

DEVELOPMENT OF FREE FATTY ACID (FFA) MONITORING DEVICE FOR EVALUATION OF OIL SAMPLES USED FOR BIODIESEL PRODUCTION

Submitted in partial fulfilment of the requirements for the award of
Bachelor of Technology degree in Chemical Engineering

by

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**DEPARTMENT OF CHEMICAL ENGINEERING
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**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

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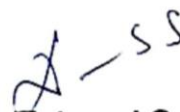
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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of Gopi Krishnan P (39190007) and Nitish S (39190022) who carried out the project entitled "DEVELOPMENT OF FREE FATTY ACID (FFA) MONITORING DEVICE FOR THE EVALUATION OF OIL SAMPLES USED FOR BIODIESEL PRODUCTION" under our supervision from November 2022 to April 2023.


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DECLARATION

We **Gopi Krishnan P (39190007)** and **Nitish S (39190022)** hereby declare that the Project Report entitled “**Development of free fatty acid (FFA) monitoring device for evaluation of oil samples used for biodiesel production**” done by me under the guidance of **Dr. M. Karthikeyan M.Tech, Ph.D.,** and **Dr. Dawn S.S. M.Tech., Ph.D.** at **SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY, CHENNAI, TAMIL NADU** is submitted in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering.

DATE: 21/04/2023

PLACE: CHENNAI

The image shows two handwritten signatures in blue ink. The top signature is 'P. Gopi Krishnan' with a long horizontal stroke extending to the right. The bottom signature is 'S. Nitish' with a circular flourish around the first part of the name.

SIGNATURE OF THE CANDIDATES

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ABSTRACT

Diversion of oil sources for biodiesel production has been gaining importance to meet the environmental concerns and energy demand. The free fatty acid (FFA) content of the feedstock is a significant factor in the biodiesel production. The FFA values determine the complexity of the biodiesel production. Until date, an experimental procedure has been used to determine the FFA concentration of an oil source; these methods are dependent on titration, which is a laborious process involving significant volumes of chemicals. Hence, in the present study, an attempt was made to develop a device for the identification of FFA. The impact of FFA and their respective methyl esters in the quality and properties of biodiesel have been investigated. Waste cooking oil samples subjected to wide range of cooking conditions including different cooking time, temperature, product to be fried, collected from different food outlets in Rajiv Gandhi Road, Chennai including Sathyabama Institute of Science and Technology mess were converted into biodiesel. Subsequently, the composition of oil samples and the variation in their quality were analysed using gas chromatography flame ionization detector (GC – FID). The respective methyl esters were also analysed. The properties of biodiesel such density, viscosity, acid value, flash point, fire point, calorific value was determined as per ASTM standards. The study was further extended to correlate the properties of biodiesel with the composition of the oil from which it was derived. The analysis evidently proved the dependence of biodiesel properties on the FFA percentage and the composition of the oil.

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LIST OF ABBREVIATIONS

FFA	Free fatty acid
FTIR spectroscopy	Fourier-transform infrared spectroscopy
NMR spectroscopy	nuclear magnetic resonance spectroscopy
GC - MS	Gas chromatography mass spectrometer
GC - FID	Gas chromatography flame ionization detector
FAME	Fatty acid methyl esters
AOCS	American Oil Chemists' Society
ASTM	American Society for Testing and Materials
EC	European Commission Regulation
AOAC	Association of Official Analytical Chemists
IR LED	Infrared light emitting diode
IR (TX)	Infrared transmitter (IR LED)
IR (RX)	Infrared receiver (photodiode)

CHAPTER – 1

INTRODUCTION

The global energy crisis is a growing concern due to the depletion of fossil fuel resources, increasing energy demand, and the negative impact of traditional energy sources on the environment. The world is currently facing an energy crisis that is affecting all aspects of global development. The energy crisis is characterized by the increasing demand for energy due to population growth, urbanization, and economic development. However, the energy supply is not keeping up with the increasing demand due to a variety of factors such as depletion of non-renewable resources, limited investment in renewable sources, and political instability in some energy-rich regions. The lack of sustainable and affordable energy sources is a significant challenge that affects economic growth, social development, and the environment.

The energy crisis has significant effects on the global economy, including an increase in energy prices, a decrease in economic growth, and an increase in debt and inflation. However, there are potential solutions to the energy crisis, including investing in renewable energy sources, increasing energy efficiency, and promoting energy conservation. Implementing these solutions will require significant investment, policy support, and behaviour change, but it is critical to mitigating the effects of the energy crisis and ensuring sustainable global development

1.1 IMPORTANCE OF NON-CONVENTIONAL ENERGY SOURCES

Non-conventional sources of energy include solar, wind, hydropower, geothermal, nuclear and biomass. These energy sources are clean and sustainable, and they have the potential to lower greenhouse gas emission that cause climate change. One of the most important non-traditional sources of energy is solar energy. It is liberal, clean, and renewable. According to a study by Balogun et al. (2019), solar energy has the potential to significantly reduce the dependence on fossil fuels for electricity generation. The study discovered that the price of solar panels has dramatically dropped in recent years, making solar energy more accessible and affordable for people and companies [1]. Furthermore, solar energy can be used to power remote areas that are not connected to the national electricity grid. This

makes it a significant source of energy in developing countries where access to electricity is limited.

Wind energy is another significant non-conventional source of energy. It is clean, renewable, and abundant. A study by Ma et al. (2020) found that wind energy has the potential to significantly reduce greenhouse gas emissions and mitigate climate change. The study highlights the need for investment in wind energy to achieve sustainable development goals [2]. In addition, wind energy can be used to power remote areas that are not connected to the national electricity grid, making it an important source of energy in developing countries.

Hydropower is another non-conventional source of energy that is significant. It is clean, renewable, and abundant. According to a study by Tadesse et al. (2019), hydropower has the potential to significantly reduce greenhouse gas emissions and mitigate climate change. The study highlights the need for investment in hydropower to achieve sustainable development goals [3]. In addition, hydropower can be used to provide electricity to remote areas that are not connected to the national electricity grid, making it an important source of energy in developing countries.

Geothermal energy is another non-conventional source of energy that is significant. It is clean, renewable, and abundant. A study by Kumaran et al. (2020) found that geothermal energy has the potential to significantly reduce greenhouse gas emissions and mitigate climate change. The study highlights the need for investment in geothermal energy to achieve sustainable development goals [4]. In addition, geothermal energy can be used to provide electricity to remote areas that are not connected to the national electricity grid, making it an important source of energy in developing countries.

Nuclear energy is an additional promising non-conventional energy source. According to a study by Bunn et al. (2017), nuclear energy can significantly contribute to supplying the world's energy demands while lowering carbon emission. The authors do point out that there are considerable difficulties with using nuclear energy, such as safety issues and the issues of disposing of radioactive waste [5].

Biomass energy is another non-conventional source of energy that is significant. It is derived from organic materials such as wood, crop residues, and animal waste. A study by Sahu et al. (2020) found that biomass energy has the potential to significantly reduce greenhouse gas emissions and mitigate climate change [6]. The study highlights the need for investment in biomass energy to achieve sustainable development goals. Furthermore, biomass energy can be used to provide electricity and heat to remote areas that are not connected to the national electricity grid, making it an important source of energy in developing countries.

1.2 BIOFUELS

Biofuel refers to fuels obtained from organic materials known as biomass. These materials can be obtained from plants, animals, and waste materials. The use of biofuels has been on the rise due to their renewable nature and potential to reduce greenhouse gas emissions. There are different types of biofuels, each with unique properties and applications.

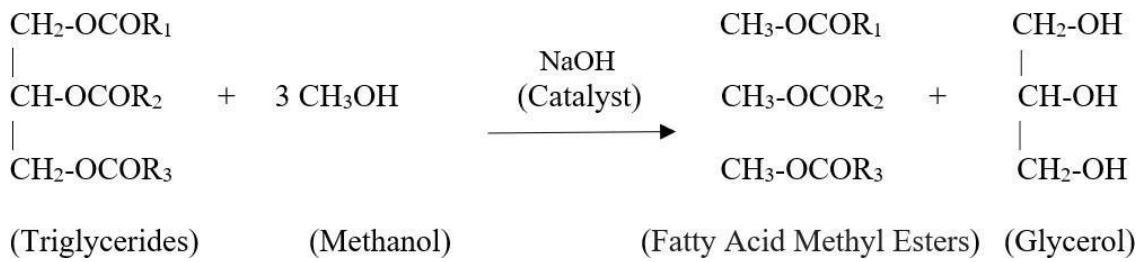
Table 1.1: Different generations of feedstocks used for biofuels

Generation of Biofuel	Type of Biofuel	Feedstock	Synthesis	Yield	Ref
First Generation	Bio-ethanol	Corn, sugarcane, wheat, barley, cassava, and other starch or sugar-rich crops	Fermentation of sugars or starches in the feedstock to produce ethanol	Varies depending on feedstock and process used, typically 100-500 L per ton of feedstock	[7]
	Bio-diesel	Soybean, canola, palm, and other vegetable oils, animal fats, and waste cooking oil	Transesterification of the feedstock with an alcohol (usually methanol) to produce biodiesel	Varies depending on feedstock and process used, typically 100-150 L per ton of feedstock	[8]
Second Generation	Bio-ethanol	Lignocellulosic biomass such as wood, grasses, and agricultural	Pre-treatment of the feedstock to break down cellulose and hemicellulose	Varies depending on feedstock and process used, typically 50-100 L per ton	[7]

		waste	into fermentable sugars, followed by fermentation to produce ethanol	of feedstock	
	Bio-diesel	Algae, jatropha, and other non-food crops	Extraction of oil from the feedstock, followed by transesterification to produce biodiesel	Varies depending on feedstock and process used, typically 200-400 L per hectare of land used	[9]
Third Generation	Bio-oil	Microalgae and other photo-synthetic organisms	Fast pyrolysis of the feedstock to produce a liquid bio-oil	Varies depending on feedstock and process used, typically 1-2 kg of bio-oil per kg of dry biomass	[10]
Fourth Generation	Bio-hydrogen	Microorganisms such as bacteria and algae	Biological or thermochemical processes to produce hydrogen gas	Varies depending on feedstock and process used, typically less than 1 kg of hydrogen per kg of feedstock	[11]

1.3 BIODIESEL

Biodiesel is a renewable fuel that is made from renewable feedstocks such as vegetable oils, animal fats, and used cooking oils. It is produced through a process called transesterification, which involves reacting the feedstock with an alcohol, such as methanol or ethanol, in the presence of a catalyst. The resulting product is a mixture of fatty acid esters, which can be used as a substitute for diesel fuel.



The chemical structure of biodiesel is like that of diesel fuel, with the main difference being the presence of fatty acid esters in biodiesel. The esters in biodiesel are composed of a long chain of carbon atoms, typically between 16 and 18, that are bonded to a glycerol molecule through an ester linkage. The esters are then separated from the glycerol molecule through the transesterification process, resulting in a pure biodiesel product.

Numerous studies had been conducted in the production, properties, and applications of biodiesel. For example, Zhang et al. (2021) Examined the application of microalgae as a possible feedstock for the production of biodiesel [12], while Bahrami et al. (2021) investigated the use of ultrasonic pre-treatment to improve the efficiency of the transesterification process [13]. Other studies have focused on the properties of biodiesel, including its viscosity, density, and cetane number [14] [15]. Additionally, studies on the use of biodiesel in other application, such as diesel engines [16] and as a blend with other fuels [17], have been done.

1.4 FEEDSTOCKS USED FOR BIODIESEL PRODUCTION

Biodiesel is produced from different generation feedstocks, ranging from first-generation feedstocks such as edible vegetable oils to second-generation feedstocks such as non-edible oils and waste oils, and third-generation feedstocks such as algae.

Due to their high oil content and accessibility, first generation feedstock like soyabean, rapeseed, and palm oils have been employed extensively in the manufacturing of biodiesel. However, the use of these feedstocks has raised concerns about competition with food production and land use changes. Second-generation feedstocks such as jatropha, camelina, and castor oils have been proposed as alternative feedstocks for biodiesel production due to their non-edible

nature and potential to grow on marginal lands. In addition, waste oils from the food industry have been used as a source of feedstocks for biodiesel production to reduce the environmental impact of waste disposal.

Third-generation feedstocks such as microalgae and macroalgae have also been studied as potential feedstocks for the manufacturing of biodiesel because of their high productivity and ability to grow in non-arable land and wastewater. Algae can also absorb carbon dioxide and nutrients from wastewater, which can reduce the environmental impact of industrial effluents.

Several studies have investigated the feasibility of using different feedstocks for biodiesel production. For example, Karmakar et al. (2010) compared the biodiesel yield of different first-generation and waste cooking oils. The authors found that waste cooking oil had a higher yield compared to the first-generation oils [18]. Li et al. (2014) reported the use of pyrolyzed rice husk as a heterogeneous catalyst to produce biodiesel from waste cooking oil. The authors found that the pyrolyzed rice husk waste catalyst had a higher conversion rate compared to other catalysts [19]. Rana et al. (2021) performed a life cycle assessment of biodiesel production from waste cooking oil and found that biodiesel produced from waste cooking oil had a lower environmental impact compared to fossil diesel [20].

Algae-based biodiesel has also been studied extensively. Alam et al. (2018) reviewed the potential of microalgae as a source of biodiesel and concluded that microalgae-based biodiesel could be a sustainable and economically viable alternative to fossil fuels [21]. Sanjaya et al. (2021) assessed the potential of palm oil biomass for bioenergy production in Indonesia and found that algae-based biodiesel had the highest energy yield compared to other bioenergy sources [22].

In addition, the use of genetically modified feedstocks for biodiesel production has also been explored. For example, Gao et al. (2019) investigated the use of a genetically modified yeast strain to produce biodiesel from waste cooking oil. The authors found that the use of the genetically modified yeast strain increased the yield of biodiesel production [23].

Table 1.2: Different generations of feedstocks used for biodiesel production

Type of Biodiesel	Feedstock	Yield	Ref.
First-generation Biodiesel	Soybean oil, rapeseed oil, palm oil, sunflower oil, etc.	95-98%	[8]
Second-generation Biodiesel	Jatropha, pongamia, camelina, etc.	70-80%	[24]
Third-generation Biodiesel	Microalgae, yeast, bacteria, etc.	30-80%	[25]

1.5 FREE FATTY ACIDS

Free fatty acid are chemically representing aliphatic hydrocarbon chain with carboxylic group, classified in many ways, such as, chain length, saturations, linear and branched [26].

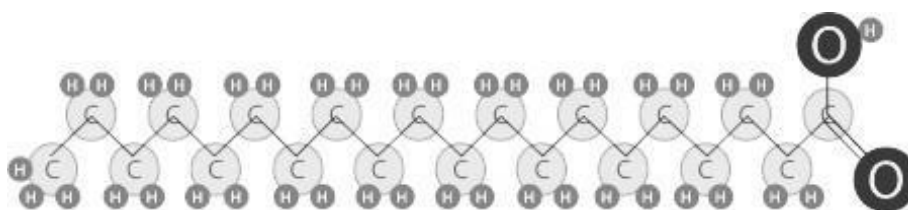


Fig 1.1: Structure of fatty acid

Based on chain length they are classified into short chained, long chained, etc. The most important classification of free fatty acids is based on double bonds present in the aliphatic chain, through this they are classified into two major categories: saturated and unsaturated fatty acids.

Saturated fatty acids possess no double bonds, owing to the fact that they are totally saturated with hydrogen molecules. Saturated fatty acids include Caprylic acid, Lauric acid, Myristic acid, Palmitic acid, and Stearic acid.

Unsaturated fatty acids are further divided into monounsaturated (one double bond) and polyunsaturated (more than one double bond) types based on the number of double bonds they contain. They include oleic acid, linoleic acid, and linoelaidic acid as unsaturated fatty acid.

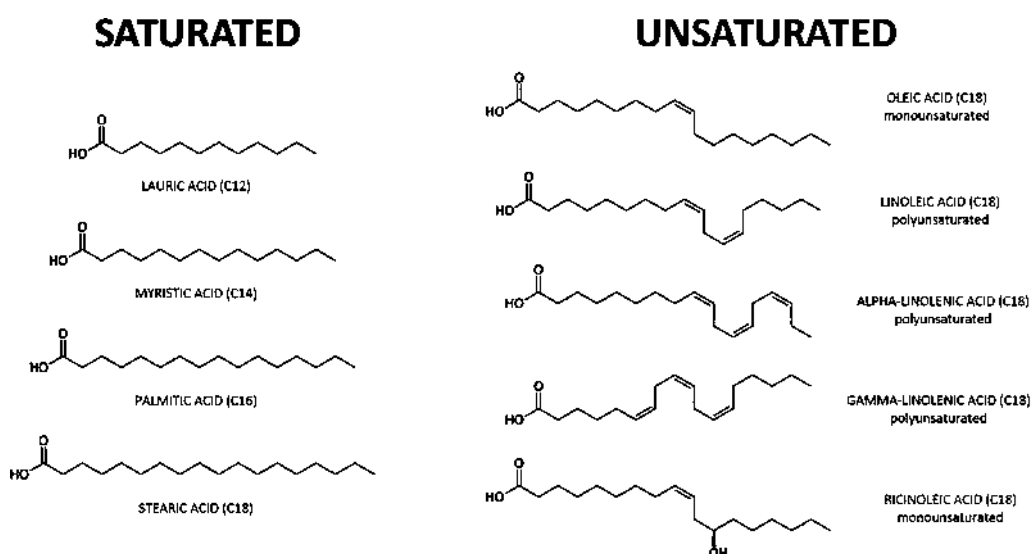


Fig 1.2: Examples of saturated and unsaturated fatty acids

These are formed by cleavage of ester bond during the hydrolysis of triglyceride in the oils by the action of high temperature and moisture content. Factors that affect the FFA content of vegetable oils include, grade of oil and its variety, storage and handling parameters, and the age of the oil. Due to high temperature and air exposure during frying or cooking operation, used cooking oil will have higher fatty acid content compared to raw vegetable oil, since these extreme conditions increases fatty acid by promoting oxidation of triacyl glycerides in the oil [27].

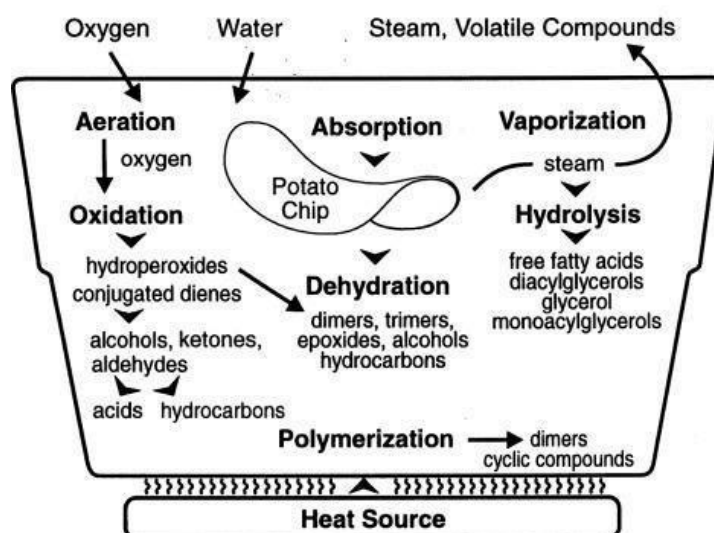


Fig 1.3: Reactions occurs during deep frying process

According to Pruszek et al. (2020) and Ribeiro et al. (2011) [28] [29] the maximum FFA content for the production of biodiesel can be around 2% by weight of the oil,

preferably 1%. Increased FFA levels can result in feedstock losses and have an adverse effect on glycerine separation due to soap formation that in turn interrupt the separation of glycerine and biodiesel by promoting stable emulsions [30]. Also, some study shows the higher FFA content acts as a poison for the catalyst in the transesterification, this directly impact conversion of triacyl glycerides [31].

According to I.M. Atadashi et al. (2012) around [32], “60-75% of the comprehensive cost of producing biodiesel fuel is revealed to be incurred by cost of feedstocks. To produce industrially feasible biodiesel in the future, it becomes mandatory to use feedstocks at lower prices, such as remains or non-edible oils or used cooking oils.”

Rancid or Non edible oils, animal fats and used cooking oils constitute the major sources biodiesel with high FFA values [33] [34]. Non edible oils such as jatropha oil [35], cotton seed oil [36], castor oil [37], rubber seed oil [38], Pongamia pinnata oil [39] are the most commonly used non edible oils in the biodiesel production. Chicken fat [40], beef tallow [41], mutton tallow, lard, are the types of animal fats that had been sources for biodiesel production.

