Study on Biodiesel Production from Used Vegetable Oil and Raw Vegetable Oils

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BY

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Nomenclature

Symbols	**Meanings**
$	United States currency, dollar
2D	2 dimensional
3D	3 dimensional
ASTM	American society for testing and materials
AV	Acid value
B0	100% diesel
B10	10% biodiesel blended with 90% diesel
B20	20% biodiesel blended with 80% diesel
B40	40% biodiesel blended with 60% diesel
B5	5% biodiesel blended with 95% diesel
BBD	Box–Behnken design
BSFC	Brake-specific fuel consumption
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
BTE	Brake thermal efficiency
C	Catalyst concentration
C.I Engine	Compression ignition engine
CCD	Central Composite Design
CCRD	Central composite rotatable design
CI	Compression ignition
CN	Cetane number
CP	Cloud point
CR	Compression ratio
DOE	Design of experiments
EGR	Exhaust gas recirculation
EGT	Exhaust gas temperature
EN	European Norm
FAME	Fatty acid methyl ester

FC	Fuel consumption
FFA	Free fatty acid
FFSAI	Food safety and standards authority of India
FID	Flame ionization detector
FMCG	Fast moving consumer goods
GC	Gas chromatography
GC-FID	Gas chromatography with flame ionization detection
GHG	Greenhouse gas
H_2SO_4	Sulphuric acid
HB	Heat of combustion of the given sample of biodiesel
hr	Hour
ISO	International Organization for Standardization
IV	Iodine value
KOH	Potassium hydroxide
LHV	Lower heating value
M	Methanol to oil ratio
MA	Mass of the specific gravity bottle
MB	Mass of the specific gravity bottle with biodiesel
MB	Mass of biodiesel to be used for combustion
Mc	Amount of fixed carbon left after combustion
MNRE	Ministry of renewable energy
M_s	Exact mass of biodiesel taking part in combustion
MW_a	Molecular weight of alcohol/acid
MW_f	Molecular weight of each component in the oil
MW_i	Molecular weight of each fatty acid alkyl ester
MW_o	Molecular weight of oil
N	Normality
NaOH	Sodium hydroxide
NO_X	Nitrogen oxides
OS	Oxidation stability
PFAME	Palmitic fatty acid methyl ester

PP	Pour point
rpm	Revolutions per minute
RSM	Response surface methodology
RUCO	Repurpose used cooking oil
RBME	Rice bran oil methyl ester
SOME	Soybean oil methyl ester
SUME	Sunflower oil methyl ester
SUFAME	Sunflower fatty acid methyl ester
SV	Saponification value
T	Temperature
t_1	The time interval in seconds of the liquid to reach from the upper mark to the lower mark of the upper bulb
t_2	The time interval in seconds of the reference liquid water to reach from the upper mark to the lower mark of the upper bulb
TLC	Thin layer chromatography
T_S	Temperature rise due to burning of given sample of biodiesel
U.S. Department of Energy	United States Department of Energy
UFO	Used frying oil
ULSD	Ultra-low Sulphur diesel
URBME	Used rice bran oil methyl ester
USA	United States of America
USOME	Used soybean oil methyl ester
USUME	Used sunflower oil methyl ester
UV	Ultraviolet
V	Volume of the biodiesel
v/v	Volume/volume
VPO	Vegetable palm oil
W	Calorimeter's energy equivalent
w/w	Weight by weight
α	Alpha
η_1	Viscosity of the liquid

η_2	Viscosity of the water
ρ_1	Densities of the liquid
ρ_2	Densities of the water
μ	Yield of biodiesel from used vegetable oil(soybean)
β_0	Offset term
β_i	Linear effect
X_i	ith independent variable
X_{ii}	Squared effect
β_{ii}	Interaction effect
β_{ij}	jth independent variable

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Chapter 1
Introduction

1.1 Introduction

The world is facing two crises: the depletion of fossil fuels and environmental deterioration. Petroleum reserves have been depleted as a result of indiscriminate extraction and consumption of fossil fuels. Petroleum-based fuels come from finite reserves. These limited deposits are concentrated in one area of the planet. As a result, countries without these resources are suffering a foreign exchange crisis, owing mostly to crude petroleum oil imports. As a result, it is vital to seek for alternate fuels that may be created using locally accessible resources as reported by Singh S.P. and Singh D, 2010. Gopinath et al., 2015 revealed that the rapid decrease in the reserves of fuels has led to exploring the fuels derived from plants. According to a report by World Oil Outlook, 2016, the rapidly expanding global energy consumption induced by population expansion, improved living standards, and greater economic activity has resulted in massive greenhouse gas (GHG) emissions. The same report also says that, global fuel oil consumption will reach 109.4 million barrels per day by 2040. However, this increased demand for oil fuel faces two significant challenges: lack of resources and detrimental environmental effects from its use.

Petroleum oil consumption is well recognised to have the second highest proportion of all energy resources because to its usage in transportation (land, air, and sea), power plants, building, and industrial operations. According to Kalam et al., 2011, the consumption of diesel fuel is larger than that of other petrol products due to the superior efficiency of diesel engines over other internal combustion engines. As a result, several research attempted to replace fossil diesel fuels with renewable fuels. At the World Exhibition in 1900, Rudolf Diesel displayed a diesel engine powered entirely by peanut oil as verified in a study by Lin et. al., 2010. Moreover, the rising concerns over the deterioration of the environment have forced researchers to think of an alternative with properties comparable to that of diesel and an alternative source that is renewable, energy efficient as well as environment-friendly as discussed by Elkelawy, et al., 2020. The study carried out by Rajkumar and Thangaraja, 2019 tells that the transportation sector is the second highest energy-consuming sector in our country. The major concerns are the emission of oxides of nitrogen and smoke which are detrimental to our health and environment. According to Workman, 2022 the third largest crude oil importer in the world is India. The Economic Times, 2022 shared the fact that India had spent USD 119.2 billion on the import of crude oil in the financial year (2021-2022) which turns out to be a huge burden on the economy of our nation. The burning of crude oil contributes to air pollution and global warming as well.

The graph shown in Fig. 1.1 from CEIC, 2022 shows the import of crude oil in terms of barrels per day from 2010 to 2021 in India. The X-axis denotes the year and the Y-axis denotes the barrel/day imported into India.

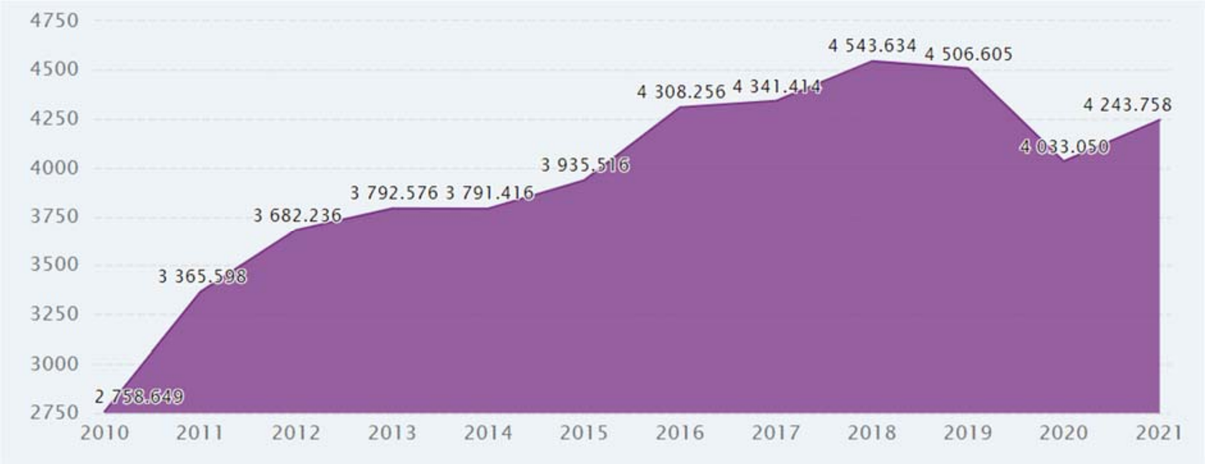


Fig. 1.1 Import of crude oil by India (barrel/day)
(Source: https://www.ceicdata.com/en/indicator/india/crude-oil-imports)

A report by International Energy Agency, 2009, suggests that in 2005, India utilised 30 million tonnes of oil in the transportation industry in 2005, with petrol accounting for 29% and diesel accounting for 71%. According to Gonsalves, 2006, Indian energy consumption is predicted to expand at a 4.8% annual pace over the next two decades. Many possibilities predict that India's oil consumption would more than treble by 2030. According to Hindustan Times, 2022, the provisional data of the Petroleum Planning and Analysis Cell, India reported that in 2019-20, India's total petroleum consumption was 194.3 million metric tonnes. According to a report by the International Energy Agency, 2006, the consumption of biofuel has been speculated to reach 92.4 mega tonnes oil equivalent by 2030. World Oil Outlook, 2016, reported that according to the Government of India's Ministry of Railways, Indian Railways utilise more than two billion gallons of diesel every year. The Ministry also adds that a slight reduction in diesel usage through biodiesel blending can result in significant fuel savings, as well as the benefits of a cleaner environment owing to fewer carbon emissions. Martinez et al. 2014. informed that the alternative renewable fuel that comes under light is biodiesel. Biodiesel is derived from the oil extract of plants or fats of animals. It is an alternative to diesel and can also be used as fuel additive.

In an extensive study by Dhyani et al., 2015, it has been reported that non-edible oil seeds are the primary source of biodiesel in India, and the method for producing it is indigenous. Bio-diesel is bio-degradable, non-toxic, and sulphur-free. Biodiesel production capacity of tree-borne oils seeds is almost 20 million tonnes per year. The estimated potential ranges from 0.1 to 20 million tonnes, but only 20 to 25% is being used. In India, there are approximately 150 non-edible tree-borne oilseeds out of which the few which are often utilised in India include Mahua, Pongamia Pinnata, Jatropha, Neem, Pilu, Sal, Kusum, Jojoba, Undi, and Bhikal. The oil content in these species ranges from 21 to 73%. Among the numerous ttree-borne oil seeds, Jatropha Curcas and Pongamia Pinnata were determined to be the most ideal for biodiesel production due to characteristics such as hardiness, ease of handling, and excellent growth in a variety of agro-climatic situations. The oils of these species are ideal for biodiesel production. Ghadge and Raheman, 2003 carried out an experiment that showed that three-step transesterification has been used in the case of transesterification of mahua oil. The biggest disadvantage of adopting biodiesel is the high production cost, which might account for 75% of manufacturing costs, raising the production cost of biodiesel to nearly 1.5 times that of the conventional diesel used as reported by Ma and Hanna, 1999. Most of the oils used for biodiesel production are edible in nature. They face tough competition between food and fuel. The non-edible feedstock is likewise useful for manufacturing biodiesel giving an appreciable yield. The conversion process of biodiesel depends upon the free fatty acid content of the oil. If it is greater than 2.5% then the two-step or three-step process is used as discussed by Strezov and Evans, 2015.

An article based on the concept of waste to energy by MNRE, 2021, (Ministry of Renewable Energy) states that being a developing nation, India is undergoing industrialization and urbanization at a rapid pace. The developments taking place all around the country have led to increased quantities of waste which are causing detrimental effects on the environment. Lahiri, 2017 reported that proper treatment of waste in any form whether solid, liquid, or gaseous is important before permanent disposal. Waste management is ensured to be significant if there is proper segregation of waste at the source itself and then the waste goes through different paths of recycling in order to safeguard the ecological balance. One of the forms of liquid waste which is disposed of without any treatment more often is the used vegetable oil which originates from vegetable oil made from biological sources such as palm, soybean, olive, and sunflower as discussed by Lam et al., 2016. A report by Economic Times, 2019 suggests that India uses 2,700 crore litres of vegetable oil, out of which 140 crore litres of used vegetable oils can be successfully collected for the production of a useful form of energy namely biodiesel. The present scenario is such that India has 850 crore litres of diesel requirement per month on average. The government targets biodiesel blending of diesel by 5 percent by the end of 2030. Biodiesel requirement is enormous which also ensures successful waste-to-energy conversion.

Lal and Sharma, 2011 revealed that continual extraction and consumption of fossil fuels have resulted in a decrease in underground carbon reserves. Sahar et al., 2018 state that the huge increase in energy demand is due to urbanization and industrialization which is decreasing the non-renewable resources gradually. Biodiesel has become an interesting alternative because of its environmental benefits. Moreover, the huge availability of used vegetable oil and animal fats can be channelized for biodiesel production as their improper disposal leads to contamination of water and land resources as investigated by Chhetri et al., 2008. Murugesan et al., 2009 confirm that biodiesel is derived from renewable, biodegradable, and non-toxic resources.

Zayed and Jehad, 2014 came to the conclusion that the price of biodiesel is significantly reliant on the raw material used in its production. Therefore, the high cost of raw materials is a major barrier to the commercialization of biodiesel. In comparison to raw oils, used vegetable oil is cheaper and also available in abundance, therefore, can be incorporated as permanent feedstock for mass-scale production of biodiesel. The production of biodiesel from used vegetable oil provides an acceptable way of disposing of fried oil. Apart from this utilizing the waste fried oil reduces the dependency on edible oils and can also reduce the farming of various plants used as feedstock for biodiesel production. The study by Shen et al., 2018 reveals that China's biofuel consumption was 2.1 million tonnes in 2014 with feedstock changing from corn oil to used vegetable oil. Evaluation by Bautista et al., confirms that biodiesel is a non-conventional fuel that is compatible with blended-form conventional diesel engines. Babaki et al., 2017 state that the substitution of diesel with biodiesel not only lowers emission and toxicity but also enhances biodegradation. Improper disposal of the oil may lead to environmental risks and adverse effects on human health. Used vegetable oil is a low-cost feedstock for biodiesel production instead of those derived from refined vegetable oils. It was confirmed in a report by Agarwal, 2016 that India is the leading importer and consumer of edible oils in the world. Soybean oil imported by India has increased four times, over the previous five years to more than 4 million tonnes in 2016 according to data published by the country's vegetable oils industry body. India's imports of soybean oil are predicted to increase by 40% over the next ten years, the U.S. Department of Agriculture estimated in May 2016. FSSAI, 2018 (Food Safety and Standards Authority of India) reported that World Biofuel Day FSSAI launched

RUCO (Repurpose Used Cooking Oil), for the collection process of used vegetable oi and for conversion of used vegetable oil to biodiesel. India though being a producer, imports soybean oil to serve the expanding consumer base.

As reported by Murugesan et al., 2009 a large percentage of this oil is used by many food chains for frying purposes as soybean is considered healthier than palm oil and likewise, they need to maintain certain food value of their products. This fried oil can be collected and used for biodiesel production without disturbing the food fuel balance. Several biodiesel synthesis techniques have been investigated, but transesterification using alkali catalysts yields a high rate of triglyceride conversion to methyl ester.

The reason biodiesel is an excellent alternative to diesel fuel is its renewability and non-pollutant nature. Recycling used vegetable oil as feedstock for biodiesel production can not only decrease the cost of production but also helps to keep the environment clean and healthy. This has been a motivation for the hypothesis that if the used vegetable oils and non-edible oils are investigated thoroughly in order to obtain optimised production of biodiesel, then it can be made economically available in blended form with diesel. A deep and detailed understanding of the whole process is required to materialize the hypothesis. This would be explained in upcoming chapters. The process of biodiesel production by optimization techniques and without the application of heat to the process of transesterification can decrease the cost of production of biodiesel further and ensure which type of feedstock is the best suited for large-scale production.

1.2 Research Motivation

A lot of work has been done in the field of biodiesel production in order to form blends with diesel, still, the cost of biodiesel remains a major drawback in this field. When raw sources like non-edible oil extract of plants is considered, the production of the plant becomes an important factor. Jatropha, being an important feedstock for biodiesel production is widely grown. But it also requires barren land for production. With the yearly production of the plant, the quality of the soil will also decrease with time if proper care is not taken. All these factors require time as well as finance. Now if used vegetable oil is considered, then this whole problem of plantation and procurement of feedstock can get sorted. Times of India, 2009 reported that Indian Railways is reportedly consuming biodiesel in large amounts. The Clean Cities Alternative Fuel Price Report, 2023 gives the national average fuel price of biodiesel as 4.95$ per gallon which stands at 1.30$ per litre and that of diesel is 4.25$ per gallon which stands at 1.12$ per litre in the USA. Another report of Indonesia known as Biofuels Annual, 2022 states that the price of biodiesel is 1.04$ per litre and the price of diesel is 0.67$ per litre in Indonesia. The calorific value of biodiesel is 12% less than that of diesel as reported by Olivera and Da Silva, 2013. Therefore, it can be said that the calorific value of 1 kg of diesel is equivalent to the calorific value 1.120 kg of biodiesel.

The question arises that despite the production of biodiesel in tonnes, why is it not still ready for the most common transport use i.e., privately owned public transports and four-wheelers? There are many important factors responsible for that. The price of the feedstock and its availability are important for the proper and continuous production of biodiesel in sufficient amounts. If used vegetable oil is used with free fatty acid content less than 2.5%, then the price of biodiesel will be less, because this will only require one step of alkali-based transesterification. If the feedstock is animal-based, the process will become costly as it will require proper pre-treatment and acid-based esterification followed by alkali-based transesterification. So here the term optimisation comes into play. Initially, the selection of the right kind of waste oil is required, depending upon the types of oil used in the area. The process of biodiesel production is very simple, but there are a set of process parameters. Change in one of the parameters can change the yield. During the process of conversion of oil to alkyl ester all the process parameters work simultaneously. Therefore, a change in one of the parameters will no longer affect the yield linearly. Keeping the cost of the reactants in mind, a set of parameters must be selected which will give the optimised yield. Hence optimisation of the process parameters is required. There are softwares like Minitab and Statgraphics which will help to achieve optimisation of the process parameters by using the statistical methodology and give the set of parameters by which optimized yield of biodiesel can be obtained.

The process of transesterification requires heat energy to move the reaction in the forward direction for a stipulated time of two hours. The transesterification can be done under ambient temperature conditions with the best-fit data. This will considerably decrease the cost of production. The structural analysis of alky esters of different types of used vegetable oils are required, to compare the difference in the compositions in with-heat and without-heat conditions. The use of biodiesel in diesel engines change the properties of the exhaust gas and the change due to the use of biodiesel from used vegetable oils from different sources has to be studied.

1.3 Aims and Objectives

The research concerns biodiesel production from used vegetable oil collected from different sources. The collection of oil is from different sources the type of oil does not remain constant. Since the yield depends upon the type of oil used, each transesterification is carried out with only one kind of oil without any mix. This research aims at the production of biodiesel from used vegetable oils and raw oils of different kinds by a very simple and economic process that can be scaled up for large-scale production. In order to achieve this, optimization of the process parameters becomes one of the crucial steps. Apart from the optimization by trial-and-error procedure, a statistical approach can also be adapted to study the interactive effect of the operating parameters on the yield of biodiesel. Depending upon the kind of oil, the yield, as well as the reaction parameters, will differ. Structural analysis of biodiesel has to be done in order to derive its correlation with the physicochemical properties of biodiesel. The constituents of fatty acid alkyl ester can be determined by gas chromatography.

Another interesting approach can be taken to decrease the cost of production of biodiesel. The ambient temperature of the tropical region enables to provide sufficient temperature for the transesterification process. This can be investigated in detail by discussing the 'with heat' and 'without heat' conditions. The properties of biodiesel can also be further investigated to determine its closeness to the standard properties. The engine performance of a compression ignition (CI) engine can be evaluated with blended samples of biodiesel from different kinds of feedstock. The aims and objectives of the study are as follows.

1. **Biodiesel production from different types of used vegetable oils and raw vegetable oils(non-edible).**
2. **To optimise the yield of biodiesel by changing the operating parameters within the given range.**
3. **Optimisation of process parameters of biodiesel production from used vegetable oils by response surface methodology.**
4. **To study the performance of a diesel engine fuelled with biodiesel blends produced from different used vegetable oils blended with diesel.**
5. **Comparison of the yield and properties of biodiesel from used vegetable oil of different plant-based feedstock.**
6. **Feasibility of biodiesel production from different used vegetable oils under ambient temperature conditions.**

7. Comparative study of the differences in the components of the fatty acid alkyl ester from each kind of source in with-heat and without-heat conditions by performing gas chromatography of each sample.

The present research comprises basically four sections. The first is the production of biodiesel from different shops selling fritters. Then the type of oil for each reaction is kept unique, without any mixing. This is done by fixing the sources of oil procurement. The second phase is the optimisation which is carried out with the oil which gave the maximum yield in the last phase. The statistical approach has been adopted to get the optimised yield. The third phase contains the synthesis of biodiesel from different kinds of used vegetable oils under with-heat and ambient temperature conditions. The difference in the fatty acid methyl ester components of the same type of oil under different operating conditions will be studied. The changes in the different physicochemical properties of the biodiesel under with-heat and without heat conditions will be analyzed. The last phase involves the engine performance of the compression ignition engine with biodiesel produced from different types of used vegetable oils.

Chapter 2
Literature Review

2.1 Review of Earlier Work

India ranked third in consumption of oil with 212.7 million tons in 2016 preceded by USA and China as mentioned in the Statistical Review of World Energy, 2021. Lack of sufficient local oil reserves in the country has led to huge import of the oil to balance the supply and demand. As a result, the economy is getting burdened. Al-Widyan and Al-Shyoukh, 2002 have confirmed that the environment and human health is getting adversely affected due to the harmful gas emissions, and this has set off the search of alternative sources of energy available within the country. Leung and Guo, 2006 have stated that biodiesel can be produced from various sources but the cost of feedstock makes the resultant cost of biodiesel high which is a major setback in its commercialization. At this stage used vegetable oil has proven itself as a significant low-cost feedstock for biodiesel production. Soybean oil import by India has increased four times in the last five years to more than 4 million tons in 2016, according to data compiled by the country's vegetable oils industry body. One of the studies by Banerjee et al., 2014 throws light on estimation of used vegetable oil thrown away by shops selling fritters in Kolkata. Chincholkar et al., 2005 explains that vegetable oils can be used as alternative fuels because they are biodegradable, nontoxic, and clean fuels. Vegetable oils and their derivatives as diesel engine fuels lead to substantial reductions in sulphur, carbon monoxide, polycyclic aromatic hydrocarbons, smoke and particulate emissions.

2.1.1 Low-Cost Feedstock

Ejaz and Younis, 2011 reviewed that more than 300 feedstocks have been identified which could be used to produce biodiesel. The conventional and non-conventional feedstock, used for the production of biodiesel, is shown in Table 2.1. These include edible oils, non-edible oils, wild oils, used vegetable oils and animal fats. Soybean oil is commonly used in USA, rapeseed oil in European countries, palm oil in Malaysia, and jatropha oil in India.

Singh S.P. and Singh D., 2010, suggested that the source of biodiesel largely depends upon the climate of a region. The climate decides the nature of the crop to be grown which indirectly infers the nature of the feedstock for biodiesel in that area. Basically, biodiesel needs to fulfil two criteria which are low cost and large-scale production.

Since the prices of edible vegetable oils are higher than that of diesel fuel, therefore waste vegetable oils and non-edible crude vegetable oils are preferred as potential low-priced biodiesel sources as reported by Ejaz and Younis, 2011.

Table 2.1 Conventional and Non-Conventional Feedstock

Conventional Feedstock		Non-Conventional Feedstock
Mahua	Used Cooking oil	Tallow
Piqui	Napus	Lard
Palm	Soybeans	Poultry fat
Karang	Rapeseed	Fish Oil
Tobacco Seed	Canola	Bacteria
Rubber Plant	Jatropha	Fungi
Barley	Jojoba Oil	Algae
Rice Bran	Laurel	Microalgae
Sesame	Babassu	Tarpenes
Sunflower	Brassica	Latexes
Coconut	Carinata	
Cynara cardunculus	Barassica	
Pongamiaglabra		

(Source: Ejaz and Younis, 2011)

In a study by Saydut, 2008, sesame (Sesamum indicum L.) seed was investigated as an alternative feedstock for the production of biodiesel fuel. The methyl ester of sesame (Sesamum indicum L.) seed oil was prepared by transesterification of the crude oil. Transesterification shows improvement in fuel properties of sesame seed oil. This study supports the production of biodiesel from sesame seed oil as a viable alternative to the diesel fuel.

Fish oil is produced in large quantities by the fish-processing industry as a by-product in Iran. As studied by Yahyaee et al., 2013, this by-product has similar calorific value to petroleum distillates and is a renewable energy source. Several studies have been carried out for using fish oil as fuel for diesel engines. The fish oil has lower content of carbon and slightly higher content of hydrogen. The fish oil also has higher flash point but much lower kinematic viscosity. As a result, the viscosity of the blend is low.

As investigated by Sinha et al., 2008, India is the second largest producer of rice in the world, next to China. Rice bran is a low value co- product of rice milling, which contains approximately 15–23% oil. Currently, the industry is processing about 3.5 million tonnes of rice bran, leading to a production of about 0.65 million tonnes of oil. This non-edible oil remains mostly underutilized. A huge quantity of rice bran is produced (approx 8% w/w of paddy), which is an agricultural waste. It has significant potential as an alternative low-cost feedstock for biodiesel production. Tomasevic and Siler-Morinkovic, 2003, reported the results of biodiesel production from waste sunflower oil with different molar ratios of methanol to oil.

Research by Alptekin et al., 2014, also suggests the use of corn oil, chicken fats and fleshing oils like animal fats as feedstock for biodiesel production. A report by Canakci and Sanli, 2008 infers that the main hindrance for commercial use of biodiesel is the high cost of feedstock. Used frying oils, yellow and brown grease have enough potential but are less expensive.

Hass, 2005 has given an option for feedstock for biodiesel production, which is the by-product of edible oil popularly known as soap stock. It is way cheaper than edible oils. And is 5 times cheaper than crude vegetable oils. Free fatty acid content being less than 15% are found in used frying oil and are known as yellow grease. Brown grease has free fatty acid content of more than 15%. With the increase in free fatty acid the transesterification process becomes complex and less productive as referred to by Canakci, 2007.

2.1.2 Chemical Structure of Oils

Review by Ejaz and Younis, 2011 claims that vegetable oils and animal fats mainly consist of triglycerides and diglycerides with a small fraction of monglyceride. The average chemical formula for common diesel fuel is C12H23. The vegetable oils consist of long chains with multiple branches resulting in molecules of large size. The molecular weight of vegetable oils ranges from 850 to 995, which is much higher than that of diesel which is 168 on average.

The Fig. 2.1 shows the chemical structure of a triglyceride molecule as in Morrison and Boyd, 1983. The main constituents of triglycerides are three sets of fatty acids and one glycerol stem. According to Canakci and Sanli, 2008, the fatty acid part comprises of 94%-95% of triglyceride which explains that the fatty acid part affects the chemical properties of the oils and fats to a great extent.

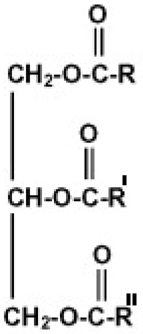


Fig. 2.1 A triglyceride (Source: Boyd, 1983)

Singh and Singh, 2010 report that there is sufficient amount of oxygen in the chemical structure of the triglyceride. If the three fatty acids are identical then it can be called a simple triglyceride, but different fatty acids give mixed triglyceride. The fully saturated ones have hydrogen with no double bonds but those having one or two double bonds are monounsaturated and polyunsaturated fatty acids respectively. The increase in the carbon deposits in engine is due to the fully saturated fatty acids. The fatty acids differ from each other with respect to their degree of unsaturation, length of their chain or reaction due to the presence of other chemical groups.

Morrison and Boyd, 1983, explains that in chemical terms fats are basically carboxylic esters derived from glycerol and are known as trialcylglycerol or trigycerides as shown in Fig 2.1. Each kind of oil has different proportions of carboxylic acids which define the characteristic property of the fat or oil and it depends upon the source of the oil. The fatty acids are straight-chain compounds with mostly even number of carbon atoms in larger amounts. The natural biosynthesis of fat results in even number of carbon atoms. Unsaturated acids along with the saturated ones are also present in the fatty acid chain of the triglyceride containing one or more double bonds in each molecule. The configuration of the unsaturated part is mostly cis which lowers the melting point of the fat as there is a bent at the cis type of double bond.

As investigated by Canakci and Sanli, 2008, the physico-chemical properties of biodiesel largely depend upon the distribution of fatty acids in the triglyceride which is used as feedstock for biodiesel production. The common fatty acids mostly found in different feedstocks is mentioned in Table 2.2.

Table 2.2 The chemical structure of common fatty acids in different types of feedstock

Fatty Acid	Chemical Structure
Myristic Acid(14:0)	$CH_3(CH_2)_{12}COOH$
Palmitic Acid(16:0)	$CH_3(CH_2)_{14}COOH$
Stearic Acid (18:0)	$CH_3(CH_2)_{16}COOH$
Oleic Acid (18:1)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic Acid (18:2)	$CH_3(CH_2)_4CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic Acid (18:3)	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$
Arachidic Acid (20:0)	$CH_3(CH_2)_{18}COOH$
Behenic Acid(22:0)	$CH_3(CH_2)_{20}COOH$
Erucic Acid(22:1)	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$

(Canakci and Sanli, 2008)

2.1.3 Procedure Adopted for Biodiesel Production

Murugesan et al., 2009 reported that presence of free fatty acids, phospholipids, water and other impurities in plant oil hinders its use directly as fuel. A little chemical modification in the structure of oil can make it work as fuel in compression ignition engines. Considerable efforts have been made to develop vegetable oil derivatives to approximate the properties and performance to that of hydrocarbon-based diesel fuels as studied by Singh and Singh,2010. The research shows that the problem with substitution of non-edible oils for diesel fuel is mostly associated with high viscosity, low volatility and polyunsaturated characters. These can be changed in at least four ways: pyrolysis, microemulsion, dilution and transesterification. Out of these, transesterification has turned out to be the most feasible one in terms of productivity and cost-effectiveness.

2.1.4 Transesterification

Canakci and Sanli, 2008 stated that transesterification is a chemical process of conversion of triglyceride to ester and glycerol. It is initiated by the bifurcation of triglyceride and the replacement of its glycerol stem with the alkyl radical of the alcohol used. This is a reversible reaction; hence it requires a catalyst to move the reaction in the forward direction and it also improvises the properties of the resultant fuel. Thus, transesterification reduces the high viscosity of the feedstock bringing it closer to that of diesel. The Fig. 2.2 below shows the mechanism of the reaction. R_1, R_2 and R_3 are the various acid chains of the triglyceride. R' denotes the alkyl alcohol used. Each mole of triglyceride reacts with three moles of alcohol to give three moles of fatty acid alkyl monoesters along with glycerol as by-product.

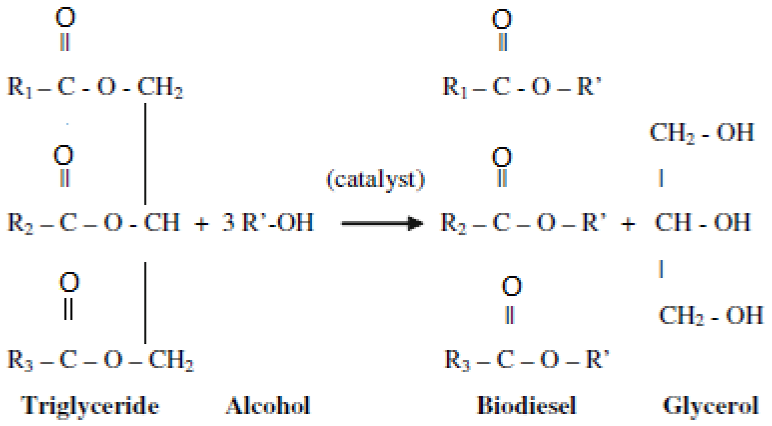


Fig. 2.2 Transesterification Reaction
(Source: Canakci and Sanli, 2008)

Fonseca et.al, 2019 reported that the used vegetable oil contains many unwanted elements which are formed during cooking such as free fatty acid in larger concentration, water, polar and non-volatile compounds. These factors adversely affect the yield of FAME and also decrease the efficiency of engines. In another study Sinha et al., 2008 verified that presence of water whether in feedstock or in alcohol can lead to saponification which consequently makes water washing difficult and decreases the yield of biodiesel.

2.1.5 Process Parameters for Biodiesel Production via Transesterification

The operating parameters are responsible for the yield of biodiesel obtained after transesterification. As discussed by Murugesan, et al., 2009. The type of catalyst also is a factor depending upon the type of feedstock, hence, can be treated as an operating parameter.

