BIODIESEL PRODUCTION FROM WASTE COOKING OILS IN IIT ROORKEE CAMPUS

A DISSERTATION

Submitted in partial fulfillment of the

requirements for the award of the degree

of

MASTER OF TECHNOLOGY

in

ALTERNATE HYDRO ENERGY SYSTEMS

By

RAVI KUMAR

(17512018)

DEPARTMENT OF HYDRO AND RENEWABLE ENERGY

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE

ROORKEE-247667 (INDIA)

JUNE, 2019

CANDIDATE'S DECLARATION

I hereby declare that the report which is being presented here as the dissertation report on the topic "**BIODIESEL PRODUCTION FROM WASTE COOKING OILS IN IIT ROORKEE CAMPUS**" in partial fulfilment of the requirements for the award of the degree of **Master of Technology** in **Alternate Hydro Energy Systems**, submitted in Department of Hydro and Renewable Energy, Indian Institute of Technology Roorkee, Uttarakhand, India, is an authentic record of my own work carried out under the supervision of **Dr. M.P. SHARMA**, Professor, Department of Hydro and Renewable Energy, Indian Institute of Technology Roorkee.

I have not submitted the matter embodied in this report for the award of any other degree or diploma.

Date:

(RAVI KUMAR)

CERTIFICATE

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

(Dr. M. P. Sharma)
Professor
Department of Hydro and Renewable Energy
Indian Institute of Technology
Roorkee -247667

ACKNOWLEDGEMENT

Date:

(RAVI KUMAR)

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

1.1 GENERAL

As the nations are developing, their energy demand is also increasing continuously whereas the conventional resources to fulfil these energy requirements are vanishing continuously. At the same time, renewable energy sources are abundant, non-exhaustive and have enough potential to fulfil large part of this energy demand. With growing technology renewable energy sources has become quite accessible and their prices have decreased over the years. Renewable energy sources use indigenous resources and have the potential to provide energy with negligible emission of air pollutants and greenhouse gases. Renewable energy technologies produce marketable energy by converting natural phenomena/resource into useful energy. It is a promising prospect for the future as an alternative to conventional energy. Hydro power, Wind, Biomass, Solar energy etc. are some of the sources which have proved to be promising.

1.2 CLASSIFICATION OF ENERGY SOURCES

The classification of energy resources with examples are given in Table 1.1

Table1.1: Types of Energy Sources [1]

Types of energy source	Description	Example
Primary energy sources	These are the sources which can be directly founds in nature or stored in nature and can be extracted. Available in raw from which needs to be processed first for utilization.	Direct – Coal, Oil, nature gas, biomass, Stored-nuclear energy from radioactive material, Thermal in earth interior.
Secondary energy sources	Secondary energy sources are derived from primary sources in a form of either final fuel or energy supply. Involvement of technological processes in this transformation in between causes drop in primary energy	Steam energy from coal, Refined crude oil products such as Gasoline, Petrol, and Electricity.

	on the way to consumers**.**	
Waste energy resources	It is possible to reuse waste energy liberated in the process of utilization of primary and secondary energy resources. Practically it is achieved by combined heat and power which is more popular as cogeneration.	Energy extracted from cooling system in power plants.
Renewable(Non-Conventional)	This is the energy acquired from never ending sources of energy available in nature. The main feature of this is, it can be extracted without causing pollution**.**	Solar power,wind energy, geothermal energy, tidal energy, biomass.
Non-renewableenergy Conventional	Non-renewable energy is the energy obtained from the conventional fuels which are exhaustible today or tomorrow with time.	Coal, oil, gas, Hydro power, Diesel power.
Commercial	This is the energy accessible from market at certain price. These arethe cardinal source for industrialized countries as its basic need for industries, commercial transport and agricultural sectors.	Electricity, lignite, coal, oil, natural, gas etc.
None commercial	These sources are not available in the market unlike previous type for a price. Instead these are traditionally gathered. Also termed as traditional fuel and mostly shrugged off in energy accounting.	Firewood , cattle, dung sugarcane crush ,solar thermal water heating etc.

1.3 RENEWABLE ENERGY SOURCES

Renewable energy is energy that is collected from renewable resources, which are naturally replenished on a human timescale, such as sunlight, wind, rain, tides, waves, and geothermal heat. Renewable energy often provides energy in four important areas: electricity generation,

air and water heating/cooling, transportation, and rural (off-grid) energy services. There are many forms of renewable energy. Most of these renewable energies depend in one way or another on sunlight. Wind and hydroelectric power are the direct result of differential heating of the Earth'ssurface which leads to air moving about (wind) and precipitation forming as the air is lifted. Solar energy is the direct conversion of sunlight using panels or collectors. Biomass energy is stored sunlight contained in plants. Other renewable energies that do not depend on sunlight are geothermal energy, which is a result of radioactive decay in the crust combined with the original heat of the Earth, and tidal energy, which is a conversion of gravitational energy [2].

Renewable energy payback to investment in the form of carbon credit for clean development mechanism wind and solar power do not produce waste and so no investment for waste management is needed during the lifecycle in such power facilities. Other potential resources are hydropower, solar energy, tidal energy, geothermal energy and biomass/bio-waste etc. Each is briefly discussed below

1.3.1 Solar Energy

Solar energy source is one of the most abundant sources with wide applications such as rural electrification, street lightening, power grid stabilization and agricultural applications. Effective utilization of solar radiation reaching earth in a year would generate 10,000 times the world energy requirement in a year. Since India is located geographically between tropic of cancer and Equator, it has an average annual temperature ranging between 25°C - 27.5°C. With this advantageous geographical location, India receive sa global solar radiation over a range of 1200 kWh/m^2/year to 2300 kWh/m^2/year. The south east coast of India is considered to be sunniest parts in the country. To harness solar energy under this geographical advantage, Ministry of New and Renewable Energy (MNRE) has targeted to install solar plants for the generation of 100 GW of Power by 2022 [2].

1.3.2 Wind Energy

The movement of wind is a complex mechanism which involves the interaction of sun and earth. It is considered to be the most widely distributed source with worldwide potential of 432,883MW. The total share of India in terms of installed capacity is 5.82%, approximately. The magnitude and direction of wind varies spatially. Thus, scientific wind mapping is done extensively in India for its effective utilization. The areas with least wind power density of 400 W/m^2 at 30 m of height are identified and considered as optimal locations

for the exploitation of wind energy. Harnessing wind energy to generate electricity involves points of interest and problems as well. Generation of electricity through wind energy is considered as a promising source as it depends on the motion of wind causing the movement of turbine blades. The source is assumed to be available throughout the year, with some fluctuations. However, noise from the gearbox and the generator are considered as major environmental impacts. It is expected that noise with an intensity of 50–60 dB is experienced within a buffer distance of 40 m.

1.3.2 Biomass Energy

Renewable source of energy other than hydropower, solar, wind and geothermal sources, currently provide only a small fraction of global energy use. The most prevalent source of energy is biomass. Biomass is biological material derived from livingorrecently living organisms. It most often refers to plants or plant-based materials which are specifically called lingo-cellulosic biomass. Biomass include wood, logging wastes and sawdust, animal dung and vegetable matter consisting of leave, crop residues and agricultural waste. According to the CEA, India had at least 3.4 GW of utility-based installed capacity in biomass power and bagasse-based cogeneration plants as of mid-2013. India's Ministry of New and Renewable Energy reports the country has 18 GW of potential biomass electricity generation capacity and 5 GW of potential bagasse-based generation. A large amount of biomass used for electricity generation comes from bagasse (crushed sugarcane or sorghum stalks), which can be used in combustion-powered generators. In India, the biomass programmes are mainly targeted to meet the needs of rural and remote areas and have helped in reaching electricity to the interior un-reached section of the population. Globally, biomass fuels accounts for 13% of total energy requirements. Biomass is one such source that can be used to provide sustainable supply of the required energy through biogas, vegetable oil, biodiesel, producer gas, and by directly burning the biomass. Biomass can be converted into suitable form of energy through different conversion technology. Biomass power generation in India is an industry that attracts investments of over Rs.600 crores every year, generating more than 5000 million units of electricity and yearly employment of more than 10 million man-days in the rural areas.

1.3.3 Geothermal Energy

The energy extracted from earth's heat is known as geothermal energy. Deepextraction bore wells are drilled to a depth of 3 Km or more to extract the entrapped heat in earth's strata, by using water under pressure as a medium to transport heat. USA, Philippines, Indonesia, Mexico, Italy and Iceland are the leading nations in utilizing their geothermal resource. The studies on geothermal energy in India were initiated in the year 1862. Geological Survey of

India has explored 340 hot springs and few potential geothermal provinces with a predicted potential of 10,600 MW. However, in practice it is still remained untapped. Among the identified geothermal provinces in India, Puga Valley located in Ladakh district is identified as most potential geothermal province.

For the effective use of geothermal energy, Ministry of New and Renewable Energy has been initiating various measures over the past 25 years.

1.3.4 Tidal Energy

Energy available in water because of the rise and fall of water level during high and low tides. Tidal energy technologies harvest energy from the seas. Power generation through tidal energy has been found to be a technically viable option, when considering the sea as a resource. In India, Gulf of Kutch and Gulf of Cambayin Gujarat and delta of Ganga in Sunder bans, Parganas district, West Bengal is potential sites for generating tidal power. The identified economic power potential is of the order of 8000 MW with about 7000 MW in the Gulf of Cambay, about 1200 MW in the Gulf of Kachchh in the State of Gujarat and about 100 MW in the Gangetic Delta in the Sunder bans region in the State of West Bengal. Installation of tidal power generation devices may cause significant disturbance to the local environment.

1.3.5 Wave Energy

Waves are formed by wind blowing over the surface of ocean. Wave energy is a renewable energy whereby we capture the energy that is being generated naturally by waves and can transmit their energy over long distances with little degradation. A number of devices have been built over the last 30 years for converting wave energy into electricity. The devices built have been located on the shore line, near the shore or off-shore. No worthwhile commercialization has taken place till date therefore, it is difficult to give any estimate for India and the chances that a significant amount of wave energy will be converted to electricity in the future are poor.

1.3.6 Ocean Thermal Energy Conversion (OTEC)

Ocean Thermal Energy Conversion (OTEC) utilizes the thermal gradient available in the ocean to operate a heat engine to produce work output. India is geographically well placed and OTEC plants are available on the Indian coast and in the island groups in the Indian Ocean, An OTEC plant was attempted off the coast of Tamil Nadu (60 kms off Tuticorin) by the National Institute of Ocean Technology (NIOT) with a gross generation capacity of 1 MW (net power 500 kW). This is the world's first floating plant. But still Ocean energy is at an

early stage of development and can be compared to the state of the wind industry in the early 1980. Ocean energy remains a wild card in the renewable power generation portfolio.

1.3.7 Small Hydro Power

Hydro power plants of capacity smaller than 25 MW are considered as small hydro power plants. To supply electricity especially in the hilly terrain, where the provision of electricity through the extension of grids becomes uneconomical, small hydro projects are preferred to meet the demand. The first small hydro project was commissioned in India during the year of 1897 with a capacity of 130 kW project at Darjeeling.

1.4 RENEWABLE ENERGY SCENARIO OF INDIA

Over the years, India has successfully created a positive outlook necessary to promote investment in, demand for and supply of renewable energy. In addition to grid power, decentralized distributed electrification using renewable energy technologies provides economical options for meeting lighting, cooking and productive energy needs in rural areas.

In the year 2015, the Government of India announced a target for 175 GW cumulative renewable power installed capacity by the year 2022. Renewable energy has started playing an increasingly important role for augmentation of grid power, providing energy access, reducing consumption of fossil fuels and helping India pursue its low carbon developmental pathway. Ahead of COP 21, India submitted its Intended Nationally Determined Contribution (INDC) to the UNFCCC, outlining the country's post-2020 climate actions. India's INDC builds on its goal of installing 175 gigawatts (GW) of renewable power capacity by 2022 by setting a new target to increase the country's share of non-fossil based installed electric capacity to 40 percent by 2030 (with the help of international support). The INDC also commits to reduce India's GHG emissions intensity per unit GDP by 33 to 35 percent below 2005 levels by 2030, and to create an additional carbon sink of 2.5 to 3 billion tonnes of carbon dioxide through additional tree cover. The installed capacity of renewable energy resources as per financial year 2018-19 is given in Table 1.2

Table1.2: Installed capacity of Renewable Energy Resources in India (up to April 2019) [3]

Sector	FY- 2018-19		Cumulative Achievements
	Target	Achievement (April 2019)	(as on 30.04.2019)
I. GRID-INTERACTIVE POWER (CAPACITIES IN MW)			
Wind Power	3000.00	189.92	35815.88
Solar Power - Ground Mounted	7500.00	445.55	26829.87
Solar Power - Roof Top	1000.00	52.95	1849.34
Small Hydro Power	50.00	1.00	4594.15
Biomass (Bagasse) Cogeneration)	150.00	28.00	9131.50
Biomass (non-bagasse) Cogeneration)/Captive Power	100.00	0.00	674.81
Waste to Power	2.00	0.00	138.30
Total	**11802.00**	**717.42**	**79033.85**
II. OFF-GRID/ CAPTIVE POWER (CAPACITIES IN MW)			
Waste to Energy	10.00	0.00	178.73
Biomass Gasifier	1.00	0.00	163.37
SPV Systems	400.00	0.73	916.34
Total	**411.00**	**0.73**	**1258.44**

As given in Table 1.2, Cumulative Achievement of Grid Interactive power is 5 times more than Cumulative achievement of Off Grid Power.

1.5 BIODIESEL/RENEWABLE DIESEL

India's energy security would remain vulnerable until alternative fuels to substitute/supplement petro-based fuels are developed based on indigenously produced renewable feed-stocks. In biofuels, the country has a ray of hope in providing energy security. Biofuels are environment friendly fuels and their utilization would address global concerns about containment of carbon emissions. Biofuels are derived from renewable bio-mass resources and, therefore, provide a strategic advantage to promote sustainable development and to supplement conventional energy sources in meeting the rapidly increasing requirements for transportation fuels associated with high economic growth, as well as in meeting the energy needs of India's vast rural population. Biofuels can increasingly satisfy these energy needs in an environmentally benign and costeffective manner while reducing dependence on import of fossil fuels [4].

Presently, India has five to six plants with capacity to produce 10,000 to 250,000 metric tons (MT) of biodiesel per year. India has targeted to produce 150 million liters of biodiesel and add another 10 million litres by 2019. Biodiesel producers utilize multiple feed-stocks such as 'WCO, animal fats, tallow's and 'other oils' (palm stearin, sludge, acidic oils, and tree oils etc.) to produce biodiesel, thereby utilizing close to 30 % of the installed capacity. While the use of animal fats and tallow's has remained constant, remaining feedstock use has shown steady growth, namely WCO and 'other oils. The trend of these feed-stocks are shown in fig 1.1 Although there is no official regulation on supply of WCO or 'other oils' for biodiesel production, biodiesel sales have shown just incremental growth in recent years, with most of it coming from food processing industries and restaurants.

Biodiesel is an alternative to Diesel in terms of combustion properties; hence it proves to be a better replacement as compared to Ethanol and Methanol. Biodiesel, amixture of mono-alkyl esters produced from edible, non-edible oils or animal fats, waste cooking oils can be produced by transesterification process. Biodiesel specified shall be mono alkyl ester long chain fatty acid from vegetable oils or animal fats with small hydrocarbon or non-hydrocarbon additives [4].