Table 1.3: FFA compositions of various feedstocks used for biodiesel synthesis

Oil source	FFA composition (%)					Ref.
	Palmitic acid C16:0	Stearic acid C18:0	Oleic acid C18:1	Linoleic acid C18:2	Linolenic acid C18:3	
Algal oil	16.6	1.9	26.9	22.8	16.1	[42]
Castor oil	0.69	0.72	2.8	4.4	0.2	[43]
Chicken Fat	19.8	6.1	34.6	30.9	2.9	[40]
Coconut oil	13.1	3.7	12.9	4.34	NA	[44]
Cottonseed oil	21.3 - 26.4	2 - 3.5	14.4 - 21.8	46.6 - 58.4	0 - 0.7	[36]
Flax seed oil	5.0 - 8.1	2.2 - 4.6	13.4 - 19.4	12.3 - 17.4	40 - 60.4	[45]
Hemp oil	5.9	2.4	9.2	55.6	18.02	[46]
Jatropha	14.5	7	46.3	31	0.2	[35]
Neem oil	15.55	18.32	42.2	19.5	0.09	[43]
Olive oil	12.3	2.4	73.7	9.4	0.41	[47]
Palm oil	44.1	4.5	39.2	10.1	0.4	[48]
Peanut oil	9.3 - 14	1.2 - 3.7	35.7 - 58.5	21 - 43	NA	[49]
Pongamia oil	7.9	4.4	49	17.2	4	[39]
Rapeseed oil	3.5	1	64.4	22.3	8.2	[50]
Rice bran oil	15	2	42.5	39	1.1	[51]
Rubber seed	10.4	8.3	24.8	40	16.5	[52]

Safflower oil	5.3 - 10.8	1.8 - 3.4	14.1 - 37.8	21 - 73.9	0.08 - 5.6	[53]
Sunflower oil	7.5	3.1	33.4	54.7	NA	[54]
Waste cooking oil Sample 1	38.35	4.33	43.67	11.39	0.3	[55]
Waste cooking oil Sample 2	32.88	5.2	38.45	10	NA	[34]

1.6 METHODS FOR THE IDENTIFICATION OF FFA

FFA content of a feedstock is crucial parameter to be identified for the biodiesel production and its commonly identified standard procedures recommended by American Oil Chemists Society (AOCS), the American Society for Testing and Materials (ASTM), the European Commission Regulation (EC) and the Association of Official Analytical Chemists (AOAC). All these protocols are comparable and are based on titration, in which the oil sample is neutralized with isopropyl alcohol and titrated against sodium hydroxide in the presence of phenolphthalein indicator.

Even though these titrimetric procedures are simple, they have several drawbacks, including excessive chemical usage, poor accuracy, and environmental concerns. A variety of instrumental techniques have been created as prospective substitutes for conventional techniques for the more precise measurement of FFA content in edible oils and fats in order to address the above-mentioned problems. These approaches can be further classified into spectroscopic methods, chromatographic methods, colorimetric techniques [56].

1.6.1 Spectroscopic techniques

Spectroscopic methods are widely used for the analytical identification of free fatty acids (FFA) in oil samples. These methods are non-destructive and offer high sensitivity and specificity, making them suitable for quantitative and qualitative analysis of complex mixtures. Some of the common spectroscopic methods used for FFA identification in oil samples include Fourier-Transform Infrared (FT-IR) Spectroscopy and Nuclear Magnetic Resonance (NMR) Spectroscopy.

FT-IR spectroscopy is a powerful tool for FFA analysis in oil samples. This technique measures the sample's infrared radiation transmission or absorption. The absorption spectra obtained from FT-IR spectroscopy can provide valuable information about the functional groups present in the sample, allowing for the

identification and quantification of FFAs. A recent study by Khan et al. (2021) demonstrated the use of FT-IR spectroscopy for the quantitative analysis of FFA in palm oil. The study showed that FT-IR spectroscopy could accurately quantify FFAs in palm oil samples with a detection limit of 0.1% and a linear range of 0.1% to 4% [57].

NMR spectroscopy is a powerful tool for FFA analysis in oil samples. This method works by measuring the nuclear magnetic resonance of the sample. The NMR spectra obtained from this method can provide information about the molecular structure and can be used for the identification and quantification of FFAs. A study by Ma et al. (2016) demonstrated the use of NMR spectroscopy for the quantitative analysis of FFA in soybean oil. The study showed that NMR spectroscopy could accurately quantify FFAs in soybean oil samples with a detection limit of 0.5% and a linear range of 0.5% to 5% [58]. However, FT-IR spectroscopy has a limitation related to the carbonyl esters ($1730 - 1750\text{ cm}^{-1}$) absorption. The carbonyl group in the FFA shifts the absorbance maxima depending on whether it is protonated ($1705 - 1710\text{ cm}^{-1}$) or ionised ($1530 - 1580\text{ cm}^{-1}$) making pH a key factor in the procedure [59].

1.6.2 Chromatographic techniques

One of the most widely used methods for the determination of FFAs in oil samples is Gas Chromatography (GC). GC is a highly sensitive and accurate method that can be used to identify and quantify individual FFAs in oil samples. GC analysis requires a sample preparation step, which involves the esterification of FFAs to their corresponding methyl esters using a strong acid, such as sulfuric acid. The resulting methyl esters are then analyzed by GC using a Flame Ionization Detector (FID) or a Mass Spectrometer (MS).

In a study by M. K. M. Kassim et al. (2017), the authors developed a GC method for the determination of FFAs in palm oil. The method involved the use of a capillary column and a FID for detection. The authors demonstrated that the method was highly sensitive and accurate, with a detection limit of 0.01%. The method was also found to be suitable for the analysis of other vegetable oils, such as soybean and sunflower oils [60].

Another analytical method that has been used for the determination of FFAs in oil samples is High-Performance Liquid Chromatography (HPLC). HPLC is a powerful analytical technique that can separate and quantify individual FFAs in oil samples. In HPLC analysis, FFAs are typically derivatized using a reagent, such as 4-dimethylaminopyridine (DMAP), to form their corresponding DMAP derivatives. The resulting derivatives are then analyzed by HPLC using a UV or fluorescence detector. In a study by Y. Cao et al. (2018), the authors developed an HPLC method for the determination of FFAs in fish oil. The method involved the use of a C18 column and a UV detector for detection. The authors demonstrated that the method was highly sensitive and accurate, with a detection limit of 0.1 µg/ml. The method was also found to be suitable for the analysis of other types of oils, such as vegetable oils and animal fats [61].

1.6.3 Colorimetric techniques

Colorimetric techniques are widely used to identify and quantify free fatty acid (FFA) content in oils. The basic principle of colorimetry is based on the reaction of specific chemical reagents with the target analyte, resulting in a colour change that can be measured spectrophotometrically. The colorimetric assays for FFA determination in oils are simple, rapid, and cost-effective, making them attractive for industrial and laboratory applications.

The so-called copper-soap colorimetry is the most used spectrophotometric technique. Its operational premise is based on two facts: (i) FFAs form blue soluble soaps with copper ions in a polar solvents, and (ii) the intensity of the resulting blue colour is directly proportional to the FFA level [59]. One of the most used colorimetric methods for the determination of FFAs in oil samples is the ferric chloride method. In this method, FFAs react with ferric chloride to produce a blue colour that can be measured using a spectrophotometer at a wavelength of 660 nm. The intensity of the colour is directly proportional to the concentration of FFAs in the sample [62].

1.7 SENSORS FOR THE OIL QUALITY ASSESSMENT

There are various parameters that are monitored to assess the oil quality, such as viscosity, acidity, and water content. Sensors play a vital role in oil quality assessment by providing real-time data on these parameters.

Viscosity sensors are used to measure the viscosity of oil, which is an important parameter that affects the performance and efficiency of machinery. A study by Bahrami et al. (2019) developed a MEMS-based viscosity sensor for oil quality assessment. The sensor was designed using micro-electro-mechanical systems (MEMS) technology and utilized a capacitive sensing mechanism to measure the viscosity of oil. The study reported a high accuracy of the sensor in measuring the viscosity of different types of oils, including motor oil and hydraulic oil [63].

Acidity sensors are used to monitor the acidity of oil, which can indicate the presence of contaminants or oxidation products. A research paper by Gao et al. (2020) proposed an acidity sensor based on a quartz crystal microbalance (QCM) for oil quality assessment. The sensor utilized a sensitive film made of polydopamine/Graphene Oxide (PDA/GO) nanocomposites, which showed a high sensitivity and selectivity towards acidic gases. The study reported that the sensor could detect the acidity of oil samples with a detection limit of 0.4 ppm [64].

Water content sensors are used to monitor the water content in oil, which can lead to equipment damage and corrosion. A study by Vaezi-Nejad et al. (2018) developed a capacitance-based sensor for water content measurement in oil. The sensor was designed using a parallel-plate capacitor configuration and utilized a thin film of water-sensitive polymer (polyvinyl alcohol) as the dielectric material. The study reported that the sensor could detect water content in oil samples with a resolution of 0.1% [65].

The objective of this study was to create a sensor module for measuring the FFA concentration of oils. However, in order to make the construction of the module more simple, infrared source of radiation was considered during the design process.

1.8 IMPORTANCE OF FATTY ACID COMPOSITIONS IN BIODIESEL PRODUCTION

The properties of biodiesel are significantly impacted by the characteristics of individual esters of fatty acids and associated structural configurations as it is a blend of several fatty acid ester molecules. With genetic engineering of the feedstock oils, it may be possible in the future to supplement a specific fatty acid or (acids) with desirable attributes to get a fuel enriched with particular fatty acids in the biodiesel fuel to enhance its general fuel properties [66].

For instance, it might be possible to enhance the presence of certain esters (such methyl caprate and methyl oleate) or decrease the amount of polyunsaturated methyl ester. According to the European biodiesel standard EN 14214, biodiesel with a high amount of methyl oleate (or monounsaturated fatty acid) may have outstanding features in terms of ignition quality, fuel stability, flow qualities at low temperatures, and iodine number [66]. Esters with saturated medium chain acids, especially those of decanoic (capric) acid, have recently been found by several authors to be appropriate [67]. This is because they exhibit acceptable cold flow characteristics and provide an alternative to long-chain saturated fatty acid esters with high melting temperatures.

Moreover, they have great oxidative stability because there are no double bounds, which makes them a better choice than those esters. In numerous research [68] [69] it had been shown that the chemical structure of the fatty acid content affects the physical and chemical properties of biodiesel. Also, several studies demonstrate a connection between exhaust emissions and the chemical makeup of fatty acids.

Reviewing the impact of the characteristics and structural arrangements of FAMES upon various properties of biodiesel such as cold flow and combustion properties is the goal of the current investigation. FAME's structural configuration encompasses its molecular make-up, chain length, degree of unsaturation, saturated or unsaturated nature, and double bond placement.

CHAPTER – 2

LITERATURE REVIEW

- In the study conducted by **Kuo-Chin Huang et al. (2013)**, they proposed a novel method for the determination of FFA in oils and fats using UV spectroscopy and copper soap colorimetry. The authors synthesized copper soap by reacting copper acetate with stearic acid, and the resulting copper soap was used as a colour reagent for the FFA determination. The UV absorbance of the FFA-copper soap complex was measured at a wavelength of 320 nm, and the FFA content was calculated based on the standard curve. The authors optimized the experimental conditions, such as the concentration of copper soap and the reaction time, to improve the accuracy and sensitivity of the method. The results showed that the method had a high accuracy and sensitivity, and it could be applied to different types of oils and fats [70].
- **Gyorik et al. (2006)** presented a new analytical method for determining the total FFA concentration of thermally processed cooking oil. The technique used a 632.8 nm He-Ne laser as the radiation source and relied upon the colorimetric copper-soap technique paired with the idea of the optothermal window. When results from this method and those from conventional spectroscopy were examined, they showed a strong concordance for FFA values greater than 2 μmol per mL [59].
- In another study by **Yiming Xu et al. (2016)**, a modified method for FFA identification using UV spectroscopy and copper soap colorimetry was reported. The authors used copper (II) chloride instead of copper acetate as the copper source to synthesize the copper soap, and the FFA-copper soap complex was measured at a wavelength of 340 nm. The authors also optimized the experimental conditions, such as the concentration of copper (II) chloride and the reaction time, to improve the accuracy and sensitivity of the method. The results showed that the modified method had a lower detection limit and a wider linear range than the traditional method [71].

- The properties of biodiesel fuel, such as density, viscosity, flash point, and cetane number, are largely influenced by the composition of FAME. Different feedstocks can result in varying compositions of FAME, which can impact the fuel's properties. **Ahmad et al. (2018)** conducted a study to investigate the influence of different feedstocks on the physio-chemical properties of biodiesel. The study found that FAME composition significantly affects fuel properties such as density, viscosity, and flash point [72].
- Furthermore, FAME can have an impact on the durability of fuel system components. **Ali et al. (2019)** evaluated the effect of FAME on the corrosion of aluminium alloys and found that FAME blends can accelerate corrosion. The study also found that the degree of corrosion depends on the composition of FAME [73].
- Furthermore, the effect of FAME on the stability of biodiesel fuel is a critical consideration for its storage and transportation. Biodiesel is susceptible to oxidative degradation, which can cause fuel quality deterioration and negatively impact engine performance. Several studies have investigated the stability of biodiesel fuel with varying FAME compositions. For example, a study by **Liu et al. (2021)** found that blends of biodiesel with high stearic acid methyl ester (SAME) content exhibited better oxidative stability than blends with high oleic acid methyl ester (OAME) content [74].

Overall, the literature survey highlights the significant influence of FAME composition on the properties of biodiesel fuel. Optimizing FAME composition is crucial for improving fuel performance and reducing its impact on the environment. Also, UV spectroscopy and copper soap colorimetry are reliable methods for the identification and quantification of FFA in oils and fats. These methods have the potential to be widely used in the food industry for the quality control of oils and fats. However, further research is needed to validate these methods for different types of oils and fats, and to investigate their applicability to complex food matrices

CHAPTER – 3

AIM AND SCOPE

3.1 AIM:

The primary objective of our project was to develop a FFA monitoring device for evaluation of oil samples used for biodiesel production, by correlate the effects of structural configurations of fatty acid present in raw oil on various properties biodiesel. This was achieved by completing following set of objectives:

- Development of a database of preliminary properties for a set of oil samples and their corresponding biodiesel samples.
- Identification of the working principle of the sensor, construction of the sensor based on the principle identified, and testing the working of the sensor by comparing the results with experimental results.
- Compositional analysis of oil samples and their respective biodiesels under gas chromatography flame ionization detector (GC - FID) to understand the variations in composition
- Identification of major components of samples by interpretation of GC results and correlating the composition of samples with the properties of biodiesel.

3.2 SCOPE:

Free fatty acids (FFA) content of an oil is an important parameter in the process of biodiesel production. FFA content determines the complexity of the biodiesel production. Till now an experimental procedure is practiced for the identification of FFA content of oil source, these methods are based on titration, which is a laborious process and involves large amounts of chemicals. Also, it depends on visual end points which in turn compromise the accuracy of the result. Since, variety of feedstock with varying structural compositions and properties being used to produce biodiesel, yields inconsistent quality of biodiesel, analysing the composition of the oil becomes essential to produce superior quality biodiesel. Therefore, A simple mechanistic decision-making approach will be attempted in simplifying the choice of the oil and grading it for its usage in biodiesel production.

CHAPTER – 4

MATERIALS AND METHODS

4.1 OIL SAMPLE COLLECTION

Different samples of waste cooking oil (WCO) which were been used under various cooking conditions such as different cooking time, food items cooked, collected from different food outlets in Chennai were collected for analysis. Information of cooking conditions were acquired from the food outlets were tabulated.

4.2 PRELIMINARY PROPERTY ANALYSIS OF OIL SAMPLES

Preliminary properties of collected oil samples, like density, kinematic viscosity, free fatty acid (FFA), was measured in laboratory under their respective ASTM standards

4.2.1 Materials and chemicals required

- Density: pycnometer, weighing machine
- Kinematic viscosity: kinematic viscometer
- FFA value: 0.1 N Sodium hydroxide, Iso propyl alcohol, thermometer, 250 mL conical flask, Phenolphthalein indicator
- Moisture content: Crucible, Hot air oven

4.2.2 Density

The density of oil sample was measured using pycnometer. A pycnometer is a glass container with a known volume and stopper. Sample was taken in the pycnometer, and the mass of the pycnometer with the sample was measured. The density was calculated by dividing the mass by the volume of the pycnometer.

$$\text{Density} = \frac{(\text{Total weight of instrument with oil} - \text{Empty weight of the instrument})}{\text{Volume of the instrument (25ml)}}$$



Fig 4.1: Density measurement using pycnometer

4.2.3 Kinematic viscosity

The viscosity is been measured under the standard of ASTM D 445. This is a standard test method for kinematic viscosity of transparent and opaque liquid. The test involves measuring the time it takes for a fixed volume of oil sample to flow through a capillary tube at a temperature of 40 °C and maintain the heat till the end of the procedure. The kinematic viscosity is then calculated based on the time and the dimensions of the capillary tube.

$$\text{Viscosity} = \text{Time in (s)} \times 0.014$$

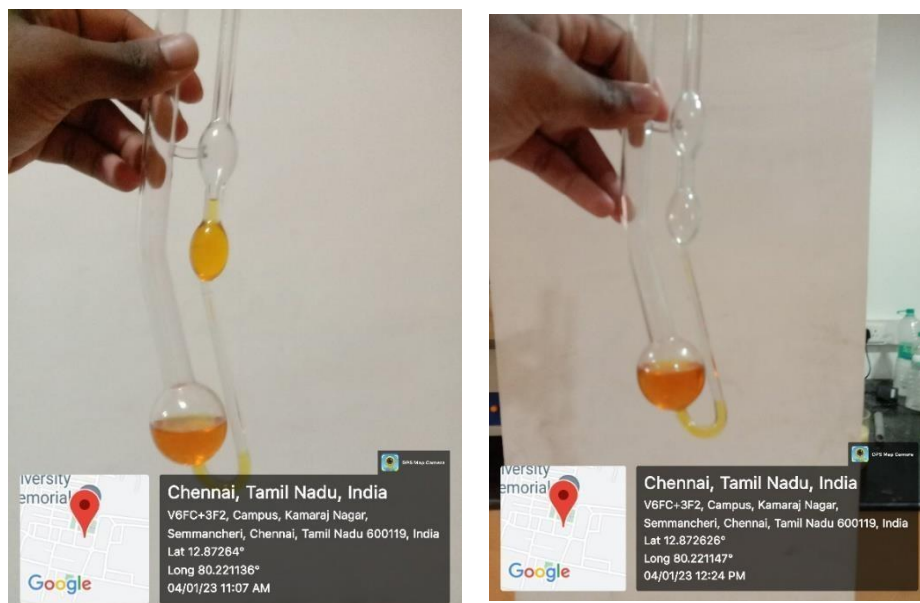


Fig 4.2: Kinematic viscosity measurement using capillary tube viscometer

4.2.4 Free fatty acid value

In the context of oils, free fatty acid (FFA) content is a measure of the acidity of the oil and is often used as an indicator of the oil's quality. The FFA content of an oil can be determined as per ASTM D 664 standards through a process called acid value (AV) determination, which involves titration with a standard solution of sodium hydroxide (NaOH).

First, a sodium hydroxide burette solution with a normality of 0.1 N is created for this titration procedure. In a conical flask, the weight of a 5 grams oil sample is measured. In addition, a conical flask containing an oil sample is filled with 25 mL of isopropyl alcohol. Four drops of burette solution are then added to the mixture. The solution is then heated until it reaches a 60 °C temperature. The sample is then left to cool until it reaches room temperature. Phenolphthalein indicator is added to the solution once it has reached room temperature. The solution is then titrated, and the results are recorded.

$$\text{FFA (\%)} = \frac{28.2 \times 0.1 \times \text{Volume of NaOH (ml)}}{\text{Weight of the sample (g)}}$$

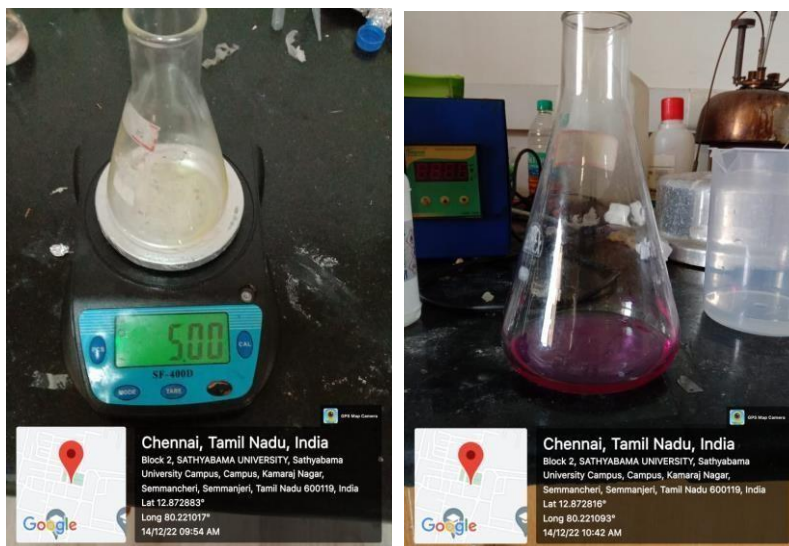


Fig 4.3: Free fatty acid value measurement through titration

4.2.5 Moisture content:

ASTM D 2709 was used to determine the moisture content. The weight of the 5 g oil sample in the crucible was measured, along with the total weight, which is recorded. Next, for three hours, the sample was placed inside a hot air oven set to

110°C. The sample is removed from the oven and let to cool to room temperature for several time. The sample's total weight was then determined. Calculating the weight difference and determining the amount of moisture present in the sample.

The moisture content (%) of the sample was calculated:

$$\frac{(\text{Initial weight of sample} - \text{Dry weight of sample})}{\text{Initial weight of the sample}} \times 100$$



Fig 4.4 Estimation of moisture content

4.3 BIODIESEL PRODUCTION

4.3.1 Materials required

Oil sample, methanol, sodium hydroxide (NaOH), heating mantle, magnetic stirrer separatory funnel, three neck flask.

