C.

5.7.6 ACID VALUE OF AN OIL

THEORY:

Acid value of an oil is defined as the number of milligrams of KOH required to neutralise the free acid content of one gram of oil. The determination is usually applicable to vegetable and animal oils and provides information regarding corrosive nature of the oil in regards to its use as lubricants and also as pharmaceutical and medical materials

PROCEDURE:

A known weight of the oil is dissolved in a known volume of ethyl alcohol and kept in a stoppered bottle or measuring flask so that the alcohol does not evaporate . Exactly 10 ml of the oil solution is taken in a conical flask and titrated with N/50 KOH solution taken in a burette (oil solution is not taken in a burette since the alcohol will evaporate) using phenolphthalein as indicator.

OBSERVATION

Table (titration value)

CALCULATION :

Let the weight of oil dissolved in 100ml of alcohol = W g

Strength of KOH = 1.05 N/50

Titration value = X ml of 1.05 N/50 KOH

Free acid present in 10 ml of the oil solution = Xml of 1.05 N/50 KOH

Hence free acid present in 100ml of the oil solution = 10 Xml of 1.05 N/50 KOH

1000 ml of N KOH = 56 g of KOH

10Xml of 1.05 N/50 KOH =56 /1000 x 10X x 1.05 / 50 x 1000 mg of KOH = A mg of KOH

Hence the free acid content of w g of the oil = A mg of KOH.

Therefore, free acid content of 1 g of oil = A/W mg of KOH.

RESULTS :

The result is expressed as the nearest whole number by convention.

CHAPTER–6

RESULT AND DISCUSSION

6.1 STANDARD OF BIODIESEL

According to ASTM- biodiesel is defined as mono alkylesters of long chain fatty acids (FA) derived from renewable lipid feedstocks for use in compression ignition (diesel) engine. Biodiesel is produced through a transterification reaction of natural oil triglycrides with a short chain alcohol in the presence of a catalyst (KOH & NaOH).
Laboratory evaluations of synthesized palon diesel were conducted using standard methods and comparing the values with European standards for biodiesel.

TABLE 6. EUROPEAN STANDARD FOR BIODESEL (EN 14214)

Property	Unit	Limits		Test Method
		Minimum	**Maximum**	
Density at 15^0 c	Kg m^3	860	900	EN ISO 3675 EN ISO 12185
Viscosity at 40^0c	mm^2 s^{-1}	3.5	5.0	EN ISO 3104
Flash point	^{0}c	120	-	ISO/CD 3679
Carbon residue	% (mm^{-1})	-	0.3	Pr EN 14104
Acid value	mg KOH g^{-1}	-	0.5	-
Sulphur content	mg kg -1	-	10	ISO 3987
Water content	mg kg -1	-	500	EN ISO 12937
Phosphorous content	mg kg -1	-	10	Pr EN 14107

A. The performance of biodiesel with different properties synthesized from palm oil was studied and the results are given in Table-7

TABLE 7. FUEL PROPERTIES OF NORMAL AND LOW POUR POINT PALM DIESEL

Property	Unit	Normal palm diesel	Low pour point palm deisel	EN 14214	ASTM D6751
Density at 15^0 c	Kg litre^{-1}	0.8783	0.87 to 0.89	0.86 to 0.90	-
Viscosity at 40^0c	mm^{2}s^{-1}	4.415	4 to 5	3.5 to 5.0	1.9 to 6.0
Flash point	^{0}c	182	150 to 200	120 (min)	130 (min)
Pour point	^{0}c	15	-21 to 0	-	-
Sulphur content	% mass	<0.001	<0.001	0.001 (max)	0.0015 (min) (grade s15) 0.05 (min) 9grade s500)
Carbon residue	% mass	0.02	0.02 to 0.03	0.3 (max)	0.05 (max)
Acid value	mg KOH g^{-1}	0.08	<0.3	0.5 (max)	0.8 (max)

B. **Table-8 (fuel properties of synthesized palm diesel)**

Sl No.	Parameter	Sample-I	Sample-II	Sample-III	Sample-IV
1.	Flash pt (^{O}C)	173	180	175	169
2.	Density (kg/l)	0.88	0.82	0.85	0.87
3.	Kinetic viscosity (mm^2 /sec)	4.71	4.76	4.52	4.67
4.	Ash content (% mass)	59 x 10^{-4}	52 x 10^{-4}	83 x 10^{-4}	71 x 10^{-4}
5.	Pour point (^{O}C)	6	6	6	6
6.	Phosphorus contact (% mass)	0.0003	0.0004	0.0004	0.0002
7.	Sulphur content (% mass)	0.031	0.048	0.036	0.045
8.	Acid no.(mg KOH/g)	1.5	1.3	1.8	1.2

6.2 GENERAL DISCUSSION

6.2.1 FLASH POINT:
It is the temperature at which the fuel becomes a mixture that will ignite when exposed to a spark of flame. It is found that the flash pt of the biodiesel are 173 , 180,175,169 ^{0}C respectively for the four samples and in general it is higher than general diesel fuel having value of 70 ^{0}C. So, it is safer than diesel.