Table1.3: India: Biodiesel Production from Multiple Feed-stocks (Million Liters) [4]

Calendar Year	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018
Beginning stocks	0	45	36	29	30	23	14	11	11	12
Production	75	99	111	121	128	132	142	148	153	161
Imports	0	0	0	0	0	2	1	3	2	3
Exports	0	0	0	0	8	64	44	53	51	60
Consumption	30	108	118	120	128	79	101	98	104	104
Ending stocks	45	36	29	30	23	14	11	11	12	12
Production capacity(million liters)										
Bio refineries	5	5	5	5	6	6	6	6	6	6
Nameplate capacity	450	450	450	460	465	480	480	500	500	500
Capacity use (%)	16.7	21.9	24.7	26.3	27.5	27.6	29.5	29.6	30.7	32.1
Feedstock use for fuel (1,000MT)										
Used cooking oil	35	38	42	48	50	55	60	65	70	75
Animal fats	3	6	6	7	7	6	5	6	6	8
Other Oils	30	50	58	60	65	65	70	70	70	70
Market penetration (MT)										
Biodiesel on road use	15	36	28	44	44	26	42	40	44	48
Diesel, on road	39,834	42,625	45,520	49,343	49,605	52,239	55,179	57,452	59,819	60,000
Blend rate (%)	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Diesel, total use	66,390	71,041	75,866	82,238	82,256	82,674	87,064	91,965	95,754	99,699
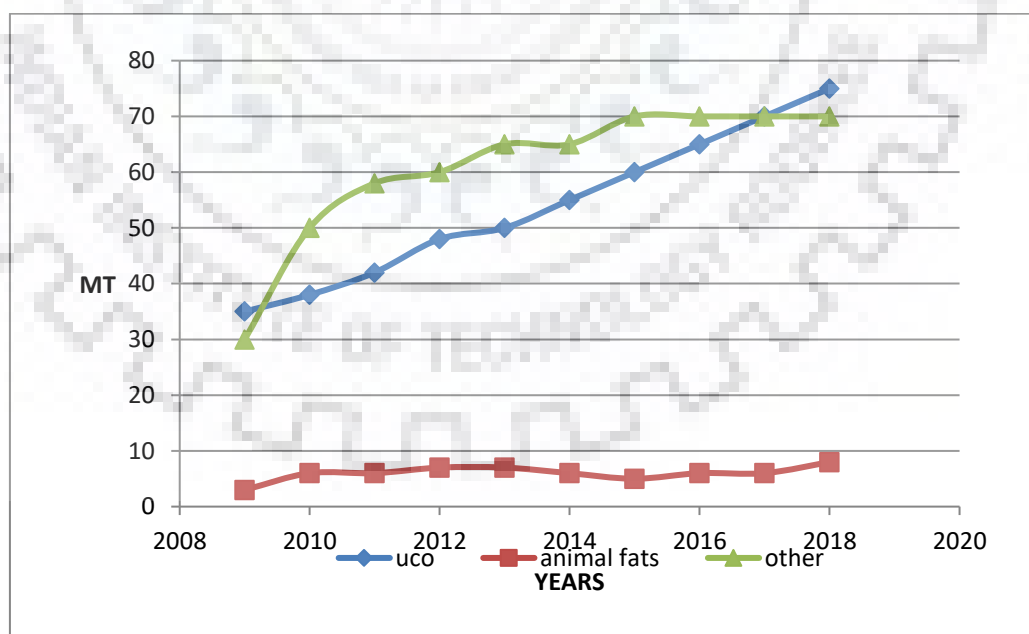
Figure 1.1: -Trend of biodiesel feed stocks

1.6 BIODIESEL QUALITY STANDARDS

Development of test methods, procedures and protocols would be taken up on priority along with introduction of standards and certification for different biofuels and end use applications. The Bureau of Indian Standards (BIS) has already evolved a standard (IS-15607) for Bio-diesel (B 100), which is the Indian adaptation of the American Standard ASTM D-6751 and European Standard EN-14214. BIS has also published IS: 2796: 2008 which covers specification for motor gasoline blended with 5% ethanol and motor gasoline blended with 10% ethanol [5].

1.7 FEEDSTOCKS FOR BIODIESEL

Currently more than 350 oils feed-stocks are available globally for biodiesel production. Different countries use different oils for biodiesel production depending on availability.

In India, biodiesel from edible oils is infeasible, as more than 68% of edible oils are imported to meet food requirement and therefore, the attention is diverted to second generation non-edible oil feed stocks like Jatropha, Pongamia, Neem, Sal etc., even though these oils suffer with limitations of low oil yields and need of large land area for their production [6].

Table1.4: -Oil feed-stocks for biodiesel production [7]

S no.	1st Generation	2nd Generation		3rd Generation
	Edible oils	Non edible oil	Animal fat	Microalgal oils
1.	Soybeans	Jatropha	Pork lard	Bacteria
2.	Rapeseed	Mahua	Beef tallow	Microalgae (Chlorellavulgaris)
3.	Safflower	Coffee ground	Poultry fat	Microalgae(Chlorellaprotothecoides)
4.	Rice bran oil	Camelina	Fish oil	Microalga
5.	Barley	Cotton seed	Chicken fat	Microalgae (Nannochloropsis sp.)
6.	Sorghum	Salmon oil		Fungi
7.	Wheat	Tall fescue		
8.	Corn	Neem		
9.	Coconut	Jojoba		
10.	Canola	Passion seed		
11.	Peanut	Moringa		

Depending on availability, the oils can be used for biodiesel production. The 1st generation edible oil are used for cooking purpose and after use of the cooking oil. The remaining oil which does not remain fit for cooking purpose is known as waste or used cooking oil. This used/waste cooking oil can be used for the production of biodiesel, after processing the waste cooking oil through chemical methods such as transesterification the mixture obtained has properties similar to the standard biodiesel.

There are many significant advantages and disadvantages as given in Table 1.5 of biodiesel over conventional diesel.

Table1.5: Some advantages and disadvantages of biodiesel production [9]

Terms	Advantages	Disadvantages
Cost	It is made from renewable resources	Currently more expensive than fossil diesel fuel
Energy Availability	Fossil diesel fuel is a limited resource, but biofuels can be manufactured from a wide range of materials	Mainly produced from edibleoil which could cause shortages of food supply and increased prices
GHG emission	Significantly less harmful carbon (CO_2*, CO, THC) emission	Reduction of fuel economy
Energy security	Viability of the first generation biofuel Production	Conflicts with food supply
Usage	Relatively less flammable compared to fossil diesel	Less suitable for use in low Temperatures
	Significantly better lubricating Properties	It can only be used in diesel-powered engines
	Significantly less harmful carbon emission compared to standard diesel	More likely than fossil diesel to attract moisture
Air pollution	Significant reduction of PM emission	Caused increases in NOx

1.8 STANDARDS FOR COMPARING BIODIESEL QUALITY

The countries like Italy, Germany, France, USA etc. have develop their own biodiesel standards. However, an Indian standard under the name IS: 15607 is also being developed. Usually ASTM standards followed all over the world. The properties of the biodiesel as per the standards are given in Table 1.6

Table1.6: Biodiesel properties as fuel in different standards [10]

S.No.	Parameter	Austria ON	India BIS	France general official	Germany DIN	Italy UNI	USA ASTM
1.	Density at 15°c (g/cm^3)	0.85-0.89	0.87-0.89	0.87-0.89	0.875-0.89	0.86-0.90	0.88
2.	Viscosity at 40°c (mm^2/s)	3.5-5	1.9-6	3.5-5	3.5-5	3.5-5	1.96
3.	Flash point °c	100	130	100	100	100	130
4.	Cetane no	≥49	≥40	≥49	≥49	-	≥47
5.	Neutralization no	≤0.8	≤0.5	≤0.5	≤0.5	≤0.5	≤0.8
6.	Pour point °c	-	-	10	-	1-5	15-18
7.	Carbon residue (%)	≤0.05	≤0.05	≤0.05	≤0.05	-	≤0.05
8.	Oxidation Stability (in hours)	4.5	3.5	4	3	6	3.5

Considerable increase in the amount of fossil fuels usage in internal combustion engines and the negative effects of exhaust emissions resulting from the burning of these fuels on the environment have led to increasing interest in alternative energy resources. Biodiesel is one of the alternative fuel sources for diesel engines. Biodiesel can be produced from many different types of raw oil materials like vegetable, animal and waste oils. When environmental cleanliness and cost is considered, most appropriate solution seems to be use of waste oil as raw material for biodiesel production. Use of waste oils in biodiesel production is very important because this process provides recycling the wastes which cause hazards to human health and the environment and providing recycling of them.

1.9 BIODIESEL STABILITY

Biodiesel is the common name given to ethyl or methyl esters of long chain fatty acids obtained from vegetable oils or animal fats. Biodiesel is renewable, non-toxic bio-degradable and usually contains no sulphur or aromatic compounds. The drawbacks of biodiesel are that it costs more than petroleum based diesel. Another very important problem associated with the biodiesel is its storage as biodiesel is vulnerable to oxidation due to environmental factors such as air, moisture light etc.

During oxidation, the biodiesel breaks into unwanted smaller chain compounds such as aldehydes, small chain esters etc. beyond tolerable limits. In other words, biodiesel becomes chemically unstable. The oxidation process deteriorates fuel quality which can cause problems such as choking of injector and fuel filter and formation of deposits in various components of the fuel system including combustion chamber [13]

Various factors that affect the stability are air, heat, light, antioxidants, minerals, peroxides; material of the storage container etc. stability of the biodiesel is its ability to resist the physical and chemical changes caused by interaction with the environment"

1.9.1   The cause of instability

During the process of transesterification, if the reaction of fatty acid is carried out with methanol, the result is methyl ester of that fatty acid and if it is implemented with ethanol, ethyl ester is formed. During the transesterification process, the fatty acid chain remains unchanged; therefore the oxidation chemistry of biodiesel is similar to that of the fatty acid or oil from which it is derived. On the basis of the carbon bonds present, Fatty acids can be classified into two types:

1. Saturated fatty acids, where no double bonds between two carbon atoms are present

2. Unsaturated fatty acids, where carbon-carbon double bonds are present

Examples of saturated fatty acids are butyric acid, myristic acid, palmitic acid and stearic acid whereas unsaturated fatty acids are oleic acid, elaidic acid and linoleic acids [12].

1.9.2 Types of stability

Stability of the biodiesel is classified into three types:

 1. Oxidation stability

 2. Storage stability

 3. Thermal stability

1.9.2.1 Oxidation stability

Biodiesel is non-resistant to oxidation when exposed to air, light and moisture etc. The quality of fuel is ultimately affected due to oxidation. Therefore, the oxidation stability studies have been the integral part of biodiesel characterization and research. The oxidation stability standards are included in the European biodiesel standards EN 14213 and EN 14214 and American standards D6751 [13] The initial products of oxidation are peroxides and hydro peroxides which further degrade into shorter chain products such as aldehydes, alcohols, ketones, and low molecular weight acids [14].The Parameters used for measuring oxidation stability are as follows

1. Iodine value
2. Peroxide value
3. Acid value
4. Kinematic viscosity
5. Oxidiability

1.9.2.2 Storage stability

Storage stability of biodiesel is the resistance offered by the biodiesel to the chemical and physical changes taking place due to the environmental factors and interaction during the long term storage [14].

Storage stability pertains to the degradation of the biodiesel and its interaction with the light, air, metal, moisture and other conditions during storage. The visible effects of oxidation during storage can be either deposit formation or the change in color of the biodiesel. The color of the biodiesel also changes from yellow to brown and starts smelling like that of paint [15]. The factors responsible for storage instability are moisture or water, particulate solids present in the sample, degradation products, light, presence of metals and microbial slimes.

1.9.2.3 Thermal stability

Thermal stability refers to the resistance offered by biodiesel to oxidation at high temperatures (>250 °C). The phenomenon of oxidation at high temperatures is different from the oxidation at low temperatures. The high temperature in biodiesel also deteriorates the natural antioxidants at a faster rate due to which the oxidation process further increases [15]

1.10   LITERATURE REVIEW

S.No.	1
Author	Knothe and Steidley (2018)
Title	The effect of metals and metal oxides on biodiesel oxidative stability from promotion to inhibition
Finding	1-Several technical problems persist when using biodiesel oxidation stability upon exposure to oxygen to air. 2- Factors affecting oxidation stability are composition of the fuel with polyunsaturated fatty acid methylesters, temperature, presence of light, storage heat space, antioxidant metal. 3- In this study a total of 26 metals for their effect on biodiesel in form of soybean oil methyl esters. Cu metal most strongly promoting oxidation.
Gaps	1-The exact reason for this differing behaviour by the various metals and metal oxides would need to be clarified in further work. Biodiesel stability during storage in and other contact with metal containers and towards "alternative" transesterification catalysts.
Ref.	[22]

S.No.	2
Author	Kolhe et.al (2017)
Title	Production and purification of biodiesel produced from used frying oil using hydrodynamic cavitation.
Finding	1- Used frying oil using a hydrodynamic cavitation reactor. 2- separation and purification of FAME 3-molar ratio 4.5:1, KOH 0.55%, conversion achieved 93.86%, in only 20 min. 3- The complete separation was observed at 70 °C temperature in just 3 hrs.
Gaps	Copper magnesium alloy is more prone to corrosion than mild steel, aluminium and stainless steel.
Ref.	[23]

S.No.	3
Author	Nadiarulah et.al (2017)
Title	Experiment on the Effects of Storage Duration of Biodiesel produced from Crude Palm Oil, Waste Cooking oil and Jatropha
Finding	1) Investigates the effects of storage duration of biodiesel. 2) There arethree types of blending 5vol% blends(5vol%plant oil 95vol% diesel), 10vol% blending(10vol% plant oil and 90vol% diesel) and 15vol% blending(15vol% plant oil and 85vol% diesel). 3) Biodiesel samples were stored at indoor condition and outdoor condition for a 3 months period.

	4) The fuel properties such as acid value, viscosity, density, water content and flash point are observed with the laboratory instrument.
Gaps	Indoor storage conditions which are less susceptible to delayed break light chain fatty acids. The physical properties majorly affected by the blending ratio and type of derivation used
Ref.	[24]
S.No.	4.
Author	Fasogbon (2016)
Title	Influence of Temperature on Corrosion Characteristics of Metals in Used Cooking Oil Methyl Ester
Finding	1- Investigating influence of temperature on the corrosion characteristics of metals in used cooking oil methyl ester. 2- The corrosion characteristics of copper-magnesium alloy, mild steel, aluminium, and stainless steel in WCO methyl ester.
Gaps	
Ref.	[25]
S.No.	5.
Author	Sinha (2016)
Title	Biodiesel production from waste cotton seed oil using low cost catalyst: Engine performance and emission characteristics.
Finding	1-Production offatty acid methyl esters from waste cotton seed oil. 2-oil/methanol molar ratio of 1:12, catalyst loading of 3 wt% Used cotton cooking oil yielded of 92% of biodiesel. The Brake thermal efficiency of the diesel was 28% at full load (100%). The specific fuel consumption of biodiesel fuel blends (B10 and B20) were 0.340 kg/kW h and 0.380 kg/kW h
Gaps	The biodiesel blends B10 and B20 resulted in considerably showed an improved emission characteristic with lower un burnt HC, CO emissions.
Ref.	[26]
S.No.	6.
Author	Dwivedi and Sharma (2015
Title	Effect of Metal on Stability and Cold Flow Property of Pongamia Biodiesel
Finding	1-The effect of metal on the stability and cold flow property of Pongamia biodiesel. 2-Stabilityof various metal varies in order of Iron> Aluminium> Zinc 3- The Pongamia biodiesel have poor oxidation stability as per IS 15607 standard.
Gaps	Pongamia Biodiesel (PB) as an alternative fuel the addition of antioxidant is necessary to improve the oxidation stability (OS) and to enhance the cloud point (CP) and pour point (PP)for PB the blending with alcohol or addition of cold flow improver to make it comparable to that of diesel.
Ref.	[27]
S.No.	7.
Author	Jain and Sharma (2014)