4.3.2 Procedure

Catalyst is an important parameter to produce biodiesel. So, the process is initiated with catalyst preparation, where 182 mL of methanol and 5 g of sodium hydroxide pellets used to prepare the catalyst. Following the catalyst preparation, 1000 mL of the oil sample was measured and added to the flask with three necks. The three-neck flask was equipped with a magnetic stirrer for continuous stirring throughout the procedure. To heat the oil sample, the three-neck flask was kept on a hot plate. The stopper, which was at the left, seals the flask's initial neck. The condenser seals off the second neck, preventing the evaporating catalysts from escaping. The final neck was then sealed off with a thermometer-equipped stopper. The prepared catalysts are introduced into the oil sample after the

temperature reaches 60°C. The reaction is continuously stirred for 90 mins. The sample was transferred to the separatory funnel for separation after the reaction completed. The sample was held for the separation process for a little while. The separation consists of two layers, the bottom layer of which was separated from the top layer of crude biodiesel and was known as glycerol. The catalyst and unreacted methanol are separated from the top layer through a process known as "washing," where the mixture is washed by mixing RO water heated to 60°C at a 1:1 ratio. The washing process is repeated until the wash water's pH is neutral. Following the washing procedure, the biodiesel was heated to 110°C to evaporate any remaining water. The purest form of biodiesel was produced after temperatures reach 110°C.

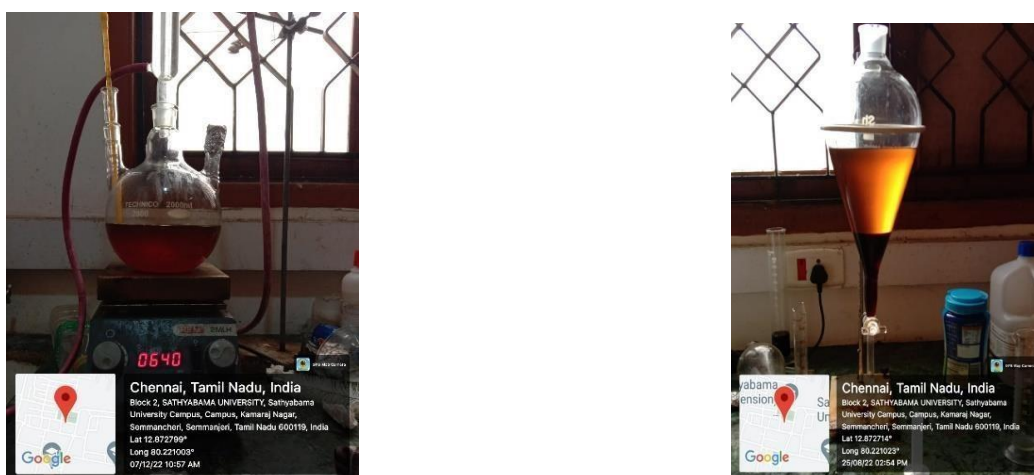


Fig 4.5: Biodiesel production: Tranesterification and Separation

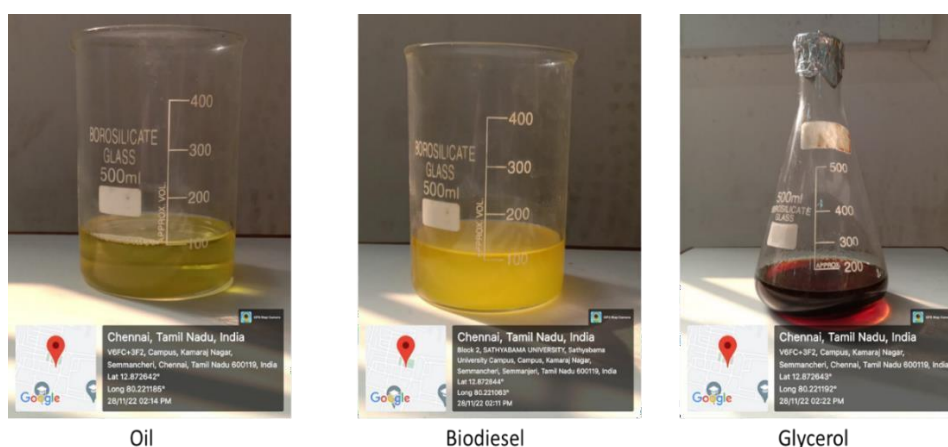


Fig 4.6: Feedstock (Waste cooking oil) and products of biodiesel production

4.4 PRELIMINARY PROPERTY ANALYSIS OF BIODIESEL SAMPLES

Biodiesel properties are analysed to ensure that the fuel meets certain quality standards and can be used efficiently in diesel engines. Preliminary properties like density, kinematic viscosity, & acid value, moisture content, and cold flow properties such as cloud point, pour point, further combustion properties such as calorific value, flash point & fire point, was measured in lab under their respective ASTM standards

4.4.1 Materials and chemicals required

- Density: pycnometer, weighing machine
- Kinematic viscosity: kinematic viscometer
- FFA value: 0.1 N Sodium hydroxide, Iso propyl alcohol, thermometer, 250 mL conical flask, Phenolphthalein indicator
- Moisture content: Crucible, Hot air oven
- Cloud point & Pour point: ASTM D 2500 apparatus for cloud and pour point.
- Flash & Fire point: Flash and fire point apparatus
- Calorific value: Bomb Calorimeter, oxygen cylinder

4.4.2 Density

The density of biodiesel was also examined using a pycnometer, like how oil density was measured as per ASTM D 1298 standards. The mass of the pycnometer with fuel was measured after the sample was acquired. By dividing the mass by the volume of the pycnometer, the density of the fuel was determined.

$$\text{Density equals} = \frac{\text{Total weight of instrument with biodiesel} - \text{Empty weight of the instrument}}{\text{Volume of the instrument (25mL)}}$$

4.4.3 Kinematic viscosity

Kinematic viscosity is a measure of the resistance of a fluid to flow, and is expressed in units of centistokes (cSt). The viscosity was measured using the ASTM D 445 standard, which is identical to measuring the viscosity of oil samples. The test entails timing how long it takes a fixed amount of fuel to pass through a capillary tube at a temperature of 40°C while maintaining the heat there until the procedure is complete. The kinematic viscosity is then determined using the time and capillary tube diameters.

$$\text{Viscosity} = \text{Time in (s)} \times 0.014$$

4.4.4 Acid value

The FFA content of the fuel can be used to determine the acid value of the fuel. The FFA content of the fuel is determined using the FFA analysis method in oil samples as per ASTM D 664 standards. For this titration process, a sodium hydroxide burette solution with a normality of 0.1 was first prepared. The weight of a 5-gram oil sample was measured in a conical flask. In addition, 25 ml of isopropyl alcohol is added to a conical flask containing an oil sample. The mixture is subsequently treated with four drops of burette solution. The solution is then heated until it reaches a temperature of 60°C. The sample is then allowed to cool to room temperature. Once the solution has reached room temperature, the phenolphthalein indicator is added. After that, the solution is titrated and the results are recorded. The acid value of biodiesel is calculated by

$$\text{Acid value (g KOH/g)} = \text{Obtained FFA value} \times 1.99$$

4.4.5 Moisture content

ASTM D 2709 was used to determine the moisture content. Biodiesel moisture content is measured using a heating process. The weight of the 5 g biodiesel sample in the crucible was determined and recorded as the total weight. The sample was then placed in a hot air oven set at 110°C for three hours. The sample was taken out of the oven and allowed to cool to room temperature for a few minutes. The total weight of the sample is then calculated. Calculating the weight difference and estimating the quantity of moisture in the sample.

The moisture content (%) of the sample was calculated:

$$\frac{(\text{Initial weight of sample} - \text{Dry weight of sample})}{\text{Initial weight of the sample}} \times 100$$

4.4.6 Cloud Point

The cloud point of biodiesel is typically measured using a test method called ASTM D 2500. The temperature at which the first visible formation of wax crystals is observed is recorded as the cloud point.

Sample of biodiesel was collected and brought to a uniform temperature, typically around 10°C. The sample jar is placed in a cooling bath, that is prepared according to ASTM standards, where temperature is lowered at a rate of 1 degree Celsius per minute. The sample is observed for the first visible formation of wax crystals. The temperature at which the first formation is observed is recorded as the cloud point.

4.4.7 Pour point

The pour point of biodiesel is typically measured using a test method called ASTM D 97. This method involves cooling a sample of biodiesel at a rate of 1 degree Celsius per minute until it stops flowing, and then recording the temperature at which this occurs as the pour point.

Sample of biodiesel was collected and brought to a uniform temperature, typically around 10°C. The sample jar is placed in a cooling bath, that is prepared according to ASTM standards, where temperature is lowered at a rate of 1 degree Celsius per minute while the sample is tilted periodically. The tilting is done to check the flow of the sample. The sample is observed for the point at which it no longer flows, and the temperature at which this occurs is recorded as the pour point.

4.4.8 Calorific Value

The calorific value of biodiesel can be measured using a device called a bomb calorimeter under ASTM D 240 standards. This device is designed to measure the heat released when a fuel is burned completely in controlled environment. First, a small sample of the biodiesel fuel is weighed and placed into a small metal container known as a bomb. Oxygen is then added to the bomb, which is then sealed and placed into the calorimeter. The bomb is ignited, and the biodiesel fuel is burned completely, producing heat. The heat produced by the burning the biodiesel fuel is absorbed by the calorimeter, which measures the temperature

changes. From the temperature change, along with the weight of the biodiesel sample and other parameters, the calorific value of the biodiesel fuel can be calculated.

Calorific value of biodiesel calculated from

$$\text{Calorific value (cal/g)} = \frac{(M_w \times C_w + W) \times T_r}{M_s} - (E_n + E_c)$$

M_w – Mass of water, g

C_w – Specific heat capacity of water, cal/g °C

T_r – Temperature rise, °C

M_s – Mass of fuel sample, g

E_n – Energy equivalent calculated with respect to nichrome wire, cal/g

E_c – Energy equivalent Energy calculated with respect to cotton thread, cal/g

4.4.9 Flash point and Fire point

Flash point Test (ASTM D 93): This test determines the flash point of a biodiesel fuel by heating a small sample of the fuel in a test apparatus. A small flame is introduced periodically to the surface of the fuel, and the temperature is gradually increased until the fuel produces enough vapor to ignite briefly, but not sustain combustion. The temperature at which this occurs is recorded as the flash point.

Fire point (ASTM D 93): This test determines the fire point of a biodiesel fuel by heating a small sample of the fuel in a test apparatus, like the flash point test. However, in this test, the temperature is gradually increased until the fuel produces enough vapour to ignite and sustain combustion for at least 5 seconds. The temperature at which this occurs is recorded as the fire point.

4.5 FREE FATTY ACID IDENTIFICATION USING UV - VISIBLE SPECTROPHOTOMETRY

4.5.1 Materials and chemicals required

250mL Conical flask, 100 mL beaker, 10 ml centrifuge tubes, centrifuge, and UV visible spectrometer, 9-octadecenoic acid or oleic acid (C18:1n9), Isooctane, copper-acetate monohydrate, pyridine, distilled water.

4.5.2 Copper acetate pyridine reagent preparation

5.5g of the copper-acetate monohydrate was dissolved in 80 mL of distilled water. The pH of the solution was initially 5.08, which was adjusted to 6.06 with pyridine, and then the solution was further diluted to 100 mL with distilled water.



Fig 4.7: pH increment of copper acetate solution using pyridine



Fig 4.8: Copper acetate pyridine reagent

4.5.3 Preparation of standard calibration solutions of oleic acid

The standard oleic acid solutions were prepared in 9 different concentrations (2 – 18 $\mu\text{mol/mL}$) for the calibration curve by dissolving stock oleic acid in a non-polar solvent, isooctane.

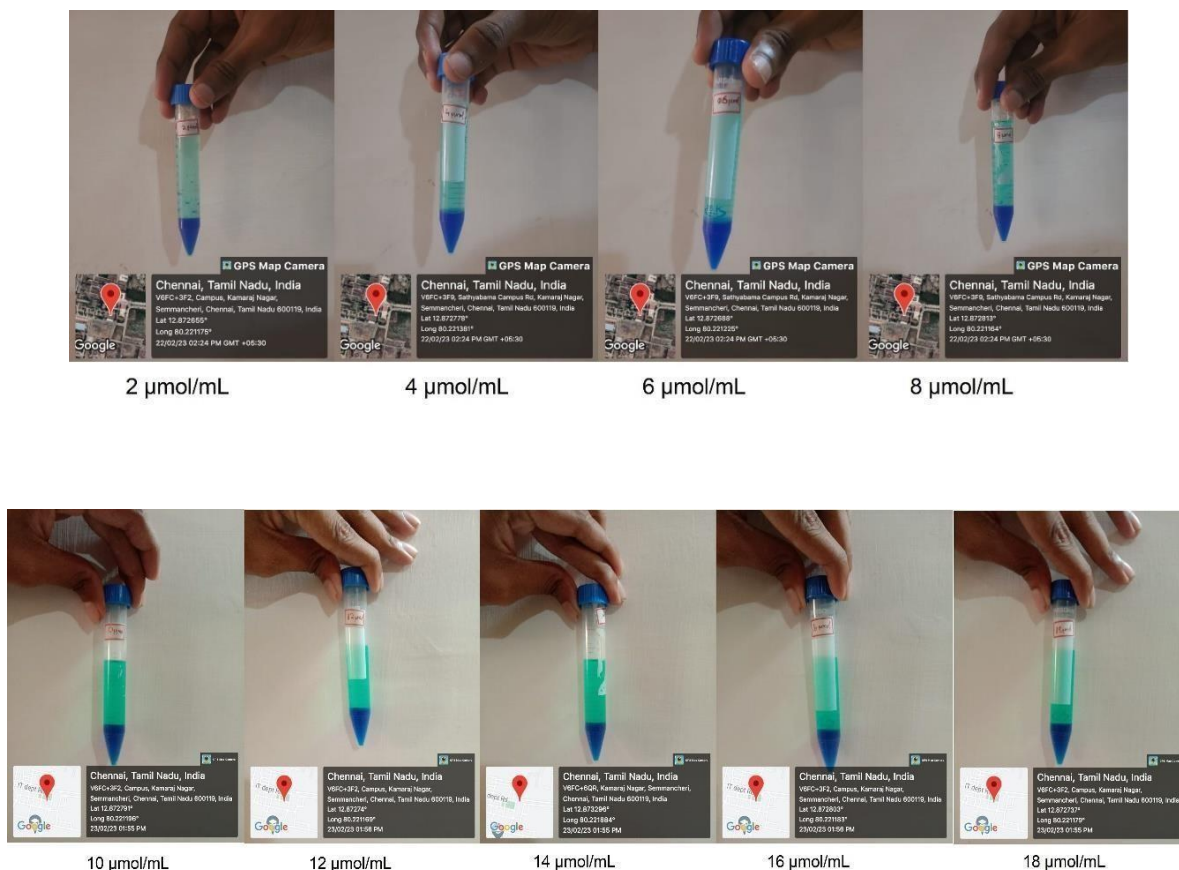


Fig 4.9: Calibration solutions of oleic acid for UV visible spectrophotometric analysis

4.5.4 Identification of free fatty acid content in raw oil sample:

Two millilitres of copper reagent were added to each calibration solution, mixed for 30 seconds then allowed to separate in a 10 mL centrifuge tubes. The top organic layer was analysed under a UV-visible spectrometer, the absorbance peak was achieved at 708 – 709 nm, and based on the analysis, a graph was plotted between the concentration of calibration solutions and the peak absorbance value. The graph was used to develop the linearity between the absorbance and concentration of fatty acid through an equation. Further, 2g of oil sample was mixed with isooctane in a 10 mL centrifuge tube, and 2 mL of copper acetate reagent was added. The mixer was then centrifuged at 2000 rpm for 5 minutes in a

centrifuge for bilayer separation, the top organic layer was analysed under a UV-visible spectrometer, such that the FFA content of the oil is predicted in terms of oleic acid ($\mu\text{mol/mL}$) based on the equation of linearity obtained from the calibration graph.

4.6 SENSOR MODULE DEVELOPMENT

4.6.1 Materials and chemicals required

5mm Infrared LED (IR LED) (TX), 5mm photodiode (RX), Arduino Uno R3 board, 10k resistor, 1k resistor, connecting wires, breadboard.

4.6.2 Construction

A simpler circuit diagram was developed to identify the components needed for the construction of the module, and the necessary components were then purchased. The initial assembly of the module was created by placing the components on a breadboard and the Arduino Uno board was used to both power the module and obtain the output readings by analysing the input signals from the module.

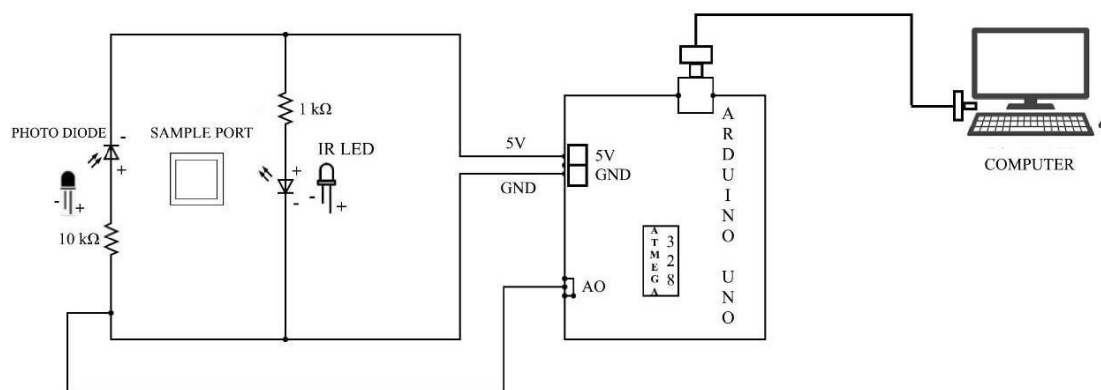


Fig 4.10: Circuit diagram of IR based sensor module

4.6.3 Working

The IR LED constantly emits IR rays, which are detected as analog signals by the photodiode that are converted as voltage measurements by a microcontroller (Arduino Uno R3). The Arduino board is powered and programmed by a computer via an OTG cable, and the reading is recorded in the computer. The intensity of the IR rays collected by the photodiode changes when samples are positioned

between the IR LED (emitter) and photodiode (collector), allowing the IR rays to pass through the sample. As a result, the output voltage also changes. When the samples were initially examined, the readings were unstable. It was later discovered that the excess light exposure to the photodiode owing to the open arrangement was the reason that contributed to the unstable readings. Hence, the module was modified into a closed assembly, which produced stable readings.

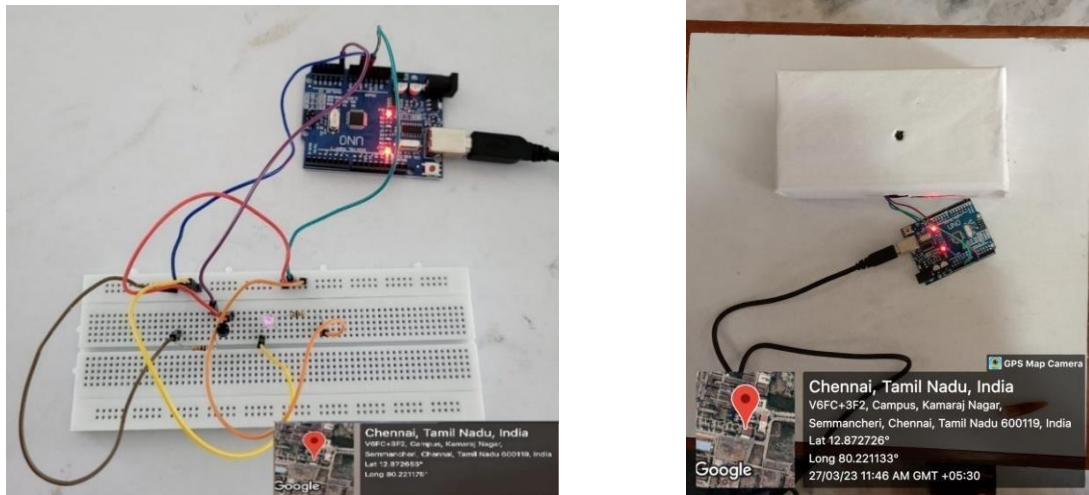


Fig 4.11: Sensor module assembly: Open and Closed assembly

4.6.4 Arduino code for the sensor

```
const int photo_diode = A0;
int input_val=0;
float volt;

void setup() {
    // put your setup code here, to run once:
    Serial.begin(9600);
}

void loop() {
    // put your main code here, to run repeatedly:
    input_val=analogRead(photo_diode);
    volt=((input_val*1.20)/1023.00)*1000;
    Serial.println(volt,4);
    delay(1000);
}
```

4.6.4 Calibration

The calibration data was obtained like the UV visible calibration, different mass percentages of oleic acid were dissolved in a non-polar solvent, isooctane, and the respective sensor outputs were recorded. The calibration graph was plotted between the sensor data and the variable concentration.

4.6.5 FFA analysis of oil samples

The oil samples were taken in the similar vials that were used for the calibration, the samples were analysed by the sensor and their respective FFA content in terms of oleic acid percentage were obtained from the equation of linearity between oleic acid concentration and output voltage readings.