- Selection of Catalyst
- Effect of free fatty acid and moisture content
- Raw oils used
- Ratio of alcohol to vegetable oil
- Amount of catalyst
- Reaction temperature
- Mixing intensity in revolutions per minute (rpm)
- Reaction time

2.1.5.1 Selection of Catalyst

Transesterification can proceed by alkali or acid catalysis, but the former one is much more convenient than the latter. Alkali catalysis is faster than acid catalysis as studied by Freedman and Pryde, 1982. There has been many view points as to which catalyst to be used for which feed stock. Base catalyst is successful only when free fatty acid (FFA) is less than one as suggested by Fangrui and Hannah, 1999.It has also been said by Crabbe et al.,2001 that base catalysts can be used in case of FFAs greater than one but a higher amount of catalyst is needed. On the other hand, Fukuda et al., 2001 advocated that base catalysts exhibit excellent results when the FFA of oil is below two. They also reported that the rate of transesterification reaction becomes thousands of times faster when base catalyst is used instead of acid catalyst. However, Gerpan, 2006 reported that base catalysts could be effectively used for feedstock having FFA up to 5. A study by Manuale et al., 2015 explains that strong basic catalyst are mostly used for industrial purpose. Lower reaction time, high rate of conversion and less amount of catalyst requirement are the main reasons behind the preference of alkali catalyst over acidic ones. Singh and Singh, 2010 explained alkali-based transesterification as shown in Fig. 2.3. The reaction mechanism has three steps as shown in the figure. Here B is the catalyst and R refers to the alkyl group of the alcohol The first step is an attack on the carbonyl carbon atom of the triglycerides molecule by the anion of the alcohol (Methoxide ion) to form a tetrahedral intermediate which reacts with the alcohol (methanol) to regenerate the anion of alcohol (methoxide ion). Lastly rearrangement of the tetrahedral intermediate, results in the formation of a fatty acid ester and a diglyceride. Then subsequently the same steps follow for diglyceride and monoglyceride consecutively giving three moles of alkyl ester and glycerol and the end. Canakci and Sanli, 2008 evaluated that alkali-based transesterification are mostly preferred as they are faster and involve less amount of catalyst use. Moreover, use of alkaline catalyst prevents any corrosion of the inner parts of engine.

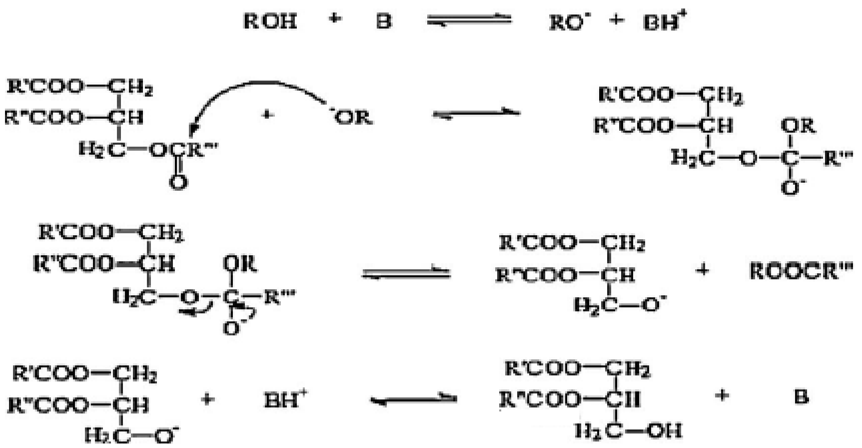


Fig. 2.3 Mechanism of the alkali-based transesterification of vegetable oils
(Source: Singh and Singh, 2010)

Sinha et al. 2008 describe that acid catalysts are used because these exhibit good results when the feedstock has water contents and its acid value is high. Base catalysts are highly sensitive to water contents, which cause soap formation, and separation becomes difficult. The acid values of most of the non-edible oils are higher than the performance range of base catalysts. So, in such cases acid catalysts are used. The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) in Fig. 2.4 involves protonation of carbonyl group of the ester leading to carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst. The mechanism is shown in the figure below for acid catalyses the H$^+$ ion involved in the reaction is that of the catalyst.

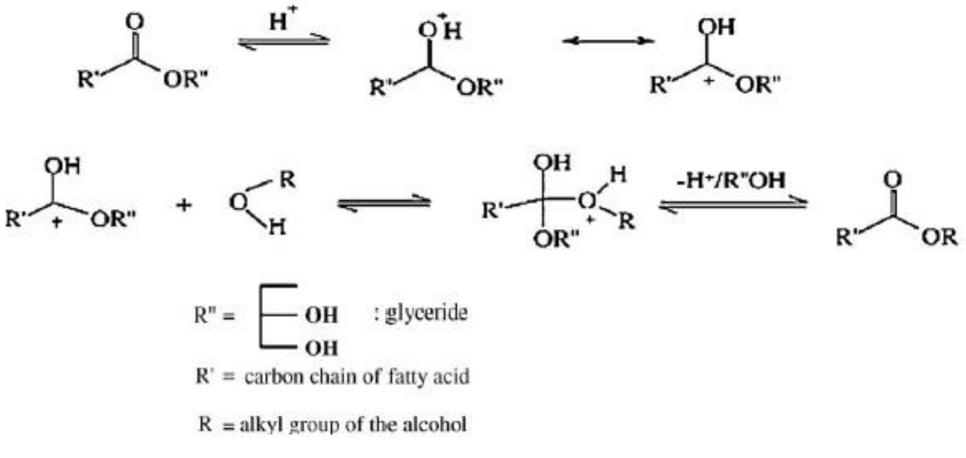


Fig. 2.4 Mechanism of acid-catalyzed transesterification (Source: Singh and Singh, 2010)

If more water and free fatty acids are in triglycerides, acid catalyst can be used. But the problems associated with these catalysts are, requirement of higher amount of alcohol, higher reaction temperature and pressure, and slower reaction rate. Reactor corrosion and environmental issues are also the hurdles in the use of acid catalysts as explained by Peng et al.,2008.

2.1.5.2 Effect of Free Fatty Acid and Moisture Content

According to Freedman et al., 1984 the yield of biodiesel highly depends upon the moisture content and free fatty acid content of the oil. If moisture is present in the feed stock, then the alkyl ester formed reacts with water to give free fatty acid. Basically, hydrolysis occurs giving free fatty acid which is not at all feasible for biodiesel production. In the reaction shown in Fig. 2.5 R is the triglyceride group of the biodiesel and R_1 is the alkyl group.

$$\text{R-COOR}_1 + \text{H}_2\text{O} \rightarrow \text{R-COOH} + \text{R}_1\text{OH}$$

Fig. 2.5 Hydrolysis of alkyl ester
(Source: Freedman et al., 1984)

As verified by Murugesan et.al, 2009 the free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. To carry the base-catalyzed reaction to complete; the three free fatty acid (FFA) value lower than 3% is needed. The higher the acidity of the oil, the smaller is the conversion efficiency. Both, excess, as well as insufficient amounts of catalyst, may cause soap formation. The materials used for base-catalyzed alcoholysis should meet certain specifications. The triglycerides should have a lower acid value. The addition of more sodium hydroxide catalyst compensates for higher acidity, but the resulting soap causes an increase in viscosity or formation of gel, which interferes in the reaction as well as with the separation of glycerol.

2.1.5.3 Raw Oils Used

As reported by Lee et al., 2017, 75% of the total cost of biodiesel production depends upon the selection of the feedstock. Murugesan et al., 2009 suggest that since different types of vegetable oil and animal fats may contain different types of fatty acids, the fuel-related biodiesel properties are generally affected by the choice of raw materials. The length and the degree of saturation of the fatty acid alkaline chains affect properties such as cetane number, oxidation, and cloud point. The final physical properties of the biodiesel will depend on the properties of the free fatty acids present and this allows biodiesel to be formulated and selected to have a specific property. It also determines the yield of the product derived from the respective raw material. Martinez et al., 2018 investigated that the choice of raw materials depends upon the availability of the feedstock. Lal and Sharma, 2011 stated that the Planning Commission of India has considered karanja, jatropha and ratanjyot as plants of great potential. Irrespective of the type of land and rainfall in a region, these crops can be easily grown. The oil extracted from these oilseeds can be used to produce high-quality biodiesel. So, these non-edible seeds act as feedstock for biodiesel production.

2.1.5.4 Ratio of Alcohol and Oil

Sinha et al., 2010 explain that the molar ratio is one of the most important parameters of biodiesel production. The molar ratio can be varied proportionately according to the stoichiometry 3:1 of the equation. They discovered that in case of rice bran oil, increase in molar ratio increases the yield to great extent as larger amount of alcohol is required to drive the reaction in forward direction. The methanol: oil ratio was varied between 6:1 and 15:1 but optimized yield was obtained at 9:1. The rate of increase of yield decreases with increase in molar ratio. Viscosity of ester does not vary significantly with molar ratio. The amount of catalyst is largely responsible for ester yield. As studied by Ahmed, 2015 for jatropha oil optimum yield was obtained at 6:1 molar ratio using methanol. At higher molar ratios like 12:1, the solubility of glycerine increases in the solution and pushes the reaction backwards resulting to lower yield. Keera 2011 reported that although the stoichiometry of the transesterification reaction requires 3:1 molar ratio, excess alcohol helps to drive the reaction forward. Higher molar ratios give higher yields up to an extent. Keeping the other parameters constant and using methanol as the alcohol, the molar ratio has been varied from 3:1 to 12:1.

Before 6:1 the reaction is not complete. The optimised yield is obtained at 6:1 for cottonseed and soybean oil. Increasing the ratio to 12:1 lowers the ester yield as the excess alcohol interferes with glycerine formation and drives the reaction backward. Refaat et al. produced biodiesel for three sets of molar ratios from waste vegetable oil giving an optimum yield of 96.5% at 6:1. Molar concentration of 6:1 has given the optimum yield of cotton seed methyl ester to Rashid et al. According to their findings, less than 6:1 has led to incompletion of the reaction whereas a molar ratio greater than 6:1 leads to dilution effect. But a note has to be taken that the optimum yield depends simultaneously on other parameters as well.

As referred to in the paper presented by Murugesan et.al, 2009 the stoichiometry of the transesterification reaction requires 3 mol of alcohol per mol of triglyceride to yield three mol of fatty ester and 1 mol of glycerol. Excess alcohol is required to drive the reaction to the right. A molar ratio of 6:1 is used in industries. The best is between 9:1 and 12:1. Molar ratio has no effect on acid or saponification. High molar ratio effects the separation of glycerin due to an increase in solubility driving equilibrium to left and thereby lowering the yield of esters.

2.1.5.5 Amount of Catalyst

As studied by Shahid and Jamal,2011 majority of researchers have used NaOH catalyst for transesterification reaction and believed that it is the best catalyst for used vegetable oil. The base catalysts are preferred over acid catalysts, owing to their capability of completion of reaction at higher speed, requirement of lower reaction temperature, and their higher conversion efficiency as compared to acid catalysts. Qi et al., 2009 reported that alkali catalyst is used the most as the process is faster and the reaction conditions are mild. Catalysts used for the transesterification of triglycerides are alkali, acid, enzyme or heterogeneous catalysts. If the oil has high free acid content and more water, acid catalyst H_2SO4, H_3PO4, HCl is suitable. Alkali catalyst is more suitable as the reaction occurs 4000 times faster than in acidic catalyst. Alkali catalyst are less corrosive to industrial equipment. The concentration in the range 0.5–1.0% (w/w) has found to yield 94–99% conversion of vegetable oils into ester as studied by Murugesan et.al, 2009. Anwar et., 2018 used KOH as catalyst creating a variation in percentage from .5% KOH to 1.5% KOH w/w of oil. This shows a variation in percentage yield of biodiesel. Biodiesel from mixed jatropha and ceiba pentandra has shown variation in yield with variation in the percentage of catalyst from 0.5 to 2 % w/w of oil as verified by Dharma et al., 2016. But here other factors are also responsible for change in yield, but amount of catalyst is one of the factors.

2.1.5.6 Reaction Temperature

The reaction is conducted close to the boiling point of the respective alcohol (60–70^0C) at atmospheric pressure for a given time. The maximum yield of esters occurs at temperatures ranging from 60 to 80^0C at a molar ratio of (alcohol to oil) 6:1 as referred to in the paper presented by Murugesan et.al, 2009. The experiment discussed in Moulita and Kalsum, 2019 demonstrates that as the reaction temperature increases, the movement and collision of the molecules also increase. This collision of particles produces heat which also adds up to increase the conversion rate of biodiesel. Hence the percentage yield increases. But a larger increase in temperature vaporizes the alcohol as its boiling point is low. This decreases the percentage yield of biodiesel.

2.1.5.7 Mixing Intensity

While discussing all the operating parameters of biodiesel Murugesan et.al, 2009 also discussed mixing intensity. Mixing is very important as oils or fats are immiscible with NaOH–MeOH or any other catalyst alcohol solution. Once mixed and the reaction is started stirring is not required. For eg, the yield of methyl esters at 360 rpm and 600 rpm are the same after 3 hours of reaction. Mashkour et al., 2016 explain that the transesterification reaction is a reversible reaction, therefore faster revolution per minute decreases the total time of the reaction process. Using used vegetable oil as feedstock, production of biodiesel, was maximum at 2 hours, 1% catalyst, and 600 rpm, giving 96% yield.

2.1.5.8 Reaction Time

Suzihaque et al., 2022 reported that the reaction time depends on other processing parameters. Lesser reaction time will not lead to homogenous mixing of the reactants. Acid transesterification takes very long time in comparison to alkali transesterification. Naik et al.,2015 explains that completion of transesterification is dependent on time. Experiments were conducted in three sets in which time varied as 40 minutes, 80 minutes and 120 minutes. The largest duration of reaction time exhibited the largest percentage yield. But excess reaction time leads to backward reaction causing hydrolysis of esters.

2.1.6 Transesterification with Respect to Changes in Process Parameters

Refaat et al., 2008 investigated biodiesel production from waste used vegetable oil with different molar ratios of methanol to oil (3:1, 6:1, and 9:1), KOH and NaOH as catalyst with different concentrations (0.5% and 1% w/w) and reaction temperatures (25 and 65ºC). Allawzi and Kandah, 2008 reported the transesterification of waste soybean oil with different ethanol concentration. Majority of researchers have used NaOH catalyst for transesterification reaction and believed that it is the best catalyst for used vegetable oil as confirmed by Encinar, 2005. Amirthavall et al., 2022 suggest that the base catalysts are preferred over acid catalysts, owing to their capability of completion of reaction at higher speed, requirement of lower reaction temperature, and their higher conversion efficiency as compared to acid catalysts. According to Lee et al., 2017, lipids in waste pepper seeds required sulphuric acid as catalyst. Bautista et al., 2009 reported that alkali catalyst is used the most as the process is faster and the reaction conditions are mild.

Sinha et al., 2008 investigated and used rice bran oil to undergo the process of transesterification which is considered as the cheapest and easiest way of biodiesel production. The parameters namely methanol: oil ratio, catalyst concentration, temperature and stirring speed have been optimized to obtain the best fit data based on percentage yield and viscosity. Research by Encinar et al., 2005 compared the performance of NaOH and KOH and found KOH better. They also reported that the separation of biodiesel and glycerol was easier when KOH was used as catalyst; hence it was preferred over NaOH. Waste palm oil has been used for producing biodiesel by acid transesterification. In such cases where free fatty acid content is high, two step transesterification or acid transesterification is done which has been discussed by Al-Widyan and Al-Shyoukh, 2002. Neat sunflower oil and waste vegetable oils have also been used as feedstock in biodiesel production by Mangus et al., 2014. They reported that more than 96% biodiesel could be obtained in 1 h by using 1% KOH and methanol/oil molar ratio 6:1 at 65^0C reaction temperature.

2.1.7 Optimisation of Process Parameters of Biodiesel Production

Dharma et al., 2016 suggests that optimisation is required as variation in operating parameters affect the yield and thereby decreases the cost of production. A statistical tool namely Response Surface Methodology (RSM) has been incorporated to study and analyze the effects of independent variables or their combinations on the dependent ones. Mohamad et al., 2017 tells that RSM is used for designing experiments, building optimization models, evaluating the effects on the variable and determining the optimum conditions that give the desired output. The study also involves RSM to observe the transesterification of vegetable palm oil (VPO) using calcium oxide, modified with titanium dioxide as catalyst under ultraviolet (UV) light. Response Surface Methodology (RSM) with Central Composite Design (CCD) enabled the optimization of the yield. Kumar et al., 2016 discussed about the Box–Behnken design (BBD) which had been applied using Design Expert software version 9.0.2.0. Total 17 experiments were carried out in sets of three and the average value was fed into the software to assess the effects of temperature, the concentration of catalyst and concentration of sludge solids in one of the research works. Optimization using RSM based on Central Composite Rotatable Design (CCRD) has been performed for transesterification of used palm oil with lipase catalyst in a packed bed reactor as investigated by Halim et al., 2009. An et al., 2012 tells that much more has to be done on the path of optimization of process parameters for maximum yield of biodiesels from non-edible oil mixtures with RSM. In another study, Hamze et, al., 2015, explains that response surface methodology based on Box–Behnken Design (BBD) analysed the effects of the main operating parameters on biodiesel yield with waste oil used for cooking. In a work by Bouaid et al., 2007, ethyl ester derived from sunflower oil which has high oleic acid content has been produced and optimized with the help of response surface methodology. Catalyst concentration of KOH was found to produce the major impact on conversion. Dharma et al., 2016 proposes that a lot of work has to be done in the field of optimization for better yield of biodiesel from non-edible feedstock.

2.1.8 Qualitative Analysis of Biodiesel

Knothe, 2008 stated that the fatty acids remain the same even after biodiesel conversion. As discussed by Still et al., 1978, chromatography is the process of separation of components in a given mixture which enables the identification of the unknown components. During the process of separation each element retains its inherent properties. Chowdhury et al., 2007 investigated that biodiesel manufactured with methanol as the catalyst and also known as fatty acid methyl ester (FAME) consists of methyl esters of saturated fatty acids, monounsaturated fatty acids and polyunsaturated fatty acids. Rabu et al., 2013 determined the composition of biodiesel produced from used vegetable oil by comparison of the retention times of the components with those of the standard mix available for comparison. The chromatogram of this biodiesel from palmitic based used vegetable oil determines the percentage each type of fatty acid as shown below.

Table 2.3 Fatty acid profile of the biodiesel from used vegetable oil (Source: Rabu et al., 2013)

FAME	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22
WCO FAME	1.2	36.9	6.7	31.6	18.9	---	0.7	0.3	0.3

Table 2.3 shows that the main component of the biodiesel is oleic acid methyl ester. Bautista et al., 2009 confirms that the qualitative analysis of biodiesel is important as it enables to decide the percentage of alkyl ester in the final product. Higher acid value of the feedstock leads to greater catalyst requirement for neutralisation and hence the methanolysis remains incomplete leading to presence of glyceride in the ester, thereby decreasing the percentage of methyl ester in the final product. Sarin et al., 2010 reported that gas chromatography has helped in determining that palm biodiesel has both saturated and unsaturated fatty acid methyl esters. Jatropha biodiesel has larger concentration of both oleic acid methyl ester and linoleic acid methyl ester.

2.1.8.1 Evaluation of Properties of the Biodiesel from Its Composition

Sarin et al., 2010 confirms the evaluation of oxidation stability which depends on the total degree of unsaturation of the FAME. The correlation can be defined as follows.

$$OS = -0.234(X) + 22.318 \ (0 < X < 84) \qquad \text{--------2.1}$$

where X is the content of total unsaturated FAME (wt%) and OS is the overall oxidation stability of the biodiesel.

As studied by, Knothe, 2005 the fatty acid alkyl esters of biodiesel determine the engine characteristics of biodiesel. The chemical structure of each fatty ester determines its property which in turn determines the overall property of biodiesel. Dunn, 2015 investigated and found out that identification of structure of fatty acids alkyl esters enable to determine the overall cold flow properties and viscosity of biodiesel.

A saturated fat contains only one C-C (carbon-carbon) bond hence cannot accept any further hydrogen. Whereas an unsaturated fat can be hydrogenated and contains one or more double bonds. Cetane Number (CN) depends upon chain length, degree of unsaturation, number of CH_2 groups in the ester moiety and position of the double bonds as reported by Graboski and McCormick, 1998. Cetane Number is the property of fuel which indicates the ignition quality of the fuel and is the measure of the time interval between fuel injection and ignition of engine, preferably known as ignition time delay. In unsaturated esters CN increases with increase in chain length. Increase in the number of double bonds decreases the CN of the unsaturated FAMEs. Also, CN increases if the double bond moves towards the end of the chain of hydrocarbon as explained by Knothe, 2014. CN also depends on the alcohol moiety showing an increase in CN with increase in the molecular weight of a particular ester for increasing group of alcohol. Higher percentage of linoleic acid and linolenic acid may denote lower CN due to high degree of unsaturation as discussed by Gopinath et al., 2010.

Table 2.4 Fatty acid profile of sunflower oil FAME composition (%)

(Source: Gopinath et al., 2010)

C 14:0	C 16:0	C 18:0	C 18:1	C 18:2	C 18:3	Others	Unsaturated	Saturated
.8	38.6	4.6	44.0	10.7	0.1	1	54.8	44.2

Here it can be seen that palmitic is higher in sunflower fatty acid methyl ester (SUFAME). Higher percentage of linoleic acid and linolenic acid may denote lower CN due to high degree of unsaturation and it has been analysed by Gopinath et al., 2010.

Mathematical modelling in one of the research papers by Choudhury et al., 2015 showed that viscosity is related to the constituents of FAME. The saturated and monosaturated parts pf FAME increases the viscosity and the polysaturated part of FAME decreases the viscosity such that increase in double bond decreases the viscosity. As reviewed in one of the studies by Gopinath et al., 2015 viscosity of all esters increases with increase in chain length and decreases with increase in the degree of unsaturation. Allen et al., 1999 reported that increase in the number of carbons in saturated methyl ester depicts increase in viscosity.

Pratas et al., 2010 investigated that density of FAMEs decreases with increase in alkyl chain length and increases with increase in saturation level. Alptekin and Canakci, 2008, reported that density of fuel largely affects the engine performance and emission characteristics as density is related to NO_x emissions and cetane number. The fact that biodiesels with higher densities show lower cetane numbers has been informed by Gopinath et al., 2015.

As stated by Nag, 2002, heat of combustion is the amount of heat liberated by complete combustion of 1 kg of fuel. Knothe, 2008 has explained that the heat of combustion depends upon the composition of the alkyl esters of the biodiesel to a larger extent as the amount of energy of fatty acid alkyl ester is directly proportional to its chain length. Freedman and Bagby, 1989 informed the energy content of fatty acid alkyl ester increases while moving towards higher alcohol for a given chain length. Increase in unsaturation results in decrease in heat of combustion due to decrease in the number of hydrogen molecules. Demirbas, 1997 stated that heat of combustion increases with increasing number of carbon atoms.

Knothe, 2002 defines that iodine value is the parameter to measure the degree of unsaturation of the FAME. Iodine value increase with alcohol moiety and increases with increase in alcohol size. As reported by Kalayasiri et al., 1999 the equation gives the iodine value of biodiesel.

$$IV = \Sigma_i \frac{254\ D\ A_i}{MW_i} \qquad \text{-------- } 2.2$$

Here IV denotes iodine value, i denotes each type of fatty acid alkyl ester, D denotes the number of double bonds of each type of fatty acid alkyl ester, A_i is the percentage of each fatty acid alkyl ester in the biodiesel and MW_i is the molecular weight of each fatty acid alkyl ester.

Gopinath et al. 2015 has discussed that the melting point of alkyl esters increases with an increase in alcohol moieties and decreases with increasing level of unsaturation. In order to calculate the cloud point (CP) and pour point (PP), the amount of saturation is considered the main factor. This is because the melting point of saturated compounds are higher than the unsaturated ones. The formula for calculation of cloud point and pour point has been shown below as described by Gopinath et al., 2015.

$$CP = 0.526(PFAME) - 4.992 \ (0\% < PFAME < 45\%) \quad \text{--------} \ 2.3$$

$$PP = 0.571(PFAME) - 12.24 \ (0\% < PFAME < 45\%) \quad \text{--------} \ 2.4$$

Here, CP is the cloud point of the biodiesel, PP is the pour point of biodiesel and PFAME denotes the percentage of palmitic fatty acid methyl ester.

The saponification value the average molecular weight of all the fatty acids in the biodiesel. It is expressed as the amount of mg of KOH (potassium hydroxide) that is required to saponify 1 gm of sample of oil. The formula below gives the saponification value as reported by Gopinath et al. 2015.

$$SV = \frac{\Sigma A_f * 56{,}106}{MW_f} \quad \text{--------} \ 2.5$$

Here SV is the saponification value (mg KOH/g oil), A_f is the percentage of each component in the mixture and MW_f is the molecular weight of each component in the oil.

The kinematic viscosity and density of vegetable oils are much higher than those of diesel due to their higher molecular weight and complex structure. The properties of biodiesel are comparable with mineral diesel. Hence it can be used as a fuel, in pure or blended form, in compression ignition engines. The fuel can be used without any major modification to the engine as reported by Ejaz and Younis, 2011. One of the studies by Cvengros and Cvengrosova, 2004 also concluded that if the acidity and water content of waste oil of any type is kept within limits naturally or by proper treatment then their transformation can be carried out similarly as fresh oils or fats of the same category. The research conducted by Qi et al., 2009 reveals biodiesel preparation from crude soybean oil by alkaline catalyzed transesterification. The viscosity, density and flash point are higher than that of diesel whereas the calorific value is lesser with respect to diesel. The higher fuel consumption reflects its lower heating value. The power output at full load is same for biodiesel and ultra-low sulphur diesel (ULSD).

The emission characteristics show that there is considerable decrease in the release of gases like carbon monoxide, hydrocarbons, nitrogen dioxides and smoke. Pradhan et al., 2016 suggests that pollution and environmental degradation has envisaged the study of engine performance with biodiesel blended diesel fuel to a great extent. Research by Fernando et al., 2006 also explains that biodiesel reduces NO_X emissions to great extent. It has been reported by Mangus et al., 2014 that the molecular structure of bio fuel affects the performance and emission of the compression ignition (CI) engine when used as a substitute for diesel in pure or blended form. Increase in unsaturation of the oil increases the NO_X emission but likewise decreases the fuel consumption due to increase in oxygen content of the oil. India is a major importer of vegetable oil. As a result, large amount of used frying oil (UFO) is generated every day. UFO has been used to evaluate the performance of a diesel engine in Brazilian conditions in various proportions of blend. Lowest fuel consumption was recorded at B5 and highest at B20 biodiesel blend by Paulo et al., 2016.

A report by Chabra et al., 2017 focuses on impact assessment of rice bran and crude rice bran biodiesel and its blends with diesel on diesel-engine performance. Performance results observed for B10 and B20 blends were closest to that of diesel whereas B40 showed lowest performance results as compared to diesel and other blends. An interesting investigation was made by Muralidharan et al., 2011 regarding the performance and emission characteristics with various blends of biodiesel from used vegetable oil. With the increase in the percentage of biodiesel, the brake thermal efficiency (BTE) decreases because of the higher fuel consumption and lower calorific value of biodiesel. The blends have higher mechanical efficiency because of the high reaction activity of the fuel.

The fuel with blend of biodiesel had higher NO_x than diesel because the plant oil naturally had the nitrogen content along with it, and this would get involved in the production of NO_x. The results by Gumus et al., 2012 confirmed that increasing the biodiesel ratio in the fuel blend leads to an increase in the brake-specific fuel consumption (BSFC). The present work concentrates on the use of only that kind of oil that is thrown away and is no longer edible so that the food market is not affected. After the production, the performance is studied for various blends in order to observe as such which oil can be used for mass production. The properties of the methyl esters of each form have also been evaluated.

2.2 Conclusion

It is very evident from the literature review that biodiesel can be produced from non-conventional feedstock like non-edible oils and used vegetable oils. The different sources of feedstock have been discussed. Biodiesel can be produced in many ways, but the most feasible one is the process of transesterification. The operating parameters of the process of transesterification determine the percentage yield of biodiesel. An attempt to optimise the process parameters has been made in this regard with respect to different types of non-edible feedstock like non-edible oils and used vegetable oils. As discussed, biodiesel can be used to run CI engines, therefore the engine performance has been kept under study by running the engine with biodiesels produced from different types of used vegetable oils. The comparison of engine performance of CI engine run on blended biodiesels produced from different sources is required to be studied. The chemical composition of raw oils is different from the used oils. Therefore, the properties of biodiesel from used vegetable oils are different from the properties of biodiesel produced from raw vegetable oils of the same origin. The gas chromatography of the alkyl esters of used vegetable oils, becomes important to study the difference in their properties although being from the same plant origin. This study tries to incorporate a modification in the conventional process of biodiesel production by utilising the ambient heat and removing the conventional heating apparatus required to supply input energy for the process of transesterification.

Chapter 3
Methodology

3.1 Materials Used for Biodiesel Production

- Methanol of 99% purity was used of Merck Ltd. Methanol is preferred over ethanol because of its cost effectiveness.
- Sodium hydroxide of 97% purity was used from Merck Ltd.
- Phenolphthalein 1% indicator solution was from Merck.
- Sodium hydroxide of 97% purity was used of Merck Ltd.
- A plastic jar of Merck Emplura Potassium Hydroxide pellets was used in later experiments as it gives greater yield when compared to sodium hydroxide.
- Distilled water for washing.
- Glassware like beaker, separating funnel, conical flask, glass rod, viscometer, and condenser of Borosil were used.
- Buschner conical flask manufactured by Borosil.
- Two plastic tubes were used for circulation of water through the condenser.
- Submersible pump was used for circulation of water during transesterification.
- Remi 5 litre Hot Plate Magnetic Stirrer was used.
- Aquarium pump
- Vacuum filtration pump
- Mercury thermometer up to 100^0C was used for temperature measurement.
- Clamp stands
- Beam Balance

Several steps are involved in biodiesel production for each kind of sample. The parameters change depending upon the requirements but the steps followed throughout the production process are the same. The flow chart in Fig. 3.1 can give an idea about the steps involved and the sequence followed.

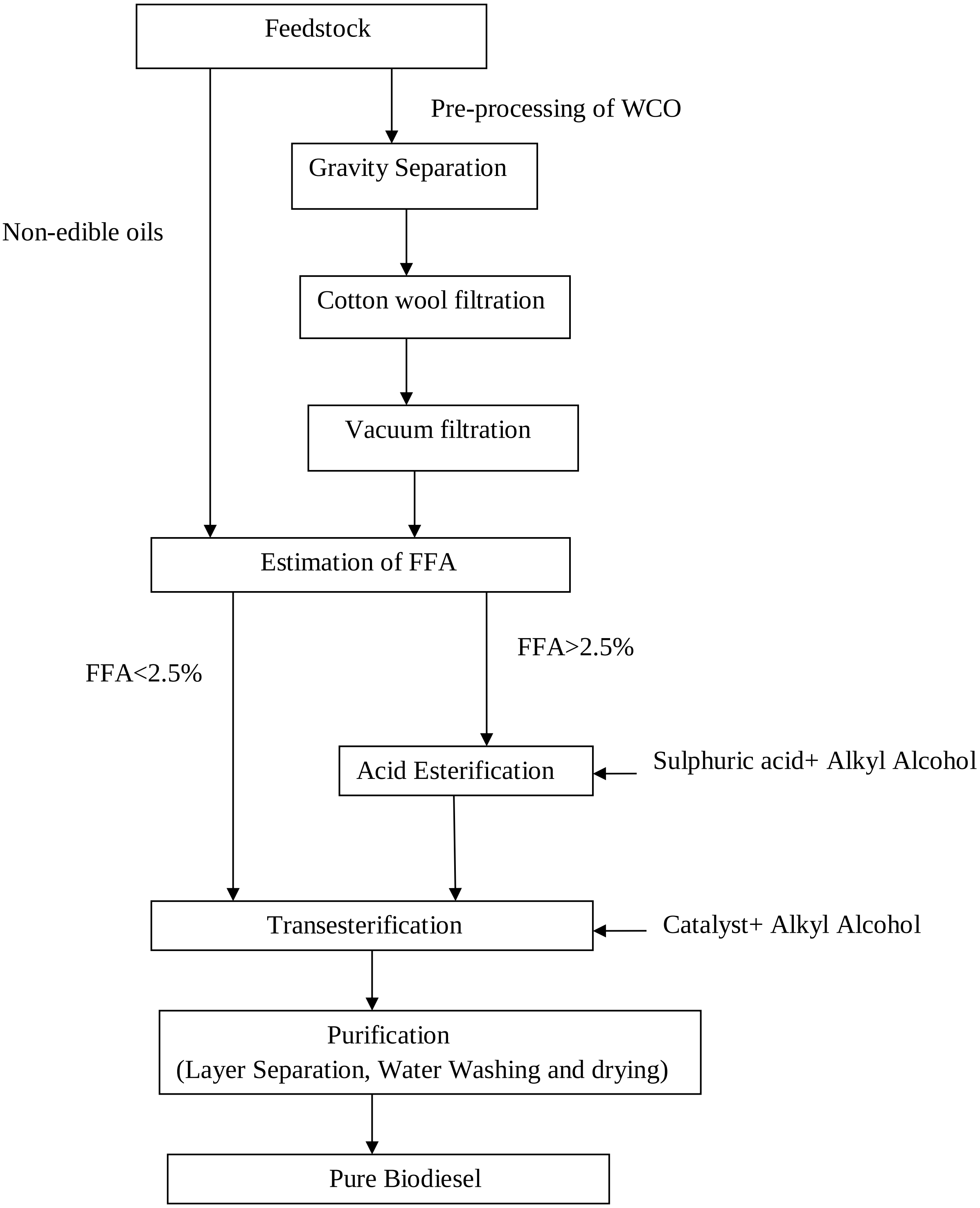


Fig. 3.1 Steps of biodiesel production

3.2 Steps to be Followed for Biodiesel Production

The following steps have been followed to produce biodiesel from used vegetable oil and raw oils in the chemical laboratory of the Department of School of Energy Studies, Jadavpur University, Kolkata.