Title	Effect of metal contents on oxidation stability of biodiesel/diesel blends
Finding	1- Evaluation of oxidation stability of metal contaminated biodiesel/diesel blend. 2- Effectiveness of different antioxidants has also been checked. 3-pyrogallol (PY) is the most effective antioxidant. 4-B100 required large amount of antioxidant for maintaining the specification followed by B30, B20, B10 and B7 samples with metal contents.
Gaps	Doping the metal deactivator with antioxidant.
Ref.	[28]
S.No.	**8.**
Author	Fernandes et.al (2013)
Title	Storage stability and corrosive character of stabilised biodiesel exposed to carbon and galvanised steels.
Finding	1-soybean biodiesel with or without TBHQ was investigated through static immersion corrosion tests. 2-Coupons of carbon steel and galvanised steel were immersed in soybean biodiesel for 12 weeks. 3-Measurements of total acid number, peroxide value, oxidation stability (Rancimat induction period), metal release, and TBHQ consumption at different stages of corrosion were performed. 4-TBHQ may have acted as a corrosion inhibitor. TBHQ was rapidly consumed in the first 3 days of experiments. 5-Biodiesel properties were not affected for a storage time of 56 days.
Gaps	1-low oxidation stability of biodiesels. 2-diffcult task to identify how metallic species came to the present of biodiesel
Ref.	[29]
S.No.	**9.**
Author	Araujo, et.al (2013)
Title	Biodiesel production from used cooking oil : A review
Finding	1-different type of used cooking oils 2-pretreatment and transesterification 3-alkaline catalysts, acid catalysts, enzymatic catalysts, non-catalysts technique are used 4-KOH catalyst recommended 5-the used cooking oil would have potential to supply up to 13% of the demand for biodiesel in Brazil
Gaps	Use of enzymatic process reaction rate is low, catalysts cost is high.
Ref.	[30]
S.No.	**10.**
Author	Yaakob et.al (2013
Title	Overview of the production of biodiesel from Waste cooking oil.
Finding	1-WCO is most promising feedstock of biodiesel. 2-It having high FFA and water content. 3-pretreatment, several method different types of reactors, various amount of alcohol and catalysts. 4- transesterification and using methanol –ethanol mixture
Gaps	
Ref.	[31]

S.No.	11.
Author	Kawentar, and Budiman (2012)
Title	Synthesis of Biodiesel from Second-Used Cooking Oil.
Finding	1. Used cooking oil collected from street seller. 2. Methanol was used as a reactant, and KOH was used as a base catalyst. 3.Several types of analysis used were free glycerol analysis, total glycerol analysis, 4. Free fatty acid (FFA) analysis, and saponification analysis. 5. Temperature 65°C molar ratio 6.18:1, KOH 1%wt.
Gaps	
Ref.	[32]

S.No.	12.
Author	Mofijur et.al (2012)
Title	Effect of biodiesel from various feed-stocks on combustion characteristics, engine durability and materials compatibility: A review
Finding	1- Impact biodiesel from different edible, non-edible and waste cooking oils feed-stocks on combustion characteristics, engine durability and materials compatibility with biodiesel. 2- Biodiesel feed-stocks biodiesel standards and advantages and challenges of biodiesel.
Gaps	Sediments found in diesel storage and engine fuel systems. These dissolved sediments may plug fuel filters or Injectors
Ref.	[33]

S.No.	13.
Author	Almeida et. al (2011)
Title	Behaviour of the antioxidant tert-butylhydroquinone on the storage stability and corrosive character of biodiesel.
Finding	1-storage stability of biodiesel was investigated with TBHQ antioxidant. 2- Static immersion corrosion tests in biodiesel (with and without TBHQ) using copper coupons. 3-TBHQ molecules adsorb at the copper surface to inhibit corrosion. 4-Tert-butylquinone (TBQ) was the main oxidation product detected.
Gaps	The formation of new molecules of high molecular weight only present in the TBHQ-doped biodiesel deteriorated by the corrosion process.
Ref.	[34]

S.No.	14.
Author	Demirbas A.(2009)
Title	Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification
Finding	Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification 2- FFA in WCO transesterified in supercritical methanol method 3-supercritical transesterification offers great advantage to eliminate the pre-treatment and operating costs. 4 -Effect of molar ratio, KOH concentration, temperature are investigated.
Gaps	Transesterification of crude waste oil gave much lower yields, due to the high levels of free fatty acids in the oil.
Ref.	[35]

S.No.	15.
Author	Phan ,and Phan (2008)
Title	Biodiesel production from waste cooking oils
Finding	1- Waste cooking oils, collected. 2-Biodiesel yield of 88–90%, methanol/oil ratios of 7:1–8:1, temperatures of 30–50 °C and 0.75 wt% KOH. 3-Carbon residue content was up to 4 wt%. 4Blends with a % of the biodiesel below 30%
Gaps	The carbon residue was 4.0 wt% for the biodiesel but only 0.05 wt% for diesel.
Ref.	[36]

As per the literature review biodiesel is obtained from the transesterification of agriculture lipids such as vegetable oils, animal fats, waste grease, waste cooking oils etc, has attracted renewed interest of researcher as substitute of biodiesel.

WCO is considering the most promising biodiesel feedstock but its drawback is having high free fatty acid and water content. Although the collection of WCO is reduce the cost of biodiesel and clean the environment. Most common process is transesterification and using methanol-ethanol mixture combine. Most commonly used alcohol is methanol because it having its lower cost.

Use of WCO is reducing the problems water pollution and blockage the drainage system.Study of various stabilities as per literature review oxidation stability, thermal stability and storage stability

1.11   GAPS IDENTIFIED

1. There is the shortage of resources of the non-edible oils so waste cooking oil (WCO) can be the replacement for that. The generation of non-edible oils is costlier also than waste cooking oil. Future scope is there in production of biodiesel from waste cooking oil.

2. The resources for production of biodiesel mainly are algae based oils which are available so there is a need to develop other resources of biodiesel.

3. The biodiesel produced from waste cooking oil has higher amount of free fatty acid (FFA) and water content.

4. The stability of biodiesel is main area where further research work is needed.

5. There are number of research papers reported on the bases on biodiesel production from WCO but little work on its oxidation, thermal and storage stability has been done.

6. Antioxidant amount has not been optimized for required oxidation, thermal and storage stability.

1.12 OBJECTIVE

Based on the literature survey and gaps identified following the present study has been carried out with the following objectives

1. To study the different techniques required to prepare biodiesel in laboratory
2. To collect waste cooking oil from various mess inside IITR campus.
3. To determine the various properties of the prepared biodiesel and compare with standards.
4. To performance testing of the engine by using prepared biodiesel and to analysis the flue gases coming from the exhaust of the diesel engine.
5. To study the oxidation and thermal stability of the biodiesel produce by WCO.

1.13 OUTLINE

This study is focused on effect of the variation of these design parameters on the power output developed by the turbine and the efficiency of turbine. The study consists of five major chapters including introduction, literature review, and design and modeling of cross flow turbine, results and discussion, and conclusion.

Chapter 1 - The explained introduction gives the better understanding of the topic and the literature is reviewed, previous studies are analyzed with the identifications of gaps and objectives

Chapter 2 -The collected waste cooking oil's properties have been found and based on these properties the mentioned methodology is identified

Chapter 3 – This chapter deals with the preparation of Biodiesel and finding the properties and comparing with standard properties. Stability has been checked based on various methods along with engine testing has been carried out to support the results.

Chapter 4–On basis of results obtained, some conclusions and recommendations are made in last chapter.

CHAPTER 2

WASTE COOKING OILS AND METHODOLOGY USED

2.1 COOKING OILS

Cooking oil consist of plant, animal, or synthetic fat which is used in frying, baking, and variety of cooking purposes. There are many varieties of cooking oils, which vary in the ratios of saturated, polyunsaturated and monounsaturated fats they contain. Some are derived from animal sources, while most are made from plants, nuts or seeds.

During the frying process foods are frying in oil with a high temperature at 150°C to 190°C. There are several times of frying oil at high temperature cannot be further use for cooking purpose. Repeated frying for preparation of food makes the edible oil no longer suitable for consumption due to high free fatty acid content. Waste oil has many disposal problems like water and soil pollution, human health concern and disturbance to the aquatic ecosystem, so rather than disposing it and harming the environment, it can be used as an effective and cost efficient feedstock for Biodiesel production as it is readily available [16]. As Compared to petroleum-based diesel, the high cost of biodiesel is a major barrier to its commercialization. It costs approximately one and a half times that of petroleum-based diesel depending on feedstock oils. A largely accepted strategy to reduce the cost of biodiesel is to minimize feedstock costs. The use of waste cooking oil for the production of biodiesel in spite of virgin oil has been an effective way of reducing feedstock costs, besides bringing substantial environmental benefits as it provides an alternative for the final disposal of the oil previously discharged of in the environment. The cost of WCO is two and three times less than that of fresh vegetable oil, which leads to a significant reduction in the total processing cost [17].

2.2 WASTE COOKING OIL (WCO)

Vegetable oil contains saturated hydrocarbons (triglycerides) which consist of glycerol and esters of fatty acids. Used vegetable oil (UVO) is a by-product from hotels, fast food restaurants and household. For having better quality food and various health hazards related to used cooking oil, they usually throw this used cooking oil without any treatment this oil is termed as waste cooking oil. The chemical and physical properties of WCO are different from those of fresh oil since some changes due to chemical reactions - such as hydrolysis, oxidation,

polymerization, and material transfer between food and vegetable oil occur during the frying process.

Chemical changes include the auto-oxidation which is the most frequent modification during the deep-frying process. It is a non-enzymatic oxidative process characterized by the oxidation of fatty acids (especially polyunsaturated fatty acids which are more sensitive than saturated fatty acids) and other unsaturated molecules when exposed to atmospheric oxygen, generating intermediate unstable compounds called hydro-peroxides or peroxides which will result in the formation of free radicals. These free radicals tend to combine with each other or with other fatty acids, and tend to form long and ramified lineal compounds, or cyclic compounds, especially when there is double bonds. The cyclization of fatty acid molecules is one of the main reactions produced due to the intense thermal treatment of the deep fat frying process.Chemical changes of the properties of biodiesel during deep frying and their reasons as discuss in Table 2.1

Table2.1 Changes in chemical parameters of oils/fat during deep-frying and the reasons for these changes [18]

Chemical Parameters	Changes during deep-frying	Causes
Anisidine value	Increases	Secondary oxidation products
Iodine value	Decreases	Formation of oxidized fat products
Peroxide value	Increases but can also Decrease	Primary oxidation products
Petrolether – insoluble oxidized fatty acids	Increase	Oxidized polymerization products
Polar compounds	Increase	Oxidized and polymerized degradation products including unchanged polar fat Components
Polymerized Triacylglycerols	Increase	Oxidized and not oxidized polymerized Triacylglycerols
Acid value	Increases	Formation of oxidation products with free carboxyl groups

2.2.1 Physical changes in oil during heating and frying

Deep-fat frying is a process of cooking and drying in hot oil with simultaneous heat and mass transfer. As heat is transferred from the oil to the food, water is evaporated from the food and oil is absorbed by the food. Many factors affect heat and mass transfer, including thermal and physical properties of the food and oil, shape and size of the food, and oil temperature.

Table2.2.Changes in some physical parameters of oils/fat during deep-frying and the reasons for these changes [18]

Physical parameters	Changes during deep frying	Causes
Refractive index/UV	Increases	Accumulation of conjugated fatty acids
Density	Increases	Polymerized Triacylglycerols
Dielectric coefficient	Decreases	Polar-oxidized components
Colour Becomes more intensive and darker	(Maillard) reaction	No
Conductivity	Increases	Polar compounds
Surface tension	Decreases	Polar compounds
Smoke point	Decreases	volatile oxidized decomposition products
Specific Heat	Increases	Polar compounds
Viscosity	Increases	Polymerized Triacylglycerols

2.3 SPECIFICATION OF WASTE COOKING OILS

Biodiesel processing costis around Rs.10 per litter, this plus landed cost of oil per litter, is cost of manufacture. Price of Bio-diesel in India should be 10% less than that of Diesel [3]. The properties of WCO can change depending on the frying conditions, such as temperature and cooking time. The usual values for Properties like density, kinematic viscosity, saponification value, acid value and Iodine value, FFA [19]. Typical specification and their properties of waste cooking oil are given in Table 2.3

Table2.3: Typical Specification for used cooking Oil[19]

S.no.	Property	Unit	Value
1.	Density (20°C)	(kg/m³)	820-900
2.	Kinematic viscosity(40°C)	(mm^2/s)	1.9-6.0
3.	Flash point	°C	130
4.	Sulphur content	%	0.05-0.005
5.	10% carbon residue	%	0.3
6.	Ash content (mass fraction)		0.020
7.	Moisture (mass fraction)		0.1
8.	Mechanical impurity		0
9.	Corrosiveness to copper-copper strip	(50°C, 3h)	1
10.	Cetane number		49

11.	Oxidation stability(110°C)	(hour)	5.0
12.	Acid value	(mg KOH/g)	0.8
13.	Free glycerol content (mass fraction)	%	0.020
14.	Total glycerine content (mass fraction)	%	0.240

Based on the above table it can be inferred that the oil is not suitable for the cooking purpose, so it can be used for the production of biodiesel.

It is derived from renewable resources, hence leads to less dependency on the conventional fuel. It has higher flash point (150–180 °C) compared to 70 °C of the conventional diesel, leading to safer handling and storage. It has good lubricity, is biodegradable, and causes reduction in exhaust emissions (except NO_x). The drawbacks of using biodiesel as CI engine fuels are its lower energy content leading to lower engine power and speed, higher viscosity, higher pour point, higher cloud point, injector coking, engine compatibility, Higher NO_x emissions, high engine wear and high price [8]

2.4 TYPES OF CATALYST USED IN PRODUCTION OF BIODIESEL

In general there are three categories of catalysts used for biodiesel production known as alkalis, acids and enzymes. As compare to enzyme catalysts, alkali and acid catalysts are more commonly used in biodiesel production. They were then categorized into homogeneous and heterogeneous catalysts. However, enzyme catalysts have become more attractive recently since it can avoid soap formation and the purification process is simple to accomplish but they are not commercially used because of the longer reaction times and higher cost. To reduce the cost, some researchers developed new biocatalysts in recent years [20].

2.4.1 Homogeneous base-catalyzed transesterification

Homogeneous alkaline catalysts are more preferable and commonly used since transesterification reaction using its acid counterpart has slower rate. The most common basic catalysts are potassium hydroxide (KOH), potassium meth oxide (KOCH3), sodium hydroxide (NaOH), sodium methoxide (NaOCH3), and sodium ethoxide (NaOCH2CH3). NaOH and KOH are the most common homogeneous base catalyst in biodiesel production.

2.4.2 Heterogeneous base catalyzed transesterification

Most of the heterogeneous catalysts developed for production of biodiesel are either alkaline oxide or alkaline earth metal oxide supported over large surface area. Heterogeneous basic catalysts are more active than heterogeneous acid catalyst, similar to their homogeneous counterparts. Solid alkaline catalysts, for instance, calcium oxide (CaO) provide many advantages such as higher activity, long catalyst life times, and could run in moderate reaction condition. Nonetheless, CaO as catalyst can also slow down the reaction rate of biodiesel production.

2.4.3 Heterogeneous acid-catalyzed transesterification

Despite of the effectiveness of homogeneous acid catalyst, it can lead to absolute contamination problems which require good separation and product purification processes. This will be resulted in higher production cost. It is believed that heterogeneous acid catalystshave the potential as alternative to homogeneous acid catalysts. Some of advantages of heterogeneous acid catalyst are insensitive to FFA content, can simultaneously conduct esterification and transesterification eliminate the washing step of biodiesel, simpler separation process of catalyst from product, regenerating and reusing the catalyst is possible and also reduce the corrosion problems.

Types of solid acid catalysts that were commonly used in esterification and transesterification reaction works include tungsten oxides, sulphonated zirconia (SZ), sulphonated saccharides, Nafionl resins, and organo-sulphoric functionalized mesoporous silicas.

2.4.4 Enzyme (Biocatalyst) catalyzed transesterification

Enzymatic transesterification has drawn researcher's attention due to the downstream processing problem posed by chemical transesterification, huge amount of wastewater generation and difficulty in glycerol recovery are some of the problems that eventually increase the overall production cost of biodiesel and being not environmental benign. In contrast, enzyme catalysis occurs without the generation of by-products, easy recovery product, mild reaction condition, insensitive to high FFA oil and catalyst can be reuse. Enzyme catalyzed biodiesel production has proven to have high potential to be an eco-friendly process and a promising alternative to the chemical process. However, enzyme catalyzed biodiesel production has some limitations especially

when implemented in industrial scale because of high cost of enzyme, slow reaction rate and enzyme deactivation. Lipase is mostly used as enzyme catalyst transesterification. Lipase is extracted from several sources, such as microbial sources (fungi and bacteria), animals, and plant [21]

2.5 MATERIAL AND METHODOLOGY

The consumption of edible oil in India is very high and still the indigenous production does not cope with the consumption and hence significant amount is imported. Therefore there is no possibility of using edible oil in biodiesel production but as consumption of edible oil is very significant so it also implies that the wastage of cooking oil is significant which can be used in the production of biodiesel it will solve the dual purpose of production of biodiesel and the handling of waste cooking oil.