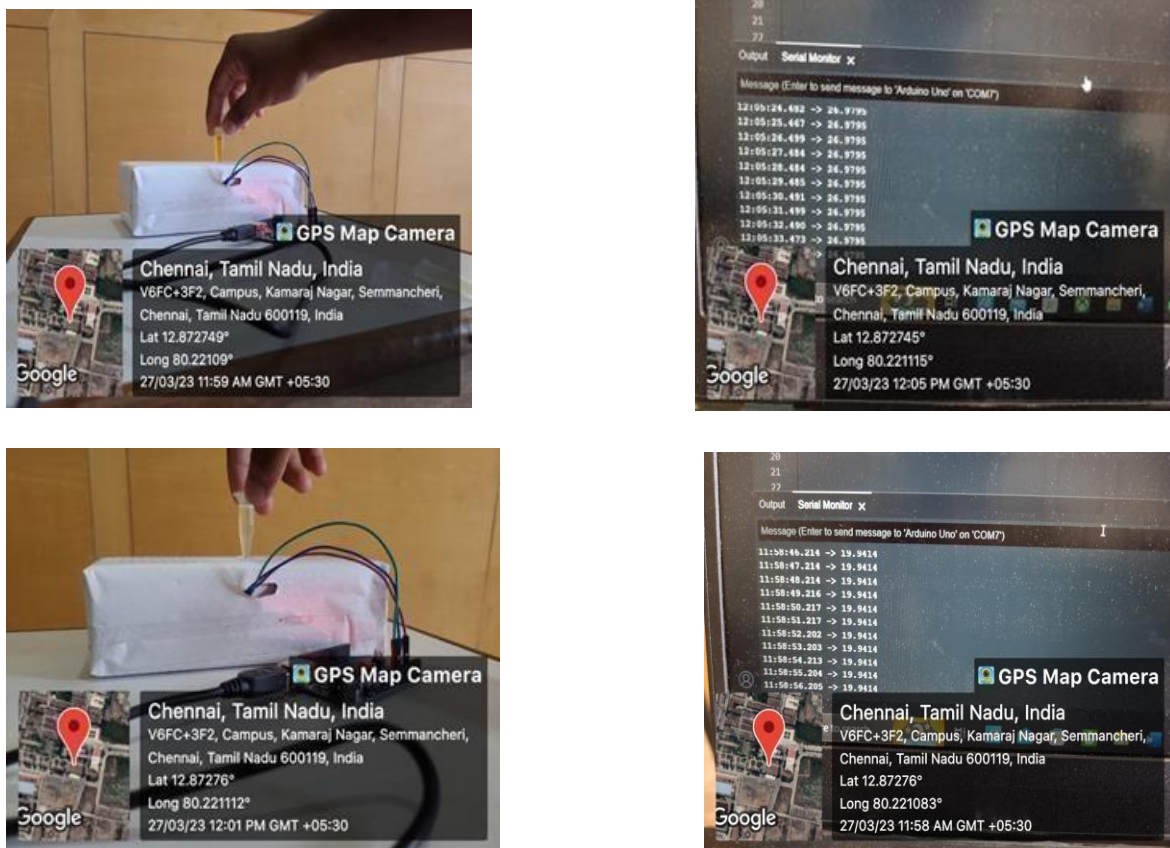


Fig 4.12: FFA measurement through the sensor module

4.7 CORRELATION OF COMPOSITION OF OIL WITH PROPERTIES OF BIODIESEL USING GC-FID ANALYSIS OF OIL AND BIODIESEL SAMPLE

4.7.1 Materials required

Raw Oil, waste cooking oil and their respective biodiesel samples, YL6500 GC, hexane,

4.7.2 Gas chromatography

The moisture removed samples were diluted with hexane before being injected into injection port of YL 6500 GC equipped with a 0.53-mm TR-WAX capillary column designed to achieve 260°C from 140°C at a rate of 10-degree Celsius per minute. Before injecting the sample, the carrier gas, helium, was adjusted to flow at a rate of 5 mL per minute. In order to determine the composition of oil and biodiesel samples, 1 µL of the sample was injected into split mode injection port. The separated components are then identified using the FID detector, which quantifies the proportion of carbon atoms in the sample. Each component will generate a distinct signal on the detector. The ignition temperature and maximum temperature of the Flame ionization detector (FID), was calibrated at 471 K and 513 K respectively. To identify the various components and their quantities, the data collected from the detector can be evaluated using software. The primary composition of oil and biodiesel samples was determined by interpreting GC - FID data and comparing it to known GC standards of fatty acid methyl esters.

4.7.3 Correlation of composition of oil samples to properties of biodiesel

The impact of the composition of the oil sample on the properties of biodiesel was studied by comparing the individual properties of selective FFAs with the properties of the biodiesel samples obtained.

CHAPTER – 5

RESULTS AND DISCUSSION

5.1 OIL SAMPLE COLLECTION

Table 5.1: Data acquired during the collection of waste cooking oil samples

ITEM	DETAILS
Restaurant details with address	Mess in Pallikaranai, Chennai
Brand of oil used	Gold winner
Types of oil	Sunflower oil
Place of buying	Pallikaranai, Chennai, Tamil Nadu
Items cooked	Veg - Poori, Vada, Appalam
Frying time of oil	5 – 6 hrs
Amount of oil generated(ml)	1000 mL per day
Amount of oil collected	1000 mL
Rate expected from the shopkeeper	Free

Waste cooking oil subjected to wide range of cooking conditions including different cooking time, temperature, product to be fried was acquired from several food outlets in Chennai including Sathyabama Institute of Science and Technology that used various types and brands of raw oil. From each outlet, about 1 litre of used cooking oil was collected, along with 100 mL of the used cooking oil's raw oil for examination. Since the frying circumstances and the amount of water in the food items can have an impact on the oil quality, such characteristics were recorded and tabulated. It was discovered that the average cooking time of oil in most outlets was 4 to 6 hours, and most outlets either discard or reuse the waste oil completely.

5.2 PRELIMINARY PROPERTY ANALYSIS OF OIL SAMPLES

The preliminary properties of the waste cooking oil sample were identified to assess the quality and understand the characteristics of the oil samples. Properties such as density, kinematic viscosity, moisture content, and FFA content were identified and recorded. All waste cooking oil samples were found to have FFA values of less than 1%, making them suitable for single-stage transesterification. Changes in properties were noticed for waste cooking oil samples and their respective raw oil samples.

Table 5.2: Preliminary properties of waste cooking oil samples

Properties		GN Oil samples				
		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Density (g/ml)		0.927	0.944	0.924	0.919	0.943
Viscosity (cSt)	Temp. (°C)	40	40	40	40	40
	Time (s)	2940	4175	2663	2949	2296
	Viscosity (cSt)	41.16	58.45	37.282	41.286	32.144
FFA (%)	Weight of oil sample(g)	5.05	5.4	5.08	5.03	5.6
	Volume of NaOH (ml)	0.6	0.8	1.1	1.4	0.9
	FFA (%)	0.335	0.418	0.611	0.785	0.453
Moisture Content (%)	Crucible Wt. without sample (g)	22.37	37.47	66.28	81.87	22.37
	Crucible Wt. with sample (g)	32.37	47.57	76.42	92.04	32.41
	Dry Wt. (g)	32.29	47.53	76.4	85.42	32.19
	Moisture content (%)	0.247	0.054	0.026	7.193	0.679

5.3 PRELIMINARY PROPERTY ANALYSIS OF BIODIESEL SAMPLES

The preliminary properties, including cold flow properties and combustion properties, for the biodiesel produced were determined and compared with ASTM D6751 in order to assess the quality and analyse the characteristics of the biodiesel.

Table 5.3: Properties of biodiesel samples

Properties	Standard*	GN – Biodiesel				
		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Density (g/cc)	no limit	0.875	0.900	0.892	0.880	0.886
Kinematic Viscosity (cSt)	1.9 – 6 (mm ² /s)	5.838	5.992	5.698	4.270	5.152
Moisture content (%)	max 0.05 (vol%)	0.083	1.234	0.319	0.186	0.301
Acid value (%)	Max. 0.50 g KOH /g	0.560	0.336	0.444	0.337	0.223
Cloud point (°C)	Report	9 °C	- 4 °C	6 °C	10 °C	5 °C
Pour point (°C)	No limit	0 °C	-14 °C	5 °C	1 °C	-10 °C
Calorific value (cal/g)	No limit	6562.3	6261.9	7764.0	4058.7	5661.0
Flash point	Min. 93 (°C)	213 °C	217 °C	195 °C	197 °C	137 °C
Fire point (°C)	No limit	235 °C	237 °C	215 °C	219 °C	159 °C

*Properties were compared with ASTM D6751 standards **

5.3.1 Density

The density of all biodiesel produced were under ASTM D6751 standards. Biodiesel density is an important feature since it influences the amount of energy that can be delivered per unit volume of fuel. Since biodiesel has a lower density than petroleum diesel, it contains less energy per gallon than petroleum diesel.

The handling and storage of biodiesel can also be impacted by density. Higher-density fuels can be trickier to pump and store, and they can need special fueling equipment.

5.3.2 Kinematic viscosity

The density of all biodiesel produced were under ASTM D6751 standards. Proper viscosity ensures good fuel atomization, complete combustion, and adequate lubrication of engine components, resulting in improved engine performance, reduced emissions, and longer engine life. Therefore, it is important to ensure that the kinematic viscosity of biodiesel falls within an appropriate range, typically between 1.9 and 6.0 cSt or mm²/s at 40 °C, depending on the application and operating conditions.

5.3.3 Moisture content

The moisture content of biodiesel is important for several reasons

The presence of moisture can indicate poor production and processing practices, which can result in impurities and reduced quality of the biodiesel. Moisture content is therefore used as a quality control parameter to ensure that the biodiesel meets the necessary standards.

Biodiesel can undergo hydrolysis when it encounters water, which can lead to the formation of free fatty acids and other impurities. This can result in increased acidity and reduced stability of the fuel, which can lead to engine damage and decreased performance. Monitoring and controlling moisture content can help prevent this.

Biodiesel can also be affected by water in cold weather condition. When water freezes, it can form ice crystals that can clog fuel filters and lines, leading to engine problems. By controlling moisture content, the risk of these issues can be minimized.

5.3.4 Cloud and pour point

The cloud point is a critical measure of biodiesel's cold-weather performance. The waxes in biodiesel can solidify and produce obstructions in gasoline filters and lines when the temperature drops, resulting in engine issues. The cloud point thus

aids in determining the lowest temperature at which biodiesel can be safely employed. Wax production in biodiesel can also boost fuel viscosity and stability. Wax in the fuel can clog fuel injectors and impair engine performance. Biodiesel manufacturers can guarantee that the fuel fulfils the appropriate quality and stability standards by monitoring the cloud point.

The pour point is an important parameter for biodiesel because it helps to ensure the fuel's cold weather performance, handling and storage, and regulatory compliance. By monitoring and controlling the pour point, biodiesel producers can ensure that the fuel meets the necessary standards and performance well in various application.

5.3.5 Calorific value

Knowing the calorific value of biodiesel is important because it helps determine the efficiency of the fuel as an energy source. For example, if the calorific value of a biodiesel fuel is high, then it means that it can produce more energy per unit than a fuel with a lower calorific value. This information can be used by engineers and researchers to optimize the performance of engines and other equipment that use biodiesel as a fuel.

5.3.6 Flash and Fire point

The flash point of a fuel is the lowest temperature at which it releases enough vapor to ignite quickly but not sustain burning. The fire point is the lowest temperature at which a fuel emits enough vapor to ignite and sustain burning. Knowing the flash and ignition points of biodiesel is crucial for various reasons. Firstly, it promotes safe fuel handling and storage. If a biodiesel fuel has a low flash point, it might ignite at low temperatures, making it more unsafe to handle and store. Secondly, the flash and fire point of biodiesel can also affect the performance of engines and other equipment that use the fuel. If the flash point is too high, it can result in poor ignition and engine performance. If the fire point is too low, it can result in the fuel igniting inside the engine, which can cause damage or failure.

5.4 FREE FATTY ACID IDENTIFICATION USING UV – VISIBLE SPECTROPHOTOMETRY

The calibration curves for the varying concentrations of oleic acid obtained from absorbance measurements are shown in Figure 5.1. The vertical axis refers to absorbance, while the horizontal axis shows the wave length of the absorbance of the calibration solution relative to that of the blank (i.e., isooctane and copper reagent). The peak absorbance for the solutions was recorded at 707-709 nm of wave length, and the absorbance increased with increasing solution concentration.

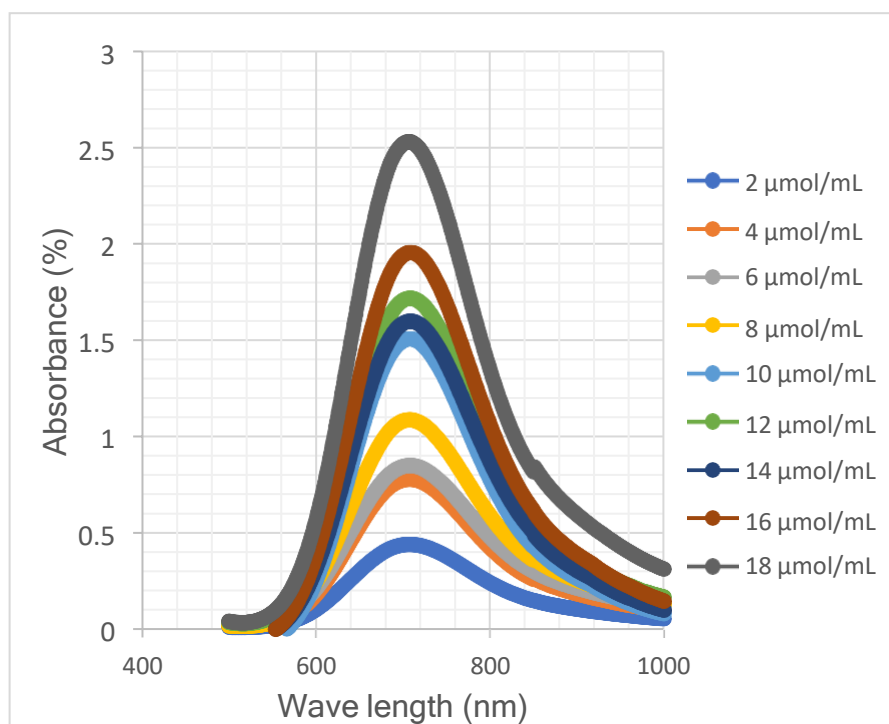


Figure 5.1: Absorbance graph for calibration solutions

The calibration curve, which was solely produced for oleic acid, is depicted in Figure. The results are also given only in terms of oleic acid. In comparison to other FFAs, oleic acid was chosen for calibration because of its superior solubility and complex formation with copper ions in non-polar solutions.

Since in the mixture of isooctane and copper acetate pyridine, only the FFAs forms a cage like complex with the copper reagent the colour development is not interfered monoacylglycerols, diacylglycerols, triacylglycerols, or another lipid.

Using the measurement results, we were able to establish linearity between the concentration and the absorbance, table, represents the calibration data obtained from the spectrophotometer results.

Table 5.4: Calibration of oleic acid for UV visible spectrophotometry analysis

Concentration ($\mu\text{mol/mL}$)	Absorbance (%)	Wave length (nm)
2	0.4	708
4	0.8	708
6	0.9	708
8	1.1	708
10	1.5	708
12	1.7	709
14	1.6	709
16	2.0	709
18	2.5	707

It was discovered that solutions with concentrations of 16 mmol/mL and above were not readily tractable to the spectrophotometry studies, since at this concentration level, the absorbance is around 2, indicating that the Lambert and Beer law no longer applies.

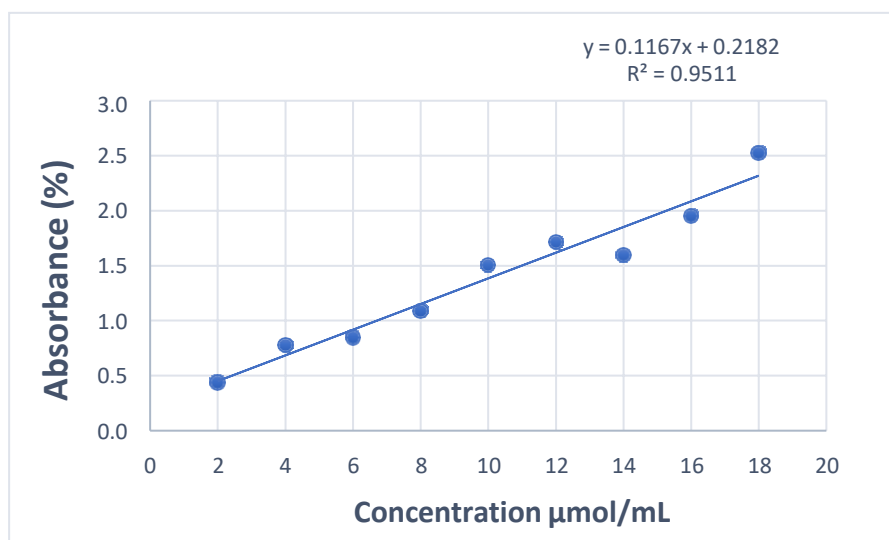


Fig 5.2: Calibration chart for UV - visible spectrophotometry

The sample 2 oil was considered for the evaluation of FFA, the FFA was predicted through the equation of linearity $y = 0.1167x + 0.2182$ from the calibration chart depicted in Figure and was comparable with FFA value obtained by titration.

5.5 SENSOR MODULE DEVELOPMENT

Since the construction of the sensor module was based on the methodology of UV visible spectrophotometry, when the oleic acid in varying concentrations dissolved in isooctane was initially analysed through the sensor, the readings obtained were seen to be linear, such that the calibration of the sensor module was done with varying concentrations of oleic in the isooctane. The sensor reading for the pure isooctane solution was considered as blank reading.

Table 5.5: Oleic acid calibration for sensor measurement

Oleic acid % (w/w) (approx.)	Output Voltage (mV)
0 (blank)	31.67
0.1	32.02
0.2	28.45
0.3	26.86
0.4	25.90
0.5	24.01
0.6	19.84
0.7	21.00
0.8	19.00
1	17.25
1.2	14.33
1.4	10.87
1.6	9.79
1.8	8.56
2	10.40

It was discovered that increasing the concentration values linearly decreased the output voltage values; this was owing to the output voltage's dependence on the amount of radiations captured by the photodiode. We try to extrapolate from this that as the FFA content of the sample grows, so does the absorption of IR rays generated by the IR LED, resulting in low transmittance to the photodiode. As a

result, the photodiode's output voltage falls. It was also discovered that because the output voltages decline linearly when the concentration exceeds 2%, the readings of the sensor were unstable; additionally, the readings of the sensor were affected by a variety of factors, such as the vial used to take the readings, the surrounding light exposure, and the temperature of the sensor.

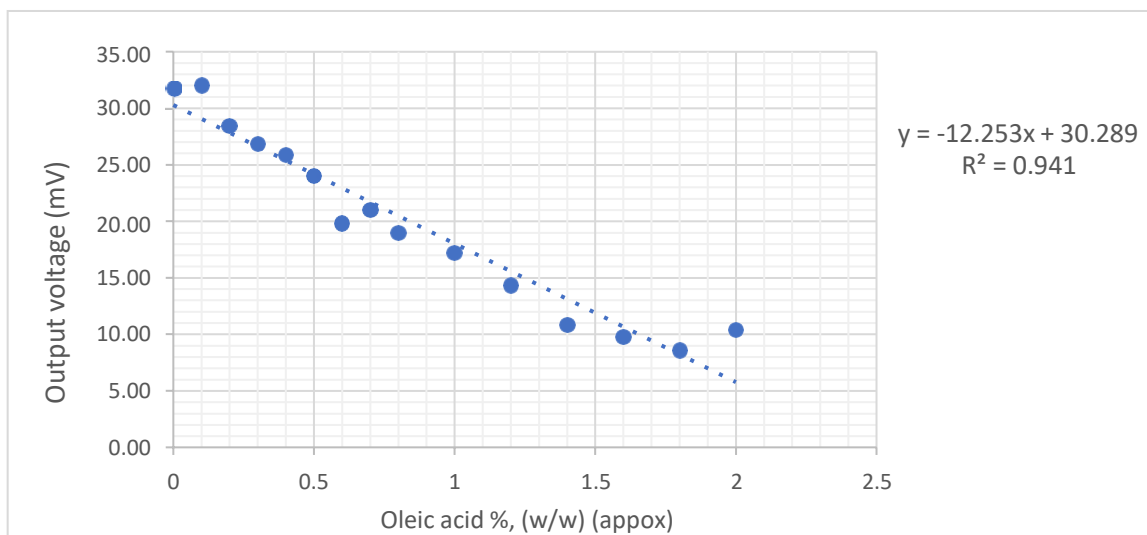


Fig 5.3: Calibration chart for the sensor reading measurement

Following the development of the calibration chart, the oil samples were analysed by the sensor module, and the FFA values of the oil samples were predicted using the equation of linearity obtained from the calibration chart and compared to FFA values derived from titration values.