3.2.1 Pre-processing of the Feedstock

The feedstock includes non-edible oils which are directly collected from seeds of different plants like mahua, karanjha and sesame. These oils do not require pre-processing. But the used vegetable oil collected from different kinds of sources contain all kinds of unwanted solid and fine particles which need to be separated from oil before undergoing transesterification. Primary filtration is done in the container itself in which it is contained. The heavy large particles are allowed to settle for 2-3 days after which the upper larger layer of the oil which is free of large heavy solid particles is passed through cottonwool. This makes the oil, free from large or small light particles of food. Now the oil only contains fine carbon particles. This can be done through vacuum filtration technique. In a Buchner conical flask, the neck is fitted with a ceramic Buchner funnel topped with a filter paper. The suction, by a pump of 1 Horsepower. The oil after filtration gets stored in the bottom of the flask whereas the black carbon particles are separated in the filter paper. Each filter paper can filter almost 0.5 to 1 litre of oil depending on the level of impurities. The Fig. 3.2, Fig. 3.3, Fig. 3.4 and Fig. 3.5 describe the process of filtration.

Fig. 3.2 Cotton wool

Fig. 3.3 Gravity Filtration through cotton wool

Fig. 3.4 Vacuum Filtration Pump

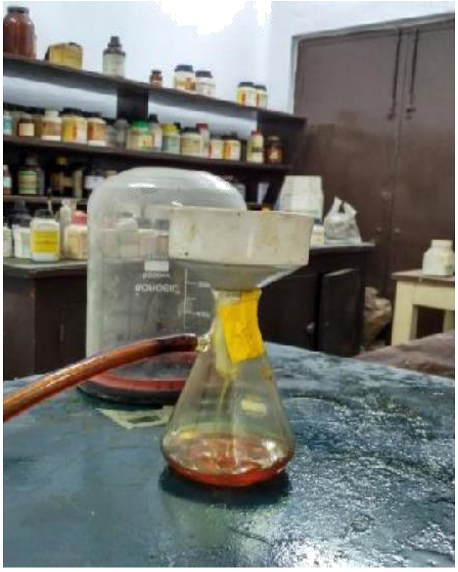


Fig. 3.5 Filtered oil obtained by vacuum filtration

3.2.2 Estimation of the FFA content

ASTM D974, 2014 describes a non-aqueous colorimetric titration with potassium hydroxide, isopropanol as a titrant, and p-naphtholbenzein as an indicator. The acid number is the amount of potassium hydroxide necessary to neutralise a 1 gm sample of oil. This acid number actually gives an estimation of the fatty acid content of the biodiesel or feedstock. Hydrolysis of ester linkages in triglyceride feedstock is responsible for the formation of fatty acid. As reported by Mahajan et al., 2006 the calculation of acid number or acid value (AV) is shown below. The acid value is expressed as mg/g.

$$acid\ value = \frac{volume\ of\ KOH\ or\ NaOH(ml) * N\ KOH\ or\ NaOH\left(\frac{mmol}{ml}\right) * 56.1(mg/mmol)}{sample\ weight(gm)}$$

--------(3.1)

Acid value is converted to percentage of free fatty acid content by multiplying it with a factor which is equal to one-tenth of the molecular weight of the fatty acid concerned divided by the molecular weight of potassium hydroxide. This is often known as the conversion factor. This value of this factor is .503. Since the sample comprises mostly of oleic acid hence the molecular weight of the fatty acid concerned is the molecular weight of oleic acid (282.4). Fatty acid content (FFA) content is expressed in percentages. Therefore, the relation between free fatty acid and acid value stands as follows:

%Free Fatty Acid (FFA) = AV*.503 -------(3.2)

3.2.3 Free Fatty Acid Estimation of the Oil

The following steps have been followed for fatty acid estimation keeping in mind the details mentioned in ASTM D974, 2014.

Note: The normality is equal to molarity in the case of KOH as well as NaOH as their equivalent weights are equal to their molecular weights. The blanking process was neglected as the KOH and iso-propyl alcohol used was from a sealed package.

Step 1: A 0.1 N solution of KOH was prepared by mixing 0.561 g of KOH with 100 ml of water. This solution was used for titration of the oil. This solution can be kept in store for almost 2-3 months. In case of NaOH the solution of same strength is prepared by mixing 40 gm of NaOH in 100 ml of water.

Step 2: 2 gm of oil was collected in an Erlenmeyer flask and mixed with 10 ml of Isopropyl Alcohol (2-Propanol) which is the titration solvent.

Step 3: 7-8 drops of Phenolphthalein were added to the mixture.

Step 4: The solution was titrated against .1 KOH/NaOH solution.

Step 5: Continuous shaking and addition of the titration solution continue till there was a visible colour change in the oil-alcohol solution which persists for at least 15 seconds.

Step 6: The amount of titrating solution for colour change is recorded. This value is used in the equation mentioned above to calculate the acid value.

Step 7: The free fatty acid content is calculated with the help of the acid value obtained.

3.2.4 Calculation of the Amount of Catalyst

Percentage of catalyst weight /weight of oil = x%

This means that 100 gm oil requires x gm of catalyst for the reaction process.

Now depending upon the amount of oil considered, the amount of catalyst required for transesterification will be calculated. In the case of two-step transesterification the percentage of catalyst volume/volume of oil.

3.2.5 Calculation of the Amount of Alcohol

Molar ratio of alcohol/acid and oil = y:1

[Note: Acid has to be considered in case of esterification.]

This means that y moles of alcohol/acid react with 1 mole of oil

Mass of oil considered = z gm (In all the cases mass of 100 ml of the corresponding oil has been considered.)

Molecular weight of oil = Mass of 1 mole of oil = MW_o

As discussed by Pubchem, 2023 the molecular weight of methanol is 32.042 gm/mol. Therefore, the molecular weight of of methanol is considered as 32 gm throughout this study.

Molecular weight of alcohol/acid = MW_a

Mass of y mole of alcohol/acid = $y^* MW_a$

Mass of alcohol/acid to react with z gm of oil $= \frac{MW_a * z * y}{MW_o}$ gm --------(3.3)

The volume of alcohol can be calculated with the help of density of alcohol. Here z gm has been considered as the mass if 100 ml of oil. Density of methanol has been considered as 791.8 kg/m^3 as discussed in Stack Exchange, 2015.

Similarly, if volume of oil is mentioned, then the corresponding mass can be calculated with the help of beam balance.

Here the molecular weight of the waste oils is same as that of the corresponding fresh oil. Although, heating causes oxidation, the fatty acid components remain more or less the same as obtained by gas chromatography in the later stages.

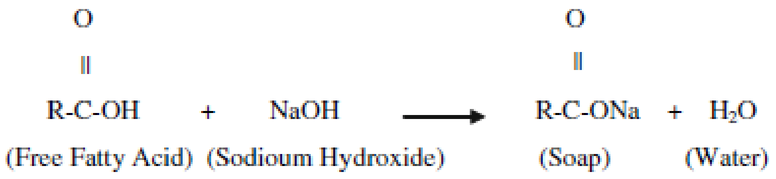
3.2.6 Acid Esterification

The free fatty acid content determines which kind of transesterification process can be adopted. In this study acid transesterification is adopted for oils having free fatty acid content more than 2.5%. Higher percentage of free fatty acid has been found in non-edible oil namely mahua oil. Therefore, acid esterification has been followed by alkali transesterification in this case. In the acid transesterification process, the acid used is sulphuric acid. The sulphuric acid carries on the esterification process, followed by the alkali-based transesterification process.

Oils having high free fatty acid content react with KOH leading to soap formation which not only decreases the yield of biodiesel but also makes it difficult for separation in the separating column. To avoid saponification, these types of oils have to be esterified in the presence of acids like H_2SO_4. H_2SO_4 reacts to the oil and produces esterified oil and water-alcohol mixture. This mixture can be separated by using a separating funnel. After the separation, transesterification may be followed. In our study Mahua (*Madhuca indica pinnata*) oil has been esterified by H_2SO_4, as the oil has 17.5% FFA content. The oil and the required methanol are slowly poured into an Erlenmeyer conical flask with a capacity of 500ml and stirred continuously with a magnetic stirrer. Then, the temperature and the stirring rate are fixed at a certain value. During the stirring process, acid is added dropwise in the flask using a dropper. After this, a reflux condenser is put on the top of the flask for preventing the escape of methanol. Water enters the reflux condenser and escapes from the top producing a cooling effect in which vaporized methanol is condensed and returned to the system. The system runs for a stipulated time and then the crude solution is poured into a separating funnel for separation. In the separating funnel, the mixture starts separating and after the given amount of time, two clear separate layers are formed. The upper darker layer is the methanol and water mixture and the lighter bottom layer is the esterified oil which is ready for transesterification. The fatty acid content of the esterified oil is confirmed by the titration method. Further transesterification is carried out since the fatty acid content reaches below 2.5%.

3.2.7 Mixing and Neutralization

The mixture of methanol and catalyst produces methoxide, which interacts with the base oils. Since most catalysts (e.g., NaOH, KOH) are solid and do not dissolve easily in methanol, it is recommended to begin mixing the methanol in a mixer and then slowly and carefully add the catalyst. The methoxide is ready to be added to the oil once the catalyst has completely dissolved in the methanol. When methoxide is introduced to oil, a neutralisation process begins instantly. During the pretreatment process, certain alkali catalysts will react with rudimental acids or free fatty acids from the oil. As a result, additional catalyst is required to complete the reaction as reported by Leung, 2010. Canacki and Sanli, 2008 also discussed that catalyst may react with the free fatty acid of the oil to form soap and water as shown in Fig. 3.6. Here the catalyst is sodium hydroxide.



$$\text{R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OH} + \text{NaOH} \longrightarrow \text{R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-ONa} + H_2O$$

Fig. 3.6 Soap formation reaction (Source: Cancki and Sanli, 2008)

3.2.8 Transesterification

A transesterification process will begin when the catalyst, alcohol, and oil are combined and stirred in a reaction vessel. The reaction vessel for continuous alkali-catalyzed biodiesel manufacturing is typically a magnetic stirred reactor. To speed up the reaction, mixing puts the oil, catalyst, and alcohol into close contact while keeping the temperature slightly below the boiling point of the alcohol (64.5°C for methanol). Normally, the reaction pressure is near to atmospheric pressure to minimise alcohol loss, and extra alcohol is utilised to guarantee that the oil is completely converted to its esters. If the free fatty acid level or the water level are too high, it may interfere with saponification and the separation of the glycerol by-product downstream. During the process, the amount of water and free fatty acids in the feedstock oil should be measured. Following the completion of the transesterification process shown in Fig 3.7, Fig. 3.8 and Fig. 3.9 two primary products exist: esters (biodiesel) and glycerol as discussed by Leung at al., 2010.

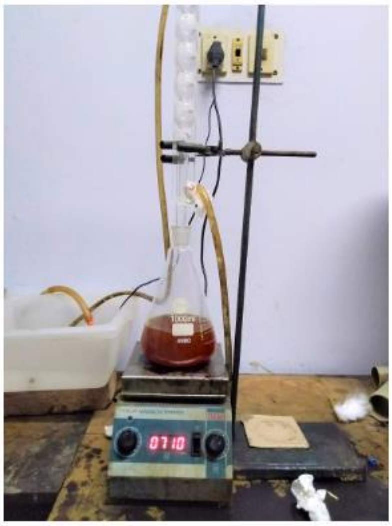


Fig. 3.7 Transesterification set up with heating and stirring

Fig 3.8 Colour of the mixture at the beginning of the reaction

Fig 3.9 Colour of the mixture at the end of the reaction

3.2.9 Separation

After completion of transesterification the reaction mixture is allowed to stand overnight for about 12 to 18 hours. The solution is poured in the separating funnel. The knob of the separating funnel is sealed with a greasy material called petroleum jelly and tied with rubber bands to prevent leakage. As the reaction mixture cools the separation becomes more and more prominent. It is observed that two layers are formed as shown in Fig. 3.10.

Fig. 3.10 Separation of biodiesel and glycerine

The upper layer is light yellow in colour and the lower layer is brown in colour. The upper layer is biodiesel or methyl ester and the lower layer is glycerol. Glycerol being denser settles at the bottom and the biodiesel floats on the top. Both layers contain some impurities like excess catalyst and excess alcohol. After the allowed settling time, opening the knob first lets out the glycerol and then the biodiesel is let out. Volumes of both biodiesel and glycerol are measured in measuring cylinders. Now the biodiesel is ready for washing to remove any excess catalyst present in it.

3.2.10 Purification of Crude Biodiesel by Water Washing

Crude biodiesel is mostly polluted by residual catalyst, water, unreacted alcohol, free glycerol, and soaps formed during the transesterification reaction after separation from the glycerol phase. Distilled water is used for bubble cleaning. Bubble washing involves placing a layer of water beneath the biodiesel and inflating the water with air bubbles. When the bubble breaks at the top of the tank, the water is pulled up into the biodiesel in a sma layer surrounding the air bubble, and it falls back down through the biodiesel. The aggressiveness of the washing process is determined by the size of the bubbles and the volume of air. Small bubbles with less flows are not aggressive, however huge bubbles with strong airflows are aggressive enough. The volume of water should be double than that of the volume of biodiesel. For this, an aquarium pump and an air stone are used as shown in Fig. 3.11. The airstone is connected to the pump by a plastic tube. The air bubbles are formed by the action of the pump. This is an efficient way of washing.

Fig. 3.11 Bubble Washing

Because glycerol and alcohol are both extremely soluble in water, water washing is an excellent method for eliminating these pollutants as well as residual salts and soaps. Distilled warm water or softened water is the basic ingredient for water cleaning. With a gentle washing action, distilled warm water avoids the precipitation of saturated fatty acid esters and delays the creation of emulsions. Softened water eliminates calcium and magnesium contamination and neutralizes any remaining alkali catalysts. After each washing, the mixture is allowed to stand in the separating funnel for some time till the oil and the residual water form separate layers. Then the pH value of the water is checked with pH paper. Washing is performed till the pH of this water shows the colour that of 7 of the pH paper. This means that there are no more dissolved acidic or basic impurities in water. Hence washing is done till the water phase becomes clear, meaning that the contaminants have been completely removed. Then, the biodiesel and water phases are separated by a separation funnel.

3.2.11 Heating

After washing the moisture present in the biodiesel has to be removed as the presence of moisture decreases the flash point and calorific value of the fuel. It also increases the viscosity of the fuel. Heating is done in two steps.

a) Firstly, three beakers are cleaned and dried. Biodiesel with moisture is kept in the first beaker. Biodiesel with moisture is an opaque yellow liquid. A little amount of this biodiesel is poured into the second beaker and heated on an electric heater. When the biodiesel becomes slightly more transparent it is poured into the third beaker. This is continued till the first beaker is empty.
b) The second step includes heating of the biodiesel kept in the third beaker. The third beaker is kept in an air oven with temperature set at 80°C for 20 minutes. Due to this heating if any excess methanol is still present also escapes. Biodiesel is now free of all impurities. Now the final biodiesel is obtained as shown below in Fig. 3.12. The volume of biodiesel obtained is measured after the oil attains ambient temperature.

Fig. 3.12 Refined biodiesel

3.3 Apparatus Used for Measurement of Different Properties of Biodiesel

3.3.1 Estimation of Density

The density was measured with the help of a pycnometer shown in Fig. 3.13. The volume of the biodiesel (V) inside the specific gravity bottle or pycnometer was measured first. Mass of the specific gravity bottle was measured both as empty (MA) and filled with biodiesel

(MB) in the beam balance. The difference between the masses was calculated and divided by the volume (V).

Density of biodiesel = $(\mathrm{M}B-\mathrm{M}A)/\mathrm{V}$ --------(3.4)

Fig. 3.13 Pycnometer

3.3.2 Flash Point and Fire Point

Flash point and fire point were measured with the help of a flash point apparatus shown in Fig. 3.14. The instrument consisted of a cup that is filled with oil up to a marked point. It consisted of a motor that stirred continuously during the process and a thermometer with upper limit of 300 °C. The bulb of the thermometer was inside the cup filled with biodiesel. There was an opening to introduce fire source inside the cup. When the power was turned on the temperature started to rise. The fire was introduced through the opening after it crossed 70°C temperature with an interval of 5°C, when the introduced fire turned off automatically that temperature was recorded. It is the flash point of the oil. After the flash point when the fire gets turned on again that temperature is the fire point and it is also recorded. Fire point is the point where the flame will be held by the biodiesel. Flash point is the point where the biodiesel gets inflamed and we see a flame then it extinguishes. This happens a couple of times before reaching the fire point as discussed by Babu and Anand, 2019.

Fig. 3.14   Pensky Martens Apparatus

3.3.3 Estimation of Viscosity

The kinematic viscosity of a fuel influences its atomization in an IC engine. The lower the kinematic viscosity value, the better the atomization of fuel. This allows for more efficient fuel combustion inside the IC engine. The viscosity of a fluid is a measure of its resistance to flow. It is measured using an Ostwald's viscometer. The Ostwald's Viscometer shown in Fig. 3.15 is made out of a U-shaped glass tube that is held vertically in a temperature-controlled bath. In a measuring cylinder, liquid is measured to a volume of 15 ml. This is done to guarantee that no errors occur. A vertical segment of an exact narrow bore (the capillary) is located in one arm of the U. Above this, is a bulb, and with another bulb in the lower portion on the other arm. Suction draws liquid into the upper bulb, which is then allowed to flow down via the capillary into the lower bulb. A known volume is indicated by two markers (one above and one below the top bulb). The time required for the liquid level to pass between these markings is related to the kinematic viscosity. The time taken for the test liquid to pass through a capillary of a specified diameter between two designated sites is measured. The kinematic viscosity is calculated by multiplying the time taken by the viscometer factor. For the viscosity measurement water is used as the reference liquid. Water is passed through the capillary and three readings are taken of the time water takes to fall from the upper mark to the lower mark. The apparatus must be dried before pouring biodiesel into it. This was done by placing the viscometer in an air oven till it dries completely at set temperature 90°C. Then biodiesel is passed through the viscometer's capillary. Again, three readings are taken of the time biodiesel takes to fall from the upper mark to the lower mark. Here the kinematic viscosity of the reference liquid, water, at 40°C is .658 mm^2/sec and at 30°C is .800 mm^2/sec as described by Joseph et al., 2009

$$\eta_1 = \eta_2 \cdot \rho_1 t_1 / \rho_2 t_2 \qquad \text{--------(3.5)}$$

where η_1 and η_2 are the viscosities of the liquid and water, respectively, and ρ_1 and ρ_2 are the densities of the liquid and water, and η_2 is the viscosity of the reference liquid, water as reported by Labmonk, 2018**.** Here t_1 and t_2 are the time interval of the liquid and reference liquid water to reach from the upper mark to the lower mark of the upper bulb.

Fig. 3.15 Viscosity measurement using Ostwald’s Viscometer

3.3.4 Estimation of Calorific Value

In a paper presented by Oliveira and Silva, 2013, calorific value is defined as the value, which denotes the amount of energy liberated in a closed chamber during the occurrence of combustion. It indicated the available energy in fuel. Bomb calorimeter is used to calculate the calorific value. Higher calorific value ensures higher yield.

As discussed by Parr Instrumentation Company, 2013 substitution procedure is used to find the heat of combustion in a bomb calorimeter. The heat obtained from the sample is compared to the heat obtained from the combustion of a similar quantity of benzoic acid or another standardising material with a known calorific value. These findings are achieved by burning a representative sample in a metal-pressure vessel or bomb at high oxygen pressure. The calorimeter absorbs the energy produced by this combustion, and the resulting change in temperature in the absorbing medium is recorded. The temperature rise in the calorimeter is then multiplied by an energy equivalent or heat capacity previously obtained through testing with a standardised substance to determine the heat of combustion of the sample.

A bomb calorimeter in Fig. 3.16 includes four essential components: (1) a bomb or container for burning the combustible charges, (2) a bucket or container to hold a given amount of water along with the bomb and equipped with a stirring mechanism, (3) an insulating jacket to shield the bucket from transitory thermal shocks during the combustion process, and (4) a thermometer or other sensor to track temperature changes inside the bucket. The parts described are numbered in the figure shown above. Parr Instrumentation Company, 2013 gives the heat of combustion of benzoic acid as 6318 calories/gram.

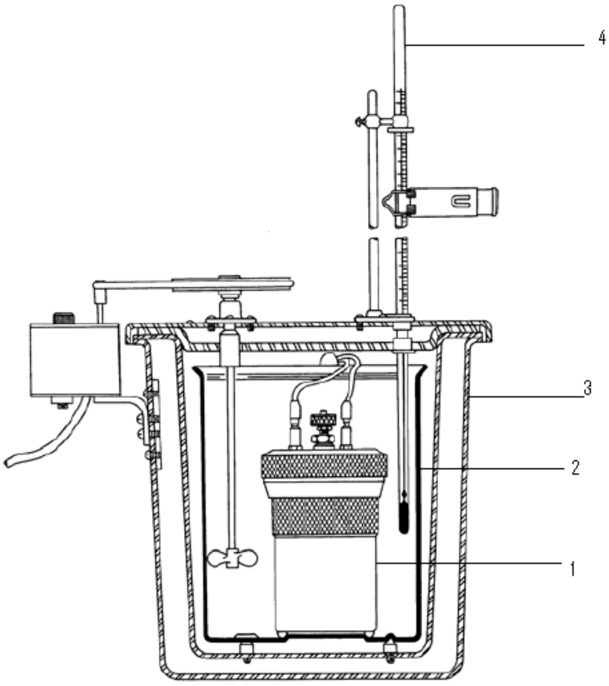


Fig. 3.16 Inner parts of a bomb calorimeter (Source: Parr Instrumentation Company, 2013)

3.3.4.1 Standardisation

As discussed by Parr Instrumentation Company, 2013, the energy equivalent or heat capacity of the bomb calorimeter must be established before testing a substance with an unknown heat of combustion. This number represents the total heat capacity of the calorimeter's elements, including the metal bomb, the bucket, and the water inside of it. By multiplying the reference material's heat of combustion by the weight of the sample burnt, one can calculate the amount of heat that was generated by the reference sample. We may then calculate the resulting energy equivalent for this specific calorimeter by dividing this amount by the temperature rise that was caused throughout the test. The parts of the calorimeter and its operating state is shown in Fig. 3.17, Fig. 3.18, Fig. 3.19 and Fig. 3.20.

The energy equivalent of the calorimeter will be calculated as follows.

Mass of benzoic acid= .8gms

Standard heat of combustion of benzoic acid=6318 cal/gm at 27°C

Temperature rise due to burning of given mass of benzoic acid=2.32°C

The calorimeter's energy equivalent (W) is then computed as follows.

$$W = (.8*6318)/2.32 = 2178.6 \text{ cal/°C} \text{ --------(3.6)}$$

Fig 3.17 Bomb or vessel in which combustion takes place

Fig. 3.18 Calorimeter in the laboratory

Fig. 3.19 Oxygen Cylinder to maintain pressure of 30kg/cm^2

Fig. 3.20 Calorimeter during operation

3.3.4.2 Fuel Test

The calorimeter can test fuel samples once the energy equivalent has been established. Burning samples with known weights causes a temperature increase, which is monitored and recorded. The observed temperature rise is then multiplied by the calorimeter's energy equivalent to calculate how much heat was produced from each sample. The sample's calorific value (heat of combustion) is then calculated on a unit weight basis by dividing this value by the sample's weight. The calorific value of biodiesel will be calculated as follows.

Here the heating value of carbon is 32.8MJ/kg as discussed by Engineering ToolBox, 2001.

Mass of biodiesel to be used for combustion = M_B gm

Temperature rise due to burning of given sample of biodiesel = T_s°C

Amount of fixed carbon left after combustion = M_c

Exact mass of biodiesel taking part in combustion = $M_s = M_B - M_c$

Heat of combustion of the given sample of biodiesel = $H_B = \frac{T_s * Ms}{W}$

Heat of combustion of carbon = 32800 joules/gm

$= \frac{32800}{4.18}$ calories/gm = 7846.889 calories/gm

=7847 calories/gm

Heat of combustion of left over carbon =$H_c = M_c * 7847$

Calorific value of the biodiesel = $\frac{H_B + H_c}{M_B}$ calories/gram --------(3.7)

3.4 Conclusion

The production of biodiesel involves a series of steps. The steps are uniform for any given set of parameters of biodiesel production. All the materials required during the process have been mentioned here. The formulae required at different stages will be used to calculate the required quantities. The equations derived in this section can be used throughout this study. The various instruments used for the calculation of various properties of biodiesel have also been discussed here. The generalised formulae have been mentioned here. They can be directly applied wherever required.

The methodologies which have been discussed here have been repeatedly used in the chapters. In order to prevent repetition of concepts, the generalised concepts have been mentioned here and they can be referred in the rest of the chapters.

Chapter 4

Experimental Studies on Biodiesel Production from Used Vegetable Oils and Non-edible Vegetable Oils

4.1 Introduction

Biodiesel is a product of a chemical reaction involving vegetable oil or animal fat, alcohol, and a catalyst. The feedstock mainly used for transesterification is edible vegetable oil. But this puts a strain on developing countries using this oil for cooking purposes. The solution to this problem would be to use used vegetable oil from the shops, hotels, and restaurants selling fried items for the production of biodiesel. Economic Times, 2019 reported that in India, 2,700 crore litres of cooking oil are consumed, of which 140 crore litres are collected from bulk customers such as hotels, restaurants, and canteens for conversion, yielding around 110 crore litres of biodiesel per year. According to Saah et al., 2021 there are 350 edible and non-edible oil-producing plants that could be used to make biodiesel worldwide. Due to the abundance of feedstock options, biodiesel manufacturing is more alluring. Based on the biomass sources, biodiesel feedstocks are classified into three types: first-generation biofuel, second-generation biofuel, and third-generation biofuel. as shown in the Fig. 4.1.

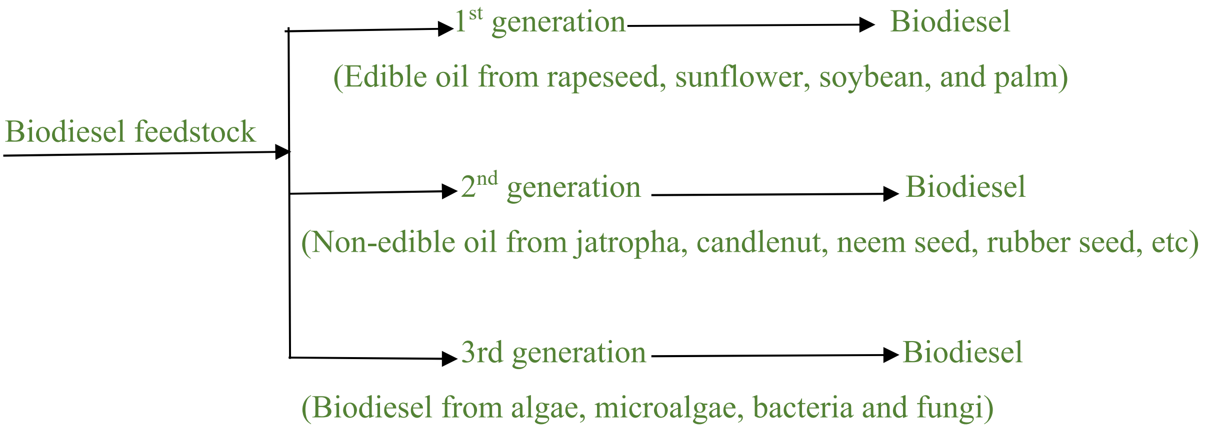


Fig. 4.1 Biodiesel production from various feedstock of different generations
(Source: Saah et al., 2021)

The fuel vs food controversy, however, was a challenge for edible oil-based biodiesel, and these issues have had a detrimental impact on the industry's ability to produce the fuel. As a result, second-generation feedstocks or non-edible vegetable oils have gained increased appeal for the manufacturing of biodiesel. To investigate non-edible feedstock for the second generation of biodiesel, several oils from non-edible plants can be used for biodiesel production as reported by Ong et al., 2013.

The present study helps to determine whether the collection of oils from various identified and non-identified sources from the streets of Kolkata can produce biodiesel or not. The mixture of oil from unknown sources will show the properties of biodiesel with reasonable productivity. But parameters giving optimum yield have to be regulated. Therefore, used oil of one kind has been adopted to study the optimisation along with other non-edible oils in the later part of this chapter. Oils of a single kind have been collected from fixed sources as well, in order to verify the properties and the cost of production. This study helps to determine whether the collection of oils from various identified and non-identified sources from the streets of Kolkata can lead to the production of biodiesel or not. It includes the comparison of the properties of biodiesel from used oils from different known and unknown sources and non-edible oils. Mostly palm oil and soybean oil are used in the market. But since palm oil can cause health-related issues, many shops are reluctant in sharing the source oil used. Hence, without knowing or having proof of the source, it cannot be used for further investigation. The used vegetable oil of one kind was readily available and was collected from Jadavpur University Guest House, Kolkata, 700132, West Bengal.

4.1.1 Objectives of the Present Chapter

- **Biodiesel production from used vegetable oil (mixed).**
- **Biodiesel production from linseed oil (raw).**
- **Biodiesel production from mahua oil (raw).**
- **Biodiesel production from used vegetable oil (soybean).**
- **Optimisation of the biodiesel produced from used vegetable oils and raw vegetable oils.**

4.2 Materials

Materials used for production are used vegetable oil (mixed), linseed oil (raw), mahua oil (raw) and used vegetable oil (soybean). The used oils have been collected from different known and unknown sources. In this study, the collection from different sources has been done for primary estimation of the potential of the used oil collected from the shops selling fritters. The non-edible oils have been collected from the local dealers. The study of the method of collection of waste oils from different sources has been discussed below.

4.2.1 Survey

In Kolkata, fritters are one of the popular snacks. The shops which sell these fritters run very successful businesses. These shops usually throw away the used oil as using it the next day decreases the quality of the fritters. The study of the method of collection of waste oils from different sources has been discussed here.

Biodiesel production from used vegetable oil handles the problem of waste management as well. A single shop can provide about 150 ml to 200 ml of impure used vegetable oil in a day. The city of Kolkata is divided into mainly 5 municipal areas namely, Kolkata Municipality, Dumdum Municipality, North Dumdum Municipality, South Dumdum Municipality and Bidhannagar Municipality. These municipalities collectively cover an area of 251.66 km^2. A total of 254 wards are under these municipalities as informed by Dum Dum Municipality, 2013, North Dum Municipality,2013, South Dum Dum Municipality, 2013 and Kolkata Municipal Corporation, 2013.

A ward has about 15 to 20 fritter shops. The used vegetable oil contains a wide variety of fatty acids in it. Used vegetable oil has more fatty acids than refined vegetable oil. Thus, the processing of the former is slightly different from the latter. But no work appears to have been reported on biodiesel production from used vegetable oil collected from shops selling fritters, especially in Kolkata. Feedstock used for this process was used vegetable oil which was collected from a number of shops in Kolkata that sell fritters. These shops used palm oil, soybean oil, and sometimes a mixture of these oils. Apart from this mass collection of oil has also been done from a single source. Used vegetable oil (soybean) was available in large amounts at regular intervals. But the quality of the oil changed from time to time. In the first attempt at collection of the feedstock, the impurities were less in comparison to the feedstock collected later.