Waste cooking oil can be useful source for the production of biodiesel. The**Food Safety and Standards Authority of India** (FSSAI) launched RUCO – Repurpose Used Cooking Oil. RUCO is an ecosystem that will enable the collection and conversion of used cooking oil to biodiesel. India is one of the largest consumers of vegetable oil and so has the potential to recover almost 220 crore litre of Used Cooking Oil (UCO) for the production of biodiesel by the year 2022. In view of waste cooking oil becoming a important source of biodiesel as substitute of diesel in India, the present work is related to the study of the oxidation, thermal and storage stability of the biodiesel produce by WCO and also the effect of metal contaminations and antioxidant on the oxidation, thermal and storage stabilities.

Present chapter deals with related to the experimental procedure employed to the biodiesel preparation from WCO and various stability methods.

Waste cooking oils (WCO) was collected from various messes of **IIT ROORKEE CAMPUS** and filtered to remove all the insoluble impurity from oil. Waste Cooking oils heating at 110°c for 10min to remove the moisture content available in the oil. Entire process chemicals are used likes H_2So_4, KOH, methanol, ethanol, KI, etc.

2.5.1Collection of Waste cooking oil from IIT Roorkee campus

Almost 120 litres of waste cooking oil obtain from the various messes in a month. After proper processing these WCO can be converted into the biodiesel which can be further used for various purposes in the campus as well as outside the campus. So by doing this we are solving

two problem at once first one is of disposal of waste cooking oil and second one is by reusing it we are keeping the environment clean. The collection of waste cooking oil from various hostel mess inside IITR campus is given in Table 2.4

Table 2.4 collection of waste cooking oils from different mess of IIT Roorkee

S.No	Mess	No of students	Brand of oil used	Oil consumption per month in kg	Amount of WCO per month in litre
1.	Cautlay Bhawan	803	Sundrop, nature drop	815	15-16
2.	Rajendra Bhawan	856	Sundrop,(refined soybean oil)	950	20-25
3.	Ganga Bhawan	403	Sundrop, nature drop	365	7-10
4.	Radhakrishnan Bhawan	515	sundrop	480	12-15
5.	Rajiv Bhawan	535	Nature drop,sundrop	515	15
6.	Azad Bhawan	420	Nature drop	380	8-10
7.	Kasturba Bhawan	717	Sundrop	600	15
8.	Sarojini Bhawan	523	Nature drop, sundrop	480	10
				Total WCO per month in Litre	120

2.6 METHODS FOR MEASURING THE PROPERTIES OF WCO

The various methods are used to investigate and analyses of the various properties of biodiesel are discussed below.

2.6.1 Viscosity Measurement

Measurement of viscosity of the WCO using the Brookfield digital viscometer apparatus450ml of filtered waste cooking oil was taken in 500ml beaker and heated at 110^0C such that water present in WCO is removed. During heating process a thermometer is kept in beaker to observe the temperature. The temperature of the sample was brought down to 40^0C and then the beaker was kept under the Brookfield viscometer DV-II+ Pro, L V spindle set. Manufactured by Brookfield Engineering Labs Inc.USA. To make a viscosity measurement,

turn the motor switch "ON". This energizes the viscometer drive motor. Allow time for the indicated reading to stabilize.

Fig 2.1Brookfield digital viscometer

2.6.2 Flash and fire point

The flash and fire points of a liquid fuel specimen are the indicators of its flammability. Flash point is the lowest temperature of the test specimen, corrected to a barometric pressure of 101.3 kPa, at which the application of an ignition source causes the vapour of the test specimen to ignite momentarily and the flame to propagate across the surface of the liquid under the specified conditions of test.

Fire point may be considered as the lowest temperature of the liquid at which vapour combustion and burning commences. Gasoline has a flash point around -43⁰ C whereas diesel has flash points higher than 52⁰ C. Flash point of biodiesel > 130⁰ C and cooking oil 204⁰ C to210⁰ C .Lower flash points are the indicators of good flammability and volatility.

Penskey Martens Flash Point Apparatus

Sample was added to the Penskey and Martens Flash Point Apparatus**.** Fill the cup with the sample to be tested to the level indicated by the filling mark and heated slowly. Insert the thermometer and supply heat with the help of the rheostat switch to ensure temperature rise rate not more than 5 to 6⁰ C per minute. Turn the stirrer with 90 to 120 rpm in a downward direction. The vapour fume of the sample was exposed to naked flame for an instant after the fixed interval of time to check. If the vapour catches fire with a peculiar sound. The lowest temperature of sample at which the vapour fumes ignites is flash point of that sample.

Fig 2.2 Penskey Martens Flash Point Apparatus

2.6.3 Acid value

The acid value is defined as the number of milligrams of Potassium hydroxide required to neutralize the free fatty acids present in one gram of fat. The value is also expressed as per cent of free fatty acids calculated as oleic acid, lauric, ricinoleic and palmitic acids.

The acid value is determined by directly Titrating the oil/fat in an alcoholic medium against standard potassium hydroxide/sodium hydroxide solution. The value is a measure of the amount of fatty acids, which have been liberated by hydrolysis from the glycerides due to the action of moisture, temperature and/or lipolytic enzyme lipase.

Accurately appropriate amount of the cooled oil sample in a 250 mL conical flask. Add 50mL of freshly neutralised hot ethyl alcohol and about one ml of phenolphthalein indicator solution. Heat the mixture for about fifteen minutes in water bath (75-80°C. Titrate while hot against standard alkali solution shaking vigorously during the titration. End point using phenolphthalein indicator shall be from colourless to light pink. The weight of the oil/fat taken for the estimation and the strength of the alkali used for titration shall be such that the volume of alkali required for the titration does not exceed 10mL.

2.6.4 Iodine number

The iodine number is defined as the percentage of iodine absorbed by a fat or wax, or the number of grams of iodine absorbed per 100 g of fat or wax. It is a measure of the unsaturated bonds present in the fat under investigation, i.e.: a low iodine number indicates few unsaturated bonds.

To 2.0 ml of the fat, add 25 ml of chloroform to dissolve the material. Pipette 5 ml sample of this solution into two separate Erlenmeyer flasks. To a third flask add 5 ml of chloroform to form a blank. Add 10 ml of halogenation reagent to each flask. Cover the flasks with aluminium foil shake and allow standing for 15 minutes. Add 7.5 ml of potassium iodide KI solution to each flask and titrate the liberated iodine using the thiosulphate solution. Titrate the test solution until a light brown colour is obtained then add 5 drops of starch indicator solution immediately and titrate to a colourless end point.

2.6.5 Density

Density is the measure of compactness of matter with in a substance and it is define as

Density =Mass/volume

The standard metric unit in use for mass and volume respectively are grams and ml or cm^3. Thus the density has the unit g/ml or g/cm^3. For the purpose for experimentation, a digital balance is used for mass measurement and a 50ml graduated cylinder is used for volume measurement of liquid.

2.6.6 Calorific value

Calorific value of fuel can be determined by the bomb calorimeter. Bomb calorimeter is used to determine the calorific value of solid fuels and non-volatile liquid fuels. Bomb calorimeter consists of a cylindrical stainless steel vessel, called bomb and is capable of withstanding high pressure. The bomb is provided with a lid that can be screwed firmly on the bomb. The lid contains two stainless steel electrodes and an oxygen inlet valve. A small ring is attached to one of the electrodes which is provided with stainless steel or nickel.

Bomb is placed in a copper calorimeter containing a known mass of water. The copper calorimeter is provided with electrically operated stirrer and The Beckmann's thermometer (it is sensitive enough to read up to 0.01^0C). This calorimeter in turn is surrounded by an air-jacket and then water jacket to prevent heat losses due to radiation

Fig 2.3 Bomb calorimeter

A known amount of fuel is placed in the crucible. The crucible is then placed over a ring and a fine Magnesium wire touching the fuel sample is stretched across the electrodes. The lid is tightly screwed and the bomb is filled with O_2 up to25atm pressure. The initial temperature is recorded. The electrodes are then connected to a 6V battery and the circuit is completed. As soon as the circuit is completed and current is switched on, the fuel in the crucible burns with the evolution of heat. Heat liberated by burning of the fuel increases the temperature of water and the maximum temperature attained is recorded. The temperature change is measured and calorific value of sample is calculated by given formula

CV = 2218* ΔT/Weight of the sample

2.6.7 Free Fatty Acid

Free fatty acids are presented in crude oils but they are removed during refining process Free fatty acids are more susceptible to autoxidation than esterified fatty acids. Thus, free fatty acids act as pro-oxidants in edible oil. These compounds have a hydrophilic and a hydrophobic group in their structure. The carbonyl group is the hydrophilic group and the hydrocarbon chain is the hydrophobic group. The carbonyl group of these compounds are preferably concentrated on the surface of edible oil, decreasing the surface tension and increasing the diffusion rate of

oxygen from the headspace into the oil, so accelerating oil oxidation. Following is the calculation procedure for FFA.

Calculation

1. Preparation of solution is done by taking KOH required for 250ml and 0.25N. Molecular weight of KOH = 56.1

    KOH required = (56.1*0.25*250)/1000 = 3.506gm /250ml of solution

2. Free fatty acid calculation using ASTM D5555-95 FFA is calculated. Oil sample of 7.05gm is added to 100ml Ethyl alcohol and phenolphthalein indicator is added to it notice the change in colour and completion of reaction. This solution is titrated with the KOH prepared in STEP 1.

    FFA = (ml of KOH*N*28.2)/Weight of the sample.

2.6.8 Cloud Point and Pour point Measurement

The oil/fuel sample is first poured into the test jar fitted with a cork, carrying a thermometer. The thermometer bulb is positioned to rest at the bottom of the jar. The entire test subject is the placed in a constant temperature cooling bath on top of a gasket to prevent excessive cooling. After every 1°C drop in the temperature, the sample is taken out and inspected for cloud then quickly replaced.

Characteristics of Waste Cooking Oil

The properties of WCO can change depending on the frying conditions, such as temperature and cooking time. Indeed, a vegetable oil subjected to thermal stress such as during frying can completely vary its chemical and physical original characteristics. The cooking process causes the vegetable oil, Triglyceride to break-down to form, Di-glycerides, Mono-glycerides, and free fatty acids (FFAs). The amount of heat and water in the frying increases the hydrolysis of triglycerides; therefore it causes a growth of the Free Fatty Acids (FFAs) in the WCO. Moreover, because of oxidation and polymerization reactions, there is an increase in the viscosity and the saponification number of the WCO when compared with the original oil. Furthermore, the transport of matter and heat between the frying food and the vegetable oil occurs and causes a higher content of water in the WCO.

2.7 FUEL PROPERTIES OF WASTE COOKING OILS

Tests are performed in the laboratory and the properties of the waste cooking oil such as viscosity, density, free fatty acid, acid value, calorific value, cloud point; pour point,

flash point, fire point etc. form the various methods and apparatus as in the Table 2.7 shows the fuel properties of waste cooking oil collected from different mess of IIT Roorkee

Table 2.7: Result showing Fuel properties of waste cooking oils

S.no.	Properties	unit	Value of WCO
1.	Density	g/ml	0.924
2.	Kinematics viscosity @ 40 °C	mm^2/sec	12.8
3.	Flash point	°C	230°C
4.	Pour point	°C	235°C
5.	FFA	%	5.00
6.	Iodine value	Mg KOH/g	13.20
7.	Saponification value	mg KOH/g	207.312
8.	Molecular weight		855.348

From the table above, it can be seen that the WCO samples had 6 times more viscosity then diesel oil. These viscosity values should be brought down to a proper value after the process so that it can be used during the cold climate. According to ASTM D6751 biodiesel viscosity ranges between 1.9-6.0mm^2/sec. Viscosity influences the ease of starting the engine, the spray quality, the size of the particles (drops), the penetration of the injected jet and the quality of the fuel-air mixture combustion. The acid value of WCO obtained by titrate the oil in an alcoholic medium against standard potassium hydroxide solution. The value came out to be 5 mg KOH/g based on acid value, the catalyst is selected.

The flash point is the minimum temperature calculated to a barometric pressure of 101.3 KPa at which the fuel will ignite (flash) on application of an ignition source under specified conditions. It is used to classify fuels for transport, storage and distribution according to hazard level. The flash point does not affect the combustion directly; higher values make fuels safer with regard to storage, fuel handling and transportation. FP varies inversely with the fuel's volatility. Biodiesel's flash point decreases rapidly as the amount of residual (un-reacted) alcohol increases (methanol's flash point is 11–12 °C, and ethanol's is 13–14 °C). Thus, measuring the biodiesel flash point helps indicate the presence of methanol or ethanol.

As the above the table shows that the content of FFA in the oil is very high 5%. Owing to large FFA content acid catalyst esterification process was adopt. For the esterification process WCO is pour into the four neck flask with reflux condenser heated at 30°C, 40°C ,

60°C, 70°C respectively and time 10 min, 20min, 30min, 60min, 90min, 120min mix with methanol to oil molar ratio 1:6, with acid catalyst H_2SO_4 (1%W/W) and 300 to 400 RPM. During the esterification FFA check at the different temperature and timeas mentioned in Table 2.7, value of FFA is higher than the standard value, therefore we adopted two step method i.e. Esterification followed by Transesterification The below flowchart as shown in Fig. 3.4, shows the process involved in converting WCO into Biodiesel via two-step.

2.8 ESTERIFICATION PROCESS

Esterification process is carboxylic acid reacts with an alcohol. This reaction can occur in the presence of an acid catalyst and temperature. This process takes lot of energy to remove the -OH from the carboxylic acid, so catalyst and heat are needed to produce the sufficient energy. The reaction between fatty acid and alcohol is the result in the production of an ester. To minimise the acid value in WCO esterification process is performed.