Table 5.6: Comparison of FFA values obtained from sensor and titration

Oil Sample	FFA measured through titration	FFA measured through sensor	Difference
Sample 1	0.33	0.27	-0.06
Sample 2	0.42	0.36	-0.06
Sample 3	0.61	0.84	0.23
Sample 5	0.45	0.557	0.107

5.6 CORRELATION OF COMPOSITION OF OIL WITH PROPERTIES OF BIODIESEL USING GC-FID ANALYSIS OF OIL AND BIODIESEL SAMPLES

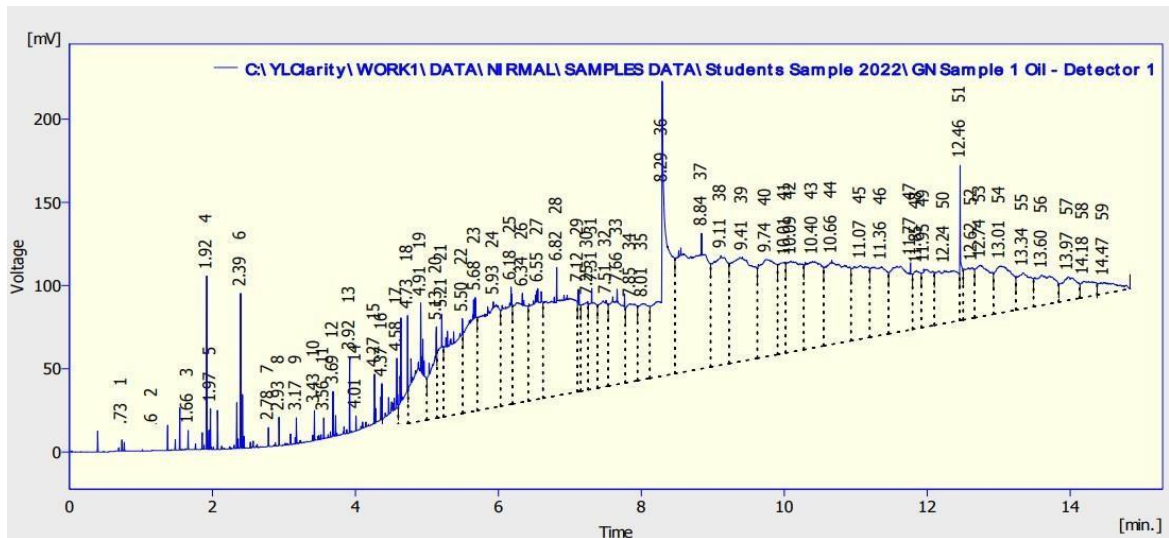
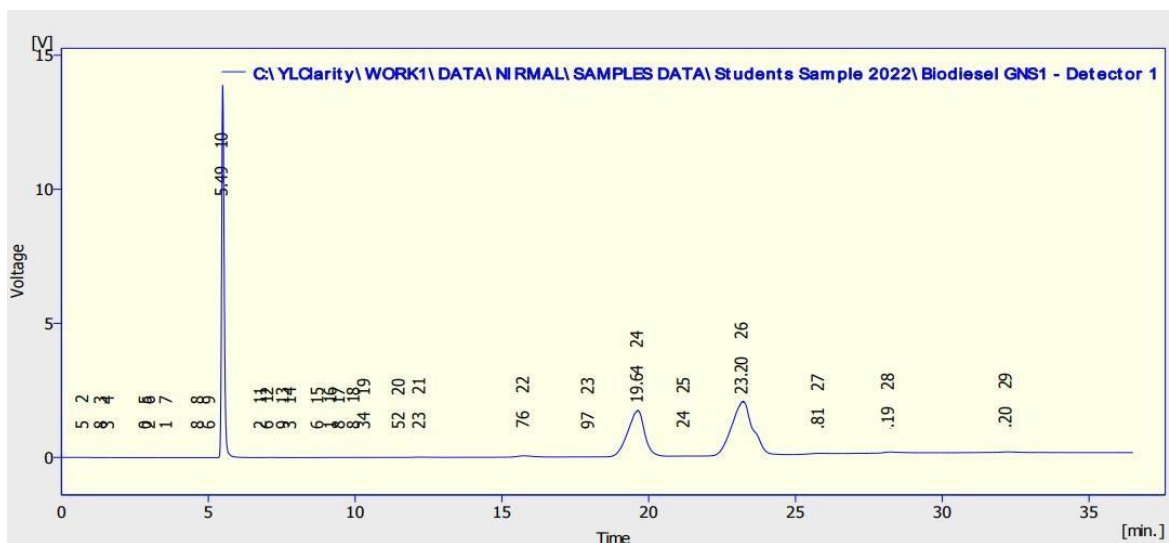


Fig 5.4: GC analysis oil sample



retention duration that can be utilized to distinguish it. The GC FID graphs was interpreted for the all the 5 collected oil samples and their respective biodiesel samples. Seven major fatty acids that were present in commonly in many oil sources were considered for the analysis

Table 5.7: Composition analysis of oil and biodiesel samples

Compound Number	Compound Name	Composition (%)					
		Sample 1		Sample 2		Sample 3	
		Oil	Biodiesel	Oil	Biodiesel	Oil	Biodiesel
C12:0	Lauric acid	0.15	0.1	0.31	0.23	0.19	0.12
C14:0	Myristic acid	0.54	0.43	0.77	0.68	0.64	0.05
C16:0	Palmitic acid	10.54	7.89	12.36	11.12	16.47	11.76
C18:0	Stearic acid	8.5	6.13	5.6	3.7	30.54	27.39
C18:1	Oleic acid	28.54	20.78	40.45	35.65	21.45	11.64
C18:2	Linoleic acid	16.47	12.54	22.37	19.56	17.96	15.23
C18:3	Linolenic acid	1.56	0.9	1.09	0.85	0.56	0.23

By comparing the individual properties of selected fatty acids with the properties of biodiesel we observed the certain impact of the fatty acid compositions over the properties of biodiesel, kinematic viscosity, density, cloud point and pour point, calorific values, etc

Kinematic Viscosity increases with increase in number of carbon atoms of fatty acids in oils, decreases with increasing degree of unsaturation. Density increases with increase in degree of unsaturation, this explains that more the presence of unsaturated fatty acids higher will be the density of the fuel.

Low temperature properties: Cloud point and pour point represents low temperature behaviour of the fuel, such that from the observation, the lower the saturation the lower the cloud and pour points. Calorific value increased with increasing chain length, and increasing unsaturation for a given chain length decrease in the heat of combustion due to the loss of hydrogen. These observations were compared and verified with various publications

CHAPTER – 6

SUMMARY AND CONCLUSION

This work was an attempt to construct a sensor to identify the FFA content in the oil sample, primarily waste cooking oil samples, that were utilized for biodiesel production. Also, the composition of oil samples and their respective biodiesel samples were analysed under GC-FID to understand the influence of the FFA composition on the properties of biodiesel. To achieve this, the preliminary properties of the waste cooking oil and respective biodiesels were identified and tabulated.

To determine the principle of the sensor, various analytical methods for the identification of FFA were compared, and a method based on copper soap UV visible spectrophotometry was finalized and experimentally performed to understand the process of identification of FFA in the oil sample. Based on the results obtained from copper soap UV visible spectrophotometry, we concluded to adapt the concept of spectroscopy as a principle for our module, but a simpler IR-based sensor module was fabricated.

Further oil samples were analysed under the sensor module, and FFA values were predicted and compared with traditional titration values. Later, the composition of oil and their respective biodiesel samples were identified and analysed under GC - FID, and the impact of the composition of the oil sample on properties of biodiesel such as viscosity, density, cloud, and pour point were analysed.

To conclude, free fatty acid content of feedstocks (oil samples) is a significant parameter to be considered to produce biodiesel, a mechanistic approach for identification of FFA content in the oil will improve the analysing procedure of oil samples and biodiesel production. Additionally, there are variations between feedstocks in the structural configuration, such as chain length, branching, degree of unsaturation, and position of double bonds, which can affect the characteristics and functionality of biodiesel. A viable alternative could be to alter fatty acid profiles, or to change their structural makeup in order to improve the properties of biodiesel fuel by genetic modification, although this requires more intensive research.

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Development of free fatty acid (ffa) monitoring device for evaluation of oil samples used for biodiesel production

by GOPI KRISHNAN P

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CHAPTER – 1

INTRODUCTION

The global energy crisis is a growing concern ¹⁵ due to the depletion of fossil fuel resources, increasing energy demand, and the negative impact of traditional energy sources on the environment. The world is currently facing an energy crisis that is affecting all aspects of global development. The energy crisis is characterized by the increasing demand for energy due to ¹¹⁹ population growth, urbanization, and economic development. However, the energy supply is not keeping up with the increasing demand due to a variety of factors such as depletion of non-renewable resources, limited investment in renewable sources, and political instability in some energy-rich regions. The lack of sustainable and affordable energy sources is a significant challenge that affects economic growth, social development, and the environment.

The energy crisis has significant effects on the global economy, including an increase in energy prices, a decrease in economic growth, and an increase in debt and inflation. However, there are potential solutions to the energy crisis, including investing in renewable energy sources, increasing energy efficiency, and promoting energy conservation. Implementing these solutions will require significant investment, policy support, and behaviour change, but it is critical to mitigating the effects of the energy crisis and ensuring sustainable global development

⁸⁶ 1.1 IMPORTANCE OF NON-CONVENTIONAL ENERGY SOURCES

Non-conventional sources of energy include solar, wind, hydropower, geothermal, nuclear and biomass. These energy sources are clean and sustainable, and they have the potential to lower greenhouse gas emission that cause climate change. One of the most important non-traditional sources of energy is solar energy. It is liberal, clean, and renewable. ¹⁰⁷ According to a study by Balogun et al. (2019), solar energy ¹¹ has the potential to significantly reduce the dependence on fossil fuels for electricity generation. The study discovered that the price of solar panels has dramatically dropped in recent years, making solar energy more accessible and affordable for people and companies [1]. Furthermore, solar energy can be used to power remote areas that are not connected to the national electricity grid. This

93 makes it a significant source of energy in developing countries where access to electricity is limited.

Wind energy is another significant non-conventional source of energy. It is clean, renewable, and abundant. A study by Ma et al. (2020) found that wind energy has the potential to significantly reduce greenhouse gas emissions and mitigate climate change. The study highlights the need for investment in wind energy to achieve sustainable development goals [2]. In addition, wind energy can be used to power remote areas that are not connected to the national electricity grid, making it an important source of energy in developing countries.

Hydropower is another non-conventional source of energy that is significant. It is clean, renewable, and abundant. According to a study by Tadesse et al. (2019), hydropower has the potential to significantly reduce greenhouse gas emissions and mitigate climate change. The study highlights the need for investment in hydropower to achieve sustainable development goals [3]. In addition, hydropower can be used to provide electricity to remote areas that are not connected to the national electricity grid, making it an important source of energy in developing countries.

Geothermal energy is another non-conventional source of energy that is significant. It is clean, renewable, and abundant. A study by Kumaran et al. (2020) found that geothermal energy has the potential to significantly reduce greenhouse gas emissions and mitigate climate change. The study highlights the need for investment in geothermal energy to achieve sustainable development goals [4]. In addition, geothermal energy can be used to provide electricity to remote areas that are not connected to the national electricity grid, making it an important source of energy in developing countries.

Nuclear energy is an additional promising non-conventional energy source. According to a study by Bunn and Heinonen (2017), nuclear energy can significantly contribute to supplying the world's energy demands while lowering carbon emission. The authors do point out that there are considerable difficulties with using nuclear energy, such as safety issues and the issues of disposing of radioactive waste [5].

Biomass energy is another non-conventional source of energy that is significant. It is derived from organic materials such as wood, crop residues, and animal waste. A study by Sahu et al. (2020) found that biomass energy has the potential to significantly reduce greenhouse gas emissions and mitigate climate change [6]. The study highlights the need for investment in biomass energy to achieve sustainable development goals. Furthermore, biomass energy can be used to provide electricity and heat to remote areas that are not connected to the national electricity grid, making it an important source of energy in developing countries.

1.2 BIOFUELS

Biofuel refers to fuels obtained from organic materials known as biomass. These materials can be obtained from plants, animals, and waste materials. The use of biofuels has been on the rise due to their renewable nature and potential to reduce greenhouse gas emissions. There are different types of biofuels, each with unique properties and applications.

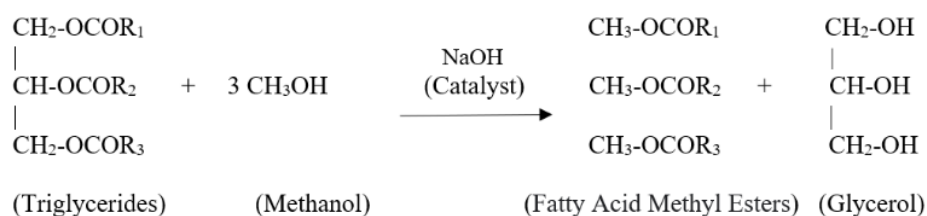
Table 1.1: Different generations of feedstocks used for biofuels

Generation of Biofuel	Type of Biofuel	Feedstock	Synthesis	Yield	Ref
First Generation	Bio-ethanol	Corn, sugarcane, wheat, barley, cassava, and other starch or sugar-rich crops	Fermentation of sugars or starches in the feedstock to produce ethanol	Varies depending on feedstock and process used, typically 100-500 L per ton of feedstock	[7]
	Bio-diesel	Soybean, canola, palm, and other vegetable oils, animal fats, and waste cooking oil	Transesterification of the feedstock with an alcohol (usually methanol) to produce biodiesel	Varies depending on feedstock and process used, typically 100-150 L per ton of feedstock	[8]
Second Generation	Bio-ethanol	Lignocellulosic biomass such as wood, grasses, and agricultural	Pre-treatment of the feedstock to break down cellulose and hemicellulose	Varies depending on feedstock and process used, typically 50-100 L per ton	[7]

		waste	into fermentable sugars, followed by fermentation to produce ethanol	of feedstock	
	Bio-diesel	Algae, jatropha, and other non-food crops	Extraction of oil from the feedstock, followed by transesterification to produce biodiesel	Varies depending on feedstock and process used, typically 200-400 L per hectare of land used	[9]
Third Generation	Bio-oil	Microalgae and other photo-synthetic organisms	Fast pyrolysis of the feedstock to produce a liquid bio-oil	Varies depending on feedstock and process used, typically 1-2 kg of bio-oil per kg of dry biomass	[10]
Fourth Generation	Bio-hydrogen	Microorganisms such as bacteria and algae	Biological or thermochemical processes to produce hydrogen gas	Varies depending on feedstock and process used, typically less than 1 kg of hydrogen per kg of feedstock	[11]

1.3 BIODIESEL

Biodiesel is a renewable fuel that is made from renewable feedstocks such as vegetable oils, animal fats, and used cooking oils. It is produced through a process called transesterification, which involves reacting the feedstock with an alcohol, such as methanol or ethanol, in the presence of a catalyst. The resulting product is a mixture of fatty acid esters, which can be used as a substitute for diesel fuel.



The chemical structure of biodiesel is like that of diesel fuel, with the main difference being the presence of fatty acid esters in biodiesel. The esters in biodiesel are composed of a long chain of carbon atoms, typically between 16 and 18, that are bonded to a glycerol molecule through an ester linkage. The esters are then separated from the glycerol molecule through the transesterification process, resulting in a pure biodiesel product.

Numerous studies had been conducted in the production, properties, and applications of biodiesel. For example, Zhang et al. (2021) Examined the application of microalgae as a possible feedstock for the production of biodiesel [12], while Bahrami et al. (2021) investigated the use of ultrasonic pre-treatment to improve the efficiency of the transesterification process [13]. Other studies have focused on the properties of biodiesel, including its viscosity, density, and cetane number [14] [15]. Additionally, studies on the use of biodiesel in other application, such as diesel engines [16] and as a blend with other fuels [17], have been done.

1.4 FEEDSTOCKS USED FOR BIODIESEL PRODUCTION

Biodiesel is produced from different generation feedstocks, ranging from first-generation feedstocks such as edible vegetable oils to second-generation feedstocks such as non-edible oils and waste oils, and third-generation feedstocks such as algae.

Due to their high oil content and accessibility, first generation feedstock like soyabean, rapeseed, and plam oils have been employed extensively in the manufacturing of biodiesel. However, the use of these feedstocks has raised concerns about competition with food production and land use changes. Second-generation feedstocks such as jatropha, camelina, and castor oils have been proposed as alternative feedstocks for biodiesel production due to their non-edible

nature and potential to grow on marginal lands. In addition, waste oils from the food industry have been used as a source of feedstocks for biodiesel production to reduce the environmental impact of waste disposal.

Third-generation feedstocks such as microalgae and macroalgae have also been studied as potential feedstocks for the manufacturing of biodiesel because of their high productivity and ability to grow in non-arable land and wastewater. Algae can also absorb carbon dioxide and nutrients from wastewater, which can reduce the environmental impact of industrial effluents.

Several studies have investigated the feasibility of using different feedstocks for biodiesel production. For example, Karmakar et al. (2010) compared the biodiesel yield of different first-generation and waste cooking oils. The authors found that waste cooking oil had a higher yield compared to the first-generation oils [18]. Li et al. (2014) reported the use of pyrolyzed rice husk as a heterogeneous catalyst to produce biodiesel from waste cooking oil. The authors found that the pyrolyzed rice husk waste catalyst had a higher conversion rate compared to other catalysts [19]. Rana and Dahiya (2021) performed a life cycle assessment of biodiesel production from waste cooking oil and found that biodiesel produced from waste cooking oil had a lower environmental impact compared to fossil diesel [20].

Algae-based biodiesel has also been studied extensively. Alam et al. (2018) reviewed the potential of microalgae as a source of biodiesel and concluded that microalgae-based biodiesel could be a sustainable and economically viable alternative to fossil fuels [21]. Sanjaya et al. (2021) assessed the potential of palm oil biomass for bioenergy production in Indonesia and found that algae-based biodiesel had the highest energy yield compared to other bioenergy sources [22].

In addition, the use of genetically modified feedstocks for biodiesel production has also been explored. For example, Gao et al. (2019) investigated the use of a genetically modified yeast strain to produce biodiesel from waste cooking oil. The authors found that the use of the genetically modified yeast strain increased the yield of biodiesel production [23].

Table 1.2: Different generations of feedstocks used for biodiesel production

Type of Biodiesel	Feedstock	Yield	Ref
First-generation Biodiesel	Soybean oil, rapeseed oil, palm oil, sunflower oil, etc.	95-98%	[8]
Second-generation Biodiesel	Jatropha, pongamia, camelina, etc.	70-80%	[24]
Third-generation Biodiesel	Microalgae, yeast, bacteria, etc.	30-80%	[25]

1.5 FREE FATTY ACIDS

Free fatty acid are chemically representing aliphatic hydrocarbon chain with carboxylic group, classified in many ways, such as, chain length, saturations, linear and branched [26].

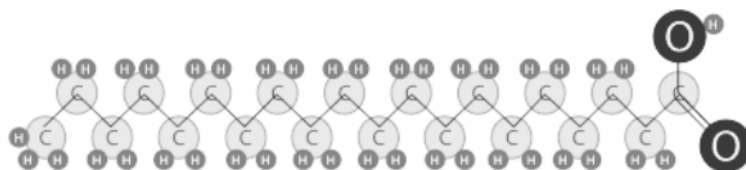


Fig 1.1: Structure of fatty acid

Based on chain length they are classified into short chained, long chained, etc. The most important classification of free fatty acids is based on double bonds present in the aliphatic chain, through this they are classified into two major categories: saturated and unsaturated fatty acids.

Saturated fatty acids possess no double bonds, owing to the fact that they are totally saturated with hydrogen molecules. Saturated fatty acids include Caprylic acid, Lauric acid, Myristic acid, Palmitic acid, and Stearic acid.

Unsaturated fatty acids are further divided into monounsaturated (one double bond) and polyunsaturated (more than one double bond) types based on the number of double bonds they contain. They include oleic acid, linoleic acid, and linoelaidic acid as unsaturated fatty acid.

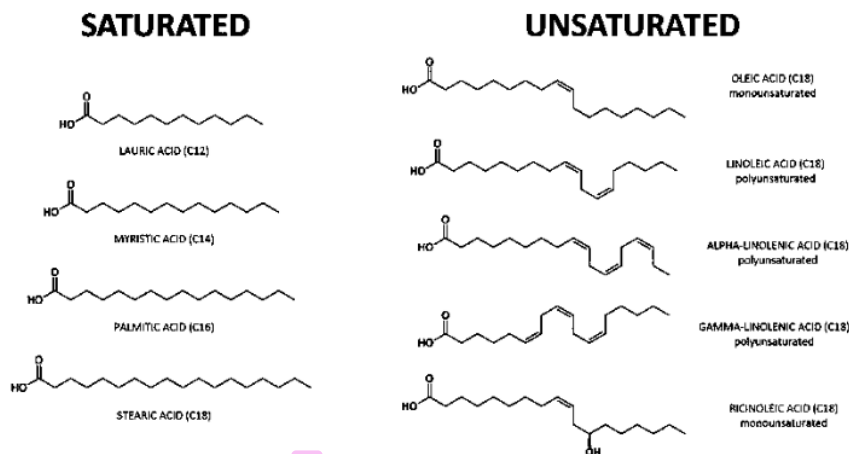


Fig 1.2: Examples of saturated and unsaturated fatty acids

These are formed by cleavage of ester bond during the hydrolysis of triglyceride in the oils by the action of high temperature and moisture content. Factors that affect the FFA content of vegetable oils include, grade of oil and its variety, storage and handling parameters, and the age of the oil. Due to high temperature and air exposure during frying or cooking operation, used cooking oil will have higher fatty acid content compared to raw vegetable oil, since these extreme conditions increases fatty acid by promoting oxidation of triacyl glycerides in the oil [27].

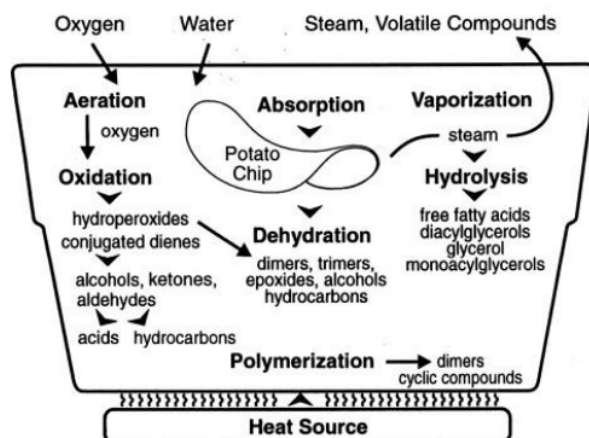


Fig 1.3: Reactions occurs during deep frying process

According to study [28] [29] the maximum FFA content for the production of According to study [28] [29] the maximum FFA content for the production of

biodiesel can be around 2% by weight of the oil, preferably 1%. Increased FFA levels can result in feedstock losses and have an adverse effect on glycerine separation due to soap formation that in turn interrupt the separation of glycerine and biodiesel by promoting stable emulsions [30]. Also, some study shows the higher FFA content acts as a poison for the catalyst in the transesterification, this directly impact conversion of triacyl glycerides [31].