It was found that flash pt of biodiesel increased as per the percentage of trighlyceride content.

6.2.2 VISCOSITY:
Viscosity is the measure of a material's resistance to flow. Viscosity is a result of the internal friction of the material's molecules. Materials with a high viscosity do not flow readily; materials with a low viscosity are more fluid.SO, it is a Measure of the fluidity of a substance.

Viscosity affects injector lubrication and fuel atomization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps or injector plungers resulting in leakage or increased wear. Fuel atomization is also affected by fuel viscosity. Diesel fuel with high viscosity tend to form larger droplets on injection which can cause poor combustion and increased exhaust smoke and emissions.The viscosity of biodiesel is found to be in the range of 4.52 to 4.76.Which is in agreement with viscocity of diesel (2.2 to 5.3 cSt at 40C).

6.2.3 ASH CONTENT:

Ash content is the nonvolatile inorganic matter of a compound which remains after subjecting it to a high decomposition temperature.

Ash is a measure of the amount of metals contained in the fuel. High concentrations of these materials can cause injector tip plugging, combustion deposits and injection system wear.The ash content of biodiesel is found to be 0.0052 -0.0083.and that of diesel is 0 .01.which is also the same for the synthesized biodisel .

6.2.4POUR POINT:

It is the Lowest temperature at which an oil will pour or flow under certain prescribed conditions.It is a measure of the ability of a diesel fuel to operate under cold weather conditions. Defined as the temperature at which the amount of wax out of solution is sufficient to gel the fuel when tested under standard conditions (ASTM D97)The Pour point is 3ºC (5ºF) above the point at which a chilled lubricant shows no movement at the surface for 5 seconds when inclined. This measurement is especially important for oils used in cold conditions.For biodiesel it is 6^{0}C.and for gasoline diesel it is 2-4 ^{0}C. for the synthesised kind it is found to be 6.

6.2.5 PHOSPHOROUS CONTENT:

Is depending much on production method for the oil. Phosphorus is dangerous for the engine due to its abrasive function. When the oil is cold pressed or refined normally the content of phosphorus is within the limits.The phosphorous content of biodiesel ranges from 0.0002 -0.0004.General diesel has phosphorous content from 0.0006 -0.0007. synthesised kind is found to be in this range.

6.2.6 SULPHUR CONTENT:

Sulphur reduces the function of catalysts and causes SOx emissions like Diesel engines. Normally vegetable oil does not contain sulphur.It is a measure of particulate emissions in diesel engine exhaust.Sulphur content of biodiesel is from 0.031 -0.045.where as gasoline diesel has a value of 0.05 -0.2. Synthesised kind is found to be in this range.

6.2.7 ACID VALUE:

The amount of free acid present in fat as measured by the milligrams of potassium hydroxide needed to neutralize it is the acid value. As the glycerides in fat slowly decompose the acid value increases. The acid value for biodiesel is1.2 -1.8.For general diesel the acid no is 0.02. Synthesised kind is found to be in this range.

6.3 Environmental benefits of synthesised biodiesel

Environmental benefits in comparison to petroleum based fuels include:

- Biodiesel reduces emissions of carbon monoxide (CO) by approximately 50% and carbon dioxide by 78% on a net lifecycle basis because the carbon in biodiesel emissions is recycled from carbon that was in the atmosphere, rather than the carbon introduced from petroleum that was sequestered in the earth's crust. However, it does produce more NOx emissions than standard diesel fuel. (Sheehan, 1998)

- 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. (Beer et al, 2004).

- Biodiesel has higher cetane rating than petrodiesel, which can improve performance and clean up emissions compared to crude petrodiesel (with cetane lower than 40).

- Biodiesel is biodegradable and non-toxic - the U.S. Department of Energy confirms that biodiesel is less toxic than table salt and biodegrades as quickly as sugar.