Esterification is carried out 1liter 3neck glass flask equipped with a measured amount of WCO was placed in reflux condenser using tap water to condense methanol vapour and the glass flask was placed in a heated water bath. This mixture was mix by stainless steel stirrer WCO is preheated in oven remove any trace amount of moisture before starting the esterification process. A sample of 500g waste cooking oil was introduced and heated to the temperature selected 30°C, 40°C, 50°C, 60°C, and 70°C the amount of acid catalyst H_2So_4 (1%w/w) 5g of the WCO. The esterification reaction performed at different molar ratio 1:4, 1:5, 1:6, 1:7 and 1:9 and rotation of the stirrer was kept 300to 400RPM because methanol is not easily dissolve in WCO. The mixture was maintained under the stirrer for the designed time (30min, 60min, 90min and 120min). At the completion of the reaction, the mixture was kept on the separating funnel for ionic liquid and methanol solution separation for 12 hours. The upper layer was removed and the remaining is contained in other flask and excess methanol was removed by vacuum distillation. And the remaining treated oil was used for transesterification process.
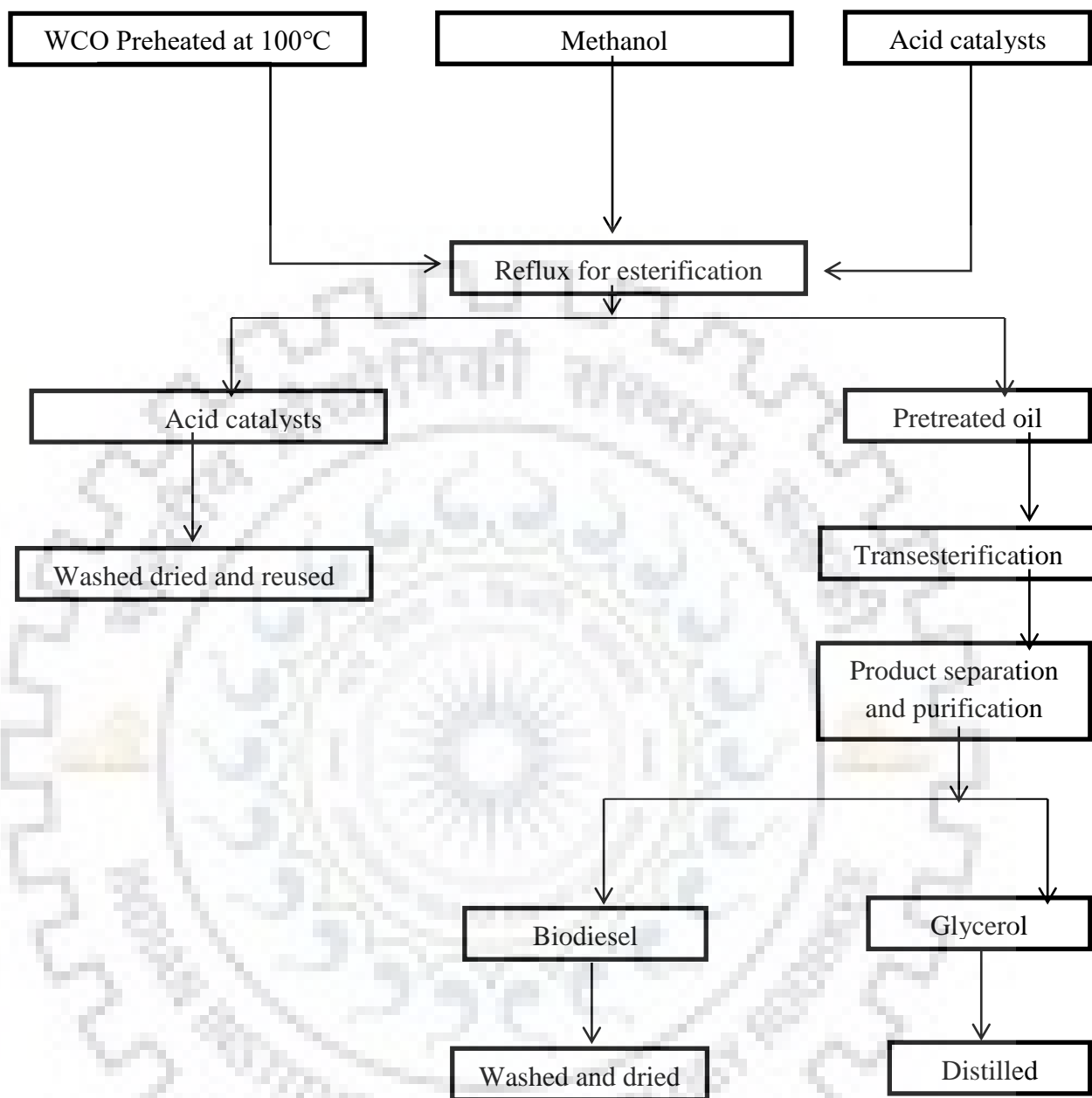
```
┌──────────────────────────┐   ┌──────────────────┐   ┌──────────────────┐
│ WCO Preheated at 100°C   │   │    Methanol      │   │  Acid catalysts  │
└──────────────────────────┘   └──────────────────┘   └──────────────────┘
                  │                     │                     │
                  │                     ▼                     │
                  │         ┌───────────────────────────┐     │
                  └────────▶│  Reflux for esterification │◀────┘
                            └───────────────────────────┘
                                        │
              ┌─────────────────────────┴─────────────────────────┐
              ▼                                                    ▼
    ┌──────────────────┐                              ┌──────────────────┐
    │  Acid catalysts  │                              │  Pretreated oil  │
    └──────────────────┘                              └──────────────────┘
              │                                                    │
              ▼                                                    ▼
┌──────────────────────────┐                        ┌──────────────────────┐
│ Washed dried and reused  │                        │  Transesterification │
└──────────────────────────┘                        └──────────────────────┘
                                                                 │
                                                                 ▼
                                                    ┌──────────────────────┐
                                                    │  Product separation  │
                                                    │     and purification │
                                                    └──────────────────────┘
                                                                 │
                                  ┌──────────────────────────────┴──────┐
                                  ▼                                      ▼
                        ┌──────────────────┐                ┌──────────────────┐
                        │    Biodiesel     │                │     Glycerol     │
                        └──────────────────┘                └──────────────────┘
                                  │                                      │
                                  ▼                                      ▼
                        ┌──────────────────┐                ┌──────────────────┐
                        │ Washed and dried │                │    Distilled     │
                        └──────────────────┘                └──────────────────┘
```

Fig 2.4: Methodology adopted for biodiesel preparation

Fig 2.5: Formation of layers by using separating funnel

Fig 2.6: Methanol recovers by vacuum distillation

Fig 2.7: Titration for free fatty acid

2.9 TRANSESTERIFICATION PROCESS

Transesterification carried out 1liter 3neck glass flask equipped with reflux condenser take the sample of esterified solution 500g and the KOH range (0.5% to 2% w/w). Oil to methanol molar ratio is 1:6 ranging temperature 75°C and the designed period of time 120min and stirred at 300-400 RPM. After 2hrs the mixture the poured into separating funnel to settle down for overnight, at the end two layers were formed. The lower layer of glycerine having high density 1.26 g/cm³ was drained off, while the upper layer of bio-diesel separated properly and the excess methanol was removed by the vacuum distillation.

2.10 WASHING OF BIODIESEL

When the biodiesel is produce by transesterification process it contains the impurities suspended particles that can be removed by the washing of biodiesel. It carried out by two step, firstly the washing with distil water heated at 40°C to 50°C, secondly added into the biodiesel shake properly and poured into the separately funnel and take it for 30min, biodiesel is on the upper layer and water left to settle down in the lower layer is removed. This process can be done 4-5 times. All the impurities of the biodiesel are removed by the washing process. After the washing biodiesel heated at 100°C for 10min to remove all the moisture contain. Prepared biodiesel is used for further testing.

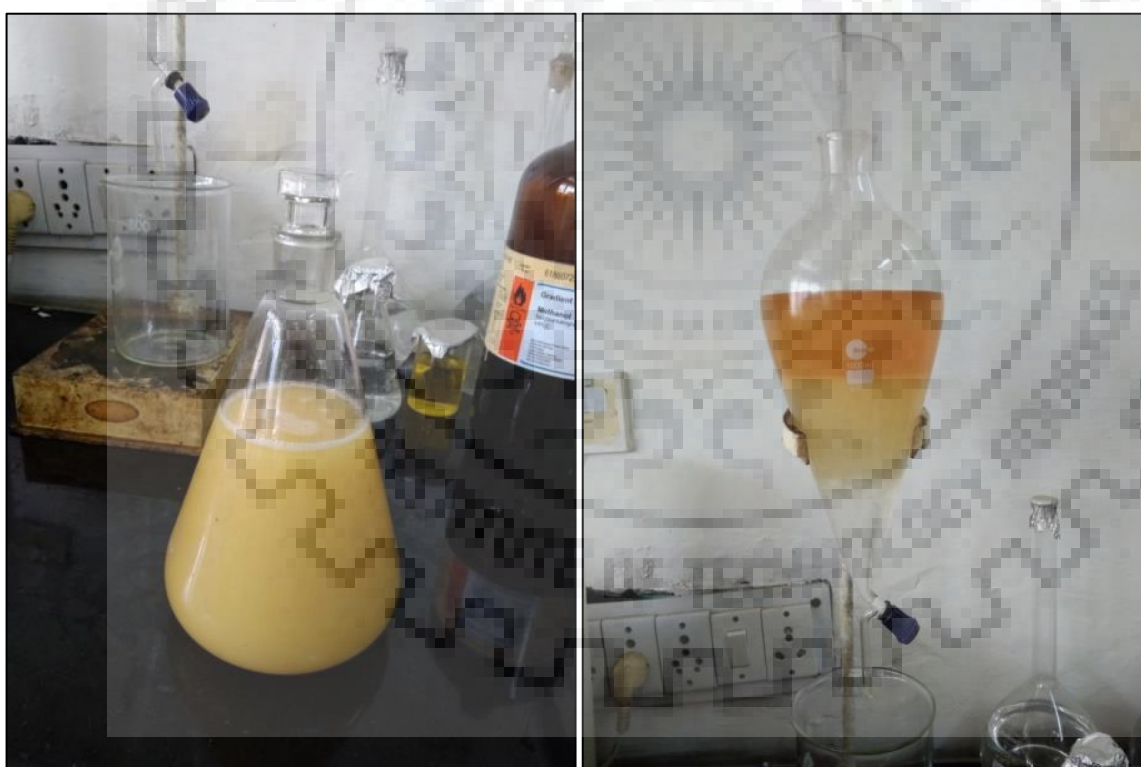**Fig 2.8 (a) Water bath (b) Separated biodiesel from glycerol**

Fig 2.9:- Washing of biodiesel

2.11 METHOD FOR MEASURING THE FUEL PROPERTIES OF BIODIESEL

2.11.1 Viscosity measurement

To measure the viscosity of biodiesel using Brookfield viscometer apparatus, 450ml of biodiesel is taken in the 500ml beaker and heated up to 40°C. During this process, spindle (model S61) is set in viscometer by dipping it at 45° so that the bubble formation does not occur and a thermometer is kept inside the beaker to measure the temperature of biodiesel. The rotation speed of spindle is 100 RPM and designed time during this process is 2 min and viscosity is measured in terms of poise.

2.11.2 Density

Density is the measure of compactness of matter with in a substance and it is defined as

Density =Mass/volume

The standard metric unit in use for mass and volume respectively are grams and ml or cm^3. Thus the density has the unit g/ml or g/cm^3.

For measuring density of biodiesel weighing machine and 10ml volumetric flask is used. Taking 10ml volumetric flask and weigh it on weighing scale. Record the weight as W_1. The flask is filled with biodiesel and weigh again and record the reading as W_2. Calculation is done by using:

2.11.3 Acid value

Acid value is defined as the number of mg of KOH is required to neutralize the FFA present in 1g of biodiesel. By the directly titrate the biodiesel in alcoholic medium against KOH solution. The apparatus for conducting the experiment consists of 250ml conical flask, burette, pipette, measuring cylinder. KOH solution, H_2SO_4+ phenolphthalein indicator solution (1g of PH indicator in 100ml of ethyl alcohol)

Formula used

Acid value = (56.1*V*N)/W

Where, V is volume of KOH solution in ml,

N is normality of KOH solution

W is weight of the sample in g.

2.11.4 Saponification value

The saponification value is the number of mg of KOH required to saponify 1 g of fat or oil. The alkali required for saponification is calculated by KOH with standard HCL. The apparatus for conducting the experiment consists of 250 ml capacity conical flask, reflux condenser, hot water bath Procedure for calculation is given below:

Step 1 To prepare alcoholic potassium hydroxide solution, take 240 ml of methanol in conical flask and then add 2.5g of KOH and then pour 1.5g of aluminium foil into the flask and mix properly and provide reflux condenser with water bath for 30min, after that solution is kept in a bottle closed tightly with rubber stopper overnight this allows the solution to decant the clear liquid.

Step 2 now dissolves 8.5g of KOH into the solution obtained after step 1 and then the solution is mixed well by stirring and titrated

Step 3 Take the 25ml of solution from step 2 into 2 flasks, In 1st flask add the sample of oil 1.7806g and in another flask solution is kept as it is, after that both flask are kept aside for condensation (1 hour). After that titrate both the flask with 0.5N HCl solution (8.8ml of HCl +200ml of distil water). Solution obtained after the titration should be colourless. Readings of titration for both the flask is noted and used for the calculation of saponification value

Formula used

Saponification value = $(56.1*(B-S)*N/w)$

Where,

B is the volume in ml of standard HCl for blank

S is the volume in ml of standard HCl for oil sample

N is the normality of HCl

W is the weight of sample in gram

2.12 METHOD USED FOR THE MEASURING THE STBILITY OF BIODIESEL

2.12.1 Oxidative stability using a modified Karl Fischer apparatus

Oxidative stability is an important parameter in the characterisation of fats and oils. The determination of this parameter with a Rancimat apparatus is very costly. The alternative modified Karl Fischer (KF) apparatus works on the same principle as the Rancimat, a conductivity based determination of volatile degradation products and automatic plotting of the

conductivity against time. The determination of the oxidation stability of oils and fats is the classical application for the Rancimat apparatus model 743. On the other hand, KF apparatus is used to calculate the moisture content in biodiesel, biofuel, diesel, engine oil, gasoline, gear oil, jet lube, and solvent or turbine oil based on EN 14214. For the purpose of testing the oxidative stability of biodiesel, the apparatus is modified for the Rancimat test.

In the Rancimat apparatus reaction vessel, a conductivity measuring cell, a heating block, and piping to pass air from the atmosphere to the biodiesel and from the biodiesel into the demineralised water are assembled as one apparatus. In order to measure the oxidation stability of the biodiesel sample by the KF apparatus, a digital conductivity meter (manufactured by Hack) and reaction vessel (24 mm in diameter, 150 mm long of quartz glass) is assembled separately with all the necessary piping to pass air.

In the Rancimat apparatus, the oxidation is induced by passing a flow of air at the rate of 150 ml/min through the biodiesel sample (3.026 g) kept at constant temperature (110°C) and the conductivity of water 1.61μs/cm at temperature (21.4°C). The vapours released during the oxidation together with the air, are passed into a flask containing 60 mL of distil water and an electrode for measuring the conductivity. The electrode is connected to a measuring and recording device. When the conductivity begins to increase rapidly, it is indicative of the end of induction period. When the conductivity of the solution is recorded continuously, an oxidation curve is obtained whose point of inflection, known as the induction period, can be calculated by the point of intersection of two tangents.

Fig 2.10Modified Karl Fischer Apparatus for Rancimat test

2.12.2 Thermal stability of biodiesel

Cooking oils have very poor thermal stability due to the presence of tertiary β-hydrogen in glycerol of triglyceride molecules. Thermal stability analysis of biodiesel produce by WCO is performed in computer controlled TGA (thermo gravimetric analyser) in isothermal mode under nitrogen atmosphere.

Thermal analysis

The thermal analysis was conducted at a heating rate of 10 °C/min from 10 °C to 700 °C in two atmospheres namely dry air atmosphere and nitrogen atmosphere (inert atmosphere) of 100 ml/min. a sample size of oil 10.50g was used. TGA curves were used to analyse the onset and offset temperatures of the samples. The TGA degradation onset temperature indicates the resistance of the sample against thermal degradation and is determined by extrapolating the horizontal baseline of TGA curve at 1% degradation and the intercept of this line with the tangent to the downward portion of the curve. The higher onset temperature for product decomposition indicates the higher thermal stability. The maximum decomposition temperature approximates the temperature at which the maximum weight loss in the sample occurred.

Fig2.11: Thermal Gravimetric Analysis (TGA) Differential Thermal Analysis (DTA)

2.13 COLD FLOW PROPERTIES OF BIODIESEL

There are two major problem associated with biodiesel when it is used in engine i.e. stability and cold flow properties. Cold flow properties are the main problem regarding the development of biodiesel as alternative fuel of diesel. Both these properties are dependent on fatty acid composition of oil saturated and unsaturated fatty acids present in oil. The presence of higher amount of saturated components increases the cloud point and pour point of biodiesel. The cloud Point and pour point of biodiesel is generally higher than for Petro diesel.

The cloud point and pour point of biodiesel were measured as per the American standards ASTM D-6751 test methods ASTM D2500, D97 IP 15, ISO 3016 respectively.

2.13.1 Measurement of cold flow properties of biodiesel

The biodiesel sample in a definite volume was cooled in a glass tube and inspected at definite intervals of 1°C until a cloud appeared. The temperature at which first cloud or haze appeared was recorded as cloud point and when sample was no longer flow is recorded as pour point.