According to I.M. Atadashi et al (2012) around [32], “60–75% of the comprehensive cost of producing biodiesel fuel is revealed to be incurred by cost of feedstocks. To produce industrially feasible biodiesel in the future, it becomes mandatory to use feedstocks at lower prices, such as remains or non-edible oils or used cooking oils.”

Rancid or Non edible oils, animal fats and used cooking oils constitute the major sources biodiesel with high FFA values [33] [34]. Non edible oils such as jatropha oil [35], cotton seed oil [36], castor oil [37], rubber seed oil [38], Pongamia pinnata oil [39] are the most commonly used non edible oils in the biodiesel production. Chicken fat [40], beef tallow [41], mutton tallow, lard, are the types of animal fats that had been sources for biodiesel production

Table 1.3: FFA compositions of various feedstocks used for biodiesel synthesis

Oil source	FFA composition (%)					Ref
	Palmitic acid C16:0	Stearic acid C18:0	Oleic acid C18:1	Linoleic acid C18:2	Linolenic acid C18:3	
Algal oil	16.6	1.9	26.9	22.8	16.1	[42]
Castor oil	0.69	0.72	2.8	4.4	0.2	[43]
Chicken Fat	19.8	6.1	34.6	30.9	2.9	[40]
Coconut oil	13.1	3.7	12.9	4.34	NA	[44]
Cottonseed Oil	21.3 - 26.4	2 - 3.5	14.4 - 21.8	46.6 - 58.4	0 - 0.7	[36]
Flax seed oil	5.0 – 8.1	2.2 – 4.6	13.4 – 19.4	12.3 – 17.4	40 –60.4	[45]
Hemp oil	5.9	2.4	9.2	55.6	18.02	[46]
Jatropha	14.5	7	46.3	31	0.2	[35]
Neem oil	15.55	18.32	42.2	19.5	0.09	[43]
Olive oil	12.3	2.4	73.7	9.4	0.41	[47]
Palm oil	44.1	4.5	39.2	10.1	0.4	[48]
Peanut oil	9.3 - 14	1.2 - 3.7	35.7 - 58.5	21 - 43	NA	[49]
Pongamia oil	7.9	4.4	49	17.2	4	[39]

Rapeseed oil	3.5	1	64.4	22.3	8.2	[50]
Rice bran oil	15	2	42.5	39	1.1	[51]
Rubber seed	10.4	8.3	24.8	40	16.5	[52]
Safflower oil	5.3 - 10.8	1.8 - 3.4	14.1 - 37.8	21 - 73.9	0.08 - 5.6	[53]
Sunflower oil	7.5	3.1	33.4	54.7	NA	[54]
Waste cooking oil Sample 1	38.35	4.33	43.67	11.39	0.3	[55]
Waste cooking oil Sample 2	32.88	5.2	38.45	10	NA	[34]

1.6 METHODS FOR THE IDENTIFICATION OF FFA

FFA content of a feedstock is crucial parameter to be identified for the biodiesel production and its commonly identified standard procedures recommended by American Oil Chemists' Society (AOCS), the American Society for Testing and Materials (ASTM), the European Commission Regulation (EC) and the Association of Official Analytical Chemists (AOAC). All these protocols are comparable and are based on titration, in which the oil sample is neutralized with isopropyl alcohol and titrated against sodium hydroxide in the presence of phenolphthalein indicator.

Even though these titrimetric procedures are simple, they have several drawbacks, including excessive chemical usage, poor accuracy, and environmental concerns. A variety of instrumental techniques have been created as prospective substitutes for conventional techniques for the more precise measurement of FFA content in edible oils and fats in order to address the above-mentioned problems. These approaches can be further classified into spectroscopic methods, chromatographic methods, colorimetric techniques [56].

1.6.1 Spectroscopic techniques

Spectroscopic methods are widely used for the analytical identification of free fatty acids (FFA) in oil samples. These methods are non-destructive and offer high sensitivity and specificity, making them suitable for quantitative and qualitative analysis of complex mixtures. Some of the common spectroscopic methods used

for FFA identification in oil samples include Fourier-transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy.

FTIR spectroscopy is a powerful tool for FFA analysis in oil samples. This technique measures the sample's infrared radiation transmission or absorption. The absorption spectra obtained from FTIR spectroscopy can provide valuable information about the functional groups present in the sample, allowing for the identification and quantification of FFAs. A recent study by Khan et al. (2021) demonstrated the use of FTIR spectroscopy for the quantitative analysis of FFA in palm oil. The study showed that FTIR spectroscopy could accurately quantify FFAs in palm oil samples with a detection limit of 0.1% and a linear range of 0.1% to 4% [57].

NMR spectroscopy is a powerful tool for FFA analysis in oil samples. This method works by measuring the nuclear magnetic resonance of the sample. The NMR spectra obtained from this method can provide information about the molecular structure and can be used for the identification and quantification of FFAs. A study by Ma et al. (2016) demonstrated the use of NMR spectroscopy for the quantitative analysis of FFA in soybean oil. The study showed that NMR spectroscopy could accurately quantify FFAs in soybean oil samples with a detection limit of 0.5% and a linear range of 0.5% to 5% [58]. However, FTIR spectroscopy has a limitation related to the carbonyl esters (1730 - 1750) absorption. The carbonyl group in the FFA shifts the absorbance maxima depending on whether it is protonated (1705 - 1710 cm⁻¹) or ionised (1530 - 1580 cm⁻¹) making pH a key factor in the procedure [59].

1.6.2 Chromatographic techniques

One of the most widely used methods for the determination of FFAs in oil samples is gas chromatography (GC). GC is a highly sensitive and accurate method that can be used to identify and quantify individual FFAs in oil samples. GC analysis requires a sample preparation step, which involves the esterification of FFAs to their corresponding methyl esters using a strong acid, such as sulfuric acid. The resulting methyl esters are then analyzed by GC using a flame ionization detector (FID) or a mass spectrometer (MS).

In a study by M. K. M. Kassim et al., the authors developed a GC method for the determination of FFAs in palm oil. The method involved the use of a capillary column and a FID for detection. The authors demonstrated that the method was highly sensitive and accurate, with a detection limit of 0.01%. The method was also found to be suitable for the analysis of other vegetable oils, such as soybean and sunflower oils [60].

Another analytical method that has been used for the determination of FFAs in oil samples is high-performance liquid chromatography (HPLC). HPLC is a powerful analytical technique that can separate and quantify individual FFAs in oil samples. In HPLC analysis, FFAs are typically derivatized using a reagent, such as 4-dimethylaminopyridine (DMAP), to form their corresponding DMAP derivatives. The resulting derivatives are then analyzed by HPLC using a UV or fluorescence detector. In a study by Y. Cao et al., the authors developed an HPLC method for the determination of FFAs in fish oil. The method involved the use of a C18 column and a UV detector for detection. The authors demonstrated that the method was highly sensitive and accurate, with a detection limit of 0.1 µg/ml. The method was also found to be suitable for the analysis of other types of oils, such as vegetable oils and animal fats [61].

1.6.3 Colorimetric techniques

Colorimetric techniques are widely used to identify and quantify free fatty acid (FFA) content in oils. The basic principle of colorimetry is based on the reaction of specific chemical reagents with the target analyte, resulting in a colour change that can be measured spectrophotometrically. The colorimetric assays for FFA determination in oils are simple, rapid, and cost-effective, making them attractive for industrial and laboratory applications.

The so-called copper-soap colorimetry is the most used spectrophotometric technique. Its operational premise is based on two facts: (i) FFAs form blue soluble soaps with copper ions in a polar solvents, and (ii) the intensity of the resulting blue colour is directly proportional to the FFA level [59]. One of the most used colorimetric methods for the determination of FFAs in oil samples is the ferric chloride method. In this method, FFAs react with ferric chloride to produce a blue colour that can be measured using a spectrophotometer at a wavelength of 660

⁵⁴ nm. The intensity of the colour is directly proportional to the concentration of FFAs in the sample [62].

1.7 SENSOR FOR THE OIL QUALITY ASSESSMENT

There are various parameters that are monitored to assess the oil quality, such as viscosity, acidity, water content, and particulate matter. Sensors play a vital role in oil quality assessment by providing real-time data on these parameters.

Viscosity sensors are used to measure the viscosity of oil, which ³⁶ is an important parameter that affects the performance and efficiency of machinery. A study by B. Bahrami et al. (2019) developed a MEMS-based viscosity sensor for oil quality assessment. The sensor was designed using micro-electro-mechanical systems (MEMS) technology and utilized a capacitive sensing mechanism to measure the viscosity of oil. The study reported a high accuracy of the sensor in measuring the viscosity of different types of oils, including motor oil and hydraulic oil [63].

Acidity sensors are used to monitor the acidity of oil, which can indicate the presence of contaminants or oxidation products. A research paper by Y. Gao et al. (2020) proposed an acidity sensor based on a quartz crystal microbalance (QCM) for oil quality assessment. The sensor utilized a sensitive film made of polydopamine/graphene oxide (PDA/GO) nanocomposites, which showed a high sensitivity and selectivity towards acidic gases. The study reported that the sensor could detect the acidity of oil samples ²⁵ with a detection limit of 0.4 ppm [64].

Water content sensors are used to monitor ⁶⁷ the water content in oil, which can lead to equipment damage and corrosion. A study by S. M. Vaezi-Nejad et al. (2018) developed a capacitance-based sensor for water content measurement in oil. The sensor was designed using a parallel-plate capacitor configuration and utilized a thin film of water-sensitive polymer (polyvinyl alcohol) as the dielectric material. The study reported that the sensor could detect water content in oil samples with a resolution of 0.1% [65]. ¹ The objective of this study was to create a sensor module for measuring the FFA concentration of oils. However, in order to make the construction of the module more simple, infrared source of radiation was considered during the design process.

1.8 IMPORTANCE OF FATTY ACID COMPOSITIONS IN BIODIESEL PRODUCTION

The properties of biodiesel are significantly impacted by the characteristics of individual esters of fatty acids and associated structural configurations as it is a blend of several fatty acid ester molecules. With genetic engineering of the feedstock oils, it may be possible in the future to supplement a specific fatty acid or (acids) with desirable attributes to get a fuel enriched with particular fatty acids in the biodiesel fuel to enhance its general fuel properties [66].

For instance, it might be possible to enhance the presence of certain esters (such methyl caprate and methyl oleate) or decrease the amount of polyunsaturated methyl ester. According to the European biodiesel standard EN 14214, biodiesel with a high amount of methyl oleate (or monounsaturated fatty acid) may have outstanding features in terms of ignition quality, fuel stability, flow qualities at low temperatures, and iodine number [66]. Esters with saturated medium chain acids, especially those of decanoic (capric) acid, have recently been found by several authors to be appropriate [67]. This is because they exhibit acceptable cold flow characteristics and provide an alternative to long-chain saturated fatty acid esters with high melting temperatures.

Moreover, they have great oxidative stability because there are no double bonds, which makes them a better choice than those esters. In numerous research [68] [69] it had been shown that the chemical structure of the fatty acid content affects the physical and chemical properties of biodiesel. Also, several studies demonstrate a connection between exhaust emissions and the chemical makeup of fatty acids.

Reviewing the impact of the characteristics and structural arrangements of FAMES upon various properties of biodiesel such as cold flow and combustion properties is the goal of the current investigation. FAME's structural configuration encompasses its molecular make-up, chain length, degree of unsaturation, saturated or unsaturated nature, and double bond placement.

CHAPTER – 2

LITRATURE REVIEW

- In the study conducted by **Kuo-Chin Huang et al. (2013)**, they proposed a novel method for the determination of FFA in oils and fats using UV spectroscopy and copper soap colorimetry. The authors synthesized copper soap by reacting copper acetate with stearic acid, and the resulting copper soap was used as a colour reagent for the FFA determination. The UV absorbance of the FFA-copper soap complex was measured at a wavelength of 320 nm, and the FFA content was calculated based on the standard curve. The authors optimized the experimental conditions, such as the concentration of copper soap and the reaction time, to improve the accuracy and sensitivity of the method. The results showed that the method had a high accuracy and sensitivity, and it could be applied to different types of oils and fats [70].
- **Gyorik et al. (2006)** presented a new analytical method for determining the total FFA concentration of thermally processed cooking oil. The technique used a 632.8 nm He-Ne laser as the radiation source and relied upon the colorimetric copper-soap technique paired with the idea of the optothermal window. When results from this method and those from conventional spectroscopy were examined, they showed a strong concordance for FFA values greater than 2 mmol mL [59].
- In another study by **Yiming Xu et al. (2016)**, a modified method for FFA identification using UV spectroscopy and copper soap colorimetry was reported. The authors used copper (II) chloride instead of copper acetate as the copper source to synthesize the copper soap, and the FFA-copper soap complex was measured at a wavelength of 340 nm. The authors also optimized the experimental conditions, such as the concentration of copper (II) chloride and the reaction time, to improve the accuracy and sensitivity of the method. The results showed that the modified method had a lower detection limit and a wider linear range than the traditional method [71].

- The properties of biodiesel fuel, such as density, viscosity, flash point, and cetane number, are largely influenced by the composition of FAME. Different feedstocks can result in varying compositions of FAME, which can impact the fuel's properties. **Ahmad et al. (2018)** conducted a study to investigate the influence of different feedstocks on the physio-chemical properties of biodiesel. The study found that FAME composition significantly affects fuel properties such as density, viscosity, and flash point [72].
- Furthermore, FAME can have an impact on the durability of fuel system components. **Ali et al. (2019)** evaluated the effect of FAME on the corrosion of aluminium alloys and found that FAME blends can accelerate corrosion. The study also found that the degree of corrosion depends on the composition of FAME [73].
- Furthermore, the effect of FAME on the stability of biodiesel fuel is a critical consideration for its storage and transportation. Biodiesel is susceptible to oxidative degradation, which can cause fuel quality deterioration and negatively impact engine performance. Several studies have investigated the stability of biodiesel fuel with varying FAME compositions. For example, a study by **Liu et al. (2021)** found that blends of biodiesel with high stearic acid methyl ester (SAME) content exhibited better oxidative stability than blends with high oleic acid methyl ester (OAME) content [74].

Overall, the literature survey highlights the significant influence of FAME composition on the properties of biodiesel fuel. Optimizing FAME composition is crucial for improving fuel performance and reducing its impact on the environment. Also, UV spectroscopy and copper soap colorimetry are reliable methods for the identification and quantification of FFA in oils and fats. These methods have the potential to be widely used in the food industry for the quality control of oils and fats. However, further research is needed to validate these methods for different types of oils and fats, and to investigate their applicability to complex food matrices

CHAPTER – 3

AIM AND SCOPE

3.1 AIM:

¹¹¹ The primary objective of our project ⁷⁶ was to develop a FFA monitoring device for evaluation of oil samples ⁷⁶ used for biodiesel production, by correlate the effects of structural configurations of fatty acid present in raw oil on various properties biodiesel. This was achieved by completing following set of objectives:

- Development of a database of preliminary properties for a set of oil samples and their corresponding biodiesel samples.
- Identification of the working principle of the sensor, construction of the sensor based on the principle identified, and testing the working of the sensor by comparing the results with experimental results.
- ⁷² Compositional analysis of oil samples and their respective biodiesels under gas chromatography flame ionization detector (GC – FID) to understand the variations in composition
- Identification of major components of samples by interpretation of GC results and correlating the composition of samples with the properties of biodiesel.

3.2 SCOPE:

⁴⁷ Free fatty acids (FFA) content of an oil ²⁹ is an important parameter in the process of biodiesel production. FFA content determines the complexity of the biodiesel production. Till now an experimental procedure is practiced for the identification of FFA content of oil source, these methods are based on titration, which is a laborious process and involves large amounts of chemicals. Also, it depends on visual end points which in turn compromise the accuracy of the result. Since, variety of feedstock with varying structural compositions and properties being used ⁸⁹ to produce biodiesel, yields inconsistent quality of biodiesel, analysing the composition of the oil becomes essential to produce superior quality biodiesel. Therefore, A simple mechanistic decision-making approach will be attempted in simplifying the choice of the oil and grading it for its usage in biodiesel production.

CHAPTER – 4

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MATERIALS AND METHODS

4.1 OIL SAMPLE COLLECTION

Different samples of waste cooking oil (WCO) which were been used under various cooking conditions such as different cooking time, food items cooked, collected from different food outlets in Chennai were collected for analysis. Information of cooking conditions were acquired from the food outlets were tabulated.

4.2 PRELIMINARY PROPERTY ANALYSIS OF OIL SAMPLES

Preliminary properties of collected oil samples, like density, kinematic viscosity, free fatty acid (FFA), was measured in laboratory under their respective ASTM standards

4.2.1 Materials and chemicals required

- Density: pycnometer, weighing machine
- Kinematic viscosity: kinematic viscometer
- FFA value: 0.1 N Sodium hydroxide, Iso propyl alcohol, thermometer, 250 mL conical flask, Phenolphthalein indicator
- Moisture content: Crucible, Hot air oven

4.2.2 Density

The density of oil sample was measured using pycnometer. A pycnometer is a glass container with a known volume and stopper. Sample was taken in the pycnometer, and the mass of the pycnometer with the sample was measured. The density was calculated by dividing the mass by the volume of the pycnometer.

$$\text{Density} = \frac{(\text{Total weight of instrument with oil} - \text{Empty weight of the instrument})}{\text{Volume of the instrument (25ml)}}$$



Fig 4.1: Density measurement using pycnometer

109 4.2.3 Kinematic viscosity

The viscosity is been measured under the standard of ASTM D 445. This is a standard test method for kinematic viscosity of transparent and opaque liquid. The test involves measuring the time it takes for a fixed volume of oil sample to flow through a capillary tube at a temperature of 40 degree Celsius and maintain the heat till the end of the procedure. The kinematic viscosity is then calculated based on the time and the dimensions of the capillary tube.

$$\text{Viscosity} = \text{Time in (s)} \times 0.014$$

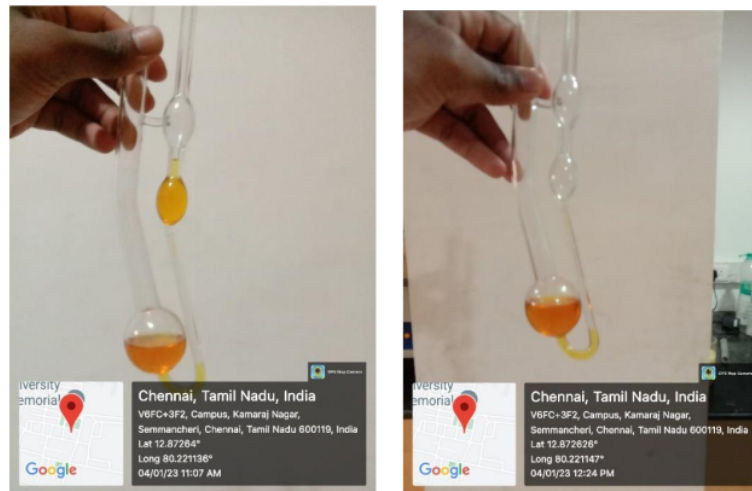


Fig 4.2: Kinematic viscosity measurement using capillary tube viscometer

4.2.4 Free fatty acid value

In the context of oils, ²⁰ free fatty acid (FFA) content is a measure of the acidity of the oil and is often used as an indicator of the oil's quality. The FFA content of an oil can be determined as per ASTM D 664 standards through a process called acid value (AV) determination, which involves titration with a standard solution of sodium hydroxide (NaOH).

First, a sodium hydroxide burette solution with a normality of 0.1 N is created for this titration procedure. In a conical flask, the weight of a 5 grams oil sample is measured. In addition, a conical flask containing an oil sample is filled with 25 mL of isopropyl alcohol. Four drops of burette solution are then added to the mixture. The solution is then heated until it reaches a 60 °C temperature. The sample is then left to cool until it reaches room temperature. Phenolphthalein indicator is added to the solution once it has reached room temperature. The solution is then titrated, and the results are recorded.

$$\text{FFA (\%)} = \frac{28.2 \times 0.1 \times \text{Volume of NaOH (ml)}}{\text{Weight of the sample (g)}}$$

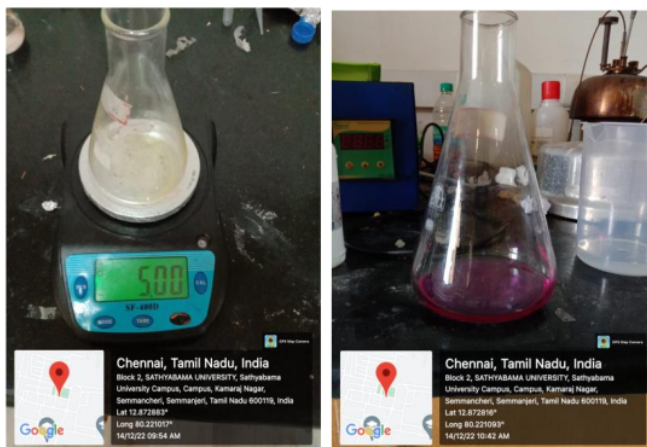


Fig 4.3: Free fatty acid value measurement through titration

4.2.5 Moisture content:

ASTM D 2709 ¹³ was used to determine the moisture content. The weight of the 5gm oil sample in the crucible was measured, along with the total weight, which is recorded. Next, for three hours, the sample was placed inside a hot air oven set to

110 degrees Celsius. The sample is removed from the oven and let to cool to room temperature for several time. The sample's total weight was then determined. Calculating the weight difference and determining the amount of moisture present in the sample.