4.2.2 Method

In this present study used vegetable oils collected from different sources were filtered. Larger particles like pieces of fried batter and vegetables were removed by passing the oil through a sieve. Then these oil samples were filtered with the help of a piece of cotton wool kept at the mouth of a funnel. Oil was passed through it into a beaker to remove the finer carbon particles. Later on, vacuum filtration was adopted for the removal of finer particles. The used vegetable oil (mixed) and used vegetable oil (soybean) have a lot of impurities of food particles and black carbon particles. Primary filtration was done in the container in which it was kept. If it is left to settle for 1-2 days, the heavier particles settle at the bottom. The top part of the oil can then be passed through waste cotton to filter the larger food particles. Secondary filtration was vacuum filtration where the oil was passed through filter paper placed in the ceramic filter fitted over a Buchner flask where the clean oil was collected. Sodium hydroxide and methanol were used during the production of biodiesel in the initial sets but later on, potassium hydroxide was used as the standard catalyst because of its inherent property of lesser possibility of soap formation.

The different oils used for this experimental study are used vegetable oil (mixed), used vegetable oil(soybean), raw linseed oil, and raw mahua oil. A survey was conducted where used vegetable oil samples were collected from fritter shops in Kolkata. In the case of used vegetable oil (mixed), these samples were mixed together as few sources were unknown and less amount of oil was obtained from different vendors. Later on, oil was collected from fixed sources to maintain the quality of the fixed type of oil. Here the molecular weight of the used vegetable oil (mixed) has been considered as 882 as reported by Leung et al., 2006. The used vegetable oil of soybean origin has been collected at different times from different sources as the oil was required in intervals. The used soybean oil has been collected from Jadavpur University, Guest House. As reported by Mihail and Zoran et al., 2011 the molecular weight of soybean oil is 874. The molecular weight of used vegetable soybean oil has been considered as 874. The consideration of the molecular weight of the used oil, the same as that of the raw oil has been adopted for all the used oils in this study in the following chapters as well. As mentioned by Singh and Sharma, 2015, the molecular weight of mahua oil is 280. The molecular weight of linseed is 878, according to Gay, 1933. The various calculation to be performed hereafter have been mentioned in Annexure I for used vegetable oil (mixed), linseed oil, mahua oil and used vegetable oil(soybean).

4.3 Determination of the Properties of the Oils

4.3.1 Density of the Oils

The density of the oil samples has been calculated as described in Eq. 3.3 of Chapter 3 for biodiesel and have been mentioned in Table 4.1.

Table 4.1 Density of oils

Types of oils	Density in kg/m^3
Used vegetable oil (mixed)	910
Linseed oil	926
Mahua Oil	886
Used vegetable oil (soybean)	897

4.3.2 Acid Value and Free Fatty Acid (FFA) Content of Oil

Acid value enables to verify the feasibility of the process selected which can be alkali transesterification or acid transesterification. As mentioned in Eq. 3.1 of Chapter 3, the acid value of the feedstock has been calculated. The FFA content is calculated as mentioned in Eq. 3.2 of Chapter 3 and is tabulated in Fig. 4.2.

Table 4.2 Acid values and FFA content of oils

Types of oils	Acid Value	% of FFA content
Used vegetable oil (mixed)	1.69	0.852
Linseed oil	2.345	1.18
Mahua Oil	34.791	17.5
Used vegetable oil (soybean)	1.809	0.910

The mahua oil has very high FFA content because of which it will be first esterified to bring down the acid value and FFA as shown in Table 4.3 and then it will undergo transesterification.

Table 4.3 Acid value and FFA content of esterified mahua oil

Type of oil	Acid Value	% of FFA content
Esterified mahua oil	3.280	1.65

4.4 Procedure of Biodiesel Production

The biodiesel conversion experiments were conducted in the bio-energy laboratory of the Department of School of Energy Studies, Jadavpur University, Kolkata, India. The filtered used vegetable oil (mixed), used vegetable oil (soybean) and linseed oil have free fatty acid content less than 2.5%. They undergo direct transesterification. The catalyst and the alcohol were completely stirred and then the calculated amount of oil was added. The experimental setup consisted of a 500 ml frosted conical flask fitted with a reflux condenser on a magnetic stirrer. Biodiesel derived from used vegetable oil (mixed) was prepared by first dissolving the catalyst NaOH which is .7% w/w of oil with the given ratio of methanol: oil without any application of heat. The amount of catalyst has been kept neither at .5% nor at 1% w/w of oil in order to check the feasibility of the reaction. The amount of alcohol is a bit more than actually required so that the forward reaction is not hindered. After complete dissolution, 100 ml of oil was added to this mixture. The reaction was carried out in a 500 ml conical flask fitted with a reflux condenser over a magnetic stirrer. The reflux condenser was used to prevent the methanol from escaping. After the reaction was completed, the reaction mixture was allowed to settle overnight in a separating funnel. The knob of the separating funnel was sealed with petroleum jelly and tied with rubber bands to prevent leakage. The mixture formed two distinct layers. The upper phase contained methyl ester (or biodiesel) and impurities like excess catalyst and methanol. The lower phase contained glycerol.

In the case of used vegetable oil (mixed), only the variation of molar ratio could be studied due to the limited availability of the sample and the reaction was carried out for 90 minutes under reflux at 55ºC. But in the case of other samples, the different parameters were varied one at a time keeping the other factors constant and the reaction was carried out at 45ºC for used vegetable oil (soybean) and at 60ºC for linseed oil (raw) and mahua oil (raw) with KOH as catalyst for obvious reasons. The reaction time has also been increased to 2 hours for allowing better conversion. The rpm was maintained at 1000 for all the sets. Mahua oil has free fatty acid content of 17.5%. To avoid saponification this oil has to be esterified in the presence of acid like H_2SO_4. In Step I, H_2SO_4 reacts to the oil and produces esterified oil and water-alcohol mixture. This mixture was separated in a separating funnel by keeping it standing for 1.5 hours. The upper darker layer was the methanol and water mixture and the lighter bottom layer was the esterified oil which is ready for transesterification in Step II. The reaction mixture was allowed to stand for overnight in a separating funnel after a stipulated duration of stirring. Two clear separate phases were obtained. Glycerol being at the bottom, methyl ester formed the upper layer. Then the oil was separated from dissolved water via separating funnel. The methyl ester obtained popularly known as the crude biodiesel underwent repeated washing with hot distilled water at 80^0C till the pH of the dissolved water became neutral. The volume of distilled water used was double the volume of crude biodiesel obtained. Bubble washing was repeated several times. Care was taken that no froth was formed. The mixture was then poured into the separating funnel and kept for half an hour. Biodiesel being lighter formed the upper layer and water formed the lower layer. The pH of water was checked with a pH strip. This process was repeated till the colour of the pH strip was green indicating a pH of 7 and complete removal of the catalyst. After washing, the biodiesel was heated to remove any moisture present. Washing was followed by heating of the oil in oven followed by heating in air oven at 90^0C for 15- 20 minutes. After the oil was cooled to normal temperature, yield of biodiesel was finally measured. Tables below show the percentage yield of biodiesel after the variation of process parameters of used vegetable oil (mixed), used vegetable oil (soybean), linseed oil and mahua oil respectively. The amount of catalyst and the amount of alcohol can be calculated as mentioned in section 3.2.4 and 3.2.5 of Chapter 3 respectively. The yield of biodiesel will be calculated as described in Eq. 4.1 of Chapter 4. In case of used vegetable oil (mixed), experiment setups were carried out for varying molar ratios of alcohol to oil (3:1, 6:1, 12:1, 15:1).

The amount of catalyst used, the reaction temperature and the stirring rate were kept constant. The limited amount of used vegetable oil (mixed) could be used to study biodiesel production for the given molar ratios. But the variation of different process parameters has been carried out for the rest of the samples of the different types of oils.

4.5 Results

4.5.1 Yield of Biodiesel

The percentage of yield has been calculated based on the volume of biodiesel and volume of oil. Table 4.4. shows the yields of biodiesels at different molar ratios.

$$\text{Percentage yield of biodiesel} = \frac{\text{Volume of biodiesel obtained}}{\text{Volume of oil considered}} \times 100 \text{ ---------(4.1)}$$

Table 4.4 Percentage yield of biodiesel prepared from 100 ml used vegetable oil (mixed) at different reaction conditions. (reaction temperature = 55^0C, stirring rate = 1000 rpm, reaction time = 1.5 hours)

Molar ratio of alcohol: oil	Catalyst concentration (%w/w)	Yield of biodiesel (%)
3:1	0.7	72
6:1	0.7	76
12:1	0.7	80
15:1	0.7	86

The amount of alcohol required for a given amount of oil was calculated as expressed in Equation 3.3 of section 3.2.5 of Chapter 3. Here the calculation for the volume of alcohol required for the molar ratio of 3:1 has been shown below and the same follows for all the other molar ratios as well.

Therefore, as described in section 3.2.5 of Chapter 3,

Density of oil = 0.91 kg/m^3

Mass of oil considered of used vegetable oil (mixed)= 91 gm

In all the cases mass of 100 ml of the corresponding oil has been considered. Therefore, 91 gm is the mass of 100 ml of the used vegetable oil(mixed).

Molecular weight of used vegetable oil (mixed) = Mass of 1 mole of used vegetable oil (mixed) = 882 gm

Molecular weight of methanol = 32

Molar ratio of methanol: oil = 3:1

Mass of 3 mole of alcohol/acid = 3 x 32

Mass of alcohol used to react with 91 gm of used vegetable oil (mixed) = $32 \text{ x } 3 \text{ x } 91/_{882}$

Volume of alcohol used to react with 100 ml of used vegetable oil(mixed)

$$= \frac{32 \text{ x } 3 \text{ x } 91}{(0.7918 \text{ x } 882)} = 12 \text{ ml}$$

Similarly, the other molar ratios have been calculated and are mentioned in the Table 4.5.

Table 4.5 Volume of alcohol for the corresponding molar ratios of alcohol: oil

Molar ratios of methanol: oil	Volume of methanol (ml)
3:1	12
6:1	25
12:1	50
15:1	63

The catalyst concentration has been calculated as discussed in section 3.2.4 of Chapter 3. Here the catalyst concentration is .7%w/w of oil which means that 100 gm oil requires .7 gm of sodium hydroxide for the reaction process. Here the mass of 100 ml of the oil is 91 gm. Therefore,

Amount of sodium hydroxide required for 100ml of oil = $\frac{0.7\times 91}{100} = 0.637$ gm.

In the same manner, the amount of alcohol(methanol) and the amount of catalyst (KOH) has been calculated for the linseed oil, mahua oil and used vegetable oil(soybean) which is required for the process of transesterification.

Table 4.6 Percentage yield of biodiesel prepared from 100ml of linseed oil (raw) at different reaction conditions. (reaction temperature of 60^0C and stirring rate of 1000 rpm)

Parameter changed	Reaction Time (hr)	Molar ratio of alcohol: oil	Catalyst concentration (%w/w)	Yield (%)
Molar ratio	2	**3:1**	1	89
	2	**6:1**	1	88
	2	**9:1**	1	90
	2	**12:1**	1	90
Catalyst concentration	2	9:1	**0.5**	85
	2	9:1	**1**	90
	2	9:1	**1.5**	84
	2	9:1	**2**	79
Reaction time	**0.5**	9:1	1	87
	1	9:1	1	87.5
	1.5	9:1	1	90
	2	9:1	1	90
	2.5	9:1	1	88

Table 4.7 Percentage yield of biodiesel prepared from 100ml of mahua oil (raw) at different reaction conditions. (reaction temperature of 60^0C and stirring rate of 1000 rpm)

Parameter changed	Reaction time (hr)	Molar ratio of alcohol:oil	Catalyst concentration (%w/w)	Yield (%)
Molar ratio	STEP I:1 STEP II:1	**STEP I: 6:1** **STEP II: 6:1**	1.24 % v/v H_2SO_4 0.7% w/w KOH	77
	STEP I:1 STEP II:1	**STEP I: 8:1** **STEP II: 6:1**	1.24 % v/v H_2SO_4 0.7% w/w KOH	92
	STEP I :1 STEP II:1	**STEP I: 8:1** **STEP II: 8:1**	1.24 % v/v H_2SO_4 0.7% w/w KOH	87.5
	STEP I:1 STEP II:1	**STEP I: 8:1** **STEP II: 9:1**	1.24% v/v H_2SO_4 0.7% w/w KOH	80
	STEP I:1 STEP II:1	**STEP I: 8:1** **STEP II: 12:1**	1.24 % v/v H_2SO_4 0.7% w/w KOH	75
Reaction time	**STEP I:1** **STEP II:1**	STEP I: 8:1 STEP II: 6:1	1.24 % v/v H_2SO_4 0.7% w/w KOH	92
	STEP I:1 **STEP II:2**	STEP I: 8:1 STEP II: 6:1	1.24 % v/v H_2SO_4 0.7% w/w KOH	80

Table 4.8 Percentage yield of biodiesel prepared from 100 ml of used vegetable oil (soybean) at different reaction conditions. (reaction temperature = 45^{0}C, stirring rate = 1000 rpm)

Parameter changed	Reaction Time (hr)	Molar ratio of alcohol:oil	Catalyst concentration (%w/w)	Yield (%)
Molar ratio	2	**6:1**	1	90
	2	**9:1**	1	97
	2	**12:1**	1	92
Catalyst concentration	2	9:1	**0.5**	90
	2	9:1	**1**	97
	2	9:1	**1.5**	89
	2	9:1	**2**	88
Reaction time	**0.5**	9:1	1	91
	1	9:1	1	93
	1.5	9:1	1	94
	2	9:1	1	97
	2.5	9:1	1	87

In Table 4.4, it can be seen that the optimum yield of 86% biodiesel has been obtained in case of used vegetable oil (mixed) at molar ratio 15:1, catalyst concentration of .7% w/w of oil, reaction temperature of 55 ^{0}C, reaction time of 1.5 hours and at 1000 rpm. Table 4.6 summarizes the optimum yield of biodiesel from linseed oil as 90% with process parameters as molar ratio 9:1, 1% w/w of oil of catalyst concentration, 60 ^{0}C reaction temperature, 2 hours of reaction time and 1000 rpm stirring rate. In Table 4.7 the biodiesel from mahua oil gives optimum yield of 92% at 1hour acid esterification with acid catalyst concentration of 1.24 % v/v of oil and molar ratio of 8:1 followed by 1 hour alkali transesterification with basic catalyst concentration of 0.7% w/w of oil and molar ratio of 6:1 at 60 ^{0}C. In case of used vegetable oil (soybean), the optimum yield of biodiesel is 97% at molar ratio 9:1, catalyst concentration of 1% w/w of oil, reaction temperature of 45 ^{0}C, reaction time of 2 hours and 1000 rpm as seen in Table 4.8. Table 4.9 below shows the optimised parameters opted for optimised biodiesel yield from different types of oil

Table 4.9 Process parameters giving optimum yield of biodiesel for the different types of feedstock

Types of feedstock	Molar ratio	Catalyst concentration	Reaction temperature(°C)	Stirring rate (rpm)	Reaction time (hr)	Percentage yield (%)
Used vegetable oil (mixed)	15:1	NaOH .7% w/w of oil	55	1000	1.5	86
Linseed oil	9:1	KOH 1% w/w of oil	60	1000	2	90
Mahua oil	STEP I: 8:1 STEP II: 6:1	STEP I: H_2SO_4 1.24% v/v of oil STEP II: KOH .7% w/w of oil	60	1000	1 1	92
Used vegetable oil (soybean)	9:1	KOH 1% w/w of oil	45	1000	2	97

Since many types of vegetable oils are used for cooking purposes, biodiesel production has been tried with other vegetable oils like used rice bran oil and used biodiesel oil. Since the data with respect to the yield of used oils was not available at the time of the study, the parameters for the corresponding raw oils have been considered with respect to the studies mentioned hereafter. Sinha et al., 2008 tell that the optimum parameters for biodiesel production from rice bran oil are 9:1 molar ratio of alcohol: oil, .75% catalyst concentration of NaOH, 1 hour reaction time, 55^0C temperature. But since the present work is based on used rice bran oil, the reaction time is kept as 2 hours. The catalyst, KOH has been used here of the same catalyst concentration as mentioned in the study of rice bran oil optimisation. As investigated by Saydut et al., 2016, the process parameters for carrying out the transesterification reaction of biodiesel production from sunflower oil were reaction time of 2 hours, with the molar ratio of alcohol: oil as 6:1 and catalyst concentration of .7% w/w of oil with reaction temperature at 60^0C. The process parameters for biodiesel production from used sunflower oil in this study are the same as mentioned above. The molecular weight of used sunflower oil was adopted from the investigation report by

Macrolgae et al., 2012, which said that the molecular weight of sunflower oil is 876.16. Similarly, 867.90 is the molecular weight of rice bran oil as reported by Li et al., 2011. Now the amount of methanol and the amount of oil with respect to the molar ratios can be calculated as described in Eq. 3.2.5 of Chapter 3 and the mass of the catalyst required is calculated as discussed in Eq. 3.2.4 of Chapter 3. The used rice bran oil was given collected from the Bakultala Canteen, Jadavpur University, Kolkata. The used sunflower oil was obtained from the Hot Chips retail outlet in Kaikhali, Kolkata. Biodiesel was produced from these two used oils as these oils are also readily available in the market and are extensively used for consumption. Therefore, the used oils of these two types can be easily collected if the collection is channelised in a proper manner. The operating parameters for used vegetable oil (rice bran) and used vegetable oil (sunflower) are shown in Table 4.10.

Table 4.10 Process parameters giving optimum yield of biodiesel for used vegetable oil (rice bran) and used vegetable oil (sunflower) at different reaction conditions

Types of feedstock	Molar ratio	Catalyst concentration	Reaction temperature(°C)	Stirring rate (rpm)	Reaction time (hr)	Percentage yield (%)
Used vegetable oil (rice bran)	9:1	KOH 0.75% w/w of oil	55	1000	2	92
Used vegetable oil (sunflower)	6:1	KOH 0.7% w/w of oil	60	1000	2	94

4.5.2 Estimation of Properties of Biodiesel Prepared from Used Vegetable Oils and Raw Oils

The tables below show the properties of used vegetable oil (mixed), used vegetable oil (soybean), linseed oil, and mahua oil respectively. The densities and viscosities of the biodiesels from the oils of used vegetable oil, linseed oil, and mahua oil have been calculated as shown in Eq. 3.3.1 and Eq. 3.3.3 of Chapter 3 respectively. Flashpoint and fire point have been measured as discussed in section 3.3.2 of Chapter 3. The calorific value of the optimum yield of biodiesel from used vegetable oil (mixed) has been calculated as described in section 3.3.4 of Chapter 3. In the case of biodiesel from the used vegetable oil (mixed) sample, the physicochemical properties of the optimum yield at 12:1 molar ratio have been discussed in

Table 4.11. For all the other samples of biodiesel, the properties of all the sets for each sample of biodiesel have been discussed.

Table 4.11 Properties of the biodiesel produced from used vegetable oil (mixed) at optimum conditions

Properties	Values
Density in kg/m^3	870
Kinematic viscosity at 30^0C in centistokes	5.9
Calorific Value in kcal/kg	7816
Flash Point in ^{0}C	179

Table 4.12 Properties of biodiesel prepared from linseed oil (raw) at different reaction conditions

Parameter changed	Magnitude of parameters	Constant parameters		Density kg/m^3	Viscosity (m^2/sec)x10^{-6}
Molar ratio	3:1	Catalyst:1% Reaction time: 2hr	Stirring rate: 1000 rpm Temperature: 60^0C	880	7.96
	6:1			878	6.05
	9:1			872	5.90
	12:1			884	8.41
Catalyst concentration	0.5	Molar ratio: 9:1 Reaction time: 2hr	Stirring rate: 1000 rpm Temperature: 60^0C	876	5.66
	1			872	5.90
	1.5			870	4.88
	2			886	5.90
Reaction time	0.5	Catalyst: 1%w/w KOH Molar ratio: 9:1	Stirring rate: 1000 rpm Temperature: 60^0C	874	6.34
	1			886	5.01
	1.5			873	5.50
	2			872	5.90
	2.5			878	5.61

Table 4.13 Properties of biodiesel prepared from mahua oil (raw) at different reaction conditions.

Parameter changed	Magnitude of parameter	Constant parameters		Density (kg/m^3)	Viscosity (m^2/sec) x10^{-6}
Molar ratio	STEP I 6:1 STEP II 6:1	Catalyst: Step I:1.24% v/v H_2SO_4 Step II:0.7%w/w KOH Reaction time-2hr	Stirring rate: 1000 rpm Temperature : 60^{0}C	846	6.46
	STEP I 8:1 STEP II 6:1			880	6.10
	STEP I 8:1 STEP II 8:1			852	6.11
	STEP I 8:1 STEP II 9:1			839	7.16
	STEP I 8:1 STEP II 12:1			841	6.49
Reaction time(hrs)	STEP I 1 STEP II 1	Molar ratio: Step I: 8:1 Step II: 6:1 Catalyst: Step I: 1.24% v/v H_2SO_4 Step II: 0.7% w/w KOH	Stirring rate: 1000 rpm Temperature: 60^{0}C	880	6.10

Table 4.14 Properties of biodiesel prepared from used vegetable oil(soybean) at different reaction conditions.

Parameter changed	Magnitude of parameters	Constant parameters		Density kg/m^3	Viscosity (m^2/sec) x10^{-6}
Molar ratio	6:1	Catalyst:1% Reaction time: 2hr	Stirring rate: 1000 rpm Temperature: 45^0C	861	5.88
	9:1			850	5.11
	12:1			845	5.10
Catalyst concentration	0.5	Molar ratio: 9:1 Reaction time:2hr	Stirring rate: 1000 rpm Temperature: 45^0C	813	5.65
	1			850	5.11
	1.5			839	5.5
	2			791	9.79
Reaction time	0.5	Catalyst:1% w/w KOH Molar ratio: 9:1	Stirring rate: 1000 rpm Temperature: 45^0C	857	5.44
	1			865	5.20
	1.5			872	5.92
	2			850	5.11
	2.5			868	5.56

4.6 Discussion

The most relevant variables in the process of transesterification are reaction temperature, molar ratio of oil to alcohol, amount of catalyst used and the stirring rate in revolutions per minute (rpm). In this particular procedure of biodiesel production from used vegetable oil (mixed), it was seen that as the molar ratio of oil to alcohol was varied from 1:3 to 1:15 the percentage of yield of biodiesel increased. Yield of biodiesel increased as the amount of alcohol used was increased. The reaction temperature was kept constant at 55^{o}C. This temperature was not increased further as it would have resulted in the loss of alcohol. The amount of catalyst used was kept between 0.5% and 1.0% (weight of catalyst/weight of oil). The final biodiesel's physical qualities will be determined by the properties of the free fatty acids present. It determines the yield of product derived from the respective raw material. The maximum yield of 86% was achieved using a greater quantity of methanol. Density is important mainly when the oil is combusted in a CI engine because it affects the efficiency of fuel atomization. The density of the biodiesel generated in this research was 870 kg/m3. When exposed to a flame or spark, a fuel's flash point is the temperature at which it will ignite. Biodiesel has a higher flash point than petrodiesel, making it suitable for transportation as reported by Ma and Hanna, 1997. The flash point was found to be 179ºC. Calorific value of a fuel is defined as the number of heat units liberated by a unit mass of a sample when burned with oxygen in an enclosure of constant volume. The calorific value of biodiesel was 7816 kcal/kg. Viscosity is a measure of a fluid's resistance to flow. The kinematic viscosity of biodiesel was measured to be 5.9 centistokes at 30ºC.

In case of biodiesels from other feedstock, the density and viscosity of all the samples have been studied to compare the properties of the other yields with the optimum yield for biodiesel of each type of oil. After calculating the value of the above-mentioned physicochemical properties of the biodiesels made from used vegetable oil (soybean), linseed oil and mahua oil, tabulated in Table 4.12, Table 4.13 and Table 4.14 respectively, the variation in the properties can be identified in the graphs Fig. 4.2, Fig. 4.3 and Fig. 4.4 respectively which are showing the change in percentage yield and change in kinematic viscosity with respect to change in the molar ratio of respective biodiesels.

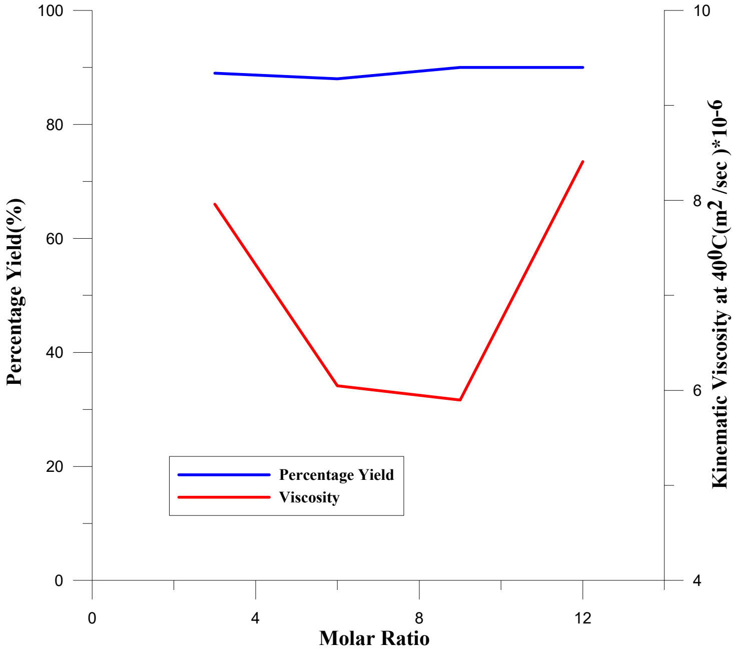


Fig. 4.2 Molar ratio (alcohol:oil) versus percentage yield and kinematic viscosity of biodiesel produced from linseed oil (raw)

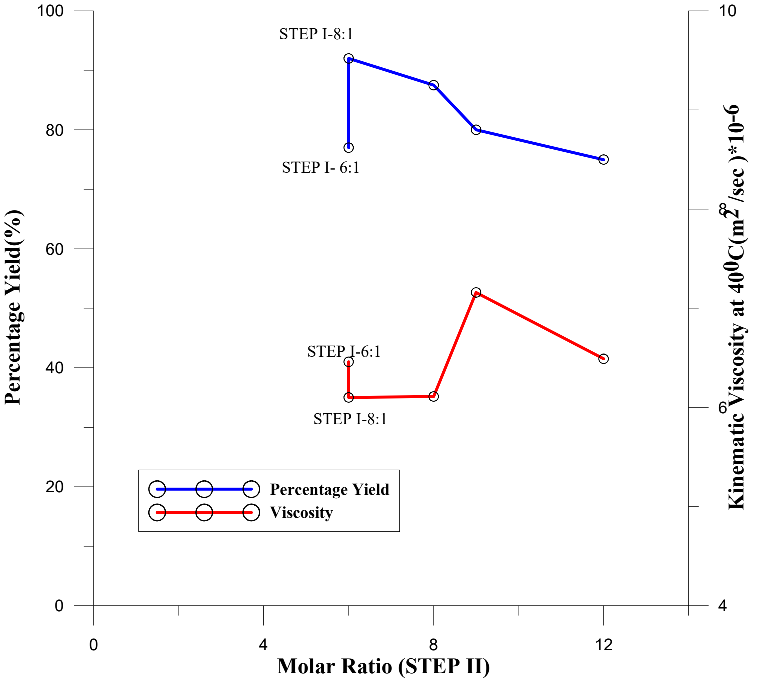


Fig. 4.3 Molar ratio (alcohol:oil) versus percentage yield and kinematic viscosity of biodiesel produced from mahua oil (raw)

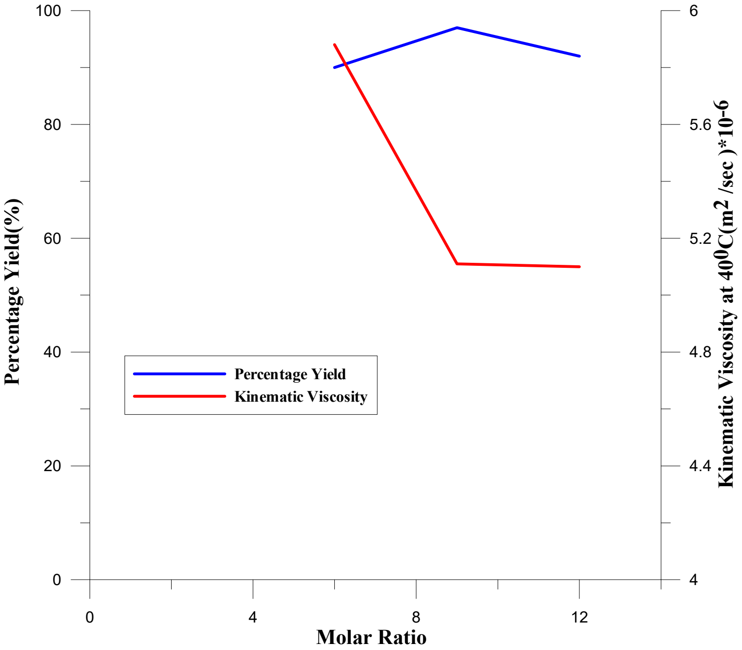


Fig. 4.4 Molar ratio (alcohol:oil) versus percentage yield and kinematic viscosity of biodiesel produced from used vegetable oil (soybean)

Biodiesel from linseed oil has very high viscosity at 12:1 although the percentage yield is the same for 9:1 and 12:1. It shows the optimum yield at 1.5 hours and at 2 hours at 9:1 molar ratio and 1% w/w of catalyst concentration. The viscosity is higher at 2 hours than at 1.5 but the density is lesser at 2 hours than at 1.5 hours. As in the case of other biodiesel samples, the reaction time of 2 hours is giving the optimum yield of biodiesel than the yield at 1.5 hours, the yield at reaction time of 2 hours has been considered as optimum for biodiesel from linseed oil. Biodiesel from mahua oil undergoes two-step process of transesterification. Increase in molar ratio in Step I till 8:1 decreases the kinematic viscosity but further increase in molar ratio in Step II does not significantly decrease the viscosity. Therefore, the molar ratio of 8:1 and 6:1 in the two subsequent steps with maximum yield (Fig.4.3) has been taken as the optimized parameter. There has been no significant increase in the kinematic viscosity of biodiesel from used vegetable oil (soybean) when the molar ratio was changed from 9:1 to 12:1. But the yield slightly decreases with an increase in molar ratio (Fig.4.4). Therefore, molar ratio 9:1 has been taken under consideration. Although maximum yield has been obtained at 0.5 hrs, viscosity is higher which may be due to incomplete reaction.

Table 4.15 shows the most optimized yield and kinematic viscosity for all three biodiesels from different sources.

Table 4.15 Optimised properties of biodiesel prepared from different types of feedstock and their yields

Oil	Density (kg/m^3)	Viscosity (m^2/sec)*10^{-6}	Yield (%)
Used vegetable oil (mixed)	870	5.90	86
Linseed oil (raw)	872	5.90	90
Mahua oil (raw)	880	6.10	92
Used vegetable oil (soybean)	850	5.11	97

The results show that transesterification improvises oil characteristics and gets them closer to those of diesel. The methyl ester of used vegetable oil can be successfully used instead of diesel or in blended form. The colour of biodiesel from used vegetable oil was bright yellow. Used vegetable oil is not that difficult to find and collect, as there are large food companies selling fried items. They need to maintain the quality of food items to sell the used oil to soap manufacturing companies. This oil can be collected as feedstock for biodiesel. Thus, there will be no competition to food as refined oil is used for cooking. But the amount of alcohol invested is very high in comparison to the yield obtained. Excess alcohol will need proper removal after the production thereby increasing the cost of production. Here NaOH has been used as a catalyst, but KOH reacts faster than NaOH, hence is preferred in the later part of the study. The yield can be increased if the used oil of one particular type can be collected from a single source. Then, the optimization can be done in a better manner. The study of raw non-edible oils is also important for comparative analysis with the used oils. In order to find the optimised source for biodiesel production, the comparison of the properties of the optimized yield of different non-edible oils and used vegetable oils has been shown in the Fig. 4.5.