Fig 2.12 Cloud and pour point measurement apparatus

Fig 2.13 Sample showing (a) haze appearance indicating cloud point (b) Solidify state for pour point

2.14 CALCULATION TABLE

Properties	Observation	Calculation	Result
Density	Weight of empty volume flask (W_1) =19.122g Weight of sample and flask (W_2) = 27.7569g Volume of flask (V) = 10ml	Density= $(W_2 - W_1)$ / V Density = (27.7569-19.122)/10	0.8635g/ml
Acid Value	Volume (V)= 0.05 mL Normality(N) =0.25 Weight (W)= 3.5 g	Acid value = (56.1*V*N)/W Acid value=(56.1*0.05*025)/3.50	0.20034 mg KOH/g
Saponification value	B is the volume in ml of standard HCl for blank 42 ml S is the volume in ml of standard HCl for oil sample 28 ml N is the normality 0.5N	(56.1*(42-28.8) *0.5/1.7860) =207.312 mg KOH/g	207.312 mg KOH/g

	of HCl W is the weight of sample in gram 1.7860g		
Molecular Weight of Biodiesel	M is the molecular weight of biodiesel = SV is the saponification value of biodiesel = 207.312 AV is the acid value of biodiesel =0.20086	M=(56.1*1000*3)/ (SV-AV) M=(56.1*1000*3)/(207.312-0.20086)	M = 270.71
Free Fatty Acid	Weight of KOH =3.506g/250ml of solution Volume consume 0.25N of the KOH solution = 0.025ml	FFA=(0.025*0.25*28.2)*100/1.754	0.10043%
Flash and Fire Point			Flash Point = 185°C Fire Point = 190°C

3.1 DETERMINATION OF FFA CONTENTS BY TITRATION

A sample of the mixture titrated six times. Titration solution was prepared adding KOH. Molecular weight of KOH is 56.1, so required KOH 3.5g/250ml of solution. In the flask oil sample of 7g is added to the 100ml Ethyl alcohol and 5-6 drop of phenolphthalein indicator added in the mixture and notice to change the colour solution is pink and reaction is complete. FFA reading recorded is given in table 4.1 and accordingly a graph plotted is shown in figure 3.1

Table 3.1 Free Fatty Acid (FFA) information from Titration

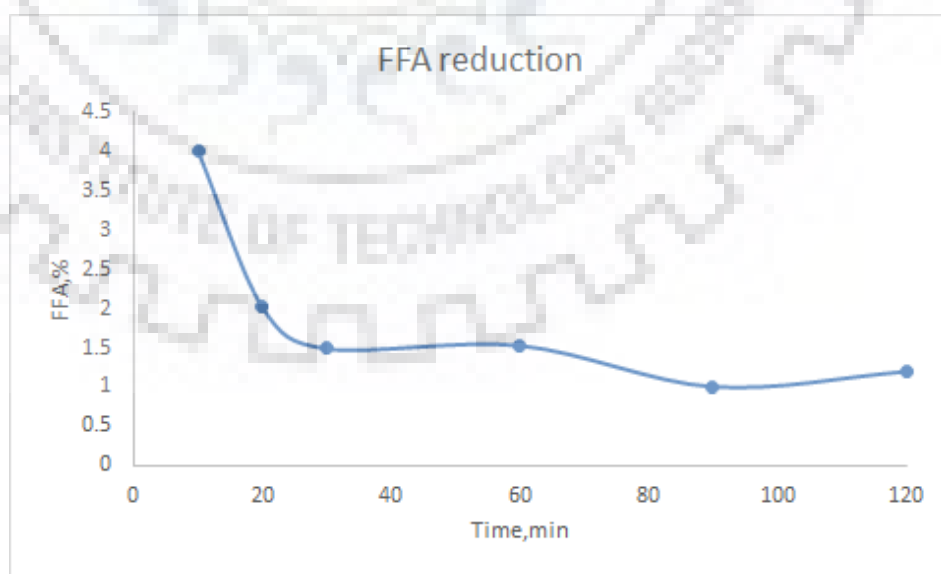| S no	Time (min)	Temperature (°C)	FFA (%)
1.	10	30	4.01
2.	20	50	2.02
3.	30	60	1.49
4.	60	60	1.53
5.	90	60	1.005
6.	120	75	1.20

Fig 3.1:- FFA reduction during esterification process

As given in the Table3.1, FFA is varying at different temperature and time. The temp of 60°C achieved at 90 min, shows that the FFA is least after 90min when the esterification process is completed. The esterified mixture poured into the separately funnel to settle down for 12 hours, two layers formation is observed, hence the upper layer having acid ionic liquidis removed and remaining mixture is used for transesterification process for the biodiesel.

3.2 OXIDATIVE STABILITY

Weight of the sample taken is 3.206g, flow of the air for proper burning is0 150ml/hr, at constant temperature 110°C and having conductivity of water 1.61µs\cm. Fig 4.2 shows the results carried out by the test and graphical determination of induction time (t) by the tangent method is shown in Fig. 3.2

Conductivity of sample biodiesel is 11.344916 µs\cm and the Induction period is 2.4667 hours

Table 3.2: Oxidative stability of biodiesel from WCO

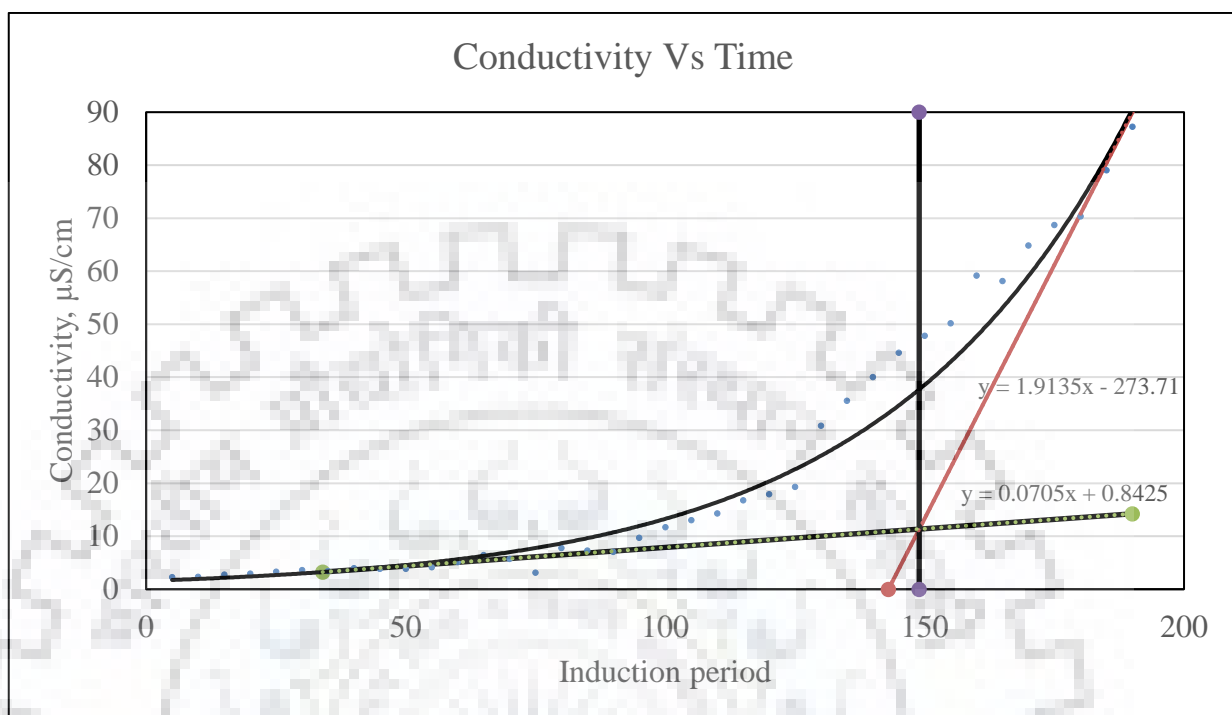| Time(min)	conductivity(µs/cm)	Time(min)	conductivity(µs/cm)
5	2.34	100	11.77
10	2.38	105	13.11
15	2.84	110	14.35
20	3.02	115	16.84
25	3.36	120	17.96
30	3.66	125	19.36
35	3.5	130	30.9
40	4.01	135	35.6
45	3.9	140	40.1
50	3.88	145	44.7
55	4.2	150	47.9
60	5.19	155	50.2
65	6.48	160	59.2
70	5.79	165	58.2
75	3.17	170	64.9
80	7.83	175	68.8
85	7.35	180	70.4
90	7.12	185	79.1
95	9.77	190	87.3

Fig 3.2Graphical determination of induction time (t) by the tangent method

3. 3 THERMAL STABILITY

Thermal stability is the indicator used to check whether Biodiesel can endure high temperature or not. High thermal stability of Biodiesel at 400^0C is shown in Fig 4.13, whereas cooking oil shows relatively less thermal stability at 300^0C in Fig. 4.12.

TGA measures change in mass - loss of weight as change in temperature. As shown in the fig 4.12 weight percentage of the oil sample decreases as increase in the temperature. In the range of temperature 200-300°C weight of the sample sharply reduce from 93.46% to 15% and after then it remains almost constant.

3.4 CLOUD POINT AND POUR POINT

As per the experimental results of the sample biodiesel, Cloud point and pour point have been closed to the standard biodiesel. If it doesn't match the specified standards then reduction as per the need is possible by adding ethanol to meet the standard specifications. Table 4.3 compares the Sample biodiesel and standard biodiesel's property.
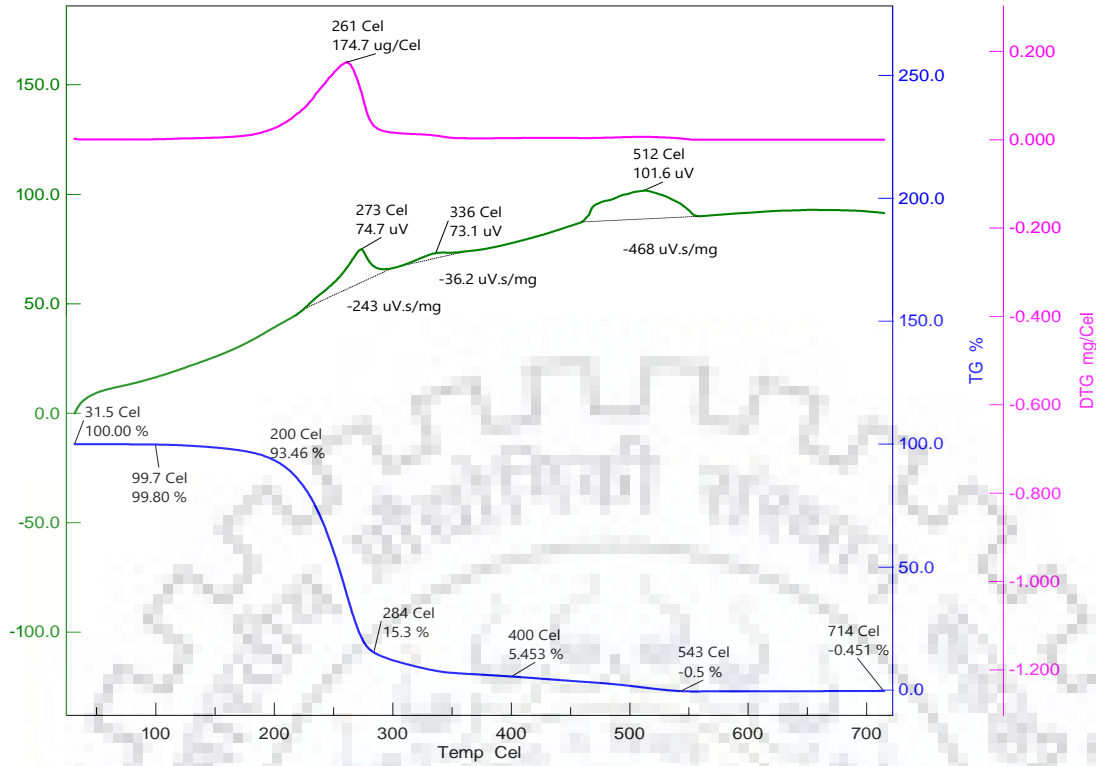
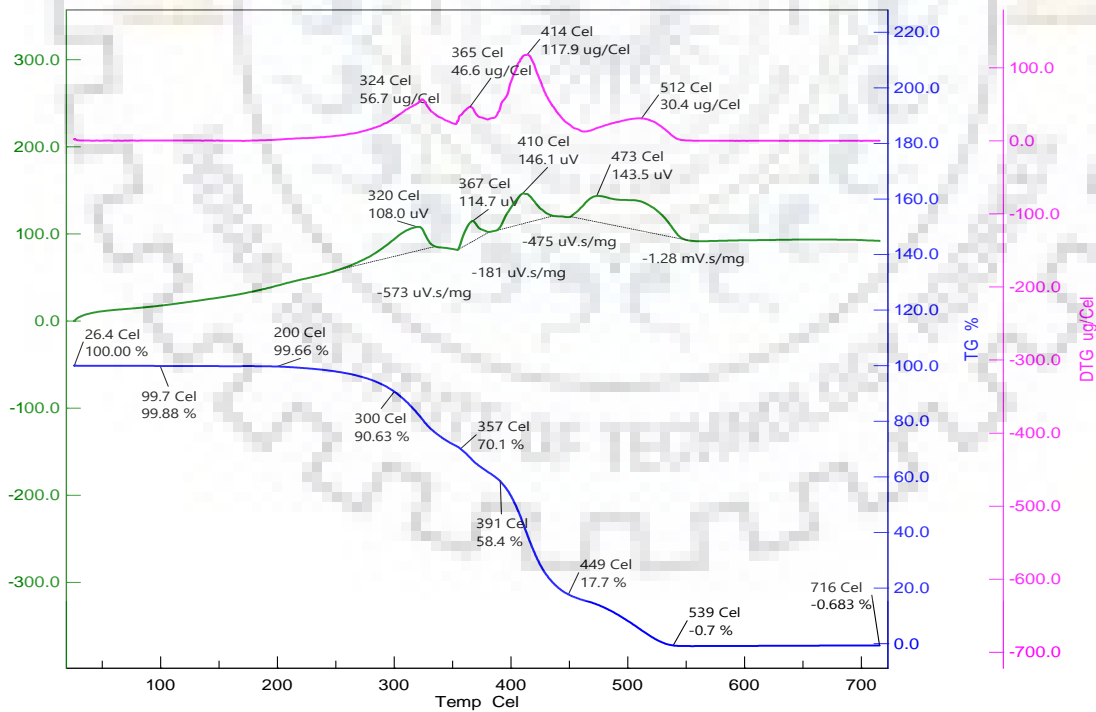**Fig3.3: TGA of waste cooking oil (dry air atmosphere)**

Fig3.4:- TGA of biodiesel produces from WCO (dry air atmosphere)

Table 3.3: Cold flow properties for biodiesel and oil sample

Cold flow property	Biodiesel sample 1	Biodiesel sample 2	WCO sample	Biodiesel ASTM 6751	Diesel IS 1460
Cloud point	14.3°C	14°C	2°C	-3 to 12	5
Pour point	11.5°C	10.5°C	-3°C	-15 to 10	3

3.5 ENGINE PERFORMANCE USING BIODIESEL

Biodiesel testing has undergone using Diesel engine whose experimental setup, measurements and results are discussed below:

3.5.1 Diesel engine

A Kirloskar made single cylinder engine generating set of 2KVA rating was used in experimentation. The filter unit of diesel engine was disconnected from its diesel tank and connected with directly fuel measuring unit.

3.5.1.1 Experimental Setup for Engine Test

Biodiesel is tested on the engine to check the performance of the engine and technical specification of engine is shown in Table

Table3.4: Technical specification of engine

S.no.	Parameters	Details
1.	Make and model	Kirloskar, AA35
2.	Type of engine	Vertical, 4-stroke, single acting high speed compression ignition diesel engine
3.	No of cylinder	1
4.	Rating @ 1500 rpm	2.6 kW (3.5 bhp)
5.	Base	30mm
6.	Stoke	76cm
7.	Cubic capacity	0.382 liters
8.	Compression ratio	15.6:1
9.	Duel timing for standard engine by spill (BTDC)	24°
10.	BMEP @ 1500 rpm	5.5 kg/mm^2
11.	Rated speed	1500rpm
12.	Direction of rotation	Clockwise when looking at flywheel end

3.5.2 Generator

A single phase synchronous generator directly coupled with diesel engine was used. The technical specification of generator is given in below table

Table3.5: Technical specification of generator

S.no	Parameters	Details
1.	Make	Kirogen alternate single phase
2.	Model	KBM-102
3.	Output	2KVA
4.	Voltage	200V
5.	Current	8.7Amp
6.	Power factor	1
7.	Frequency	50Hz
8.	Speed	1500 RPM

3.5.3 Emission meter/smoke meter

With regard to the exhaust emission, MRU air emission monitoring system is used to measure the CO, HC and NO_x emission.

3.5.4 Resistive type load panel

The resistive type load panel was fabricated which is connected with voltmeter, current meter and wattmeter.