The moisture content (%) of the sample was calculated:

$$\frac{(\text{Initial weight of sample} - \text{Dry weight of sample})}{\text{Initial weight of the sample}} \times 100$$



Fig 4.4 Estimation of moisture content

4.3 BIODIESEL PRODUCTION

4.3.1 Materials required

Oil sample, methanol, sodium hydroxide (NaOH), heating mantle, magnetic stirrer separatory funnel, three neck flask.

4.3.2 Procedure

Catalyst is an important parameter to produce biodiesel. So, the process is initiated with catalyst preparation, where 182 mL of methanol and 5 grams of sodium hydroxide pellets used to prepare the catalyst. Following the catalyst preparation, 1000 mL of the oil sample was measured and added to the flask with three necks. The three-neck flask was equipped with a magnetic stirrer for continuous stirring throughout the procedure. To heat the oil sample, the three-neck flask was kept on a hot plate. The stopper, which was at the left, seals the flask's initial neck. The condenser seals off the second neck, preventing the evaporating catalysts from escaping. The final neck was then sealed off with a

thermometer-equipped stopper. The prepared catalysts are introduced into the oil sample after the temperature reaches 60 degrees Celsius. The reaction is continuously stirred for 90 mins. The sample was transferred to the separatory funnel for separation after the reaction completed. The sample was held for the separation process for a little while. The separation consists of two layers, the bottom layer of which was separated from the top layer of crude biodiesel and was known as glycerol. The catalyst and unreacted methanol are separated from the top layer through a process known as "washing," where the mixture is washed by mixing RO water heated to 60 °C at a 1:1 ratio. The washing process is repeated until the wash water's pH is neutral. Following the washing procedure, the biodiesel was heated to 110 degrees Celsius to evaporate any remaining water. The purest form of biodiesel was produced after temperatures reach 110 degrees Celsius.

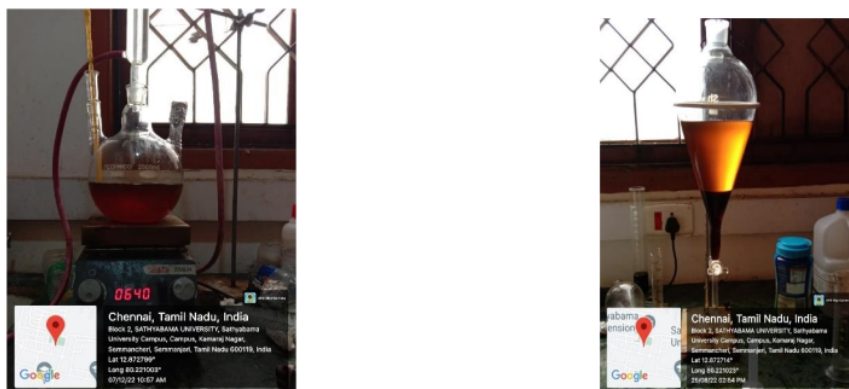


Fig 4.5: Biodiesel production: Tranesterification and Separation

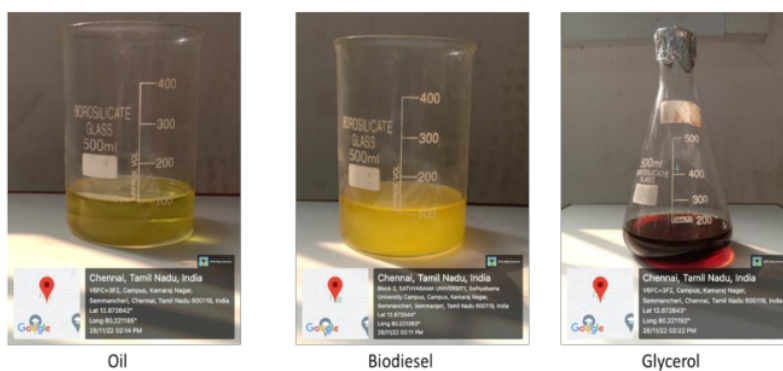


Fig 4.6: Feedstock (Waste cooking oil) and products of biodiesel production

4.4 PRELIMINARY PROPERTY ANALYSIS OF BIODIESEL SAMPLES

Biodiesel properties are analysed to ensure that the fuel meets certain quality standards and can be used efficiently in diesel engines. Preliminary properties like density, kinematic viscosity, & acid value, moisture content, and cold flow properties such as cloud point, pour point, further combustion properties such as calorific value, flash point & fire point, was measured in lab under their respective ASTM standards

4.4.1 Materials and chemicals required

- Density: pycnometer, weighing machine
- Kinematic viscosity: kinematic viscometer
- FFA value: 0.1 N Sodium hydroxide, Iso propyl alcohol, thermometer, 250 mL conical flask, Phenolphthalein indicator
- Moisture content: Crucible, Hot air oven
- Cloud point & Pour point: ASTM D 2500 apparatus for cloud and pour point.
- Flash & Fire point: Flash and fire point apparatus
- Calorific value: Bomb Calorimeter, oxygen cylinder

4.4.2 Density

The density of biodiesel was also examined using a pycnometer, like how oil density was measured as per ASTM D 1298 standards. The mass of the pycnometer with fuel was measured after the sample was acquired. By dividing the mass by the volume of the pycnometer, the density of the fuel was determined.

Density equals=
$$\frac{\text{Total weight of instrument with biodiesel} - \text{Empty weight of the instrument}}{\text{Volume of the instrument (25mL)}}$$

4.4.3 Kinematic viscosity

Kinematic viscosity is a measure of the resistance of a fluid to flow, and is expressed in units of centistokes (cSt).

The viscosity was measured using the ASTM D 445 standard, which is identical to measuring the viscosity of oil samples. The test entails timing how long it takes a fixed amount of fuel to pass through a capillary tube at a temperature of 40 degrees Celsius while maintaining the heat there until the procedure is complete.

⁸ The kinematic viscosity is then determined using the time and capillary tube diameters.

$$\text{Viscosity} = \text{Time in (s)} \times 0.014$$

4.4.4 Acid value

⁵⁶ The FFA content of the fuel can be used to determine the acid value of the fuel. The FFA content of the fuel is determined using the FFA analysis method in oil samples as per ASTM D 664 standards. For this titration process, a sodium hydroxide burette solution with a normality of 0.1 was first prepared. The weight of a 5-gram ⁸ oil sample was measured in a conical flask. In addition, 25 ml of isopropyl alcohol is added to a conical flask containing an oil sample. The mixture is subsequently treated with four drops of burette solution. The solution is then heated until it reaches a temperature of 60 °C. The sample is then ⁴⁹ allowed to cool to room temperature. Once the solution has reached room temperature, the phenolphthalein indicator is added. After that, the solution is titrated and the results are recorded. The acid value of biodiesel is calculated by

$$\text{Acid value (g KOH/g)} = \text{Obtained FFA value} \times 1.99$$

4.4.5 Moisture content

ASTM D 2709 was used to determine the moisture content. Biodiesel moisture content is measured using a heating process. The weight of the 5 g biodiesel sample in the crucible was determined and recorded as the total weight. ²⁵ The sample was then placed in a hot air oven set at 110 degrees Celsius for three hours. The sample was ⁵⁷ taken out of the oven and ¹²¹ allowed to cool to room temperature for a few minutes. The total weight of the sample is then calculated. Calculating the weight difference and estimating the quantity of moisture in the sample.

⁹⁶ The moisture content (%) of the sample was calculated:

$$\frac{(\text{Initial weight of sample} - \text{Dry weight of sample})}{\text{Initial weight of the sample}} \times 100$$

⁵⁸ **4.4.6 Cloud Point**

The cloud point of biodiesel is typically measured using a test method called ASTM D 2500.³⁴ The temperature at which the first visible formation of wax crystals is observed is recorded as the cloud point.

Sample of biodiesel was collected and brought to a uniform temperature, typically around 10 degrees Celsius. The sample jar is placed in a cooling bath, that is prepared according to ASTM standards, where temperature is lowered at a rate of 1 degree Celsius per minute. The sample is observed for the first visible formation of wax crystals.⁶¹ The temperature at which the first formation is observed is recorded as the cloud point.

³¹ **4.4.7 Pour point**

The pour point of biodiesel is typically measured using a test method called ASTM D 97. This method involves cooling a sample of biodiesel at a rate of 1 degree Celsius per minute until it stops flowing, and then recording the temperature at which this occurs as the pour point.¹⁰

Sample of biodiesel was collected and brought to a uniform temperature, typically around 10 degrees Celsius. The sample jar is placed in a cooling bath, that is prepared according to ASTM standards, where temperature is lowered at a rate of 1 degree Celsius per minute while the sample is tilted periodically. The tilting is done to check the flow of the sample. The sample is observed for the point at which it no longer flows, and the temperature at which this occurs is recorded as the pour point.¹⁰

4.4.8 Calorific Value

⁶⁸
The calorific value of biodiesel can be measured using a device called a bomb calorimeter under ASTM D 240 standards. This device is designed to measure the heat released when a fuel is burned completely in controlled environment. First, a small sample of the biodiesel fuel is weighed and placed into a small metal container known as a bomb. Oxygen is then added to the bomb, which is then sealed and placed into the calorimeter. The bomb is ignited, and the biodiesel fuel is burned completely, producing heat. The heat produced by the burning the biodiesel fuel is absorbed by the calorimeter, which measures the temperature

changes. From the temperature change, along with the weight of the biodiesel sample and other parameters, the calorific value of the biodiesel fuel can be calculated.

Calorific value of biodiesel calculated from

$$\text{Calorific value (cal/g)} = \frac{(M_w \times C_w + W) \times T_r}{M_s} - (E_n + E_c)$$

M_w – Mass of water, g

C_w – Specific heat capacity of water, cal/g °C

T_r – Temperature rise, °C

M_s – Mass of fuel sample, g

E_n – Energy equivalent calculated with respect to nichrome wire, cal/g

E_c – Energy equivalent Energy calculated with respect to cotton thread, cal/g

4.4.9 Flash point and Fire point

Flash point Test (ASTM D 93): This test determines the flash point of a biodiesel fuel by heating a small sample of the fuel in a test apparatus. A small flame is introduced periodically to the surface of the fuel, and the temperature is gradually increased until the fuel produces enough vapor to ignite briefly, but not sustain combustion. The temperature at which this occurs is recorded as the flash point.

Fire point (ASTM D 93): This test determines the fire point of a biodiesel fuel by heating a small sample of the fuel in a test apparatus, like the flash point test. However, in this test, the temperature is gradually increased until the fuel produces enough vapour to ignite and sustain combustion for at least 5 seconds. The temperature at which this occurs is recorded as the fire point.

4.5 FREE FATTY ACID IDENTIFICATION USING UV - VISIBLE SPECTROPHOTOMETRY

4.5.1 Materials and chemicals required

250mL Conical flask, 100 mL beaker, 10 ml centrifuge tubes, centrifuge, and UV visible spectrometer, 9-octadecenoic acid or oleic acid (C18:1n9), Isooctane, copper-acetate monohydrate, pyridine, distilled water.

4.5.2 Copper acetate pyridine reagent preparation

5.5g of the copper-acetate monohydrate was dissolved in 80 mL of distilled water. The pH of the solution was initially 5.08, which was adjusted to 6.06 with pyridine, and then the solution was further diluted to 100 mL with distilled water.



Fig 4.7: pH increment of copper acetate solution using pyridine



Fig 4.8: Copper acetate pyridine reagent

4.5.3 Preparation of standard calibration solutions of oleic acid

The standard oleic acid solutions were prepared in 9 different concentrations (2 – 18 $\mu\text{mol/mL}$) for the calibration curve by dissolving stock oleic acid in a non-polar solvent, isooctane.

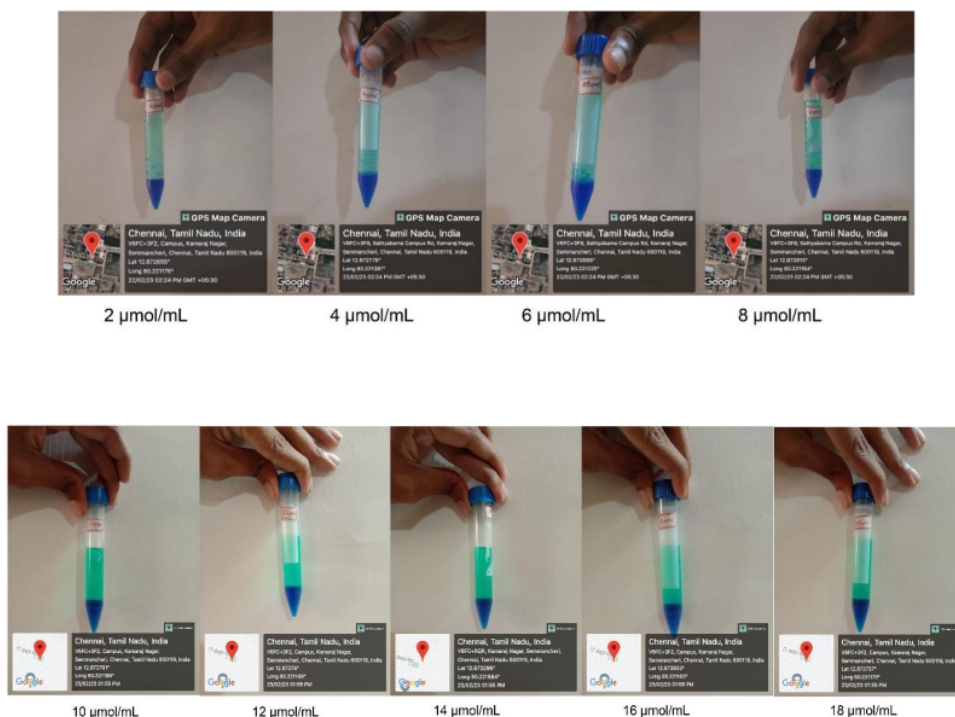


Fig 4.9: Calibration solutions of oleic acid for UV visible spectrophotometric analysis

4.5.4 Identification of free fatty acid content in raw oil sample:

Two millilitres of copper reagent were added to each calibration solution, mixed for 30 seconds then allowed to separate in a 10 mL centrifuge tubes. The top organic layer was analysed under a UV-visible spectrometer, the absorbance peak was achieved at 708 – 709 nm, and based on the analysis, a graph was plotted between the concentration of calibration solutions and the peak absorbance value. The graph was used to develop the linearity between the absorbance and concentration of fatty acid through an equation. Further, 2g of oil sample was mixed with isooctane in a 10 mL centrifuge tube, and 2 mL of copper acetate reagent was added. The mixer was then centrifuged at 2000 rpm for 5 minutes in a

centrifuge for bilayer separation, the top organic layer was analysed under a UV-visible spectrometer, such that the FFA content of the oil is predicted in terms of oleic acid ($\mu\text{mol/mL}$) based on the equation of linearity obtained from the calibration graph.

4.6 SENSOR MODULE DEVELOPMENT

4.6.1 Materials and chemicals required

5mm Infrared LED (IR LED) (TX), 5mm photodiode (RX), Arduino Uno R3 board, 10k resistor, 1k resistor, connecting wires, breadboard.

4.6.2 Construction

A simpler circuit diagram was developed to identify the components needed for the construction of the module, and the necessary components were then purchased. The initial assembly of the module was created by placing the components on a breadboard and the Arduino Uno board was used to both power the module and obtain the output readings by analysing the input signals from the module.

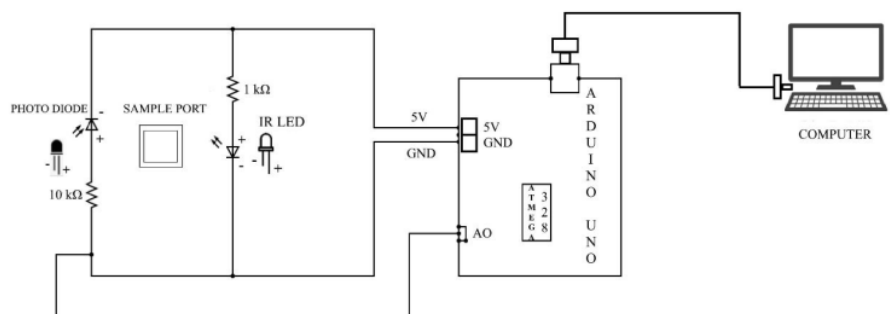


Fig 4.10: Circuit diagram of IR based sensor module

4.6.3 Working

The IR LED constantly emits IR rays, which are detected as analog signals by the photodiode that are converted as voltage measurements by a microcontroller (Arduino Uno R3). The Arduino board is powered and programmed by a computer via an OTG cable, and the reading is recorded in the computer. The intensity of the IR rays collected by the photodiode changes when samples are positioned

between the IR LED (emitter) and photodiode (collector), allowing the IR rays to pass through the sample. As a result, the output voltage also changes. When the samples were initially examined, the readings were unstable. It was later discovered that the excess light exposure to the photodiode owing to the open arrangement was the reason that contributed to the unstable readings. Hence, the module was modified into a closed assembly, which produced stable readings.

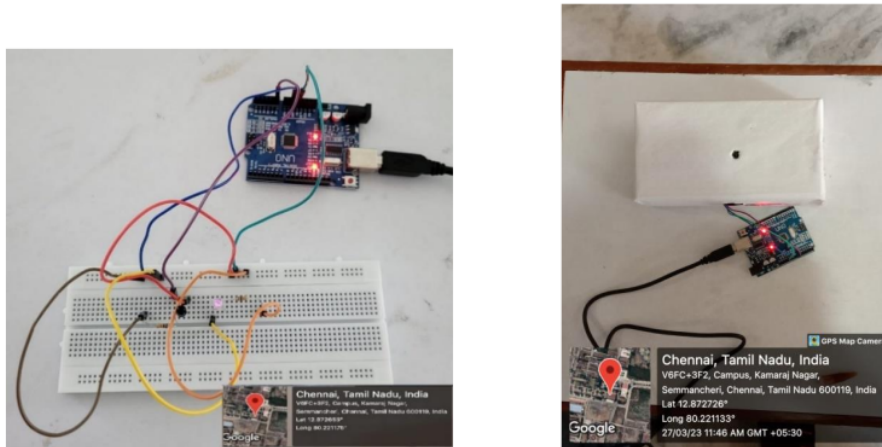


Fig 4.11: Sensor module assembly: Open and Closed assembly

4.6.4 Arduino code for the sensor

```
const int photo_diode = A0;
int input_val=0;
float volt;

void setup() {
    // put your setup code here, to run once:
    Serial.begin(9600);
}

void loop() {
    // put your main code here, to run repeatedly:
    input_val=analogRead(photo_diode);
    volt=((input_val*1.20)/1023.00)*1000;
    Serial.println(volt,4);
    delay(1000);
}
```

4.6.4 Calibration

The calibration data was obtained like the UV visible calibration, different mass percentages of oleic acid were dissolved in a non-polar solvent, isooctane, and the respective sensor outputs were recorded. The calibration graph was plotted between the sensor data and the variable concentration.

4.6.5 FFA analysis of oil samples

The oil samples were taken in the similar vials that were used for the calibration, the samples were analysed by the sensor and their respective FFA content in terms of oleic acid percentage were obtained from the equation of linearity between oleic acid concentration and output voltage readings.

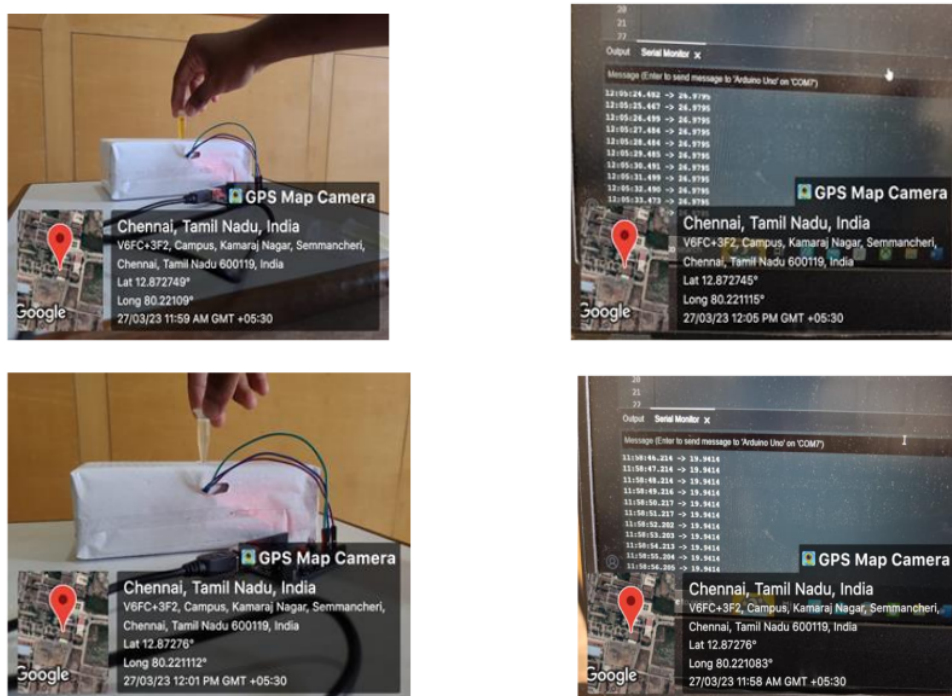


Fig 4.12: FFA measurement through the sensor module

4.7 CORRELATION OF COMPOSITION OF OIL WITH PROPERTIES OF BIODIESEL USING GC-FID ANALYSIS OF OIL AND BIODIESEL SAMPLE

4.7.1 *Materials required*

Raw Oil, waste cooking oil and their respective biodiesel samples, YL6500 GC, hexane,

4.7.2 *Gas chromatography*

The moisture removed samples were diluted with hexane before being injected into injection port of YL 6500 GC equipped with a 0.53-mm TR-WAX capillary column designed to achieve 260 °C from 140 °C at a rate of 10-degree Celsius per minute. Before injecting the sample, the carrier gas, helium, was adjusted to flow at a rate of 5 millilitres per minute. In order to determine the composition of oil and biodiesel samples, 1 µL of the sample was injected into split mode injection port. The separated components are then identified using the FID detector, which quantifies the proportion of carbon atoms in the sample. Each component will generate a distinct signal on the detector. The ignition temperature and maximum temperature of the Flame ionization detector (FID), was calibrated at 471 K and 513 K respectively. To identify the various components and their quantities, the data collected from the detector can be evaluated using software. The primary composition of oil and biodiesel samples was determined by interpreting GC - FID data and comparing it to known GC standards of fatty acid methyl esters.