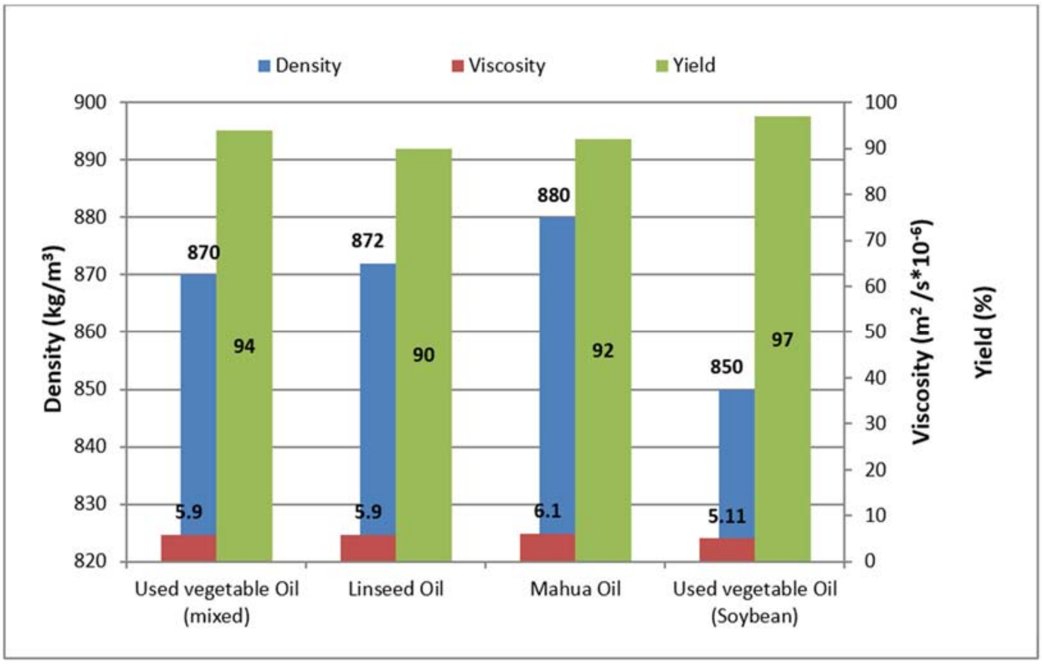


Fig. 4.5 Comparison of properties of biodiesel produced from used vegetable oil (mixed), linseed oil, mahua oil, used vegetable oil (soybean oil)

It can be very well observed that the density and viscosity are the least and yield is the highest in case of biodiesel from used vegetable oil (soybean). Therefore, it can be concluded that, out of all the raw oils and mixed oils, the biodiesel from used oil (soybean) has given the optimum yield and has shown impressive results in terms of physicochemical properties.

4.7 Conclusion

Used vegetable oil collected from shops selling fritters can be used to produce biodiesel as it is not a food source and is mostly thrown away. The collection of oil has to be streamlined for the procurement of oil. The optimised yield has to be obtained for in order to decrease the cost of production. The optimised yield of biodiesel prepared from used vegetable oil (soybean) obtained is 96% - 97%.

Oil from different kinds of feedstock can be utilized for biodiesel production. Depending upon the process parameters, the yield and kinematic viscosity vary. The molar ratio of 9:1 is the optimized parameter for the used vegetable oil (soybean) undergoing single-step transesterification. The complete transesterification takes 2 hours and the catalyst concentration of 1% is giving optimized yield for the single-step process. If FFA content is high then a two-step process is mandatory as in the case of mahua oil. The other parameters like time and temperature can also be varied and the yield of fatty acid methyl ester can be studied. The best properties are seen in the biodiesel from used oil than the biodiesels from other non-edible oils. Therefore, used vegetable oil can be accepted as the best source for biodiesel production if collected in a proper manner.

In the first part of the study of optimisation, biodiesel has been produced from used vegetable oil collected from mixed sources. The requirement for alcohol is very high in that case. The reason might be that all the sources were not known. Viscosity is close to 6 mm/sec^2. But when used vegetable oil (soybean) is used as feedstock then, the yield is comparatively higher with lower viscosity. Therefore, it can be concluded that the optimization has enabled to choose the right kind of used oil for biodiesel production for a country like India, where there is a huge requirement of blending of diesel with biodiesel to improvise the emission characteristics.

Chapter 5

A Statistical Approach for Optimisation of Process Parameters for Biodiesel Production

5.1 Introduction

A systematic, effective strategy called design of experiments (DOE) enables scientists and engineers to investigate the link between several input variables (also known as factors) and important output variables or responses. It is a methodical process for gathering information and developing discoveries as discussed by JMP statistical discovery, 2023. They have also discussed the reasons for requirement of DOE which have been mentioned below.

DOE is required because:

- it ascertains whether a particular factor—or a group of factors—has an impact on the response.
- it ascertains whether variables interact while influencing the response.
- it simulates the response's behaviour in relation to the factors.
- it helps in optimising the reaction as reported by JMP statistical discovery, 2023.

According to Kumari and Gupta, 2019, a collection of statistical and mathematical tools called the response surface methodology (RSM), which is based on the design of experiments, are used to plan trials and optimise the impact of process factors. RSM recognises the influence of process factors on the removal process and minimises the number of trials. Manojkumar et al., 2022 suggested that a helpful statistical tool for experiment design, optimization, and analysis in any process is called the Response Surface Methodology. The specifics of interactions and quadratic effects between the process variables that are involved in the process and cannot be exposed by the conventional optimisation methods which one variable at a time, are provided by RSM. Both the central composite design (CCD) and the Box-Behnken design (BBD), which are used to examine the process variables at five and three levels, respectively, are part of RSM. CCD is an effective and frequently used design that has been documented in the literature for the optimization of numerous processes. The highlights of the methodology have been shown in Fig. 5.1.

Fig. 5.1 Highlights of RSM (Source: Manojkumar, et al., 2022)

The influence of reaction temperature, catalyst concentration, and circulation flow rate on membrane reactor-based biodiesel synthesis was examined using response surface technique modelling as investigated by Moyo et al., 2021. To maximise biodiesel yield, various reaction conditions were also adjusted using RSM and Box-Behnken design (BBD). The resulting biodiesel's physical and chemical properties were then determined based on ASTM standards and contrasted with those of proven fuels in accordance with ASTM and EN standards as studied by Almasi et al., 2021. The response surface methodology (RSM) has been used to optimise the procedure in this investigation. To determine the impact of two or more independent factors on the dependent variables, the method uses multiple regression and correlation analysis. Its key benefit is that fewer experiments are needed to gather enough data for results that are statistically valid. The production of biodiesel has frequently utilised RSM, one of the most widely used techniques for process optimization as referred in a paper presented by Sahedi et al., 2021.The input parameters of a dual fuel engine running on honge oil methyl ester and producer gas were effectively optimised using a DoE-based RSM statistical tool, and the economics of such an optimised system were also explored as investigated by Kashyap et al., 2021.

5.1.1 Objectives of the Present Chapter

a. Prediction of the optimum level of the process parameters
b. Study of the interactive effects of the operating parameters on the yield
c. Selection of the optimum parameters for optimum yield based on statistical analysis
d. Determination of the properties of the optimum biodiesel sample

The main objective of the present chapter is to compare the experimental yield with the predicted yield obtained via statistical analysis. This optimization has been done using RSM. In the design matrix, the operating parameters are varied in different ranges at three levels in order to find the optimized yield of the product.

5.2 Materials

Used vegetable oil (soybean) was obtained from the guest house canteen of Jadavpur University thereby maintaining a single source of the feedstock throughout the experiment. This used vegetable oil (soybean) collected contained a lot more impurities in the form of large particles and fine granules. This shows that the oil underwent repeated heating. The colour of the oil was also darker in comparison to the used vegetable oil of soybean origin collected earlier. Filtration is carried out as discussed in section 4.4 of Chapter 4. The secondary filtration took a lot of time in comparison to the earlier sample. After the pretreatment, the acid value of the oil was determined and the refined feedstock was used for further reaction process.

5.3 Properties of the Oil

5.3.1 Determination of the density of the used vegetable oil (soybean)

Density of the oil has been calculated as described in equation 3.4 of Chapter 3.
Density of the sample = 9.1/10 = .918 gm/cc = 918 kg/m^3

5.3.2 Determination of acid value and FFA content of oil

As mentioned in equation 3.1 and equation 3.2 of Chapter 3, the acid value and free fatty acid content of the oil has been calculated respectively and mentioned in Table 5.1.

Table 5.1 Acid Value of feedstock

Type of oil	Acid Value	% of FFA content
Used vegetable oil(soybean)	1.683	.846

5.4 Procedure of Biodiesel Production

The system used for the transesterification reaction consisted of 1000cc Erlenmeyer flask equipped with condenser, thermometer and magnetic stirrer. For each run 200cc of used vegetable oil(soybean) was preheated to some extent. Next the premixed solution of catalyst and alcohol was added to the oil and the reaction proceeded on the arranged setup. The reaction time is 2 hours. The temperature range lies from 25^0C to 60^0C depending upon the parameters of the respective run. The catalyst concentration ranges from .5% to 1.5% w/w of oil keeping the agitation speed of 1000 rpm for each set of runs. The products of the reaction were allowed to settle for a night into a separating funnel in which it was transferred. The ester layer was separated as crude biodiesel. This crude biodiesel was washed with distilled water at 65-70^0C by the process of bubble washing. This crude biodiesel undergoes bubble washing till the ph of the washed water becomes neutral. The biodiesel was then heated in small amounts to make it free from dissolved water. This heating had to be done safely in order to avoid the scattering of heated biodiesel due to the presence of water in small quantities. The biodiesel was then kept in air oven at 100^0C for 7-8 hours. After, cooling the percentage yield is estimated. The various calculation to be performed hereafter have been mentioned in Annexure II for used vegetable oil(soybean).

5.5 Properties of the Oils

5.5.1 Determination of the Required Amount of Catalyst from Catalyst Concentration

The amount of catalyst can be calculated as described in section 3.2.4 of Chapter 3. The amount of catalyst will be different; hence it has to be tabulated for maintaining the data in a proper manner.

5.5.2 Determination of the Required Amount of Alcohol from the Molar Ratio

As reported by Mihail and Zoran et al., 2011 the molecular weight of soyabean oil is 874. The molecular weight of used vegetable soyabean oil has been considered as 874. The alcohol:oil ratio will enable the calculation of the amount of alcohol required for the required amount of oil as described in section 3.2.5 of Chapter 3.

The volume of alcohol can be calculated with the help of density of alcohol which is said to be 791.3 kg/m^3 according to Kumar, et al., 2016. The density of alcohol was measured in the laboratory and was found to be 791.8 kg/m^3.

5.6 Design of Experiments

The experimental design of 15 set of runs was optimized using response surface methodology originally by the Box-Behnken Design. The statistical analysis of experimental data was done using Minitab Software Version 17.0. The link between a response and a collection of experimental variables or factors is investigated using RSM. The first and second-order coefficients may be estimated efficiently using this approach. BBD can be less expensive to operate than central composite design with the same number of elements since it contains fewer design points. The influence of key operational factors such as temperature (T), catalyst concentration (C), and methanol-to-oil ratio (M) was investigated. The parameters and their values were chosen based on prior experimental investigations. made by Mohamad et al., 2017, Hamze et al., 2015 and Razack, 2016. Table 5.1 displays the real and coded values for the ranges and levels of three independent parameters. The three-level three-factor BBD has been employed in this study as mentioned in Table 5.2

Table 5.2 Operating parameters along with their levels

Code	Parameters	Levels		
		-1(Low)	0(Medium)	+1(High)
T	Temperature	25	42.5	60
C	Catalyst concentration	.5	1	1.5
M	Methanol to oil ratio	3	6	9

5.7 Statistical Analysis

The experimental runs to be performed in the laboratory was obtained from the BBD design. A mathematical model following a second-order polynomial equation (5.1) was used to generate the predicted response as reported by Hamze et al., 2015.

The general form of full quadratic model is mentioned below:

$$\mu = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j \qquad \text{---------------(5.1)}$$

where the volumetric yield of biodiesel produced from used vegetable oil(soybean) is μ, β_0 represents the offset term, β_i represents the linear effect, β_{ii} represents the squared effect , β_{ij} represents the interaction effect, X_i is the ith independent variable and X_j is the jth independent variable. The F-test was used to analyse the coefficients. The best conditions for biodiesel yield from used vegetable oil(soybean)were determined using analysis of variance (ANOVA), regression analysis, and contour plot. The value of the coefficient of R^2 determines the model's accuracy. The experimental yield was calculated as mentioned in equation 4.1 of Chapter 4 and the results have been shown in Table 5.3.

Table 5.3 Experimental design for the optimization of process parameters of biodiesel production from used vegetable oil(soybean). (Minitab Software Version 17.0)

Experimental Run	Temperature (T)	Catalyst Concentration (C)	Molar ratio (M)	Experimental Yield(%v)	Predicted Yield(%v)
1	60.0(1)	1.0(0)	9(1)	89.0	90.181
2	60.0(1)	0.5(-1)	6(0)	83.0	80.108
3	25.0(-1)	1.0(0)	9(1)	65.7	62.142
4	42.5(0)	1.5(1)	3(-1)	72.5	70.842
5	42.5(0)	0.5(-1)	3(-1)	63.0	62.335
6	42.5(0)	1.5(1)	9(1)	86.7	87.180
7	42.5(0)	1.0(0)	6(0)	87.4	87.577
8	42.5(0)	1.0(0)	6(0)	87.6	87.577
9	25.0(-1)	0.5(-1)	6(0)	47.6	49.420
10	42.5(0)	1.0(0)	6(0)	88.0	87.577
11	25.0(-1)	1.0(0)	3(-1)	56.3	54.942
12	25.0(-1)	1.5(1)	6(0)	67.0	69.715
13	42.5(0)	0.5(-1)	9(1)	71.0	72.493
14	60.0(1)	1.0(0)	3(-1)	67.5	70.885
15	60.0(1)	1.5(1)	6(0)	85.0	83.008

5.8 Results and Discussion

5.8.1 Development of Quadratic Regression Model

BBD was used to prepare the quadratic regression model of biodiesel yield from used vegetable oil(soybean). In the present work the relationship between biodiesel yield and the three variable parameters namely, temperature, catalyst concentration and molar ratio were evaluated using RSM. The result at each point based on BBD along with the predicted values is given in Table 5.6. This statistical software was used to assess the statistical significance of the coefficients of the entire regression mode equation as investigated by Hamze et al., 2015. In this case, the predicted yield of the used vegetable oil(soybean) biodiesel is given in equation 5.2 below.

$$\text{Percentage yield} = -82.7 + 3.651\,T + 79.9\,C + 8.99\,M - 0.03378\,T*T - 26.68\,C*C - 0.855\,M*M - 0.497\,T*C + 0.0576\,T*M + 1.03\,C*M \quad \text{----------------------}\ (5.2)$$

Positive sign with the coefficients of each terms how synergistic effect in increase of FAME yield, whereas negative sign indicates antagonistic effect as reported by Babaki et al., 2017.

Table 5.4 gives the result of the statistical analysis of variance which is used to establish the significance and fitness of the quadratic model, as well as the influence of individual and interacting factors on the responses selected. Regression analysis is frequently used to examine how the response varies when the value of a variable changes.

Table 5.4 Analysis of variance (ANOVA) for the fitted quadratic polynomial model for optimization of transesterification parameters. (Minitab Software Version 17.0)

```
Analysis of Variance

Source              DF   Adj SS   AdjMS  F-Value  P-Value
Model                9  2391.79  265.755    23.68    0.001
  Linear             3  1589.70  529.899    47.22    0.000
    T                1   965.80  965.801    86.07    0.000
    C                1   271.45  271.445    24.19    0.004
    M                1   352.45  352.451    31.41    0.002
  Square             3   680.19  226.731    20.21    0.003
    T*T              1   395.21  395.211    35.22    0.002
    C*C              1   164.31  164.308    14.64    0.012
    M*M              1   218.68  218.680    19.49    0.007
  2-Way Interaction  3   121.90   40.634     3.62    0.100
    T*C              1    75.69   75.690     6.75    0.048
    T*M              1    36.60   36.603     3.26    0.131
    C*M              1     9.61    9.610     0.86    0.397
Error                5    56.10   11.221
  Lack-of-Fit        3    55.92   18.639
  Pure Error         2     0.19    0.093
Total               14  2447.90



Model Summary
         S    R-sq  R-sq(adj)  R-sq(pred)
       3.34975  97.71%     93.58%      63.43%
```

F-value is the statistic which is used to check the hypothesis that the means of all the factor level are equal. It is calculated as the mean square for the factor divided by the mean squares for error. F-value is used to determine the p-value. The F-value for regression is used to test the null hypothesis that all the coefficients in a regression model are zero. The p-value is used to determine which of the effects in the model are statistically significant. When the null hypothesis is true and is rejected, then a particular type of error occurs. The probability of this type of error is called alpha (α) and is sometimes referred to as the level of significance. A commonly used α -level is 0.05. If the p-value is less than or equal to α, the impact is considered significant. But if the p-value is greater than α, then the effect is not significant. The regression model is significant as p-value =.001. That is at least one of the model's terms influences the mean response.

The linear and the squared effects have p-value<.05 which shows that these parameters are effective in the modeling of the system. In the linear effect, temperature has the lowest p-value and the highest F-value which signifies that it is the most important parameter in biodiesel production from used vegetable oil(soybean). The p-value of squared terms have significant evidence of a quadratic effect. This denotes that the relationship between these parameters and yield follows a curved line. In the two interactive terms of temperature-molar ratio and molar ratio-catalyst concentration, the p-value >.05. denotes that they do not have a significant interaction effect. (Minitab StatGuide, Minitab Software Version 17.0)

F-test and ANOVA (analysis of variance) were used to determine the statistical significance of the equation, which revealed that the model was statistically significant at 95% confidence level (p< 0.0001). The model F-value was reported to be 23.68, indicating that the model is significant. S, R^2 and adjusted R^2 indicate how well the model matches the data. These values might assist you in selecting the best-fitting model. S is measured in response variable units and indicates the standard deviation of data values from fitted values. The smaller the S, the better the projected response, and the better the model. Here the S has a low value of 3.34975. R^2(R-Sq) how much variance in observed response values can be explained by the independent factors.

A high R^2 value suggests that the model accounts for more data variability, and hence the data points will be closer to the regression line as discussed by Dharma et al., 2016. Here the value of R^2 indicates 97.71% of the variability in the used vegetable oil(soybean) biodiesel yield which can be explained by its relationship with the independent variables mentioned in the quadratic regression model. Adjusted R^2 is an R^2 that has been adjusted to account for the number of variables in the model. R^2 can be unnaturally high if unimportant variables are included. In contrast to R^2, adjusted R^2 may decrease when more variables are added to the model. The corrected R^2 value is 93.58%, indicating that the factors included are significant. R^2 (pred) is the measurement that indicates how well the model predicts the reaction to fresh observations. Significant disparities between projected R^2 and the other two R^2 values may suggest that the model is an overfit. An overfit model does not predict fresh observations as well, as it predicts the already existing data. Adjusted R^2 is a modified R^2 that has been adjusted for the number of variables in the model. If unnecessary variables are included, R^2 can be artificially high. Unlike R^2, adjusted R^2 may get smaller when you add unnecessary variables to the model. The value of adjusted R^2 is 93.58% which indicates that the variables considered are important.

R^2 (pred) is a measure of how well the model predicts the response for new observations. Large differences between predicted R^2 and the other two R^2 statistics can indicate that the model is over fit. An over fit model does not predict new observations nearly as well as the model fits the existing data.

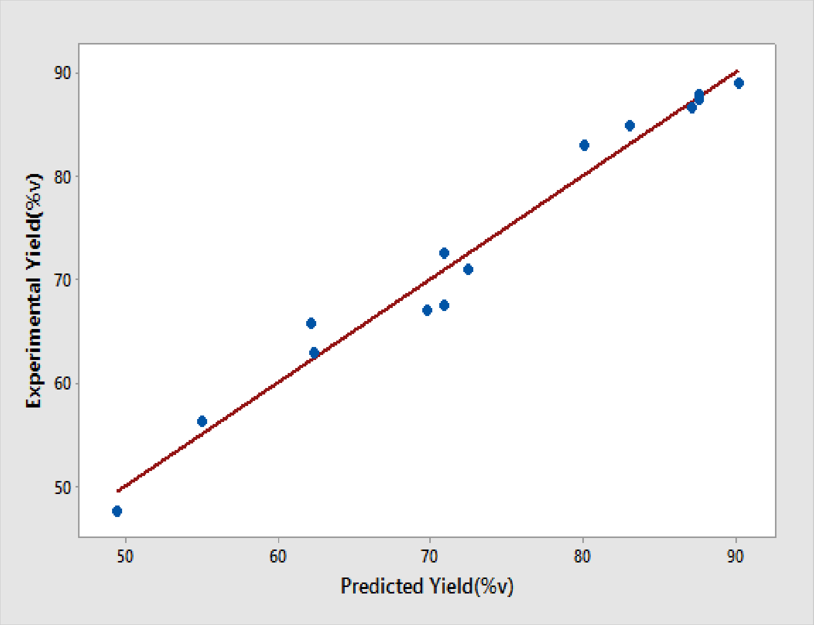


Fig. 5.2. Parity plot for experimental yield versus predicted yield of biodiesel produced from used vegetable oil (soybean)

The parity plot in Fig.5.2 compares the experimental yield and the predicted yield of methyl ester from used vegetable oil(soybean). R^2 being the coefficient of determination value for the yield of methyl ester is 0.9771 which indicates 97.71% of the variability of data can be explained by the model. It also suggests that there is a good fit between the given model and the experimental data as informed by Dharma et al., 2016. Omar and Amin, 2011reported that the empirical model explains the majority of the variability in the assay reading, which should be at least 0.75.

5.8.2 Interactive Effects of Variables on Biodiesel Yield

The interactive effects of the variables are graphically shown in 2D and 3D formats as contour plots and surface plots respectively. Fig. 5.3 and Fig .5.4 show the effect of interaction T (temperature) and C (catalyst concentration) on the yield of biodiesel keeping the M(molar ratio) at a hold value of 6. The contour plot and the surface plot depicts that with increase in T and C there is an increase in the yield up to a certain optimum level after which further increase in their value depicts decrease in the yield. Larger increase in temperature leads to the vaporization of methanol thereby showing to gradual decrease in the yield. Further increase in catalyst concentration also decreases the amount of biodiesel obtained as at times it leads to soap formation which decreases the yield. Keeping the value of M at 6 the optimized yield of 91.080% is obtained at T of 50.808^{0}C and C of 1.136% w/w of oil.

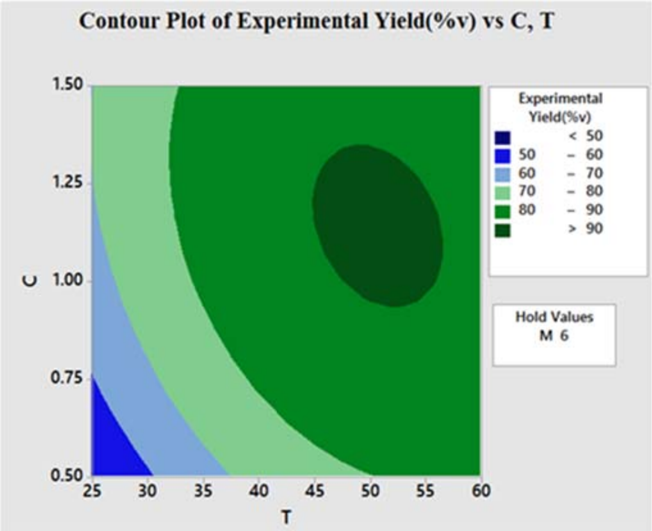


Fig. 5.3 Contour plot of biodiesel yield (%) at different catalyst concentration and different temperatures

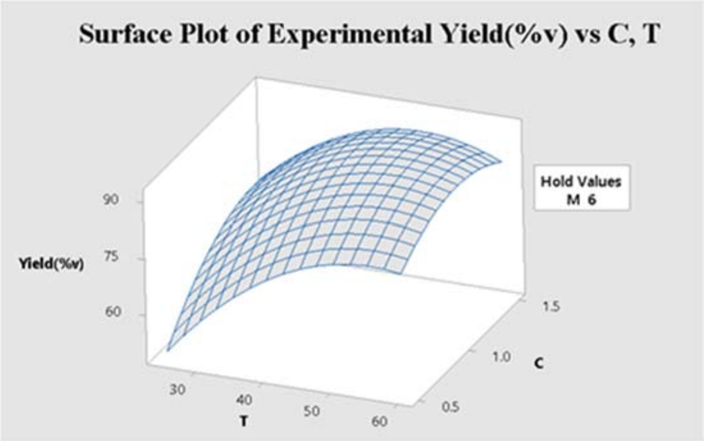


Fig. 5.4 Surface plot of biodiesel yield (%) for combined effects of catalyst concentration and temperature

Fig. 5.5 and Fig. 5.6 show the interactive effect of M and C keeping a hold value of T as 42.5^{0}C. It can be observed that even large increase in M does not significantly increase the yield at lower values of C but as the value of C is increased along with M the yield gradually increases. This shows that catalyst is the most important parameter for transesterification of biodiesel in this study. Apart from this, increased molar ratio makes separation of methyl ester and glycerin difficult due to formation of emulsion and this was investigated by Anw et al., 2012 and Hamze et al., 2015. The optimized yield of 90.696% is obtained at C of 1.247% w/w of oil and M of 7.424:1 at the hold value of T as 42.5^{0}C.

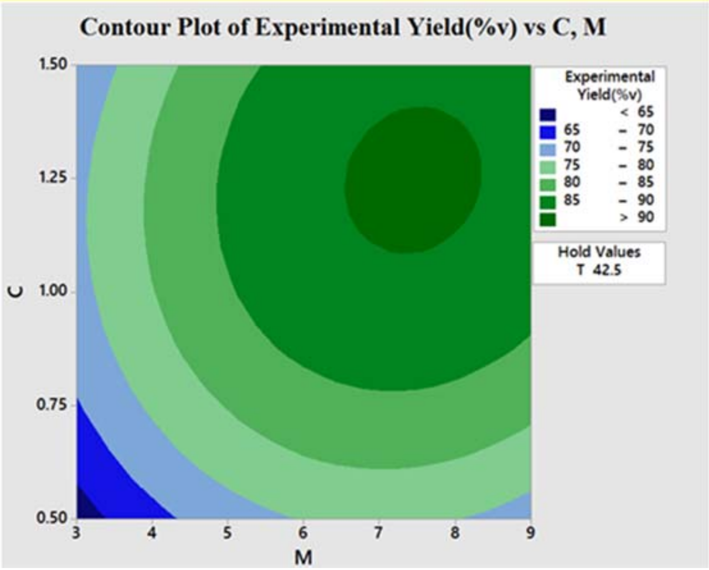


Fig. 5.5 Contour plot of biodiesel yield (%) at different catalyst concentration and different molar ratios of alcohol and oil

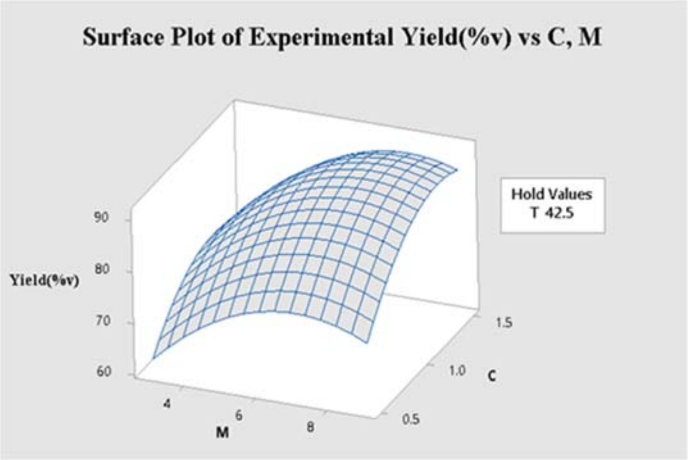


Fig. 5.6 Surface plot of biodiesel yield (%) for combined effects of catalyst concentration and molar ratios of alcohol and oil

Fig. 5.7 and Fig. 5.8 denotes the interactive effect of temperature and molar ratio on the yield of biodiesel with a hold value of C as 1. Even with increase in M, the yield is not showing any considerable rise at lower values T. But as T is increasing along with M, there is significant rise in the biodiesel yield from used vegetable oil(soybean). At medium values of T the yield is considerable even at lower values of M. The optimized yield of biodiesel is obtained at T of 53.282^{0}C and M of 7.667:1 keeping the hold value of C at 1%.

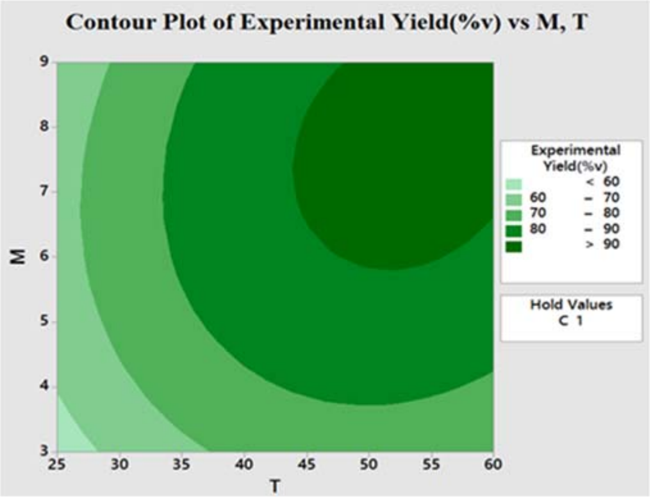


Fig. 5.7 Contour plot of biodiesel yield (%) at different molar ratios of alcohol and oil and different temperatures

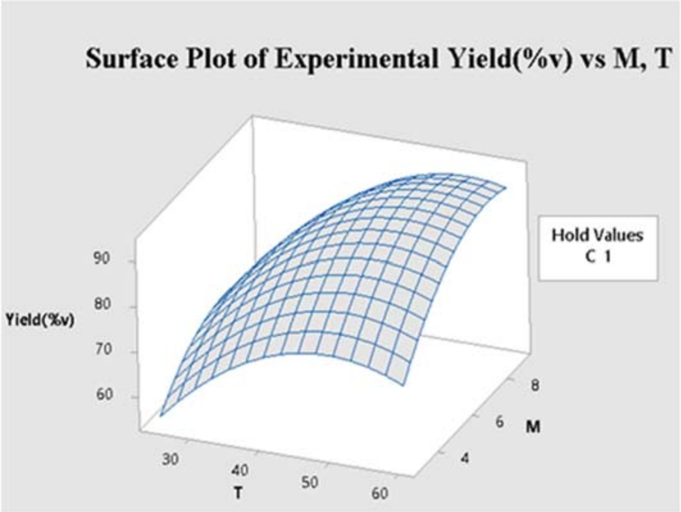


Fig. 5.8 Surface plot of biodiesel yield (%) for combined effects of molar ratios of alcohol and oil and temperatures

5.8.3 Validation of the Model

The optimized condition to produce methyl ester from used vegetable oil(soybean) was inferred from the regression model of RSM with statistical software. The amount of methyl ester obtained was determined from model Equation (3). In order to confirm the accuracy of the model for transesterification of used vegetable oil(soybean)experiments were carried out under optimized conditions. These optimized conditions were obtained from the response optimizer of the statistical software. The optimal conditions are temperature as 52^0C, catalyst concentration as 1.157% w/w of oil and molar ratio as 7.7:1. The yield predicted is 93.408%

using regression model. The experiments were performed in the laboratory in triplicates and the average experimental yield of biodiesel form used vegetable oil(soybean) was 93.60%. Therefore, the minimal error in the yield is .205%. Since the predicted and experimental yields are close to each other therefore the model is considered to be highly accurate for production of biodiesel from used vegetable oil(soybean). Here the optimised yield is less in comparison to the sample of biodiesel derived from used vegetable oil(soybean) in the Chapter 4. The reason is the low quality of the feedstock because of the larger amount of impurities. But here the main concern is the difference between the predicted yield and the experimental yield which proves the validation of the model.

5.9 Estimation of Physico-chemical Characteristics

5.9.1 Determination of the Density of the Biodiesel

Density of the oil has been calculated as described in equation 3.4 of Chapter 3.

Density of oil = 8.81/10 = 0.881 gm/cc

5.9.2 Determination of Viscosity of the Biodiesel

Viscosity of the sample of biodiesel has been calculated as described in equation 3.5 of Chapter 3. Kinematic viscosity of biodiesel = 3.989 mm^2/sec

5.9.3 Determination of the Calorific Value of the Biodiesel

Calorific value of biodiesel has been calculated as described in equation 3.7 of Chapter 3 and the value was 38.194 MJ/kg

5.9.4 Flash Point

The flash point has been determined as discussed in section 3.3.2 of Chapter 3. The average value of the flash point of biodiesel from used soyabean oil was 162^0C. The properties have been mentioned in Table 5.5.

Table 5.5 Physical and chemical properties of biodiesel produced from used vegetable oil(soybean) and comparison with the standards as mentioned by Singh et al., 2018 and Barbaras and Todorut, 2011.