3.5.5 Fuel flow measuring unit

The fuel measuring unit consist of graduated transparent glass cylinder. The cylinder is attached with wood stand and top end of the cylinder was open and bottom end is connected with the stop valve. The outlet stop valve is connected with PVC pipe.

3.5.6 Experimental procedure for testing of engine

The engine was prepared to bring it in starting condition and it was coupled directly to the alternator and the loads are provided by electrical resistance. The connection was made between the separate fuel measurement units with the engine. A resistive load panel was attached with the output of the generator. The engine-generator set run initially using diesel for

15minutes at each part load of 0%, 25%, 50%, 75% and 100% of 2kW. The RPM of the generator was maintained at 1500. The fuel consumption at each case was measured by stopwatch. Different sample of diesel and blends of biodiesel were prepared. Samples were mixed properly before using in the engine. During each sample, the filter of the diesel engine was opened and complete mixture of biodiesel and diesel was drained out so that it could not impure with next sample. The diesel is blended with the biodiesel prepared in the different quantities namely B_0, B_5, B_{10}, B_{20}, B_{30}, B_{50}, and B_{80} where subscript indicates the percentage of biodiesel in mixture with diesel. During the experiment, the flue gases are measured by smoke meter (flue gas analyser) and these flue gases were O_2, CO, NO, NO_x and SO_2. Flue gas temperature was also measured by smoke meter. After conducting the experiments the results are obtain. The graphical representation of the results are given below

Table 3.6: Emission of flue gas at 0% load

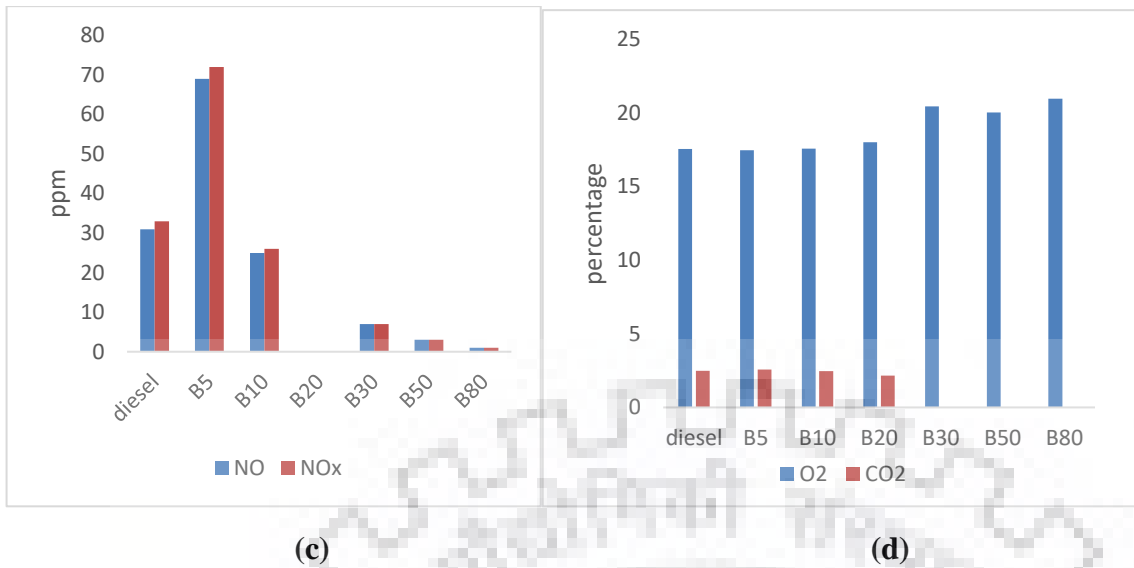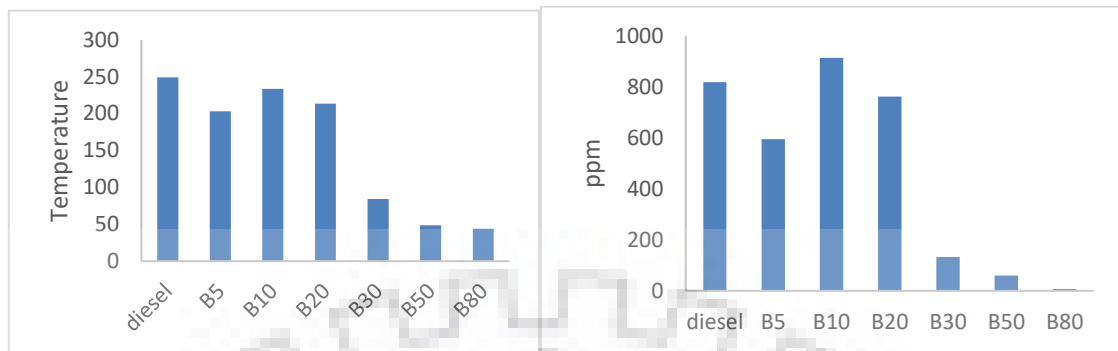| Properties	B_5	B_{10}	B_{20}	B_{30}	B_{50}	B_{80}	diesel
O_2	17.47	17.59	18.02	20.46	20.04	20.97	17.56
CO	696	993	717	117	30	5	1012
NO	69	25	0	7	3	1	31
CO_2	2.57	2.46	2.16	0	0	0	2.48
FT	153	165.9	165.8	87.9	44	43.5	148.9
No_x	72	26	0	7	3	1	33

(a)

(b)

(c) (d)
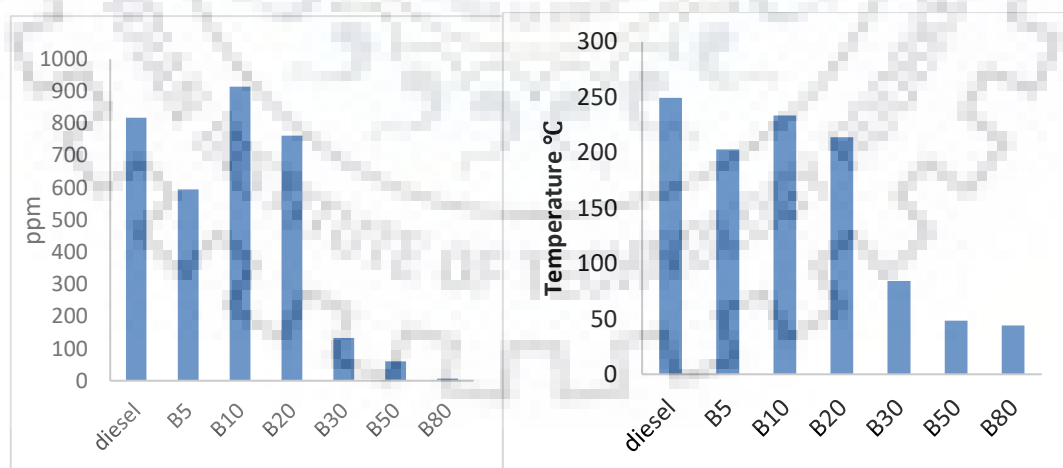
Fig 3.5: Emissions of (a) CO (b) flue gas temperature (c) NO and NOx (d) O₂ and CO₂ at 0% load

As shown in the Fig 4.15 decrement in the emission of flue gases were obtained for all types of biodiesel blends used, which were B_0, B_5, B_{10}, B_{20}, B_{30}, B_{50} and B_{80}. As shown in fig (a) the emission of CO gas decreases along with the increasing biodiesel blends. It was also observed that at after B_{20}, the CO emission decreases drastically for B_{30}, B_{50} and B_{80} denoting that with addition of more biodiesel, the blend burns more efficiently after B_{20}. Same phenomena can be observed from Fig 4.15(b) for flue gases temperature. For B_0, B_5, B_{10} and B20 the flue gas temperature remains between 200—250 ^{0}Cwhereas, for B_{30}, B_{50} and B_{80} the flue gas temperature drastically decreases to around 50 ^{0}C. This denotes that there with the increase in the blend quantity the unburnt fuel decreases. As shown in Fig 4.15(c), the NO_x emission also follows the footsteps of CO. After B_{10}, increasing the quantity of biodiesel, the NO_x drastically reduces and reaches value of below 10ppm. As temperature also decreases around B_{20}, it indicates the lower combustion value for the decrease in the amount of NO_x gases. As far as emission of Co_2 is concerned, it attains a value of 0 for bled above B_{20} as shown in Fig 4.15(d) denoting hardly any combustion of the fuel. Hence it is not suggested to use blends above B_{20} for practical purposes.

Table 3.7: Emission of flue gases at 25% load

Properties	B₅	B₁₀	B₂₀	B₃₀	B₅₀	B₈₀	diesel
O₂	15.96	15.88	16.43	20.2	20.86	20.93	15.8
CO	595	914	762	133	60	7	818
NO	134	106	88	14	5	1	134
CO₂	3.7	3.47	3.34	0	0	0	3.8
FT	203	233.4	213.7	84.1	48.5	44	249.3
NOₓ	142	111	92	15	5	1	141

(a)(b)
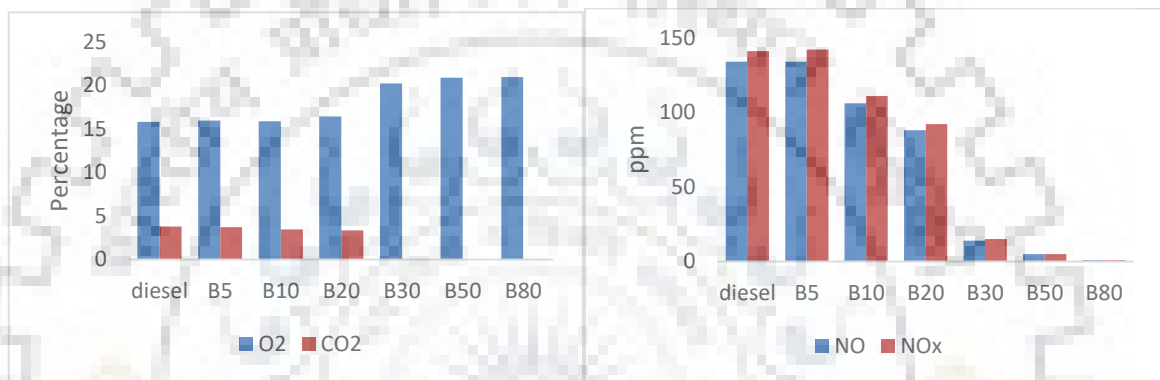
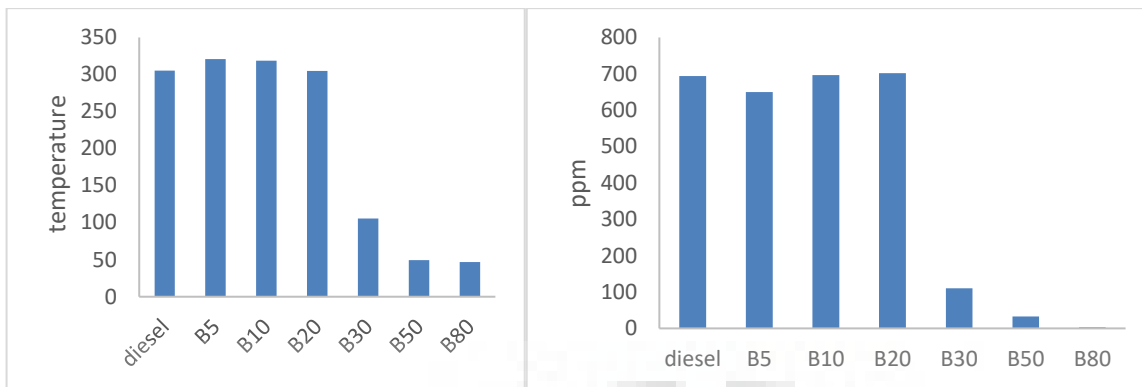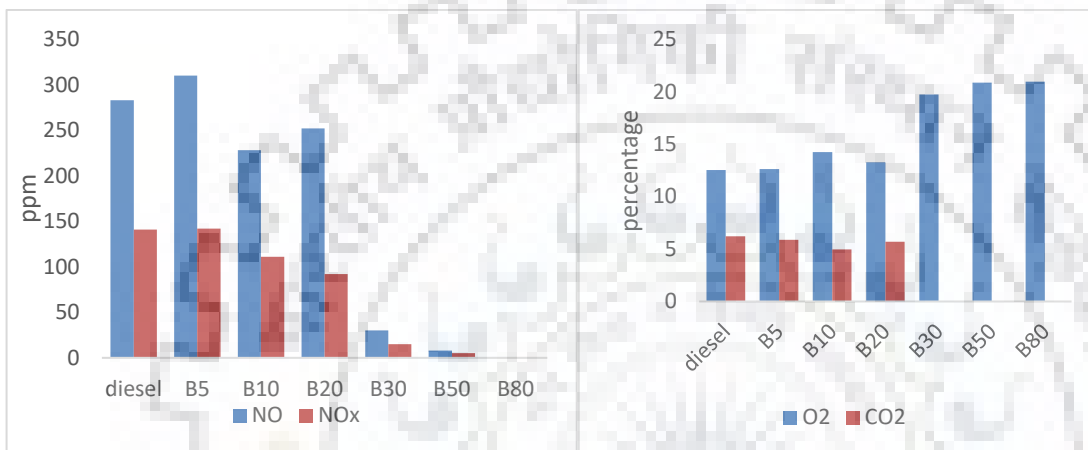**(c)**   **(d)**

Fig 3.6: Emissions of (a) flue gas temperature (b) CO(c) O_2 and CO_2 (d) NO and NO_x at 25% load

Table 3.8: Emission of flue gases at 50% load

	50% load						
Properties	**B_5**	**B_{10}**	**B_{20}**	**B_{30}**	**B_{50}**	**B_{80}**	**Diesel**
O_2	12.61	14.24	13.28	19.75	20.86	20.95	12.54
CO	650	697	702	110	33	3	694
NO	310	228	252	30	8	1	283
CO_2	5.89	4.97	5.69	0	0	0	6.23
FT	321	318.6	305	105.74	49.2	47	305.2
NO_x	295	239	265	35	8	1	297

55

(a)(b)

(c)   **(d)**

Fig 3.7: Emissions of (a) flue gas temperature (b) CO(c) NO and NO_x(d) $O_2$and CO_2at 50% load

Table 3.9: Emission of flue gases at 75% load

Properties	B_5	B_{10}	B_{20}	B_{30}	B_{50}	B_{80}	Diesel
				75% load			
O_2	9.21	10.07	10.56	19.64	20.91	20.91	9.9
CO	650	795	724	75	12	4	958
NO	520	432	424	45	4	3	468
CO_2	8.4	8.06	7.7	0.5	0	0	8.18
FT	402	446.1	422.9	123	51.4	52.7	460.1
NO_x	475	454	445	43.5	4	3	491