. The flash point of biodiesel (>150 °C) is significantly higher than that of petroleum diesel (64 °C) or gasoline (−45 °C). The gel point of biodiesel varies depending on the proportion of different types of esters contained. However, most biodiesel, including that made from palm oil, has a somewhat higher gel and cloud point than petroleum diesel. In practice this often requires the heating of storage tanks, especially in cooler climates.

- Pure biodiesel can be used in any petroleum diesel engine, though it is more commonly used in lower concentrations.

- Carbon dioxide emission , TPM (total particulate matter), Carbon monoxide emission are reduced with biodiesel when NOx emissions seem to be increased. However catalytic converter technology is more effective at counter acting nitrogen oxide emission because biodiesel does not contain sulphur. It degrades quickly in environment and is non- toxic in nature.

6.4 COST EFFECTIVENESS

The real cost of biodisel technology is contained in the oil feed stock. Batch processing methods used for transesterification (the chemical reaction) are not greatly affected by economies of scale. A small – scale producer would see about the same benefit as large – scale production, assuming oil costs were the same. A biodiesel producer may be able to obtain sufficient qualities of waste vegetable oil to supply their fuel requirements at zero or minimum charge.

CHAPTER – 7

BIODIESEL: FUEL OF THE FUTURE

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7.1 BIODIESEL : FUEL OF THE FUTURE

Biodiesel resources can provide energy security with the upsurge in economic activities, India is consuming over a whopping 127 million tonnes of crude oil a year and is forced to import about 70 per cent of its needs. The current yearly consumption of diesel alone is approximately 40 million tonnes in India constituting about 40 per cent of all petro-products.

In the current scenario, exploring energy alternatives in the form of bio-fuels, namely, ethanol and biodiesel assumes top priority.

Biodiesel, derived from the plants (bearing oils) like palm, sunflower, rapeseed, canola or Jatropha Curcas, can be used as a substitute or an additive to diesel. Biodiesel can provide power similar to conventional diesel and thus can be used in diesel engines. Biodiesel is non-toxic and environment friendly as it produces substantially less carbon monoxide and the combustion gases contain no sulphur dioxide and unburnt hydrocarbons.

7.2 CANCER RISK REDUCED

Because of these properties cancer risks and neonatal defects are reduced. Biodiesel mixed (5-20 per cent) with conventional diesel can extend engine life. It has good potential for rural employment generation.

7.3 RETURN ON INVESTMENT

For an optimal capacity of 10,000 TPA of biodiesel, the capital cost for oil extraction and transesterification would be Rs.20,000/tonne capacity. The return on investment (ROI) has been arrived at 15 per cent pre tax on the capital cost. The efficient storage of biodiesel resources can provide energy security to the country. Biodiesel can safely be stored for up to 6 months. The existing storage facilities and infrastructure for petrol and diesel can be used for the biodiesel with minor alterations
.
India has vast stretches of degraded land, mostly in areas with adverse agro-climatic conditions, where species of jatropha,canola,palm etc can be grown easily. Use of 11 million hectares of wasteland for jatropha ,palm cultivation can lead to generation of a minimum of 12million jobs. Production of bio-fuel from plant materials is a major step toward harnessing one of the world's most-prevalent, yet least-utilised renewable energy resources. India, with its huge waste/non-fertile lands, has taken a well-noted lead in biodiesel production from plant materials cultivated in these waste lands for sustainable industrial development.

CHAPTER – 8

CONCLUSION

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In order to make the world greener , the renewable resource are used to replace non-renewable starting materials. So an alternative way is required to convert the biomass based energy to useable fuel. It is the principle of green chemistry.

This process deals with the manufacture of biodiesel an alternative to diesel fuel from vegetable oils.

Biodiesel is a fuel made from organic oils & chemically known as free fatty acid methyle ester (FAME) depending on the general characteristic value of the common vegetable oil found in he market it is found that palm oil is the best alternative to produce the biodiesel due to its high carbon content, could point , kinetic viscosity & relative density.
. Moreover, it is the relatively cheaper in the market.

Alkali transesterification procedure is adopted for the conversion & then the synthesized biodiesel is used for characterisation .Due to larger fatty acid carbon chain of raw material the produced biodiesel contains high carbon content & cetane no. Testing indicated that there will be some problem with palm biodiesel in operating with low temperature due to having higher pour point perhaps due to greater degree of saturation .
But high flash point & high viscosity indicate a high level of safety for biodiesel.

It is biodegradable & non-toxic in nature. The finished product may be less cost effective than conventional diesel with respect to the present market price. So, this can be burnt in normal diesel engine just like the usual diesel.

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