Parameters	Standard Test Method for Biodiesel			Limit			Biodiesel sample produced from used vegetable oil (soybean)	Diesel
	European Standard EN141214	US Standard ASTM D6751	India IS15607	EN14214	ASTM D6751	India		
Density at 15^0C (kg/m^3)	EN ISO 3675 ENISO 12185	----	ISO 3675/P32	860-900	----	860-900	881.3	839.0
Viscosity at 40^0C (mm^2/sec)	EN ISO 3104 ISO 3105	D445	ISO 3104/P25	3.5-5.0	1.9-6.0	2.5-6.0	3.989	2.91
Flash Point(^{0}C)	EN ISO 3679	D93	P21	120 min	93 min	120 min	162	76
Calorific Value(MJ/Kg)	----	D240	----	35 min	35 min	----	38.194	43.981

5.10 Conclusion

This study has been conducted to minimise the cost of production and obtain the best-fit data for obtaining the optimised yield. The main focus of this study is to verify the yield obtained statistically and study the interactive effects of the process variables which ultimately decide the yield for each set of parameters. According, to the ANOVA results catalyst concentration and temperature are the most effective factors regarding biodiesel production. RSM based on Box Benkhen Design was used to obtain the optimum conditions for optimised yield. The optimised yield of 93.408% was obtained at the temperature of 52^0C, catalyst concentration of 1.157% w/w of oil and molar ratio of 7.7:1. Here the molar ratio is lesser than that of Chapter 4 for biodiesel from used vegetable oil(soybean). The properties of the feedstock are responsible here for the amount of each parameter required for the optimised yield. As discussed, the feedstock used for this study had a greater percentage of impurities. This affects the percentage yield of biodiesel. With the change in the sample of feedstock, the yield gets affected. The properties and chemical analysis of biodiesel give a detailed idea about the nature of the oil that has been produced. The properties fall within the standard ranges mentioned; hence it qualifies for commercial use in engines in blended form.

Chapter 6

A Study on the Performance of Diesel Engine Fueled with Biodiesel Blends Produced from Different Used Vegetable Oils

6.1 Introduction

The diesel engine inspired by Rudolf Diesel is a compression-ignition engine because it ignites fuel by heating the air in the cylinder as a consequence of mechanical compression (CI engine). This is in contrast to engines that use spark plugs to ignite the air-fuel combination, such as petrol or petrol engines (which use a gaseous fuel such as natural gas or liquefied petroleum gas). Diesel engines work by compressing either air alone or air mixed with exhaust combustion gases (exhaust gas recirculation, or EGR). Air is pulled into and compressed in the chamber during the induction and compression strokes. The air within the cylinder gets extremely hot due to the pressure increase, to the point that atomized diesel fuel is poured into the cylinder and it ignites. Before combustion, a heterogeneous air-fuel mixture occurs when the fuel disperses unevenly after being delivered into the air tank. Instead of adjusting the intake air, the air-fuel ratio is modified to manage the torque produced by the diesel engine. The diesel engine is dependent on altering the amount of fuel injected since the air-fuel ratio is higher as discussed by Reif, 2014.

Suppes and Storvick, 2016 explained that biodiesel has recently replaced diesel as the primary fuel for compression-ignition engines. Diesel fuel has a number of beneficial performance traits, including: (i) a rapid heat release rate during burning; (ii) volatility, which keeps it liquid until the temperature is well over the boiling point of water; (iii) rapid compression When the compression ratio is around 15 to 1 or higher, ignition (without a spark) happens; and (iv) when fuel is supplied via the fuel injectors in each cylinder, a fine, uniform mist formed. Diesel fuel regulations are nearly polar opposites of those for gasoline. When squeezed in an engine cylinder, the gasoline readily evaporates and does not ignite. To prevent preignition, air is compressed in the diesel engine's cylinder before fuel is supplied. The diesel fuel evaporates when minute mist particles from the fuel injectors ignite in the hot, compressed air. The gasoline also lubricates the fuel injector pump. The propensity of diesel fuel to ignite is described by its cetane rating. The minimum cetane number for diesel fuel required by US standards is 40.

D.H. Qi et al., 2009 reported that alkali catalyzed transesterification process was used to create biodiesel from raw soybean oil. The comparison of characteristics of diesel and biodiesel was performed. The compression ignition engine's performance, emissions, and combustion properties were examined while using diesel and biodiesel as fuels. Diesel and biodiesel have slightly different fuel characteristics. Clearly, biodiesel has a higher viscosity than diesel, especially at low temperatures. Biodiesel has a specific gravity that is roughly 6.1% greater than diesel. Compared to diesel, biodiesel's LHV (Lower Heating Value) is around 10.2% lower. In comparison to diesel, the flash point of biodiesel is higher. This biodiesel has an acid value of 1.8 mg KOH/g. The biodiesel has a small boiling range, and between 310 and 360 °C, 95% of it is boiled out. Diesel and biodiesel display varied combustion characteristics with changing engine loads because their respective qualities are different. At lower engine loads, biodiesel has somewhat greater peak cylinder pressure, peak rate of pressure rise, and peak rate of heat release. Peak cylinder pressures are approximately comparable for both fuels at higher engine loads; however, biodiesel has a lower peak rate of pressure rise and heat release. The crank angles at which the greatest values emerge in biodiesel are known in advance. Due to a shortened ignition delay and enhanced injection time at all engine load types, biodiesel combustion begins earlier.

Under speed characteristics and at full load, the power output of biodiesel is approximately identical to that of diesel. Compared to diesel, biodiesel has a greater Brake special fuel consumption (BSFC). Its lesser heating value is reflected in the increased fuel usage. Both fuels have brake-specific energy consumption that is quite similar. Under speed characteristics at full load, the emissions of carbon monoxide, hydrocarbons, nitrogen oxides, and smoke are typically reduced by 27, 27, 5, and 52%, respectively. According to the study, biodiesel made from soybean crude oil can be used in place of diesel in diesel engines.

The study by Chhabra et al., 2016 examined the effects of rice bran and crude rice bran biodiesel on the performance of diesel engines. The experimental study gives comprehensive information on the biodiesel production process, an analysis of the fuel's characteristics, and its effects on engine performance. The study also looks into how to best optimise the Compression Ratio (CR) of a compression ignition engine running on biodiesel mixtures. Experiments were carried out at various CRs ranging from 12 to 18 in order to determine the engine's ideal CR. After that, studies were carried out in which at CRs of 12 and 14, B10, B20 and B40 blends of crude rice bran bio-diesel and diesel were evaluated, and the results were compared to those obtained when the same engine was tested using standard diesel fuel. The results of the experiment revealed that the most ideal CR is 14, as shown by the following findings. Brake Thermal Efficiency (BTE) was discovered to be at its highest value with CR of 14. The lowest fuel usage and BSFC were discovered at CR of 14. Maximum cylinder pressure increase and ignition delay reduction were seen at CR of 14 with increasing load. At a CR of 12, the BTE of the B10 and B20 blend is essentially identical to that of ordinary diesel fuel. Maximum BTE for B10 was higher at CR 14 than it was at CR 12. For CR 14, the specific fuel consumption for B10 at full load settings showed a small decline. For both CRs, B40 had the highest BSFC. Diesel and B10 both reached their maximum cylinder pressures at CR 12 and CR 14, respectively. Increases in CR were associated with shorter ignition delays. With a longer ignition delay, B40 reached minimum cylinder pressure at both the mentioned CRs. While B40 showed the lowest performance results when compared to diesel and other blends, B10 and B20 blends were closest to diesel in terms of performance. For both B20 and diesel at CR 12 and CR 14, hydrocarbon emissions were detected. In both instances, the highest hydrocarbon emission was B40. Diesel had worse carbon monoxide and carbon dioxide emissions at both the CRs than B10 and B20. In comparison to diesel, higher (nitrogen oxides) NO_X emissions were noted. For B10 and B20, comparable performance values to diesel were seen. B10 and B20 both had lesser emissions than diesel, with the exception of NO_X emissions, which were greater in the cases of B10 and B20. Comparing B40 against diesel and other mixes, it demonstrated the lowest performance and higher emission results. Hence, fuel blends made from crude rice bran methyl ester can be utilized in diesel engines without needing to be modified.

As assessed by Muralidharan et al., 2011, the exhaust gas temperature (EGT) decreased as the load was increased. The EGT fell as the percentage of biodiesel in the blend increased because it had a lower calorific value. For all combinations of used cooking oil, the mechanical efficiency of the biodiesel utilised in this experiment rose as the load increased. Due to the strong fuel reaction activity, the mixes exhibited better mechanical efficiency. Due to the plant oil's naturally occurring nitrogen content, which contributes to the formation of NOx, the fuel containing a biodiesel blend had greater NO_x content than diesel.

It has been confirmed in Chapter 4 that when compared to non-edible oils, used soyabean oil gives an appreciable yield in comparison to non-edible oils. This chapter deals with the study of CI engine performance with biodiesel from used soyabean oil, used rice bran oil, and used sunflower oil as discussed in Chapter 4.

6.1.1 Objectives of the Present Chapter

- **Study of engine performance when run on diesel blended with biodiesel produced from used soybean oil.**

- **Study of engine performance when run on diesel blended with biodiesel produced from used sunflower oil.**
- **Study of engine performance when run on diesel blended with biodiesel produced from used rice bran oil.**

  The various calculation to be performed hereafter have been mentioned in Annexure III for different types of used vegetable oils. The calculation of the BSFCs from the fuel consumption has also been mentioned in Annexure III. The properties have been mentioned in Table 6.1.

6.2 Physicochemical Properties of Biodiesel

6.2.1 Determination of the Density of the Biodiesel

The density of the oil has been calculated as described in equation 3.4 of Chapter 3.

6.2.2 Determination of Viscosity of the Biodiesel

The viscosity of the oil has been calculated as described in equation 3.5 of Chapter 3. Here the reference liquid is water.

6.2.3 Determination of the Calorific Value of the Biodiesel

Calorific value of biodiesel has been calculated as described in equation 3.7 of Chapter 3.
The standard conversion of joule to calorie has been done as discussed in section 5.5.4 of Chapter 5.

6.2.4 Flash Point

The flash point has been determined as discussed 3.3.2 of Chapter 3.

Table 6.5 gives tabulated data on the properties of biodiesel samples compared to that of diesel. The standards have been discussed in Table 5.2 of Chapter 5. Here USOME = Used Soybean Oil Methyl Ester, URBME = Used Rice Bran Oil Methyl Ester, USUME = Used Sunflower Oil Methyl Ester.

Table 6.1 Physicochemical properties of biodiesels produced from different types of used vegetable oils and diesel

Parameters	Diesel	USOME	URBME	USUME
Density at 15^{0}C (kg/m^3)	839.0	868.80	886.1	873.7
Viscosity at 40^{0}C (mm^2/sec)	2.91	3.910	4.281	4.317
Flash Point (^{0}C)	76	164	180	172
Calorific Value (MJ/Kg)	43.98	38.7	39.20	38.4

6.3 CI Engine Performance Study with Biodiesel Blended with Diesel

6.3.1 Operation of the Diesel Engine

In this study, the experiments were conducted on a four-stroke, single-cylinder, diesel engine coupled with a generator by using different blends of USOME, USUME, and URBME at fixed injection timing and compression ratio. After the biodiesel was prepared in the laboratory different blends of the three samples of the biodiesel and diesel were prepared based on the volume. The trial of the engine was performed with three types of blends of each type of biodiesel namely, 5% biodiesel + 95% diesel(B5), 10% biodiesel + 90% diesel(B10), 20% biodiesel + 80% diesel(B20), 0% biodiesel + 100% diesel(B0). The performances were compared with the results of CI engine run by normal Petrodiesel. Different loads have been applied in the form of tungsten filament lamps of wattage 500W and 200W. Firstly, the engine RPM was set to 3950 at no load condition. RPM is reduced as the load increases. Fuel consumption and EGT were measured for 200,500,1000,1500 and 2000 W Load. For 500W load, only one lamp of 500W was switched ON and keeping the other lamps off. For 1000W load, two lamps of 500W each are kept ON. For 1500W load, three lamps of 500W are kept ON. Again, for the 2000W load, four lamps of 500W were switched ON. The experiments were started after 30 minutes of no-load run. Before beginning a new test, the engine was run long enough to utilise the remaining gasoline from the previous experiment.

A schematic representation of the experimental setup used for investigating the engine characteristics during different tests is presented in Fig. 6.1. The detailed specifications of the test engine are shown in Table 6.6. Initially, the engine was started with diesel and run at least for 30 min until it reached a steady state. For each trial, three sets of experiments were performed. As discussed by Paul and Jash, 2017, the mass of fuel consumed per unit of brake power output per hour is brake-specific fuel consumption at a given load.

The BSFC for the different blends of the three different types of methyl esters along with B0 have been discussed here. B100 has not been mentioned due abnormal behaviour of the engine in terms of sound and vibration.

Fig. 6.1 shows the schematic diagram of the experimental setup of the CI engine under study. Fig. 6.2 and Fig. 6.3 shows the engine in running condition in the Bio-energy Lab of the department. Table 6.2 gives the specifications of the test engine.

Table 6.2 Specifications of Test Engine

Model	Z170f
Type	Single cylinder, horizontal,4-stroke
Bore*stroke(mm)	70*70
Rated power	2.94kw/4hp
Rated speed(r/min)	2600
Max power	3.23kw/4hp
Cooling method	Air-cooled
Starting method	Hand-cranking
Net weight(kg)	44

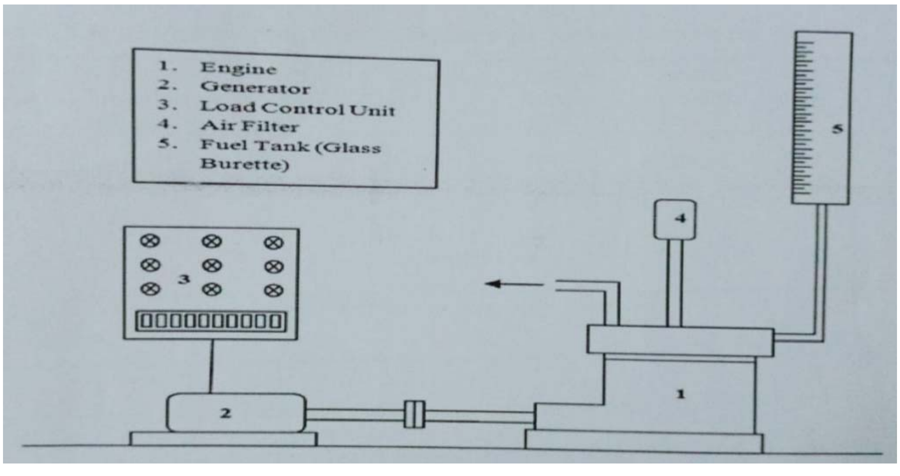


Fig. 6.1 Schematic diagram of the experimental setup of the test engine

Fig. 6.2 Test engine setup run by biodiesel blends and diesel

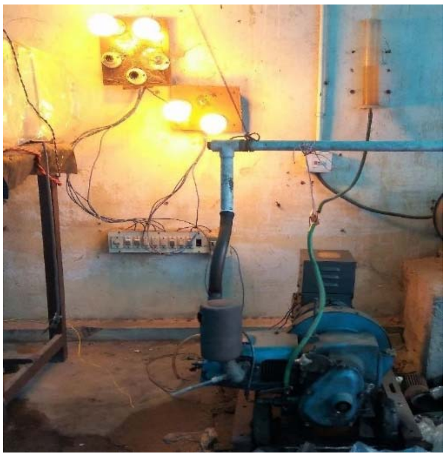


Fig. 6.3 Lighting load run by the test engine

6.4 Results and Discussion

6.4.1 Break Specific Fuel Consumption vs Load on the Engine

As discussed by Paul and Jash, 2017, brake-specific fuel consumption is defined as the amount of fuel consumption per unit brake power output per hour. Figures 6.3, 6.4 and 6.5 show the variations in brake-specific fuel consumption (BSFC) with engine loads for different blends of USOME, URBME and USUME.

Specific Fuel Consumption is used to describe the fuel consumption with respect to power output. The fuel consumed in 1 hour was calculated for each sample of biodiesel blends and diesel. Brake specific fuel consumption was been calculated with the help of specific fuel consumption and the load. The specific fuel consumption was calculated with the value of fuel consumption and density of the fuel. The density of the blends was calculated with respect to the percentage of biodiesel and diesel in the mix. The variation of BSFC with increase in load for diesel and different blends of biodiesel produced from used vegetable oil (soybean), used vegetable oil(rice bran) and used vegetable oil(sunflower) have been shown in tabular form below in Table 6.3, Table 6.4, Table 6.5 and Table 6.6.

Table 6.3 Brake-specific fuel consumption of diesel at different loads on the engine

Load(W)	Brake Specific Fuel Consumption BSFC (kg/kWh)
500	0.478
1000	0.292
1500	0.226
2000	0.178

Table 6.4 Brake-specific fuel consumption of biodiesel blends prepared from used vegetable oil (soybean) at different loads on the engine

Load(W)	BSFC(kg/kWh) B5	BSFC(kg/kWh) B10	BSFC(kg/kWh) B20
500	0.499	0.509	0.516
1000	0.293	0.301	0.308
1500	0.229	0.230	0.230
2000	0.181	0.184	0.191

Table 6.5 Brake-specific fuel consumption of biodiesel blends prepared from used vegetable oil (rice bran) at different loads on the engine

Load(W)	BSFC(kg/kWh) B5	BSFC(kg/kWh) B10	BSFC(kg/kWh)B20
500	0.483	0.504	0.518
1000	0.298	0.301	0.304
1500	0.231	0.235	0.237
2000	0.189	0.198	0.207

Table 6.6 Brake-specific fuel consumption of biodiesel blends prepared from used vegetable oil (sunflower) at different loads on the engine

Load(W)	BSFC(kg/kWh) B5	BSFC(kg/kWh) B10	BSFC(kg/kWh) B20
500	0.482	0.487	0.496
1000	0.296	0.305	0.311
1500	0.233	0.236	0.241
2000	0.181	0.191	0.194

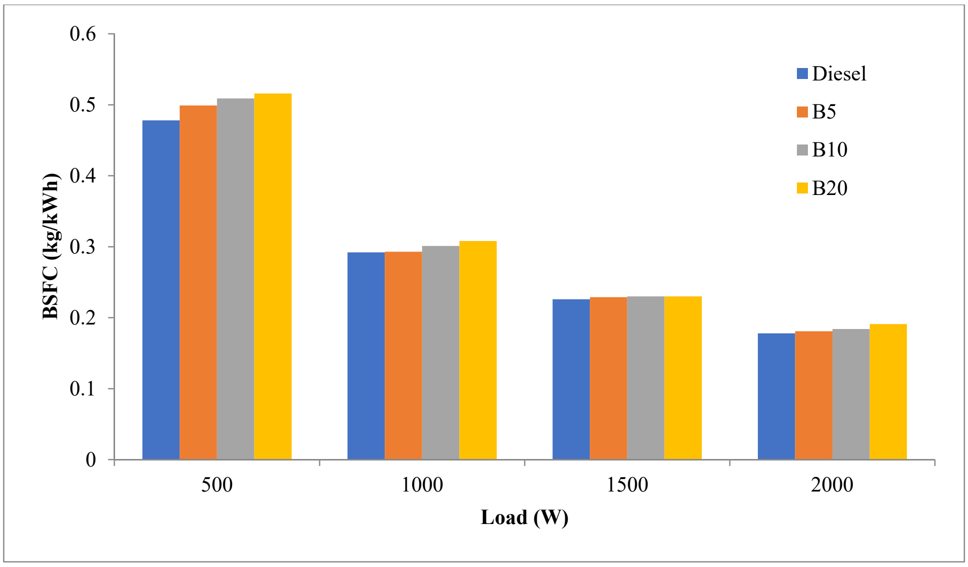


Fig. 6.4 Variation of BSFC vs. Load for biodiesel from used vegetable oil (soybean)

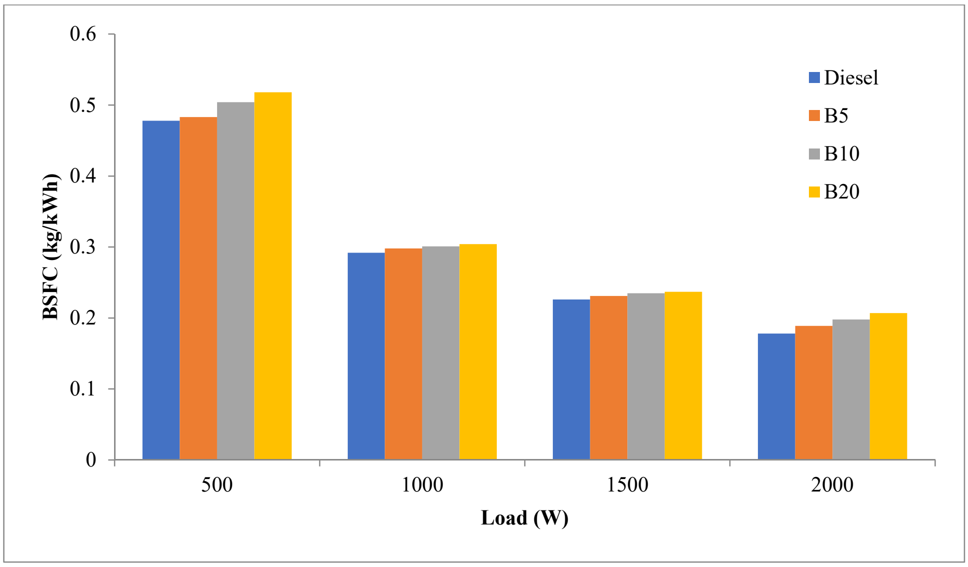


Fig. 6.5 Variation of BSFC vs. Load for biodiesel from used vegetable oil (rice bran)

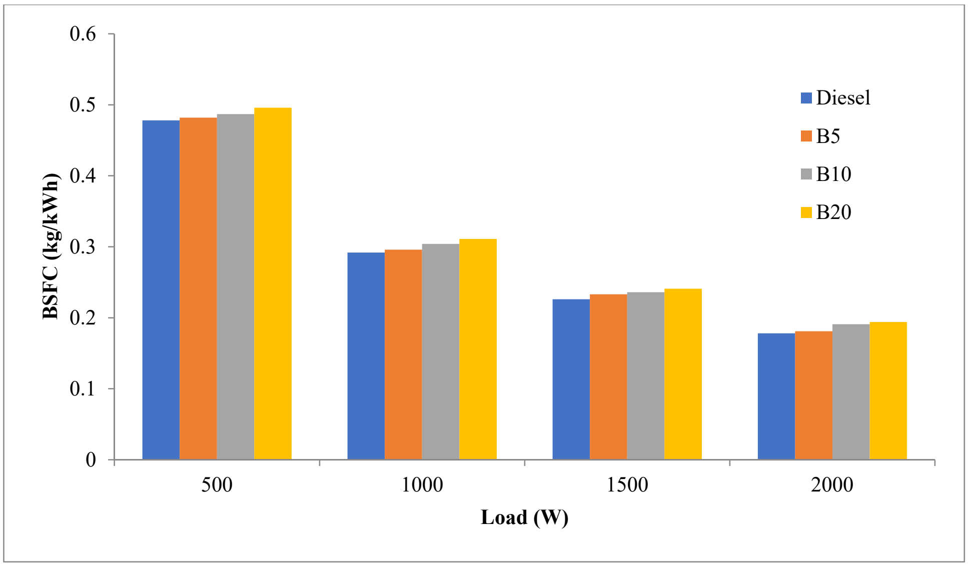


Fig. 6.6 Variation of BSFC vs. Load for biodiesel from used vegetable oil(sunflower)

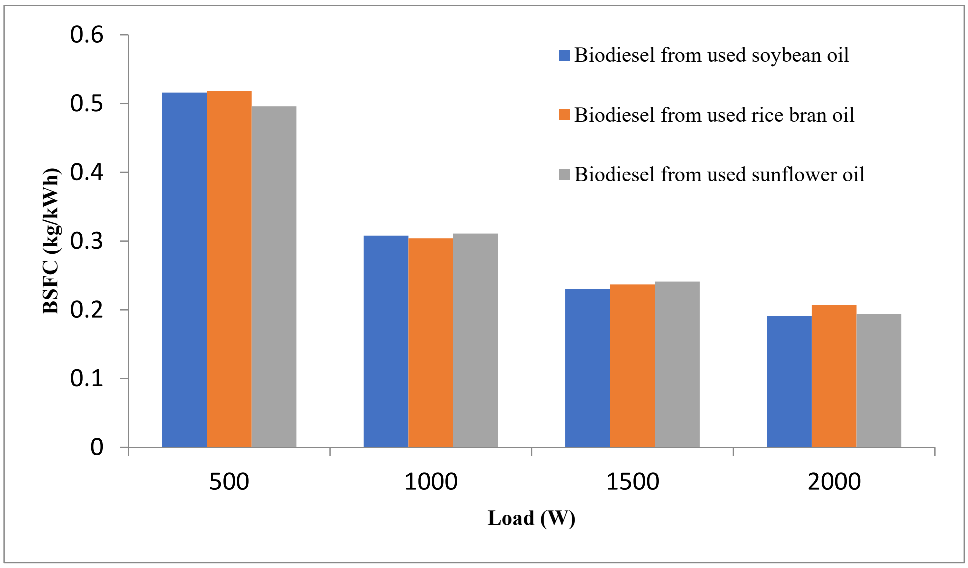


Fig. 6.7 Comparison of BSFC vs Load for B20 blend of the three different biodiesels

The bar graphs Fig. 6.4, Fig. 6.5, Fig. 6.6 and Fig. 6.7 show that the BSFC decreases with an increase in load on the engine for all three types of biodiesel blends (B5, B10, B20) as well as diesel (B0). The increase in the percentage of blending increases the BSFC at any given load for different types of biodiesels. For all three types of biodiesel blended fuels, the BSFCs are higher than that of diesel under all loading conditions and are higher than diesel for all the blends at a given load. It was observed that BSFC reduces with an increase in engine load. As the load of the engine increases, the efficiency and combustion quality of the engine also increases.

BSFCs for B-5, B-10, B-20 blends of USOME were found higher by 1.68%, 3.37%, and 7.3% respectively compared to diesel and corresponding blends of UBRME were found higher by 6.17%,11.2% and 16.3% respectively in comparison to diesel at 62% of the rated output. For the same blends of USUME BSFCs were higher by 1.68% ,7.3% and 8.98% when compared to diesel at 62% of the rated load. The calorific values of pure biodiesel oil are less than mineral diesel. Therefore, an increase in the proportion of biodiesel in the blend would decrease the calorific value of the resultant fuel. It was found that SOME has the lowest BSFC at high load conditions which can be explained by the fuel properties like lower density and viscosity which improves fuel spray for better mixing and better combustion performance. Paul and Jash, 2017 discussed that the calorific value of biodiesel blend decreases with an increase in the percentage of blending of the biodiesel for the same amount of power output. Figure 6.6 compares the blend form B20 of each type of biodiesel at different loads. At 15.47% of the rated load the BSFC of the blended USOME is the highest, but as the load increases and reaches 62% of the rated output the graph shows that the BSFC of the blended form of SOME is the lowest in comparison to the B20 blends of URBME and USUME. At lesser output load URBME and USUME are suitable for use, but at higher output loads USOME is suitable for use as biodiesel in blended form.

6.5 Conclusion

The objective of this study was to study the engine performance of biodiesel produced from three used vegetable oil sample, i.e. soybean oil , sunflower oil and rice branoil . Based on the experimental results, the following conclusions can be drawn.

The density, viscosity and flash point of biodiesels are higher than that of diesel fuel. Although they have different fuel values, they can be used in a diesel engine by mixing in various blend ratios. As expected, when the load was increased the values of BSFC decreases. Due to lower heating value of biodiesel, BSFC of all blends of biodiesel are higher in comparison to diesel. This is which leads to use of higher amount of fuel to generate the same power. Among three biodiesels, USOME has the lowest BSFC value at high load, It can be seen that at high load BSFC for B10 and B20 of USOME is 3.8% and1.57% lower than USUME, along with this 7.6% and 8.37% lower than URBME. Though the calorific value of URBME is a little higher than USOME but the viscosity of USOME is lower than the other two.

Liaquat et al., 2012 reported that due to the lower calorific value and low density of blended fuel, the BSFC of the blended jatropha biodiesel was less than that of fuel. So, it can be concluded that the combined effect of viscosity and calorific value causes the lesser burning of fuel in blended form of USOME. Hence, we can conclude that biodiesel from used soybean oil is the preferable one of the three types. Nowadays in order to maintain food value, these three types of oils are mostly in use. The used form of palm oil is cheaper, but it solidifies in winter, which makes it unsuitable for use.

The results obtained in the study confirmed that biodiesel produced from used vegetable oils could be used as a fuel in diesel engines after blending with diesel fuel. In India, soybean oil, rice bran oil, and sunflower are mostly used for frying purposes. Therefore, the used forms of these three types of oils are readily available in the market.

Chapter 7

Gas Chromatography Study for Qualitative Analysis of Biodiesel Produced from Different Types of Used Vegetable Oils by Addition of Heat and Without Addition of Heat

7.1 Introduction

In order to measure and identify specific components in biodiesel samples, such as pollutants and fatty acids methyl esters, chromatographic analysis has been utilized in a variety of ways. Chromatography is widely used in the field of research to know the biodiesel composition since it is essential in today's quality control analysis of biodiesel as mentioned by Yahaya et al., 2013. It also explains that chromatography is the study of mixture separation, and it is frequently used to find hidden components in mixtures. The elements in a mixture migrate along a stationary phase in chromatography. Each component in a mixture maintains its unique properties and hence flows at a speed set by those properties. When a mixture needs to be separated, it is done so by passing it through the stationary phase and into the mobile phase, using the rate of migration as the basis for separation.

By using gas chromatography in accordance with EN 14103 and internal calibration with methyl hepta-decanoate, Rabu et al., 2013 established the purity of the methyl esters. Hydrogen was used as the carrier gas at a pressure of 70 kPa in an FID detector with a Thermo Scientific TR-FAME column. The fatty acid composition was compared to a known composition and concentration of Supelco Analytical Grain fatty acid methyl ester (FAME) mix. Each sample was examined three times. For the purpose of peak recognition and quantification, the FAME compositions in biodiesel from used vegetable oil were examined and compared to those of a standard grain FAME Mix. In a study by Bautista et al., 2009, Thin Layer Chromatography (TLC) was used to identify methyl derivatives of fatty acids. The detection of monoglyceride, diglyceride, triglyceride, and free fatty acids was also conducted using this technique. One of the techniques that can be used to analyse methyl esters of biodiesel derived from used cooking oil, rapeseed oil, sunflower oil and soybean oil is gas chromatography with flame ionisation detection (GC-FID), which does not require any modifications of the methyl ester as discussed by Chen et al., 2010.

In the study conducted by Dias et al., 2012, the order of mono-, di-, and triglyceride elution is dependent on the carbon content. Double-bonded molecules with the same number of carbon atoms coelute, but molecules with the same number of carbon atoms that are saturated and unsaturated are divided; the unsaturated molecules elute first. As investigated by Sarin et al., 2010, the fatty acid composition of the methyl esters and their blends with other methyl esters enabled the derivation of a correlation between oxidation stability and the total percentage of saturated methyl esters. Based on the results of the study reported by Gopinath et al., 2010, it can be inferred that each of the biodiesel's fatty acids has a significant impact on the cetane number of its fuels. Lower cetane levels are a result of an increase in double bonds. With longer chains cetane number increases and with more unsaturation, the cetane number decreases. If the content of alkyl esters of lauric, myristic, palmitic, and stearic fatty acids rise, the cetane number rises as well. However, the cetane number decreases with an increase in the content of oleic, linoleic, and linolenic fatty acid alkyl ester. It also claims that the cetane number of saturated esters grows with chain length, but the cetane number of unsaturated FAMEs decreases with the number of double bonds.

The technique for predicting the viscosities of biodiesel fuels from their fatty acid composition is presented by Allen et al., 1999 and has been experimentally verified. Controlled mixtures of standard fatty acid esters and biodiesels were used to demonstrate the application of a logarithmic mixture equation. It was observed by Gopinath et al., 2015 that the structure and characteristics of FAMEs affect the properties of biodiesel. The FAME compounds' chemical structure, chain length, saturated and unsaturated nature, amount of unsaturation, and placement of the double bonds all have an impact on properties like viscosity, cetane number, the heat of combustion, and oxidation stability. As discussed by Canakci and Sanli, 2008 the fatty acid composition of some biodiesel feedstocks is mentioned below in Table 7.1.

A report by Rodrigues et al., 2006 suggested that single double bond increases viscosity whereas double bond or triple bond tends to show decrease in viscosity. In comparison to stearic methyl ester viscosity of methyl oleate is greater. But moving on to linoleic methyl ester and linolenic methyl ester the viscosity decreases. The argument in support to this suggests that a single double bond creates stronger intermolecular interaction between p electrons whereas in case of methyl stearate only weak vander waal forces exist. The study by Wang and Briggs, 2002 shows that increase in saturation and increase in the length of the chain increases the viscosity.