(a)   **(b)**
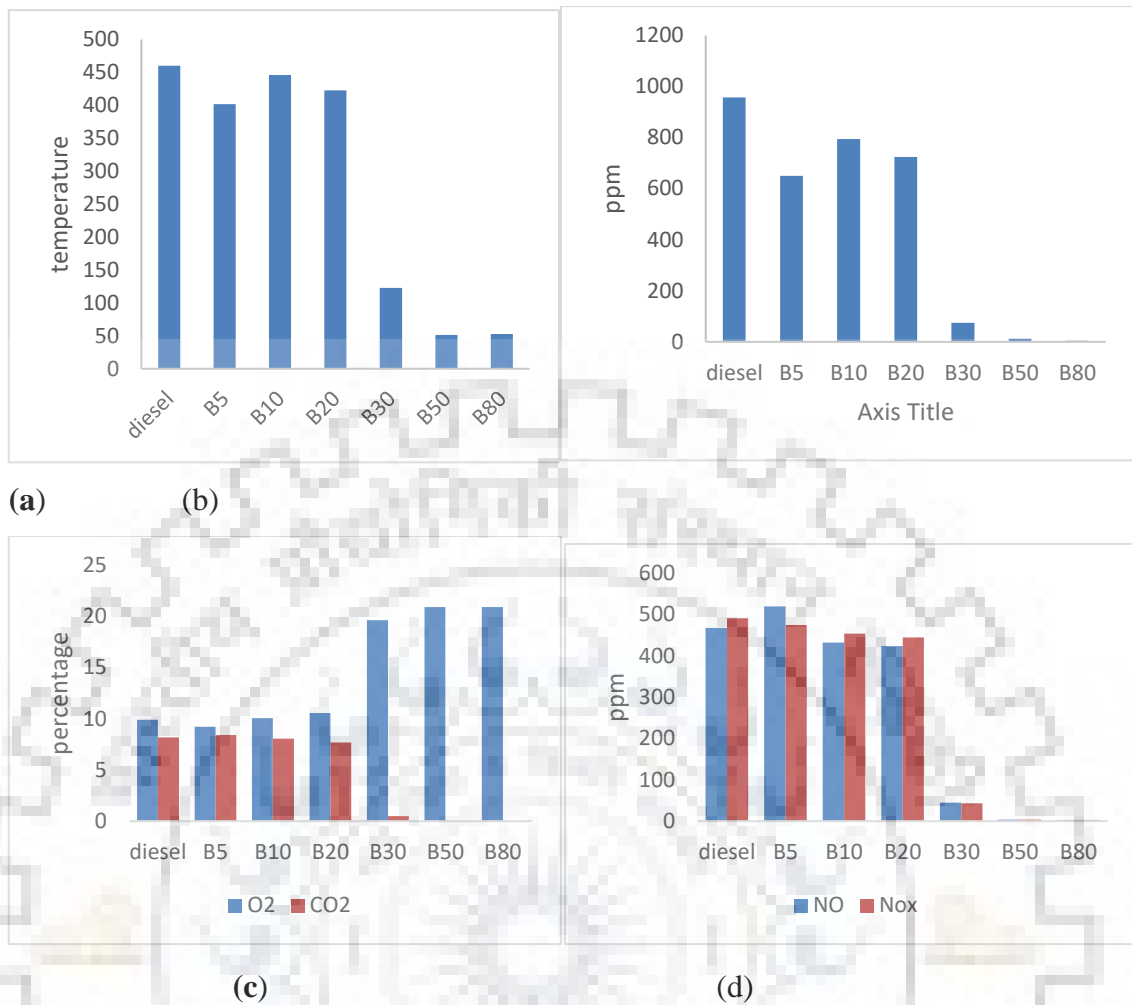

(c)   **(d)**

Fig 3.8: Emissions of (a) flue gas temperature (b) CO (c) O_2 and CO_2 (d) NO and NO_x at 75% load

Table 3.10: Emission of flue gases at 100% load

Properties	B_5	B_{10}	B_{20}	B_{30}	B_{50}	B_{80}	Diesel
				100 % load			
O_2	15.96	7.12	18.34	19.35	20.87	20.93	11.07
CO	595	1415	260	145.87	15	4	441
NO	134	550	150	75	7	3	398
CO_2	3.7	10.5	1.75	0.5	0	0	7.35
FT	203	475	220.6	138.2	55.9	52.7	360
NO_x	142	575	125.8	82	7	3	418

(a)(b)

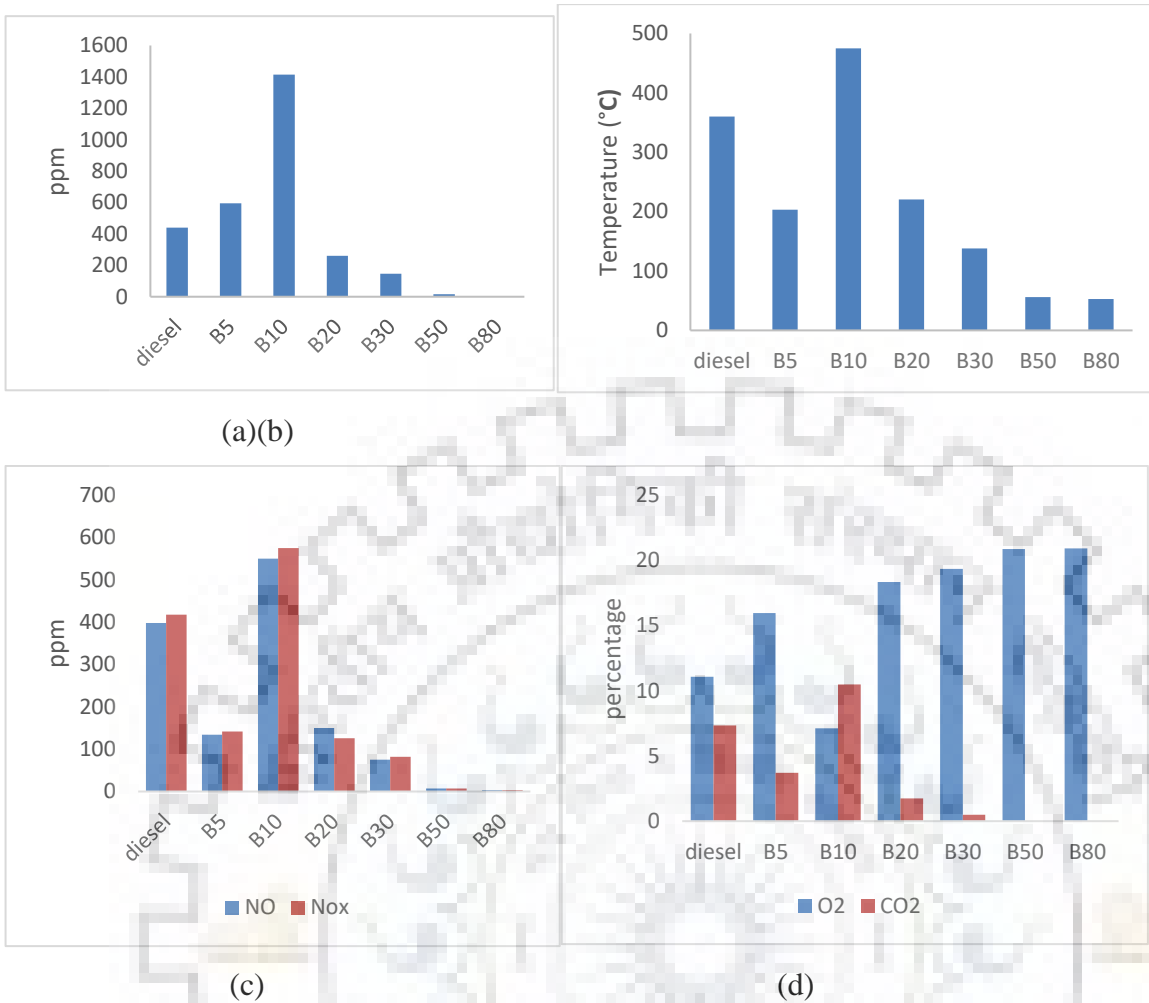(c)   (d)

Fig 3.9: Emissions of (a) CO (b) flue gas temperature (c) NO and NO$_x$ (d) O$_2$ and CO$_2$ at 100% load

From the Fig4.15 (a), Fig4.16 (a), Fig4.17 (a) and Fig4.18 (a), it can be observed that with the increase in the blend, NO$_x$ emission decreases and after B20, it remains minimal. But after increasing load, blends B$_5$, B$_{10}$ and B$_{20}$ show a constant increase in the value of NO$_x$ as well for temperature denoting increasing combustion rate but for B30, B50 and B80 both NO$_x$ and temperature values decreases again denoting lesser and lesser combustion.

From the Fig4.15(d), Fig4.16(c), Fig4.17(d), Fig4.18(c) and Fig4.19(d), it can be observed that with the increase in the blend, CO$_2$ emission decreases and after B$_{20}$, becomes almost 0 while for O$_2$ it reaches value equivalent to environment denoting negligible combustion. But after increasing load, blends B$_5$, B$_{10}$ and B$_{20}$ show a constant increase in the value of CO$_2$and decreasing trend in O$_2$ emission denoting increasing combustion rate.

From analysis of all the three parameters, it can be concluded that combustion decreases after increasing blend after B$_{20}$ for any load

4.1 CONCLUSIONS

Based on the objectives, the following conclusions are drawn:

- The value of FFA for the waste cooking oil was 5%.To reduce it within the standard limit two step processes was adopted which comprises of treatment with acid catalyst, followed by transesterification.

- Properties of waste cooking oil such as viscosity, FFA , flash point , Cloud Point, pour point, Saponification value, acid value, density and iodine value was determined using various experimental setups and result of all these test lead to the conclusion that esterification process should be used for biodiesel production.

- This study produced biodiesel from the waste cooking oil collected from IIT Roorkee messes and their chemical properties were found with kinematic viscosity value of 4.32 as compared to the standard range of 1.9-6, the acid no is 0.25 as compared to the standard value of 0.5. Glycerine value is almost same to the standards. Hence found it of good quality and within the array of specified standards. As per the experimental results of the sample biodiesel, Cloud point and pour point have been closed to the standard biodiesel

- IIT Roorkee campus generates 120 litres of waste cooking oil per month just from messes. Hence the campus has potential to produce at least around 1500 litres of biodiesel annually which will be of good quality. With 93% yield, campus has potential to produce 1395 Litres of Biodiesel

- After conducting performance tasting of oil, it is concluded that higher blends decrease the combustion rate drastically as a result, decrease in CO_2, NO_x and temperature of the flue gases. Moreover, with the increase in the blend of biodiesel, the time taken for consumption increase throughout any load category indicating the decrease in the specific fuel consumption.

- After the comparative analysis with other blending standards, it has been found that B_{20} has produced the best results with maximum combustion and with maximum power.

4.2   RECOMMENDATIONS

This study is limited to biodiesel production from waste cooking oil collected from IIT Roorkee campus hence, the study areas can also be expanded to city level. More efforts can also be put in reducing the cloud point for the biodiesel produced to prevent it from freezing at lower temperature. There is a need for further study regarding finding alternative quick and cost-effective method for FFA treatment.

[1] Classification of energy sources: www.polytechnichub.com/classification-energy-sources.

[2] Alternative energy solution for the 21st century   www.altenergy.org/

[3] Annual Report of (Government of India ministry of new renewable energy mnre.gov.in)

[4] mnre.gov.in/file-manager/User Files/biofuel_policy.pdf (national policy on biofuel)

[5] petroleum.nic.in/sites/default/files/biofuelpolicy2018_1.pdf. (The Gazette of India extraordinary part-1 section-1 NEW DELHI, FRIDAY, JUNE 8, 2018

[6]Sharma, M.P., 2016.Selection of potential oils for biodiesel production. *Renewable and Sustainable Energy Reviews*, *56*,1129-1138.

[7] Kumar, M. and Sharma, M.P., 2013. Production methodology of biodiesel from microalgae. *Int J Appl Eng Res*, *8*(15),1825-1832

[8] Leung, D.Y., Wu, X. and Leung, M.K.H., 2010. A review on biodiesel production using catalyzed transesterification. *Applied energy*, *87*(4), 1083-1095

[9] Jain, S. and Sharma, M.P., 2010. Prospects of biodiesel from Jatropha in India: a review. *Renewable and Sustainable Energy Reviews*, *14*(2), 763-771.

[10] Gaffney, J.S. and Marley, N.A., 2009. The impacts of combustion emissions on air quality and climate–From coal to biofuels and beyond. *Atmospheric Environment*, *43*(1), 23-36.

[11] Behçet, R., Oktay, H., Çakmak, A. and Aydin, H., 2015. Comparison of exhaust emissions of biodiesel–diesel fuel blends produced from animal fats. *Renewable and Sustainable Energy Reviews*, *46*, 157-165.

[12] Amini-Niaki, S.R. and Ghazanfari, A., 2013. Comparison of fuel and emission properties of petro diesel and sunflower biodiesel prepared by optimized production variables. *Fuel*, *109*, 384-388.

[13] Dhanasekaran, R., Krishnamoorthy, V., Rana, D., Saravanan, S., Nagendran, A. and Kumar, B.R., 2017. A sustainable and eco-friendly fueling approach for direct-injection diesel engines using restaurant yellow grease and n-pentanol in blends with diesel fuel. *Fuel*, *193*, 419-431.

[14] Véras, I.C., Silva, F.A., Ferrão-Gonzales, A.D. and Moreau, V.H., 2011. One-step enzymatic production of fatty acid ethyl ester from high-acidity waste feedstocks in solvent-free media. *Bioresource technology*, *102*(20), 9653-9658

[15] Knothe G.2006, Analyzing biodiesel: standards and other methods. Journal of the American Oil Chemists' Society. 83(10):823-33.

[16]Lam, M.K., Lee, K.T. and Mohamed, A.R., 2010. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. *Biotechnology advances*, *28*(4), 500-518.

[17] Phan, A.N. and Phan, T.M., 2008. Biodiesel production from waste cooking oils. *Fuel*, *87*(17-18), pp.3490-3496.

[18] (fats and fatty acids) www.chemistryexplained.com/Di-Fa/Fats-and-Fatty-Acids.html

[19] Sharma, R. and Mann, B., Module 13: Changes occurring in oils and fats during frying.

[20] Raqeeb and Bhargavi R. 2015, Journal of Chemical and Pharmaceutical Research, 7(12):670-681 Biodiesel production from waste cooking oil Department of Chemical Engineering, SRM University, Chennai, India.

[21] Cordero-Ravelo, V. and Schallenberg-Rodriguez, J., 2018. Biodiesel production as a solution to waste cooking oil (WCO) disposal. Will any type of WCO do for a transesterification process? A quality assessment. *Journal of environmental management*, *228*, 117-129

[22] Talha, N.S. and Sulaiman, S., 2016. Overview of catalysts in biodiesel production. *ARPN Journal of Engineering and Applied Sciences*, *11*(1),439-448.

[23]   Knothe, G. and Steidley, K.R., 2018. The effect of metals and metal oxides on biodiesel oxidative stability from promotion to inhibition. *Fuel Processing Technology*, *177*, 75-80.

[24] Kolhe, N.S., Gupta, A.R. and Rathod, V.K., 2017. Production and purification of biodiesel produced from used frying oil using hydrodynamic cavitation. *Resource-Efficient Technologies*, *3*(2), 198-203.

[25] Nanihar, N., Khalid, A., Mustaffa, N., Jaat, N., Sapit, A., Razali, A. and Sunar, N.M., 2017, October. Experiment on the Effects of Storage Duration of Biodiesel produced from Crude Palm Oil, Waste Cooking oil and Jatropha. In *Journal of Physics: Conference Series* (Vol. 914, No. 1, p. 012007). IOP Publishing.

[26] Sinha, D. and Murugavelh, S., 2016. Biodiesel production from waste cotton seed oil using low cost catalyst: Engine performance and emission characteristics. *Perspectives in science*, *8*, 237-240

[27] Dwivedi, G. and Sharma, M.P., 2015. Effect of metal on stability and cold flow property of pongamia biodiesel. *Materials Today: Proceedings*, *2*(4-5), 1421-1426.

[28] Jain, S. and Sharma, M.P., 2014. Effect of metal contents on oxidation stability of biodiesel/diesel blends. *Fuel*, *116*, pp.14-18.

[29] de Araújo, C.D.M., de Andrade, C.C., e Silva, E.D.S. and Dupas, F.A., 2013. Biodiesel production from used cooking oil: A review. *Renewable and Sustainable Energy Reviews*, *27*, 445-452.

[30] Kawentar, W.A. and Budiman, A., 2013. Synthesis of biodiesel from second-used cooking oil. *Energy Procedia*, *32*, pp.190-199.

[31] Mofijur, M., Masjuki, H.H., Kalam, M.A., Atabani, A.E., Shahabuddin, M., Palash, S.M. and Hazrat, M.A., 2013. Effect of biodiesel from various feedstocks on combustion characteristics, engine durability and materials compatibility: a review. *Renewable and Sustainable Energy Reviews*, *28*, 441-455.

[32] Almeida, E.S., Portela, F.M., Sousa, R.M., Daniel, D., Terrones, M.G., Richter, E.M. and Muñoz, R.A., 2011. Behaviour of the antioxidant tert-butylhydroquinone on the storage stability and corrosive character of biodiesel. *Fuel*, *90*(11), 3480-3484.

[33] Demirbas, A., 2009. Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. *Energy Conversion and Management*, *50*(4), 923-927.

[34] Zhang, Y., Dube, M.A., McLean, D.D.L. and Kates, M., 2003. Biodiesel production from waste cooking oil: Process design and technological assessment. *Bioresource technology*, *89*(1), 1-16