4.7.3 *Correlation of composition of oil samples to properties of biodiesel*

The impact of the composition of the oil sample on the properties of biodiesel was studied by comparing the individual properties of selective FFAs with the properties of the biodiesel samples obtained.

CHAPTER – 5

RESULTS AND DISCUSSION

5.1 OIL SAMPLE COLLECTION

Table 5.1: Data acquired during the collection of waste cooking oil samples

ITEM	DETAILS
Restaurant details with address	Mess in Pallikaranai, Chennai
Brand of oil used	Gold winner
Types of oil	Sunflower oil
Place of buying	Pallikaranai, Chennai, Tamil Nadu
Items cooked	Veg – Poori, Vada, Appalam
Frying time of oil	5 – 6 hrs
Amount of oil generated(ml)	1000 mL per day
Amount of oil collected	1000 mL
Rate expected from the shopkeeper	Free

Waste cooking oil subjected to wide range of cooking conditions including different cooking time, temperature, product to be fried was acquired from several food outlets in Chennai including Sathyabama Institute of Science and Technology that used various types and brands of raw oil. From each outlet, about 1 litre of used cooking oil was collected, along with 100 mL of the used cooking oil's raw oil for examination. Since the frying circumstances and the amount of water in the food items can have an impact on the oil quality, such characteristics were recorded and tabulated. It was discovered that the average cooking time of oil in most outlets was 4 to 6 hours, and most outlets either discard or reuse the waste oil completely.

5.2 PRELIMINARY PROPERTY ANALYSIS OF OIL SAMPLES

The preliminary properties of the waste cooking oil sample were identified to assess the quality and understand the characteristics of the oil samples. Properties such as density, kinematic viscosity, moisture content, and FFA content were identified and recorded. All waste cooking oil samples were found to have FFA values of less than 1%, making them suitable for single-stage transesterification. Changes in properties were noticed for waste cooking oil samples and their respective raw oil samples.

Table 5.2: Preliminary properties of waste cooking oil samples

Properties		GN Oil samples				
		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Density (g/ml)		0.927	0.944	0.924	0.919	0.943
Viscosity (cSt)	Temp. (°C)	40	40	40	40	40
	Time (s)	2940	4175	2663	2949	2296
	Viscosity (cSt)	41.16	58.45	37.282	41.286	32.144
FFA (%)	Weight of oil sample(g)	5.05	5.4	5.08	5.03	5.6
	Volume of NaOH (ml)	0.6	0.8	1.1	1.4	0.9
	FFA (%)	0.335	0.418	0.611	0.785	0.453
Moisture Content (%)	Crucible Wt. without sample (g)	22.37	37.47	66.28	81.87	22.37
	Crucible Wt. with sample (g)	32.37	47.57	76.42	92.04	32.41
	Dry Wt. (g)	32.29	47.53	76.4	85.42	32.19
	Moisture content (%)	0.247	0.054	0.026	7.193	0.679

5.3 PRELIMINARY PROPERTY ANALYSIS OF BIODIESEL SAMPLES

The preliminary properties, including cold flow properties and combustion properties, for the biodiesel produced were determined and compared with ASTM D6751 in order to assess the quality and analyse the characteristics of the biodiesel.

Table 5.3: Properties of biodiesel samples

Properties	Standard*	GN – Biodiesel				
		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Density (g/cc)	no limit	0.875	0.900	0.892	0.880	0.886
Kinematic Viscosity (cSt)	1.9 – 6 (mm ² /s)	5.838	5.992	5.698	4.270	5.152
Moisture content (%)	max 0.05 (vol%)	0.083	1.234	0.319	0.186	0.301
Acid value (%)	Max. 0.50 g KOH /g	0.560	0.336	0.444	0.337	0.223
Cloud point (°C)	Report	9 °C	- 4 °C	6 °C	10 °C	5 °C
Pour point (°C)	No limit	0 °C	-14 °C	5 °C	1 °C	-10 °C
Calorific value (cal/g)	No limit	6562.3	6261.9	7764.0	4058.7	5661.0
Flash point	Min. 93 (°C)	213 °C	217 °C	195 °C	197 °C	137 °C
Fire point (°C)	No limit	235 °C	237 °C	215 °C	219 °C	159 °C

*Properties were compared with ASTM D6751 standards **

5.3.1 Density

The density of all biodiesel produced were under ASTM D6751 standards. Biodiesel density is an important feature since it influences the amount of energy that can be delivered per unit volume of fuel. Since biodiesel has a lower density than petroleum diesel, it contains less energy per gallon than petroleum diesel.

³⁴ The handling and storage of biodiesel can also be impacted by density. Higher-density fuels can be trickier to pump and store, and they can need special fueling equipment.

5.3.2 Kinematic viscosity

The density of all biodiesel produced were under ASTM D6751 standards. Proper viscosity ensures good fuel atomization, complete combustion, and adequate lubrication of engine components, resulting in improved engine performance, reduced emissions, and longer engine life. Therefore, it is important to ⁷¹ensure that the kinematic viscosity of biodiesel falls within an appropriate range, typically between 1.9 and 6.0 cSt or mm²/s at 40 degrees Celsius, depending on the application and operating conditions.

5.3.3 Moisture content

The moisture content of biodiesel is important for several reasons

The presence of moisture can indicate poor production and processing practices, which can result in impurities and reduced quality of the biodiesel. Moisture content is therefore used as a quality control parameter to ensure that the biodiesel meets the necessary standards.

Biodiesel can undergo hydrolysis when it encounters water, which can lead ¹⁵to the formation of free fatty acids and other impurities. This can result in increased acidity and reduced stability of the fuel, which can lead to engine damage and decreased performance. Monitoring and controlling moisture content can help prevent this.

Biodiesel can also be affected by water in cold weather condition. When water freezes, it can form ice crystals that ⁴⁰can clog fuel filters and lines, leading to engine problems. By controlling moisture content, the risk of these issues can be minimized.

⁹¹5.3.4 Cloud and pour point

The cloud point is a critical measure of biodiesel's cold-weather performance. The waxes in biodiesel can solidify and produce obstructions in gasoline filters and lines when the temperature drops, resulting in engine issues. The cloud point thus

110 aids in determining the lowest temperature at which biodiesel can be safely employed. Wax production in biodiesel can also boost fuel viscosity and stability. Wax in the fuel can clog fuel injectors and impair engine performance. Biodiesel manufacturers can guarantee that the fuel fulfils the appropriate quality and stability standards by monitoring the cloud point.

The pour point is an important parameter for biodiesel because it helps to ensure the fuel's cold weather performance, handling and storage, and regulatory compliance. By monitoring and controlling the pour point, biodiesel producers can ensure that the fuel meets the necessary standards and performance well in various application.

15 5.3.5 Calorific value

Knowing the calorific value of biodiesel is important because it helps determine the efficiency of the fuel as an energy source. For example, if the calorific value of a biodiesel fuel is high, then it means that it can produce more energy per unit than a fuel with a lower calorific value. This information can be used by engineers and researchers to optimize the performance of engines and other equipment that use biodiesel as a fuel.

9 5.3.6 Flash and Fire point

The flash point of a fuel is the lowest temperature at which it releases enough vapor to ignite quickly but not sustain burning. The fire point is the lowest temperature at which a fuel emits enough vapor to ignite and sustain burning. Knowing the flash and ignition points of biodiesel is crucial for various reasons. Firstly, it promotes safe fuel handling and storage. If a biodiesel fuel has a low flash point, it might ignite at low temperatures, making it more unsafe to handle and store. Secondly, the flash and fire point of biodiesel can also affect the performance of engines and other equipment that use the fuel. If the flash point is too high, it can result in poor ignition and engine performance. If the fire point is too low, it can result in the fuel igniting inside the engine, which can cause damage or failure.

5.4 FREE FATTY ACID IDENTIFICATION USING UV – VISIBLE SPECTROPHOTOMETRY

The calibration curves for the varying concentrations of oleic acid obtained from absorbance measurements are shown in Figure. The vertical axis refers to absorbance, while the horizontal axis shows the wave length of the absorbance of the calibration solution relative to that of the blank (i.e., isooctane and copper reagent). The peak absorbance for the solutions was recorded at 707–709 nm of wave length, and the absorbance increased with increasing solution concentration.

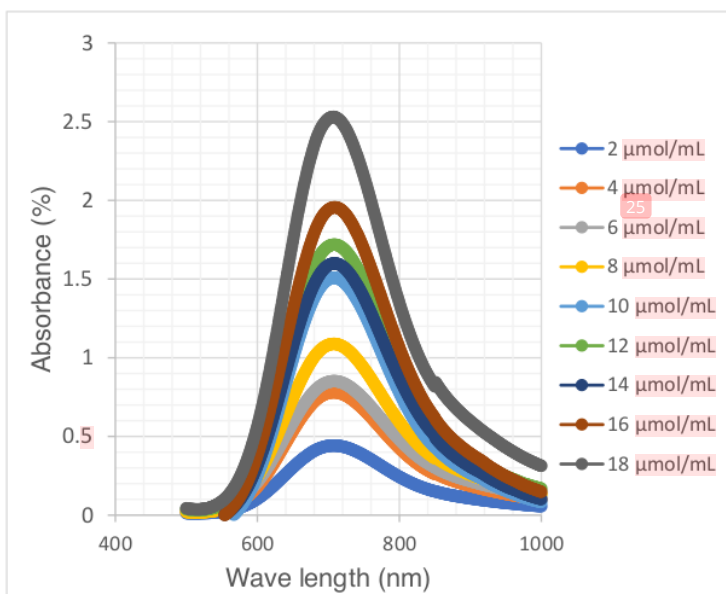


Figure 5.1: Absorbance graph for calibration solutions

The calibration curve, which was solely produced for oleic acid, is depicted in Figure. The results are also given only in terms of oleic acid. In comparison to other FFAs, oleic acid was chosen for calibration because of its superior solubility and complex formation with copper ions in non-polar solutions.

Since in the mixture of isooctane and copper acetate pyridine, only the FFAs forms a cage like complex with the copper reagent the colour development is not interfered monoacylglycerols, diacylglycerols, triacylglycerols, or another lipid.

Using the measurement results, we were able to establish linearity between the concentration and the absorbance, table, represents the calibration data obtained from the spectrophotometer results.

Table 5.4: Calibration of oleic acid for UV visible spectrophotometry analysis

Concentration (μmol/mL)	Absorbance	Wave length (nm)
2	0.4	708
4	0.8	708
6	0.9	708
8	1.1	708
10	1.5	708
12	1.7	709
14	1.6	709
16	2.0	709
18	2.5	707

It was discovered that solutions with concentrations of 16 mmol/mL and above were not readily tractable to the spectrophotometry studies, since at this concentration level, the absorbance is around 2, indicating that the Lambert and Beer law no longer applies.

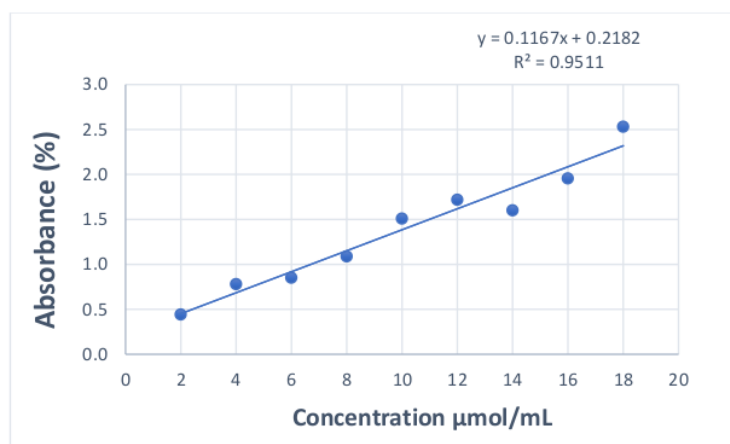


Fig 5.2: Calibration chart for uv - visible spectrophotometry

The sample 2 oil was considered for the evaluation of FFA, the FFA was predicted through the equation of linearity $y = 0.1167x + 0.2182$ from the calibration chart depicted in Figure and was comparable with FFA value obtained by titration.

5.5 SENSOR MODULE DEVELOPMENT

Since the construction of the sensor module was based on the methodology of UV visible spectrophotometry, when the oleic acid in varying concentrations dissolved in isooctane was initially analysed through the sensor, the readings obtained were seen to be linear, such that the calibration of the sensor module was done with varying concentrations of oleic in the isooctane. The sensor reading for the pure isooctane solution was considered as blank reading.

Table 5.5: Oleic acid calibration for sensor measurement

Oleic acid % (w/w) (approx.)	Output Voltage (mV)
0 (blank)	31.67
0.1	32.02
0.2	28.45
0.3	26.86
0.4	25.90
0.5	24.01
0.6	19.84
0.7	21.00
0.8	19.00
1	17.25
1.2	14.33
1.4	10.87
1.6	9.79
1.8	8.56
2	10.40

It was discovered that increasing the concentration values linearly decreased the output voltage values; this was owing to the output voltage's dependence on the amount of radiations captured by the photodiode. We try to extrapolate from this that as the FFA content of the sample grows, so does the absorption of IR rays generated by the IR LED, resulting in low transmittance to the photodiode. As a

result, the photodiode's output voltage falls. It was also discovered that because the output voltages decline linearly when the concentration exceeds 2%, the readings of the sensor were unstable; additionally, the readings of the sensor were affected by a variety of factors, such as the vial used to take the readings, the surrounding light exposure, and the temperature of the sensor.

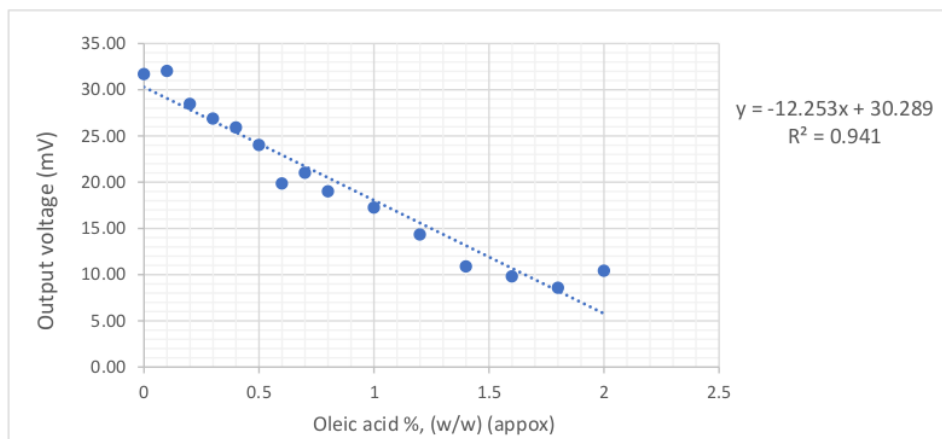


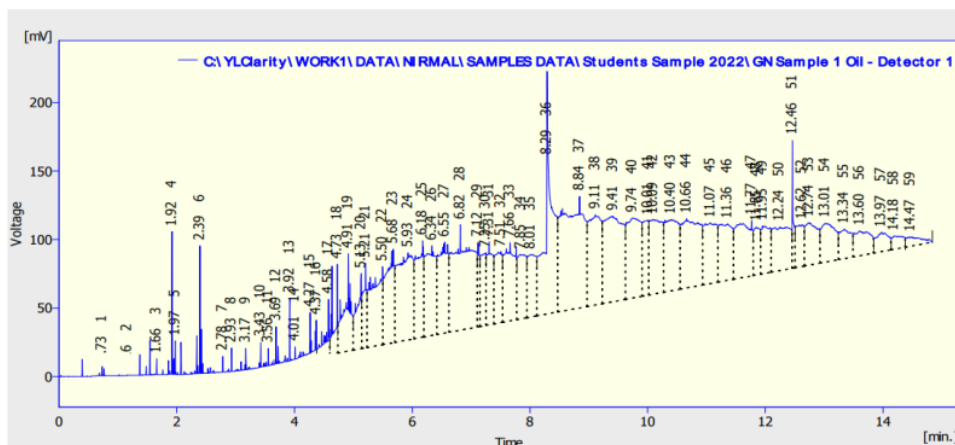
Fig 5.3: Calibration chart for the sensor reading measurement

Following the development of the calibration chart, the oil samples were analysed by the sensor module, and the FFA values of the oil samples were predicted using the equation of linearity obtained from the calibration chart and compared to FFA values derived from titration values.

Table 5.6: Comparison of FFA values obtained from sensor and titration

Oil Sample	FFA measured through titration	FFA measured through sensor	²² Difference
Sample 1	0.33	0.27	-0.06
Sample 2	0.42	0.36	-0.06
Sample 3	0.61	0.84	0.23
Sample 5	0.45	0.557	0.107

5.6 CORRELATION OF COMPOSITION OF OIL WITH PROPERTIES OF BIODIESEL USING GC-FID ANALYSIS OF OIL AND BIODIESEL SAMPLES



retention duration that can be utilized to distinguish it. The GC FID graphs was interpreted for the all the 5 collected oil samples and their respective biodiesel samples. Seven major fatty acids that were present in commonly in many oil sources were considered for the analysis

Table 5.7: Composition analysis of oil and biodiesel samples

Compound Number	Compound Name	Composition (%)					
		Sample 1		Sample 2		Sample 3	
		Oil	Biodiesel	Oil	Biodiesel	Oil	Biodiesel
C12:0	Lauric acid	0.15	0.1	0.31	0.23	0.19	0.12
C14:0	Myristic acid	0.54	0.43	0.77	0.68	0.64	0.05
C16:0	Palmitic acid	10.54	7.89	12.36	11.12	16.47	11.76
C18:0	Stearic acid	8.5	6.13	5.6	3.7	30.54	27.39
C18:1	Oleic acid	28.54	20.78	40.45	35.65	21.45	11.64
C18:2	Linoleic acid	16.47	12.54	22.37	19.56	17.96	15.23
C18:3	Linolenic acid	1.56	0.9	1.09	0.85	0.56	0.23

By comparing the individual properties of selected fatty acid acids with the properties of biodiesel, we observed the certain impact of the fatty acid compositions over the properties of biodiesel, kinematic viscosity, density, cloud point and pour point, calorific values, etc

Kinematic Viscosity increases with increase in number of carbon atoms of fatty acids in oils, decreases with increasing degree of unsaturation. Density increases with increase in degree of unsaturation, this explains that more the presence of unsaturated fatty acids higher will be the density of the fuel.

Low temperature properties: Cloud point and pour points represents low temperature behaviour of the fuel, such that from the observation, the lower the saturation the lower the cloud and pour points. Calorific value increased with increasing chain length, and increasing unsaturation for a given chain length decrease in the heat of combustion due to the loss of hydrogen. These observations were compared and verified with various publications

CHAPTER – 6:

SUMMARY AND CONCLUSION

This work was an attempt to construct a sensor to identify the FFA content in the oil sample, primarily waste cooking oil samples, that were utilized for biodiesel production. Also, the composition of oil samples and their respective biodiesel samples were analysed under GC-FID to understand the influence of the FFA composition on the properties of biodiesel. To achieve this, the preliminary properties of the waste cooking oil and respective biodiesels were identified and tabulated.

To determine the principle of the sensor, various analytical methods for the identification of FFA were compared, and a method based on copper soap UV visible spectrophotometry was finalized and experimentally performed to understand the process of identification of FFA in the oil sample. Based on the results obtained from copper soap UV visible spectrophotometry, we concluded to adapt the concept of spectroscopy as a principle for our module, but a simpler IR-based sensor module was fabricated.

Further oil samples were analysed under the sensor module, and FFA values were predicted and compared with traditional titration values. Later, the composition of oil and their respective biodiesel samples were identified and analysed under GC - FID, and the impact of the composition of the oil sample on properties of biodiesel such as viscosity, density, cloud, and pour point were analysed.

To conclude, free fatty acid content of feedstocks (oil samples) is a significant parameter to be considered to produce biodiesel, a mechanistic approach for identification of FFA content in the oil will improve the analysing procedure of oil samples and biodiesel production. Additionally, there are variation between feedstocks in the structural configuration, such as chain length, branching, degree of unsaturation, and position of double bonds, which can affect the characteristics and functionality of biodiesel. A viable alternative could be to alter fatty acid profiles, or to change their structural makeup in order to improve the properties of biodiesel fuel by genetic modification, although this requires more intensive research.

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