Unsaturation is the reason for low cetane number as discussed by Knothe et al., 2003. Geller and Goodrum, 2004 revealed that higher saturation ensures higher cetane number. Knothe, 2006 also explained that the presence of unsaturation makes the biodiesel more susceptible to oxidation. Dunn, 2008 tells that polyunsaturation is more prone to auto-oxidation than monosaturated ester because they have more allylic methylene positions. Mc Cormick and Alleman, 2005 explained that unsaturated ester has lower energy content depending on weight. But when higher density is considered then energy per unit volume is higher. These factors when acting together in a mixture of different alkyl esters exhibit small differences which become difficult to be segregated. One of the reports by Sharma, 2008 suggests that biodiesel can be produced from used vegetable oil at room temperature by mixing 10 % biodiesel with used vegetable oil, which undergoes transesterification with potassium hydroxide and methanol for 3 hours. In this study, the stirring is carried out for three hours with a certain amount of biodiesel in the used raw oil. This will increase the cost of production of biodiesel. It can be said that not much work has been done in the field of biodiesel production from used vegetable oil at room temperature which can reduce the cost of production.

Table 7.1 Fatty acid composition of different feedstocks used for biodiesel production

	Fatty Acids (% w/w)						
Feedstock	C 14:0 Myristic Acid	16:0 Palmitic Acid	C 16:1 Palmitoleic Acid	C 18:0 Stearic Acid	C 18:1 Oleic Acid	C 18:2 Linoleic Acid	C 18:3 Linolenic Acid
Sunflower	-	6.08	-	3.26	16.93	73.73	-
Rapeseed	-	3.49	-	0.85	64.40	22.30	8.23
Soybean	-	10.58	-	4.76	22.52	52.34	8.19
Soybean Soapstock	-	17.2	-	4.4	15.7	55.6	8.19
Used frying oil	-	12	-	-	53	33	1
Tallow	3-6	24-32	-	20-25	37-43	2-3	-
Lard	1-2	28-30	-	12-18	4-50	7-13	-
Yellow grease	2.43	23.24	3.79	12.96	44.32	6.97	0.67
Brown grease	1.66	22.83	3.13	30.73	12.30	1.64	16.43

Source: Canakci and Sanli, 2008.

7.1.1 Objectives of the Present Chapter

1. Qualitative analysis of biodiesel produced from used vegetable oil (soybean) by the method of gas chromatography with and without application of heat.
2. Qualitative analysis of biodiesel produced from used vegetable oil (rice bran) by the method of gas chromatography with and without application of heat.
3. Qualitative analysis of biodiesel produced from used vegetable oil (sunflower) by the method of gas chromatography with and without application of heat.
4. Comparison of the properties of the biodiesel produced from different types of vegetable oils based on the percentage of saturation and unsaturation of the fatty acid methyl esters.
5. Justification for the biodiesel produced under ambient temperature conditions from used vegetable oil (soybean).
6. Comparison of the fuel properties of biodiesel produced from fresh vegetable oils and used vegetable oils.

In this study biodiesel from each used vegetable oil has been produced with and without the application of heat during the process of transesterification keeping the process parameters the same as discussed in section 6.1.3 of Chapter 6. The chromatographic analysis of the biodiesel produced under ambient temperature conditions helps to look into the feasibility of the process. The percentage composition of the constituents has to be known to treat the product as biodiesel. This adaptation decreases the cost of production as well. The ambient heat helps in the transesterification process thus decreasing the cost of production. The energy balance for the decrease in the cost has been discussed in the later part of this study. In research by Paul and Jash, 2017 it has been discussed that unsaturation is responsible for the good quality of biodiesel as they are preferred than biodiesel with a larger percentage of saturated alkyl ester.

7.2 Methodology

7.2.1 Materials Used

Used vegetables oils derived from different types of feedstock have been used in the qualitative analysis process. The source of collection of the oils, their properties along with their acid values, the process parameters, transesterification and purification have been discussed in section 6.4 of Chapter 6. Only one additive fact is that each oil with the same process parameters is also run under ambient temperature conditions without the application of any heat. Gas chromatography has been performed here to study the constituents of the biodiesel produced under with-heat and without-heat conditions. The equipment in the laboratory of the Bose Institute, Manicktala, Kolkata, West Bengal was used for GC-MS (gas chromatography and mass spectra) analysis with model number TRACE_GC_ULTRA and MS POLARIS _Q of Thermo Fischer Scientific India Private Limited. The carrier gas in the equipment is helium with 99.99% purity. The conditions of the chromatographic system are as follows. The column used was TR_WAX_MS COLUMN with dimensions of 30 m in length,.25 mm in internal diameter, and 0.25 m in film thickness. The initial temperature was 50°C and the hold time was of 1 minute. The final temperature was 270°C with 5 minutes hold time. The methyl esters were identified by their retention time and likewise quantified by their corresponding peak areas. The optimized yield was analyzed in triplicate. Standard FAME MIX was used to study and analyze the biodiesel methyl ester from used soybean oil. The ambient temperature during the production of biodiesel under without-heat conditions was between 38°C and 42°C which was the temperature of the mixture undergoing transesterification.

7.2.2 Chromatographic Results

Altogether there were six samples of biodiesel of three types of feedstock namely used soybean oil, used sunflower oil and used rice bran oil. Methyl esters of each kind of used oil were produced under with-heat and without-heat conditions respectively. The ambient temperature during the production of biodiesel under without-heat conditions was between 38°C and 42°C which was the temperature of the mixture undergoing transesterification. The yields of the methyl esters and the composition of the methyl esters obtained by transesterification under different temperature conditions has been shown in Table 7.2 and Table 7.3. The fatty acid composition of the methyl esters produced from USOME, URBME and USUME has been mentioned in Table 7.3. Here,

Used Soybean oil methyl ester = USOME, Soybean oil methyl ester = SOME
Used Sunflower oil methyl ester = USUME, Sunflower oil methyl ester = SUME
Used Rice bran oil methyl ester = URBME, Rice bran oil methyl ester = RBME

Kumar and Negi, 2015 discussed the effects on vegetable oil after undergoing repeated cooking. The thermal oxidation of vegetable oil under cooking conditions gives rise to free radical mechanism of chain reactions. It has been reported that the concentration of refined uncooked oil is reduced by approximately fifty percent after the oil undergoes repeated cooking. This oxidation of linolenic acid to stearic acid and oleic acid had taken place through free radical mechanism. It therefore can be concluded that double bonds break into single bonds after heating oil several times.

Table 7.2 Yields of biodiesels

Types of biodiesels	Percentage Yield (%)
Used soybean oil methyl ester with heat	96.5
Used soybean oil methyl ester without heat	89
Used rice bran oil methyl ester with heat	92
Used rice bran oil methyl ester without heat	87
Used sunflower oil methyl ester with heat	94
Used sunflower oil methyl ester without heat	93

Table 7.3 Fatty acid composition of methyl esters (biodiesel) prepared from different used vegetable oils expressed in terms of the percentage(%) area occupied by the peaks in the chromatogram

Methyl ester of feedstock	C 16:0 Palmitic Acid Methyl Ester	C 18:0 Stearic Acid Methyl Ester	C 18:1 Oleic Acid Methyl Ester	C 18:2 Linoleic Acid Methyl Ester	C 18:3 Linolenic Acid Methyl Ester	Others
Used Soybean Oil Methyl Ester with heat	29.58	0.73	19.22	38.61	6.25	5.61
Used Soybean Oil Methyl Ester without heat	33.15	0.96	19.94	31.94	9.13	4.88
Used Rice Bran Oil Methyl Ester with heat	37.44	---	20.60	29.08	---	12.88
Used Rice Bran Oil Methyl Ester without heat	36.56	---	18.81	30.89	---	13.74
Used Sunflower Oil Methyl Ester with heat	24.87	---	22.23	34.13	5.89	12.88
Used Sunflower Oil Methyl Ester without heat	38.90	---	30.73	12.30	1.64	16.43

The chromatograms of the three types of methyl esters produced under different operating conditions are shown below. The peaks in the graphs determine the presence of the methyl esters of unsaturated fatty acids and saturated fatty acids at the given retention times when compared to the retention times of the methyl esters of fatty acids of the standard FAME grain mix.

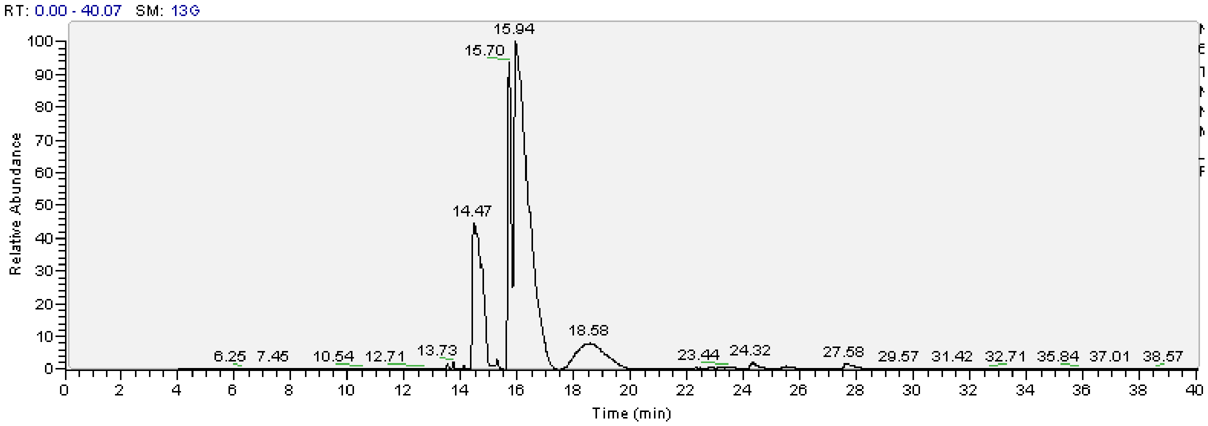


Fig. 7.1 Chromatogram of used soybean oil methyl ester under with-heat conditions

In Fig. 7.1, the first peak was observed at the retention time of 14.47 minutes which detects the presence of palmitic acid methyl ester with 29.58% of the area occupied by the peaks in the chromatogram. The subsequent peaks of methyl ester of stearic acid, methyl ester of oleic acid, methyl ester of linoleic acid, and methyl ester of linolenic acid were observed at the retention times of 15.29 minutes, 15.70 minutes, 15.94 minutes and 18.43 minutes of the subsequent methyl esters and percentage peak areas of 0.73%, 19.22%, 38.61% and 6.25% respectively.

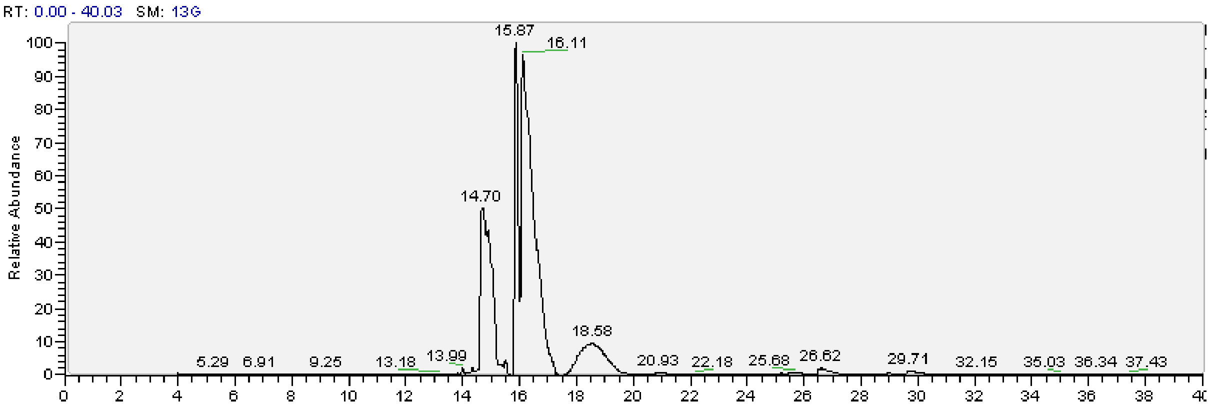


Fig. 7.2 Chromatogram of used soybean oil methyl ester prepared at ambient temperature without addition of heat

In Fig. 7.2 the first peak was observed at the retention time of 14.9 minutes which detects the presence of palmitic acid methyl ester with 33.15% of the area occupied by the peaks in the chromatogram. The subsequent peaks of methyl ester of stearic acid, methyl ester of oleic acid, methyl ester of linoleic acid, and methyl ester of linolenic acid were observed at the retention times of 15.50 minutes, 15.87 minutes, 16.10 minutes and 18.58 minutes of the subsequent methyl esters and percentage peak areas of 1.00 %, 19.94%, 31.94% and 9.13% respectively.

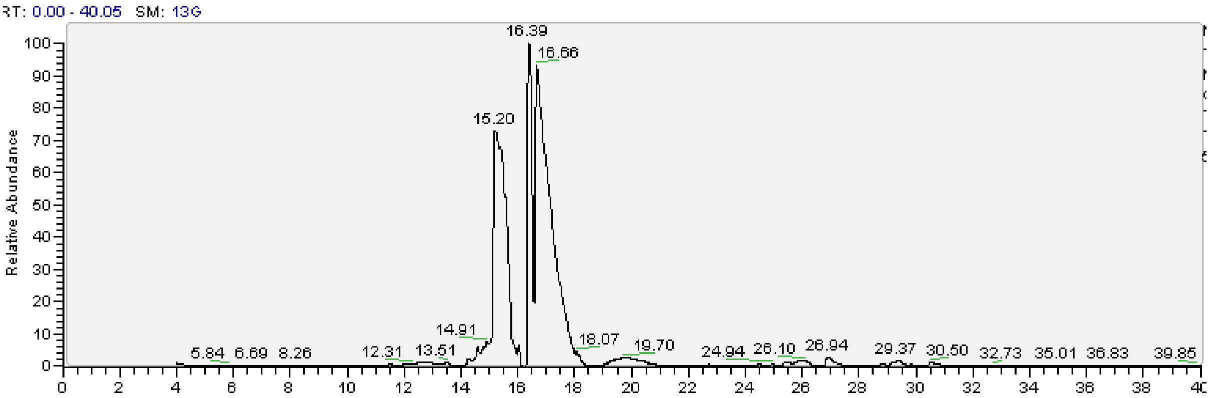


Fig. 7.3 Chromatogram of used rice bran oil methyl ester under with-heat conditions

In Fig. 7.3 the first peak was observed at the retention time of 15.20 minutes which detects the presence of palmitic acid methyl ester with 37.44% of the area occupied by the peaks in the chromatogram. The subsequent peaks of methyl ester of oleic acid and methyl ester of linoleic acid were observed at the retention times of 16.38 minutes and 29.08 minutes of the subsequent methyl esters and percentage peak areas of 20.60% and 6.25% respectively. The stearic acid methyl ester and the linolenic acid methyl ester could not be detected which confirms their absence in the feedstock of used rice bran oil.

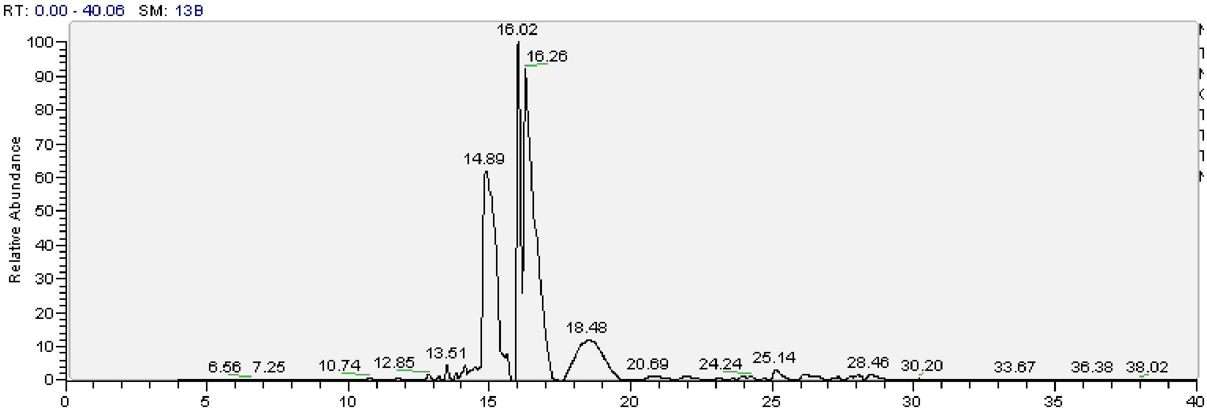


Fig. 7.4 Chromatogram of used rice bran oil methyl ester at ambient temperature without addition of heat

In Fig. 7.4 the first peak was observed at the retention time of 14.86 minutes which detects the presence of palmitic acid methyl ester with 36.56% of the area occupied by the peaks in the chromatogram. The subsequent peaks of oleic acid methyl ester and linoleic acid methyl ester were observed at the retention times of 16.02 minutes and 16.26 minutes of the subsequent methyl esters and percentage peak areas of 18.81% and 30.89% respectively. The stearic acid methyl ester and the linolenic acid methyl ester could not be detected in the URBME produced under without-heat conditions.

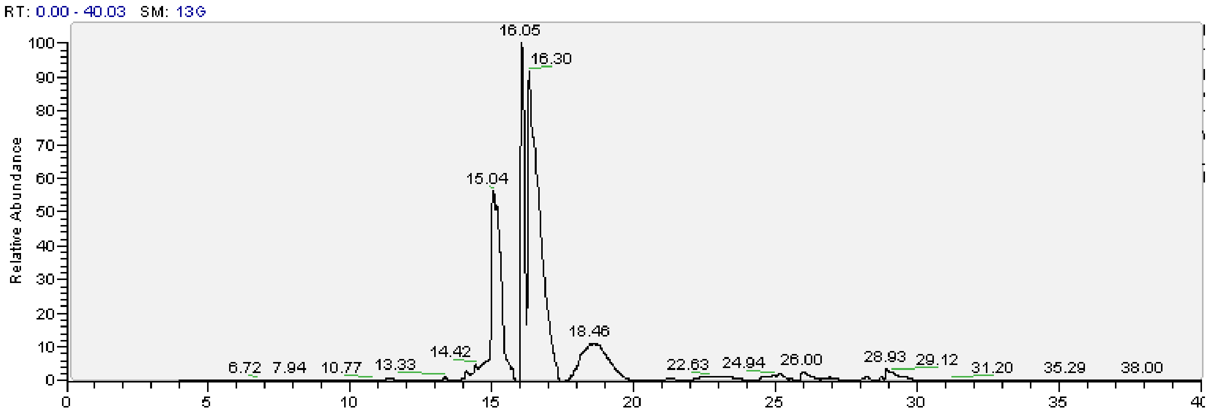


Fig. 7.5 Chromatogram of used sunflower oil methyl ester under with-heat conditions

In Fig. 7.5 the first peak was observed at the retention time of 15.04 minutes which detects the presence of palmitic acid methyl ester with 24.87% of the area occupied by the peaks in the chromatogram. The subsequent peaks of methyl ester of oleic acid, methyl ester of linoleic acid, and methyl ester of linolenic acid were observed at the retention times of 16.05 minutes, 16.30 minutes, and 18.59 minutes of the subsequent methyl esters and percentage peak areas of 22.23%, 34.13% and 5.89% respectively. The stearic acid methyl acid remains undetected in this biodiesel which proves that sunflower oil does not contain stearic acid.

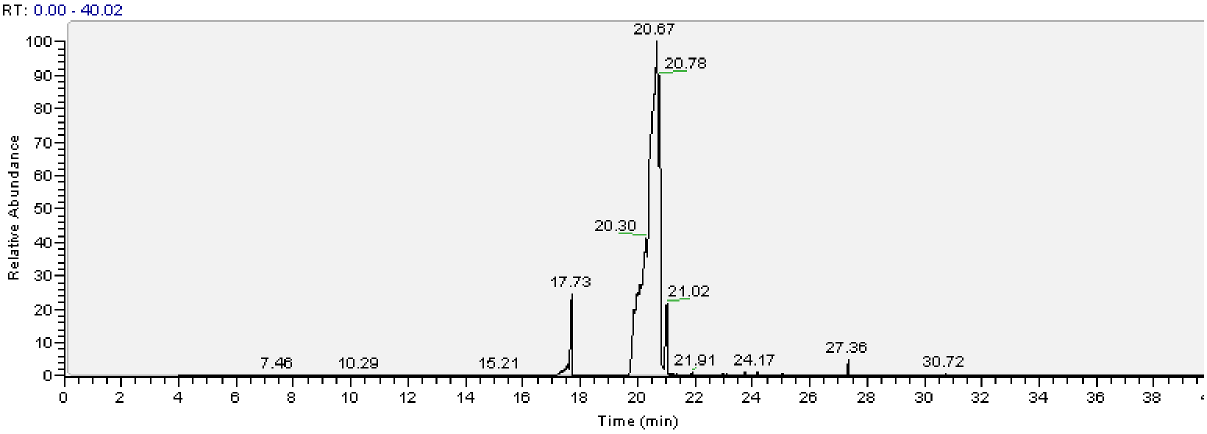


Fig. 7.6 Chromatogram of used sunflower oil methyl ester at ambient temperature without addition of heat

In Fig. 7.6 the first peak was observed at the retention time of 17.73 minutes which detects the presence of palmitic acid methyl ester with 38.90% of the area occupied by the peaks in the chromatogram. The subsequent peaks of methyl ester of oleic acid, methyl ester of linoleic acid and methyl ester of linolenic acid were observed at the retention times of 20.67 minutes, 20.78 minutes, and 21.02 minutes of the subsequent methyl esters and percentage peak areas of 30.73%, 12.30% and 1.64% respectively. The chemical composition of the biodiesel samples was used to calculate few properties of the methyl esters.

7.2.3 Chromatographic Analysis

The saturated part of the methyl esters is higher in the case of the samples produced under without-heat conditions. In case of URBME, the saturated part remains more or less the same as with or without heat. But the USOME and USUME show greater saturation in the case of production under ambient temperature conditions. As discussed, the degree of unsaturation is an important criterion in deciding the fuel properties of biodiesel.

As seen in Table 7.1 the percentage of oleic acid methyl ester in fresh soybean oil is 22.52% whereas in Table 7.3 the percentage of oleic acid methyl ester in biodiesel from used soybean oil produced in heat and ambient temperature conditions are 19.22% and 19.94% respectively. It can be seen that there has been a decrease in the percentage of oleic acid methyl ester in case of biodiesel from used soybean oil. But the decrease is not very large. The amount of linoleic acid in the case of biodiesel from used soybean oil and used sunflower oil has decreased considerably when compared to their corresponding raw forms.

A report by Kumar and Negi, 2015 suggests that the reheating of the oils for cooking purposes leads to free radical mechanism of chain reactions which can highly be the reason for the decrease in the percentage of linoleic acid in the used vegetable oils and its oxidation to either oleic acid or stearic acid. Therefore, the percentage of linoleic acid methyl ester is found to be less in the biodiesel produced from used vegetable oils.

The amount of oleic acid methyl ester and linoleic acid methyl ester in all the sets of combinations tells that the biodiesels produced are appropriate for use in diesel engines. It also shows that linolenic acid methyl ester is absent in rice bran oil and the saturated methyl ester is higher in amount. Even in the biodiesel produced under ambient temperature conditions (38°C - 42°C), the percentage composition of the fatty acid methyl esters of each type of biodiesel is close to the corresponding composition of their respective methyl esters produced under with-heat conditions. Therefore, it can be concluded that under ambient temperature conditions, biodiesel production is readily possible in case of used oils which can decrease the production cost of the biodiesel produced.

The percentage composition of the biodiesel also helps to theoretically calculate the oxidation stability (OS), iodine value (IV), cloud point (CP) and pour point (PP) of the six samples of biodiesel as mentioned in equation 2.1, equation 2.2, equation 2.3 and equation 2.4 of section 2.8.1 of Chapter 2. These values have been tabulated in Table 7.4. The percentage of unsaturation of the biodiesels helps to calculate the oxidation stability, cloud point, pour point and iodine value of the biodiesel samples. The chemical properties of biodiesel which depend upon the degree of saturation or unsaturation have been tabulated below. Pubchem, 2023 gives the molecular weight of each fatty acid methyl ester. The molecular weight of oleic acid methyl ester, linoleic acid methyl ester and linolenic acid methyl ester are 296.5, 294.5 and 292.5 respectively. The various calculation to be performed hereafter have been mentioned in Annexure IV.

Table 7.4 Properties of biodiesel with respect to the percentage of unsaturation in the composition

Methyl ester of feedstock	Oxidation Stability (h)	Iodine Value	Cloud Point (°C)	Pour Point (°C)
Used Soybean Oil Methyl Ester with heat	7.32	99.348	10.56	4.65
Used Soybean Oil Methyl Ester without heat	8.04	95.962	12.44	6.69
Used Rice Bran Oil Methyl Ester with heat	10.70	67.809	14.70	9.13
Used Rice Bran Oil Methyl Ester without heat	10.69	69.398	14.23	8.63
Used Sunflower Oil Methyl Ester with heat	7.70	93.433	8.09	1.96
Used Sunflower Oil Methyl Ester without heat	11.87	51.815	15.46	9.97

The oxidation mechanism of biodiesel as explained by Botella et al., 2014 was that the composition of the feedstock determines the oxidation stability, where the unsaturated and polyunsaturated methyl esters are the most reactive species. The higher the unsaturation level in an alkyl ester, the more susceptible it is to oxidation. This suggests that the raw material composition has a direct relationship with the oxidative stability of the biodiesel produced notably in terms of the concentrations of certain unsaturated fatty acids (linolenic, linoleic and oleic). Thus, the raw materials with the lowest oleic acid concentration and the greatest linoleic and linolenic acid content had the lowest oxidation stabilities, indicating a greater percentage of compounds with multiple unsaturation as opposed to those with a single unsaturation.

In this part of the study, the lowest oxidation stability is of USOME produced by the application of heat. The percentage of oleic acid methyl ester is 19.22% and the combined percentage of linoleic acid methyl ester and linolenic acid methyl ester is 44.86%. The highest oxidation stability is of USUME produced without the application of heat. Here the percentage of oleic acid methyl ester is 30.73% and the combined percentage of linoleic acid methyl ester and linolenic acid methyl ester is 14.04%.

The iodine value is a critical quality criterion for determining the oxidative stability of biodiesel as described by Rocha and Soares, 2018. The iodine value of a product is proportional to its degree of unsaturation and shows its oxidative stability. The iodine value of USOME produced by the application of heat is the highest and that of the USUME produced without heat is the lowest. The percentage of unsaturation of USOME produced by the application of heat is 64.08% which is the highest degree of unsaturation and the percentage of unsaturation of USUME produced without the application of heat is 44.77% which has the lowest degree of unsaturation. This fact synchronises with the value of iodine value which is highest for USOME produced by the application of heat and lowest for USUME produced without the application of heat.

Khethiwe et al., 2020 observed that the quantity of saturated fatty acids in biodiesel fuels influences both the cloud point and the pour point of biodiesel fuels. Increased unsaturation, particularly monounsaturated fatty acids, enhances the cold flow properties. Bahubali and Gopalan, 2019 explained that cloud point is primarily determined by the saturated ester content of the fuel. The high unsaturation of fatty acid methyl esters, on the other hand, causes polymerisation and oxidation of the fuel. The presence of unsaturation has the greatest impact on the pour point and cloud point. All of these traits are thought to be influenced by intermolecular forces of attraction, which increase with chain length. The existence of double bonds disrupts the attractive forces that operate between molecules along the hydrocarbon chain, lowering the value of certain physical qualities.

As seen in Table 7.4, the best CP (Cloud Point) and PP (Pour Point) have been provided by USUME produced by the application of heat as the percentage of saturation or the saturated chain length is minimum in case of this methyl ester. This shows that higher percentage of saturated fatty acids alkyl ester in biodiesel is responsible for the poor low-temperature properties of the biodiesel. All three types of oils are mostly used for cooking purposes at homes or restaurants in India. Therefore, bulk collection of used vegetable oils can increase the production of biodiesel even in the absence of heat. As the study has been carried out in Kolkata, West Bengal, India, the ambient temperature of the hot and humid climate has aided the process of transesterification.

7.2.4 Justification for Production of Biodiesel at Ambient Temperature Conditions

The percentage yields of USOME, USUOME and URBME under with-heat conditions are higher than those under without-heat conditions. But the amount of thermal energy required to be provided for the process of transesterification is saved during the without conditions. The process of transesterification involves the supply of heat to the mixture of oil, alcohol and catalyst for a stipulated amount of time. Now if the heat supply is not required then, the amount of energy saved can be estimated. The calculation of the amount of energy saved in the process of running the production under ambient temperature conditions in case of biodiesel produced from used vegetable oil(soybean) with heat and without heat has been shown below.

The heat input for transesterification for 2 hours = 150 x 2 Wh

= 0.3 kWh

Since 1kWh = 861.2 kcal,

Therefore, 0.3kWh = 861.2 x 0.3 = 258.36 kcal

Calorific Value of USOME produced with application of heat = 38.7 MJ/kg (Table 7.5)

Calorific Value of USOME produced without application of heat = 38.49 MJ/kg (Table 7.5)

Percentage yield of USOME produced with application of heat = 96%

Percentage yield of USOME produced without application of heat = 89%

The percentage decrease in the yield = (96 – 89) = 7.8%.

The chemical energy of 96 ml of USOME with application of heat =0 .771 kcal.

(Density of USOME produced with application of heat = .868 kg/m^3) (Table 7.5)

The chemical energy of 89 ml of USOME without application of heat = 0.717 kcal.

(Density of USOME produced without application of heat = .875 kg/m^3) (Table 7.5)

Therefore, the decrease in the output energy of the biodiesel in without-heat conditions

= 0.771 kcal- 0.717 kcal = .054 kcal.

So, we can say that the amount of energy saved by inhibiting the supply of heat for 2 hours is 258.36 kcal - .054 kcal = 257.820 kcal per 100 ml of raw used vegetable oil, which is much more than the energy loss due to the decrease in the volume of biodiesel produced.

It can therefore be concluded that the process of biodiesel production without the application of heat is more energy efficient than the conventional method of application of heat for biodiesel production.

7.3 Conclusion

The properties of the fuels produced from different feedstock and different temperature conditions in this study have been compared with the biodiesel produced from the same sources in fresh form as discussed in a study by Sinha et al., 2008. The comparative analysis of the properties from this investigation and from the literature survey has been shown in Table 7.5.

Table 7.5 Fuel properties of biodiesel

	Biodiesel produced in this study from used vegetable oil						Biodiesel produced from fresh vegetable oil (Sinha et al., 2008)		
Property	Used SOME with heat	Used RBME with heat	Used SUME with heat	Used SOME without heat	Used RBME without heat	Used SUME without heat	SOME	SUME	RBME
Density kg/m^3(30^{0}C)	.868	.886	.873	.875	.879	.878	.884	.880	.877
Viscosity cSt (40^{0}C)	3.91	4.317	4.281	3.767	4.310	4.410	4.08	4.2	5.29
Flash Point (^{0}C)	154	178	170	159	180	172	141	164	183
Fire Point (^{0}C)	170	186	182	175	198	192	171	183	196
Calorific Value (MJ/Kg)	38.7	39.20	38.40	38.49	39.05	38.00	39.8	40.1	42.2

The comparative analysis can be done here with the help of the properties of biodiesels produced from the corresponding fresh vegetable oils studied by Sinha et al., 2008. The data here shows that the viscosity of soybean oil methyl ester is the lowest even when without heat data is considered. The others have viscosity a little higher than that of SOME. The flash point of SOME is 154^{0}C and under without heat condition is 159^{0}C, which is the lowest when compared to the flash points of other samples of biodiesel. The fire point also shows the same trend. But the calorific value of URBME under with heat and without heat conditions is the highest.

The properties of the biodiesel as discussed by Sinha et al., show that out of all the oils, the biodiesel from soybean oil gives the best result, but the biodiesel from two other oils which are sunflower oil and rice bran oil shows fuel properties that ensures their use as biodiesel in the diesel engines as well. A similar trend has been found in the biodiesels from the used vegetable oils in this study. 97% yield of biodiesel from used vegetable oil at room temperature has been obtained in an investigation by Piker et al., 2016 but the catalyst used is calcinated egg shells which denotes an increase in the production cost.

USOME under with-heat and without-heat conditions show the best result to be used in diesel engines. In fact, the other two oils, USUME and URBME have properties that ensure their use as biodiesel. This proves that the ambient temperature in West Bengal has been useful in biodiesel production from the used vegetable oils of three different kinds which are collected from the canteens and shops.

Moreover, the amount of energy saved is much more in comparison to the decrease in the percentage yield under with heat and without heat conditions. Under without heat conditions, the process becomes simpler and easier as the heating is not required and the condenser is also no more required for water flow in the outside glass wall to prevent the escape of alcohol which is otherwise required during heating. Therefore, all the used vegetable oils explained here can be used for biodiesel production under ambient temperature conditions.

Chapter 8
Conclusions

8.1 Study Outcome

The present study deals with the analysis of the total process starting from the production of biodiesel from used vegetable oils and non-edible oils till its end use. This study has been divided into four parts. It involves the process of biodiesel production and optimization of process parameters, statistical analysis to obtain an optimized yield, performance of diesel engine with the biodiesel produced and comparative chemical analysis of the biodiesel produced with application of heat and without any application of heat from different types of used vegetable oils.

Biodiesel produced from linseed oil and mahua oil has given yields of 90% and 92% respectively. But the yields of biodiesels from used vegetable oils collected from different sources varied between 97% to 86%. The difference in the yields of biodiesels from used vegetable oils is due to the difference in the quality of feedstock and the difference in the amount of catalyst and alcohol used for the reaction. It can be seen here that by the process of transesterification, the properties of biodiesel produced from used vegetable oils and non-edible oils can be brought close to that of diesel. The process parameters when varied produce changes in the percentage of yield. Therefore, variables like catalyst concentration, molar ratio and reaction time have been varied in different proportions to observe the changes in the yield in each type of feedstock for biodiesel production keeping few parameters constant for each set run for transesterification.

The collection of used vegetable oil at times is a difficult process because the sources of the feedstock are unknown at times and people prefer throwing the used oils rather than selling them at low prices. But bigger companies that produce fried food items have large amount of used oil which they sell to manufacturers of soap companies. Apart from this, Fast Moving Consumer Goods (FMCG) manufacture a large variety of products like chips, sweets and many other items at cheaper rates. The products under FMCGs are present in every household and touch each part of the life of the consumer as reported by Wikipedia. 2023. If initiative is taken by the companies of FMCG, then the collection of the used vegetable oil can become much easier. Therefore, it can be seen that the oils which are not for consumption or are discarded after use of their raw form can act as potential feedstock for biodiesel production.

As it can be observed that changes in process parameters changes yield, it is necessary to find a set of values for the process parameters which can give the optimised yield. Statistical analysis has helped in this study to provide sets of combinations of the process variables. Biodiesel production for each set of parameters has given a set of predicted yields which have been compared to the corresponding experimental yields. The various designs provided by the mathematical tool Response Surface Methodology (RSM) can be used to examine the process parameters at five and three levels. The interactive and the quadratic effects of the parameters can be studied by this method. From the graphs the optimized parameters are obtained and the transesterification is performed with the set of the optimized parameters. It can be seen that the there is a difference of 0.205% between the experimental yield and the predicted yield. This validates the process. Thus, the statistical analysis method minimizes the use of the trial-and-error method of selection of values of operating parameters for biodiesel production. Since the mixed oil has given lesser yield previously, the used vegetable oil of one soybean origin has been used in this part of the study. This oil has been used as it was readily available from a single source and could be easily collected for experimental purpose.

The production of biodiesel can be validated only when the internal combustion engine can be run in the form of its blends with diesel in various proportions. The engine has been run with biodiesel blends (B5, B10 and B20) in which the biodiesel has been produced from used vegetable oil(soybean), used vegetable oil (rice bran) and used vegetable oil(sunflower). The physical and chemical properties of the biodiesels from USOME, URBME and USUME have been presented in tabular form which shows that their densities are comparable to that of diesel. It has also observed that viscosities have values which enable their use as blends with diesel. The brake specific fuel consumption of all the blends is less than that of diesel as the viscosities of the blends is greater than that of pure diesel. Brake specific fuel consumption (BSFC) of blended biodiesels produced from different sources is slightly greater than that of diesel at all loads. The BSFCs of all the biodiesels from used vegetable oils decreases with increase in load. With increase in blending the calorific value of the blended form of biodiesel decreases at any given load.

Since biodiesel can be produced from various sources the qualitative analysis becomes important to know the composition of the biodiesel produce from used oils from different sources. The biodiesels have been produced from used soybean oil, used rice bran oil and used sunflower oil with and without application of heat. The various properties depending upon the degree of unsaturation and saturation of the methyl esters have been calculated and verified. It has also been proved that 2578.20 kcal of energy is saved per litre of use vegetable oil processed if the biodiesel is produced without the application of heat by the process of transesterification for 2 hours.

At present, transesterification system is incorporated with a heating system and stirring arrangement. If the production is done without application of heat, then no heating arrangement will be required and only the stirring unit will be needed for stirring purpose. It has also been studied that the chemical composition and the fuel properties of biodiesel produced without application heat can be readily used to run in diesel engines in blended form.

With the elimination of the usage of heat, the capital cost for the transesterification reactor will be less with respect to the present technology. Along with this not only the input cost will also decrease, but the capital investment for the production system will be less as this is much simplified in construction. Various heating elements like thermostat control system and a few other elements which were required during heating are no more required.

Decrease in yield leading to a decrease in output energy in the form of calorific value of the produced biodiesel can be compensated by the decrease in heat input for the production process which is much larger in terms of amount of energy. The decrease in calorific value of the decreased yield of biodiesel is much less in comparison to the heat saved by removing the heater. Therefore, the production cost decreases as the running cost and capital cost will be less. This will make the production unit simpler than the conventional one.

Biodiesel production uses reactants which are oil, alcohol and catalyst. In this study, methanol has been used as alcohol which is highly flammable in nature as it has the tendency to form explosive mixture with air and its boiling point is 64.9°C as reported by Editors of the Encyclopedia Britannica, 2023. Therefore, if heat input is eliminated then any kind of hazardous accident can be prevented and no elaborate safety measure will be required for protection. Small-scale production can be done by small-scale entrepreneurs without adopting any kind of elaborate safety measures. The following schematic diagram in Fig. 8.1 will give an idea of the setup for biodiesel production without any arrangement for heat input.

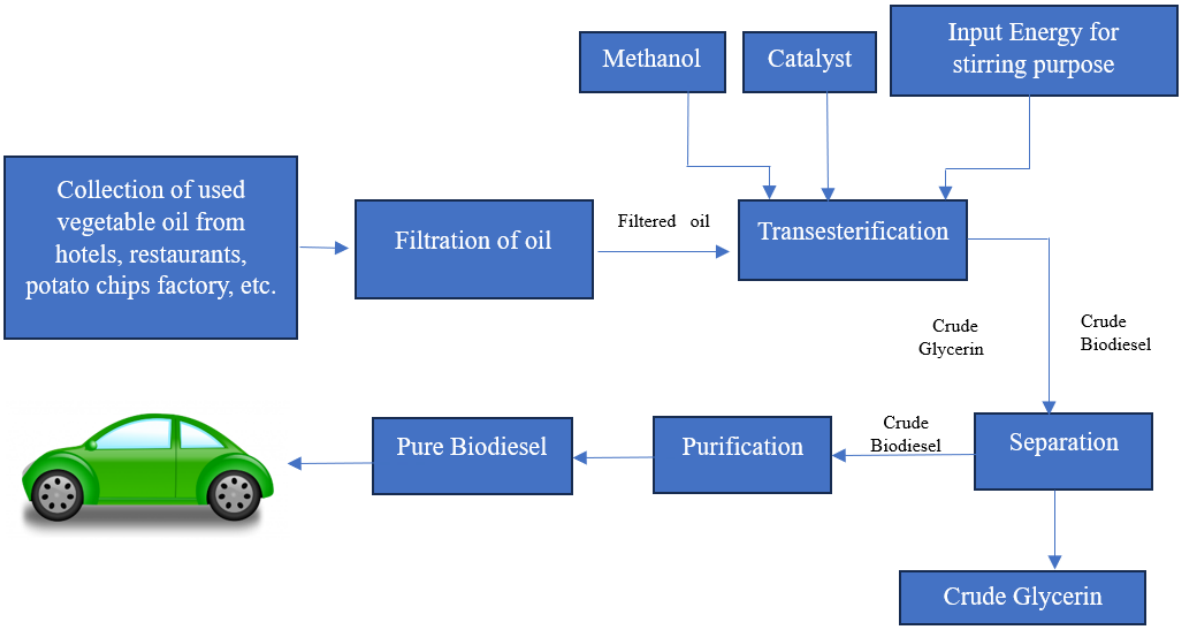


Fig. 8.1 Proposed biodiesel production from used vegetable oil at ambient temperature without application of heat

Thus, from the above outcome of the study, it can be suggested that biodiesel can be readily produced from cheaper sources like used vegetable oils if the collection of the oil is channelized in a proper manner. It has also been concluded that heat is not mandatory to produce biodiesel as it can be produced without any application of heat under ambient temperature conditions. Further methanol, diesel and biodiesel can be tried together to run the CI engine and the study can be carried over further.

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ANNEXURE I

Determination of the density of the used vegetable oil (mixed)

Density of the oil has been calculated as described in Eq. 3.3 of Chapter 3.

Mass of specific gravity bottle =9.284 gm

Volume of the specific gravity bottle = 10 ml

Mass specific gravity bottle and oil = 18.384 gm

Therefore, Mass of oil = (18.384 -9.284) gm = 9.10 gm

Density of oil = 9.1/10 = 0.91 gm/cc

Therefore, density of linseed oil, mahua oil and used vegetable oil(soybean) have been calculated with the help of the following data

Type of oil	Mass of specific gravity bottle and oil (gm)	Mass of oil (gm)	Density (gm/cc)
Linseed oil	18.559	9.275	0.9275
Mahua Oil	18.140	8.856	0.8856
Used vegetable oil (soybean)	18.254	8.970	0.8970

Acid Value of used vegetable oil (mixed)

The acid value and FFA content are calculated as described in Eq. 3.1 and Eq. 3.2 of Chapter 3.

Volume of NaOH	Mass of sample of oil	Acid Value	% of FFA content
1.51 ml	5 gm	1.69	0.852

For rest of the oils acid value is calculated with .1 N KOH solution and their values are as under.

Type of oil	Volume of KOH (ml)	Mass of sample of oil (gm)	Acid Value	% of FFA content
Linseed oil	2.1	5	2.345	1.18
Mahua Oil	31.4	5	34.791	17.5
Used vegetable oil (soybean)	1.6	5	1.809	0.910

Acid value and FFA content of esterified mahua oil

Type of oil	Volume of KOH (ml)	Mass of sample of oil (gm)	Acid Value	% of FFA content
Esterified mahua oil	2.9	5	3.280	1.65

Amount of alcohol corresponding to each molar ratio in case of 100 ml of used vegetable oil(mixed)

Molar ratio of oil: alcohol	Amount of alcohol approximate values (ml)
1:3	14
1:6	28
1:12	43.537
1:15	55

Determination of viscosity of the biodiesel from used vegetable oil(mixed) for the optimised yield of 86%

As mentioned in Eq. 3.5, the viscosity of biodiesel is calculated.

$\eta_2 =$ .800 mm^2/sec

Average time taken for water to fall from upper to lower mark = 178 seconds

Average time taken for biodiesel to fall from upper to lower mark = 1508 seconds

Density of this sample of biodiesel = 0.87 g/cc.

Density of water = 1 g/cc.

Kinematic viscosity of biodiesel = $\frac{(.800 \times 0.87 \times 1508)}{(178 \times 1)}$

= 5.896 centistokes = 5.9 centistokes

= 5.9 mm^2/sec

Determination of the calorific value of the biodiesel from used vegetable oil(mixed) for the optimised yield of 86%

Calorific value of biodiesel has been calculated as described in Eq. 3.7 of Chapter 3.

Mass of biodiesel = 0.8gms

Temperature rise due to burning of given sample of oil T_s=2.78^{0}C

(Here a correction has to be made in the mass of the fuel burnt since certain amount of fixed carbon was left after the combustion process)

Therefore,

Amount of fixed carbon left after combustion M_{cl}=.025gms

Heat of combustion of the given sample of biodiesel =T_s*W/M_s

=2.78 x 2178.6/.775=7807.354 calories/gram

Heat of combustion of left over carbon =8084 calories/gm

Now, Calorific value of biodiesel = (7807.354 x 0.775+.025 x 8084)/0.8

= 7815.999 calories/gm = 7816 calories/gm

Average time of fall for calculation of viscosity for biodiesel from used vegetable oil (soybean)

η_2 = 0.658 mm^2/sec at 40°C

ρ_2 = 1 gm/cc

Parameter changed	Magnitude of parameters	Constant parameters		Average time taken by the biodiesel to reach from upper mark to the lower mark of the viscometer (secs)
Molar ratio	6:1 9:1 12:1	Catalyst-1% Reaction time-2hrs	Stirring rate-1000 R.P.M Temperature = 45^0C	1600 1461 1467
Catalyst concentration	0.5 1 1.5 2	Molar ratio-9:1 Reaction time-2hrs		1690 1462 1594 3009
Reaction time	0.5 1 1.5 2 2.5	Catalyst-1% w/w KOH Molar ratio-9:1		1543 1462 1650 1461 1558

Properties of biodiesel prepared from used vegetable oil (soybean)

Parameter changed	Magnitude of parameters	Constant parameters		Density kg/m^3	Viscosity (m^2/sec) x 10^{-6}
Molar ratio	6:1 9:1 12:1	Catalyst-1% Reaction time-2hrs	Stirring rate-1000 R.P.M Temperature = 45^0C	861 850 845	5.88 5.11 5.10
Catalyst concentration	0.5 1 1.5 2	Molar ratio-9:1 Reaction time-2hrs		813 850 839 791	5.65 5.11 5.5 9.79
Reaction time	0.5 1 1.5 2 2.5	Catalyst-1% w/w KOH Molar ratio-9:1		857 865 872 850 868	5.44 5.20 5.92 5.11 5.56

Average time of fall for calculation of viscosity for biodiesel from linseed oil

Parameter changed	Magnitude of parameters	Constant parameters		Average time taken by the biodiesel to reach from upper mark to the lower mark of the viscometer (secs)
Molar ratio	3:1 6:1 9:1 12:1	Catalyst- 1% w/w KOH Reaction time- 2hrs	Stirring rate- 1000 r.p.m. Temperature- 60^0C	2199 1675 1645 2313
Catalyst concentration	0.5 1 1.5 2	Molar ratio- 9:1 Reaction time- 2hrs		1571 1645 1364 1619
Reaction time	0.5 1 1.5 2 2.5	Catalyst- 1%w/w KOH Molar ratio- 9:1		1764 1374 1532 1645 1553

Properties of biodiesel prepared from linseed oil

Parameter changed	Magnitude of parameters	Constant parameters		Density Kg/m^3	Viscosity (m^2/sec) x 10^{-6}
Molar ratio	3:1	Catalyst-1% Reaction time-2hrs	Stirring rate-1000 r.p.m. Temperature-60^{0}C	880	7.96
	6:1			878	6.05
	9:1			872	5.90
	12:1			884	8.41
Catalyst concentration	0.5	Molar ratio-9:1 Reaction time-2hrs		876	5.66
	1			872	5.90
	1.5			870	4.88
	2			886	5.90
Reaction time	0.5	Catalyst-1%w/w KOH Molar ratio-9:1		874	6.34
	1			886	5.01
	1.5			873	5.50
	2			872	5.90
	2.5			878	5.61

Average time of fall for calculation of viscosity for biodiesel from mahua oil

Parameter changed	Magnitude of parameter	Constant parameters		Average time taken by the biodiesel to reach from upper mark to the lower mark of the viscometer (secs)
Molar ratio	STEP I 6:1 STEP II 6:1	Catalyst- Step I-1.24 v/v H_2SO_4 Step II-0.7%w/w KOH Reaction time-2hrs	Stirring rate-1000 R.P.M Temperature-60^{0}C	1858
	STEP I 8:1 STEP II 6:1			1685
	STEP I 8:1 STEP II 8:1			1744
	STEP I 8:1 STEP II 9:1			2075
	STEP I 8:1 STEP II 12:1			1876
Reaction time(hrs)	STEP I 1 STEP II 1	Molar ratio- Step I-8:1 Step II-6:1 Catalyst- Step I-1.24%v/v H_2SO_4 Step II-0.7% w/w KOH	Stirring rate -1000 R.P.M Temperature-60^{0}C	1685
	STEP I 1 STEP II 2			1875

Properties of biodiesel prepared from mahua oil

Parameter changed	Magnitude of parameter	Constant parameters		Density (kg/m^3)	Viscosity (m^2/sec) x 10^{-6}
Molar ratio	STEP I 6:1 STEP II 6:1	Catalyst- Step I-1.24 v/v H_2SO_4 Step II-0.7%w/w KOH Reaction time-2hrs	Stirring rate-1000 R.P.M Temperature-60^{0}C	846	6.46
	STEP I 8:1 STEP II 6:1			880	6.10
	STEP I 8:1 STEP II 8:1			852	6.11
	STEP I 8:1 STEP II 9:1			839	7.16
	STEP I 8:1 STEP II 12:1			841	6.49
Reaction time(hrs)	STEP I 1 STEP II 1	Molar ratio- Step I-8:1 Step II-6:1 Catalyst- Step I-1.24 v/v H_2SO_4 Step II-0.7% w/w KOH	Stirring rate - 1000 R.P.M Temperature-60^{0}C	880	6.10
	STEP I 1 STEP II 2			869	6.70

ANNEXURE II

Determination of the density of the oil

Density of the oil has been calculated as described in Eq. 3.4 of Chapter 3.

Mass of specific gravity bottle =9.284 gm

Volume of the specific gravity bottle = 10 ml

Mass specific gravity bottle and oil = 18.464 gm

Therefore, Mass of oil = (18.464 -9.284) gm = 9.18 gm

Density of oil = 9.1/10 = .918 gm/cc

Determination of acid value and FFA content of oil

Acid value enables to verify the feasibility of the process selected i.e alkali transesterification or acid transesterification. As mentioned in Eq. 3.1 and Eq. 3.2 of Chapter 3, the acid value of the oil has been calculated.

Acid Value of oil

Type of oil	Volume of KOH (ml)	Mass of sample of oil (gm)	Acid Value	% of FFA content
Used vegetable oil	1.5	5	1.683	.846

Estimation of physico-chemical characteristics of biodiesel produced from used vegetable oil (soybean).

Determination of the density of the biodiesel

Density of the oil has been calculated as described in Eq. 3.4 of Chapter 3.

Mass of specific gravity bottle =9.284 gm

Volume of the specific gravity bottle = 10 ml

Mass specific gravity bottle and oil = 18.464 gm

Therefore, Mass of oil = (18.464 -9.654) gm = 8.81gm

Density of oil = 8.81/10 = .881 gm/cc

Determination of acid value and FFA content of oil

Acid value enables to verify the feasibility of the process selected i.e alkali transesterification or acid transesterification. As mentioned in Eq. 3.1 and Eq. 3.2 of Chapter 3, the acid value of the oil has been calculated.

Acid Value of oil

Type of oil	Volume of KOH (ml)	Mass of sample of oil (gm)	Acid Value	% of FFA content
Used vegetable oil	.336	5	.378	.846

Determination of viscosity of the biodiesel

$$\eta_1 = \eta_2 \cdot \rho_1 t_1 / \rho_2 t_2$$

where η_1 and η_2 are viscosities of the biodiesel and water, and ρ_1 and ρ_2 are the densities of the biodiesel and water, respectively and η_2 is the viscosity of the reference liquid as reported by Labmonk, 2018**.** Here t_1 and t_2 are the time interval of the liquid. Viscosity of the oil has been calculated as described in Eq. 3.5 of Chapter 3. Here the reference liquid is water.

η_2 = 0.658 mm^2/sec at 40°C

ρ_2 = 1 gm/cc

Average time of fall of water = 172

Average tie of fall of biodiesel = 1184

Kinematic viscosity of biodiesel = $\frac{(0.658*.881*1183.5)}{(172*1)}$

= 3.989 centistokes = 3.989 centistokes

= 3.989 mm^2/sec

Determination of the calorific value of the biodiesel

Calorific value of biodiesel has been calculated as described in Eq. 3.6 of Chapter 3.

Mass of biodiesel =0.8gms

Temperature rise due to burning of given sample of oil Ts=2.78^{0}C

(Here a correction has to be made in the mass of the fuel burnt since certain amount of fixed carbon was left after the combustion process)

Therefore,

Amount of fixed carbon left after combustion Mcl=0.02gms

Heat of combustion of the given sample of biodiesel =Ts x W/Ms

=3.28 x 2178.6/.78=9164.328 calories/gram

Heat of combustion of left over carbon =8084 calories/gm

Now, Calorific value of biodiesel = (9164.328 x .78+.025 x 8084)/.8

= 9137.32 calories/gm

According to britannica.com, 2023, 1 calorie = 4.18 joules

Therefore, 9137.32 calories/gm = 38.19399 MJ/kg = 38.194 MJ/kg

ANNEXURE III

Density of oils

Mass of specific gravity bottle =9.284 gm

Volume of the specific gravity bottle = 10 ml

Type of oil	Mass of specific gravity bottle and oil (gm)	Mass of oil (gm)	Density (gm/cc)
Used vegetable oil (soybean)	18.454	9.170	.9170
Used vegetable oil (rice bran)	18.534	9.250	.9250
Used vegetable oil (sunflower)	19.274	9.990	.9990

Acid value and FFA content of oils

Type of oil	Volume of KOH (ml)	Mass of sample of oil (gm)	Acid Value	% of FFA content
Used vegetable oil (soybean)	1.67	5	1.907	.959
Used vegetable oil (rice bran)	1.30	5	1.458	.733
Used vegetable oil (sunflower)	1.6	5	1.719	.864

Determination of viscosity of the biodiesel

$$\eta_1 = \eta_2 \cdot \rho_1 t_1 / \rho_2 t_2$$

where η_1 and η_2 are viscosities of the biodiesel and water, and ρ_1 and ρ_2 are the densities of the biodiesel and water, respectively and η_2 is the viscosity of the reference liquid as reported by

Labmonk, 2018**.** Here t_1 and t_2 are the time interval of the liquid. Viscosity of the oil has been calculated as described in Eq. 3.5 of Chapter 3. Here the reference liquid is water.

η_2 = .658 mm^2/sec at 40°C

ρ_2 = 1 gm/cc

Average time of fall of water = 180 seconds

Average time of fall of biodiesel from used vegetable oil (soybean) = 1232 seconds

Average time of fall of biodiesel from used vegetable oil (rice bran) = 1396 seconds

Average time of fall of biodiesel from used vegetable oil (sunflower) = 1353 seconds

Determination of the calorific value of the biodiesel

Calorific value of biodiesel has been calculated as described in Eq. 3.7 of Chapter 3.

The standard conversion of calorie to joule can be referred at Britannica, 2023.

Mass of biodiesel =.8gms

Type of oil for biodiesel production	Temperature rise due to burning of given sample of oil T_s (^{0}C)	Amount of fixed carbon left after combustion M_{cl} (gms)
USOME	3.40	0
URBME	3.44	0
USUME	3.37	0

The calorific values have been rounded off.

Calculation of BSFCs for USOME, URBME and USUME at different loads.

Densities of B5, B10 and B20 for USOME, URBME and USUME

Density of diesel = 839 kg/m^3

Density of B5 of USOME = .05 x 868.80 + .95 x 839 = 840.49 kg/m^3

Similarly, all the required values have been calculated and tabulated as given below.

Type of biodiesel	Density of B5 blend (kg/m^3)	Density of B10 blend (kg/m^3)	Density of B20 blend (kg/m^3)
USOME	840.49	841.98	844.96
URBME	841.33	843.71	848.72
USUME	840.73	842.47	845.94

The densities of the blends are used to calculate the corresponding BSFCs from the values of the fuel consumption given.

The specific fuel consumption(ml/kWh) of diesel/biodiesel at the given value of Output Power

= fuel consumption (ml/h) ÷ Output Power (kW)

The BSFC (kg/kWh) of diesel/biodiesel at the given value of Output Power

= specific fuel consumption(ml/kWh) x density of diesel/blended biodiesel(kg/ml)

(To convert kg/m^3 to kg/ml the density has to be divided by 10^6.)

Brake-specific fuel consumption of diesel at different loads on the engine

Load(W)	Fuel Consumption (ml/hr)
500	280
1000	348
1500	405
2000	424

Fuel consumption of biodiesel blends prepared from used vegetable oil (soybean) at different loads on the engine

Load(W)	FC(ml/h) B5	FC(ml/h) B10	FC(ml/h) B20
500	297	302	305
1000	348	357	364
1500	410	410	408
2000	430	438	452

Fuel consumption of biodiesel blends prepared from used vegetable oil (rice bran) at different loads on the engine

Load(W)	FC(ml/h) B5	FC(ml/h) B10	FC(ml/h) B20
500	287	299	305
1000	354	357	358
1500	412.5	417	419
2000	450	472	488

Fuel consumption of biodiesel blends prepared from used vegetable oil (sunflower) at different loads on the engine

Load(W)	FC(ml/h) B5	FC(ml/h) B10	FC(ml/h) B20
500	287	289	293
1000	352	362	368
1500	416	420	427
2000	430	454	458

ANNEXURE IV

Calculation of oxidation stability, iodine value, CP and PP of FAMEs.

The calculation has been shown for used soybean oil methyl ester with heat, The calculation procedure for other methyl esters will be the same.

Value for the properties of used soybean oil methyl ester produced by application of heat

$OS = -0.234(64.08) + 22.318 = 7.32\text{h}$

$IV = 254\{(1\text{x}19.22 \div 296.5) + (2 \text{ x } 38.61 \div 294.5) + (3 \text{ x } 6.25 \div 292.5)\} = 99.348$

$CP = 0.526 \text{ x } 29.58 - 4.992 = 10.56\ °\text{C}$

$PP = 0.571 \text{ x } 29.58 - 12.24 = 4.65\ °\text{C}$

In the same manner, the values of the above properties for all the mentioned fatty acid methyl esters can be calculated as these properties are based on the structural composition of the fatty acid methyl esters.

Paper Publications

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Waste To Energy Conversion Through Biodiesel Production From Waste Cooking Oil And Its Optimization

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The study comprises one of the methods of waste management by conversion of waste cooking oil to a sustainable form of energy. It carries out the production of biodiesel from waste oil which is disposed of in such a manner that it can be a serious threat to the environment in near future. Large scale production of biodiesel from this waste oil can be a permanent solution of waste to energy conversion. In this study, the operating parameters, namely catalyst concentration, methanol: oil ratio and reaction temperature were varied at three different levels using response surface methodology (RSM). The R^2 value is 0.9771 which indicates that there is a good fit between the given model and the experimental data. Based on the experimental results, the optimum operating parameters from transesterification of waste soybean oil at a stirring rate of 1000 rpm and 2 hr reaction time at a temperature of 52^0C, the molar ratio of 7.7:1 and catalyst concentration of 1.157% w/w of oil. Biodiesel production has been carried out with the optimized parameters to obtain the corresponding laboratory yield. The predicted and laboratory yields were 93.408% and 93.06%, respectively which denotes that variation is 0.348%. 2D and 3D contour plotting has been done using MINITAB17 for the prediction of optimized yield. The physical and the chemical properties have been compared and the relationship has been studied.

KEYWORDS

Biodiesel, Waste, Energy, Response surface methodology, Transesterification, Used soybean oil

1. INTRODUCTION

Being a developing nation, India is undergoing industrialization and urbanization at a rapid pace. This is leading to changed life patterns accompanied by economic growth. The developments taking place all around the country has led to increased quantities of waste which is causing a detrimental effect on the environment [1]. Proper treatment of waste in any form whether solid, liquid or gaseous is important before permanent disposal. Waste management is ensured to be significant if there is proper segregation of waste at the source itself and then the waste goes through different paths of recycling in order to safeguard the ecological balance [2]. One of the forms of liquid waste which is disposed of without any treatment more often is the waste cooking oil which originates from the cooking oil made from biological sources, such as palm, soybean, olive and sunflower [3]. India uses 2,700 crore litres of cooking oil, out of which 140 crore litres can be successfully collected for the generation of a useful form of energy, namely biodiesel.

The present scenario is such that India has 850 crore litres of diesel requirement per month on average. The government targets biodiesel blending of diesel by 5% by the end of 2030. The requirement of biodiesel is enormous which also ensures successful waste to energy conversion [4]. The continuous extraction and consumption of fossil fuel have led to a reduction in underground reserves of carbon sources [5]. The huge increase in energy demand is due to urbanization and industrialization which is decreasing the non-renewable resources gradually [6]. Biodiesel has become an interesting alternative because of its environmental benefits. Moreover, the huge availability of waste cooking oil and animal fats can be channelized for biodiesel production as their improper disposal leads to contamination of water and land resources [7]. Biodiesel is derived from renewable, biodegradable and non-toxic resources [8]. The cost of biodiesel is highly dependent on the raw material used for manufacturing. Therefore, the high cost of raw material is a major barrier to the commercialization of biodiesel [9].

China's biofuel consumption was 2.1 Mt in 2014 with feedstock changing from corn-oil to waste cooking oil [10]. In comparison to raw oils, the used vegetable oil is cheaper and also available in abundance, therefore, can be incorporated as permanent feedstock for mass-scale production of biodiesel. The production of biodiesel from waste cooking oil provides an acceptable way of

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Optimization of process parameters of biodiesel production from different kinds of feedstock

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Abstract

An experimental study has been carried out to produce biodiesel from different kinds of feedstock. Operating parameters have been optimized with respect to percentage yield of production and viscosity. The most common method for production of biodiesel is transesterification. Palm, karanja, mahua, linseed and castor oil are among the few of the non-edible oils. Along with this waste cooking oil can also be considered as non-edible oil as it is mostly thrown away. The process of transesterification depends on various factors like reaction temperature, stirring rate, molar ratio, amount of catalyst and reaction time. Depending upon the acid value, the number of steps of transesterification was determined. If free fatty acid is greater than 2.5% then two step transesterificaton is carried out. Karanja and mahua oil undergo two-step process because of high FFA content. The main objective of the study was to optimize the reaction parameters for production of biodiesel from different kinds of oil based on kinematic viscosity and percentage of yield obtained.

Selection and Peer-review under responsibility of the Conference Committee Members of International Conference on Advances in Energy Research 2015 (ICAER-2015).

Keywords: : biodiesel; feedstock; transesterification; non-edible; acid value

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1. Introduction

The world is confronted with the twin crisis of fossil fuel depletion and environmental degradation. The indiscriminate extraction and consumption of fossil fuels have led to a reduction in petroleum reserves. Petroleum

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Biodiesel production from used vegetable oil collected from shops selling fritters in Kolkata

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Abstract

Used vegetable oil is an important feedstock for biodiesel production. Biodiesel has been produced from used vegetable oil collected from shops selling fritters in Kolkata. Transesterification is affected by factors like oil to alcohol ratio, concentration of catalyst used, temperature, stirring rate and reaction time. The process parameters were optimized and a maximum biodiesel yield of 94% has been achieved. Important properties of the biodiesel like density, flash point, calorific value and viscosity have also been estimated.

Selection and peer-review under responsibility of Organizing Committee of ICAER 2013

Keywords: Used vegetable oil; transesterification; fritters shops; biodiesel.

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1. Introduction

Energy consumption of the world is ever increasing. This has caused the fuel resources like petroleum dwindle. An alternative for petroleum is biodiesel. It has the same properties as fossil fuel diesel, is biodegradable and has lower emissions. Biodiesel is a product of a chemical reaction involving vegetable oil or animal fat, alcohol and a catalyst. The feedstock mainly used for transesterification is edible vegetable oil. But this puts a strain on developing countries using this oil for cooking purposes. The solution to this problem would be to use used vegetable oil for production of biodiesel. Used vegetable oil is a by-product from hotels, restaurants and shops selling fritters. In Kolkata, fritters are a popular snack. The shops selling these fritters run very successful businesses. These shops usually throw away the used oil as using it the next day decreases the quality of the fritters.

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Chapter 34

An Evaluation of Engine Performance of a Compression Ignition Engine with Biodiesel Produced from Different Kinds of Feedstock

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Introduction

The indiscriminate extraction of fossil fuel has led to depletion of petroleum reserves to a great extent [1]. The insufficient local oil reserves in the country has led to huge import of the oil to balance the supply and demand. As a result, the economy has burdened. Apart from this the environment and human health is getting adversely affected due to the harmful gas emissions. This has set off the search of alternative sources of energy available within the country [2]. Biodiesel can be produced from various sources but the cost of feedstock makes the resultant cost of biodiesel high which is a major setback in its commercialization. At this stage waste cooking oil has proven itself as a significant low-cost feedstock for biodiesel production [3]. Soybean oil import by India increased to more than 4 million tons in 2016, according to data provided by the industrial body keeping records of the total vegetable oil imported and consumed. As estimated by the U.S. Department of Agriculture in 2016 India's import of soybean oil is expected to rise over the next 10 years by 40% [4]. Most part of this oil is used for frying purpose thereby creating a huge hub of waste cooking oil if collected in proper manner. One study throws light on estimation of waste cooking oil thrown away by shops selling fritters in Kolkata [5]. One study uses rice bran oil to undergo the process of transesterification which is considered as the cheapest and easiest way of biodiesel production. The parameters namely methanol: oil ratio, catalyst concentration,

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