

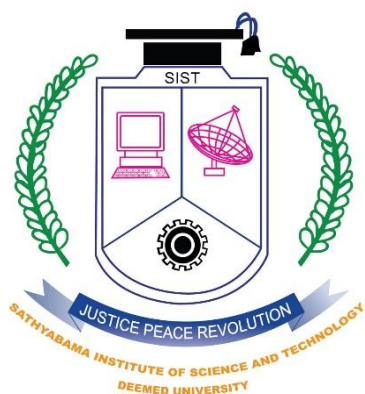
PRODUCTION OF PRASINOS FUEL FROM *BLUE – GREEN* ALGAE LIPIDS

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

by

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**DEPARTMENT OF CHEMICAL ENGINEERING
SCHOOL OF BIO AND CHEMICAL ENGINEERING**

**SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

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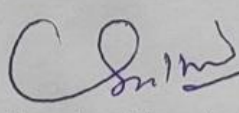
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BONAFIDE CERTIFICATE

This is to certify that this project Report is the bonafide work of **NITHISH S (40190015), RAAJA VEERAPPAN S (40190018)**, Who carried out the project entitled "**PRODUCTION OF PRASIONOS FUEL FROM BLUE – GREEN ALGAE LIPIDS**" under my supervision from November 2023 to April 2024.


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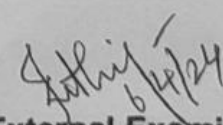
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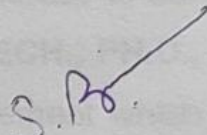
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DECLARATION

We, NITHISH S (40190015) and RAAJA VEERAPPAN S (40190018) hereby declare that the Project Report entitled "PRODUCTION OF PRASIONOS FUEL FROM BLUE – GREEN ALGAE LIPIDS" done by us under the guidance of Dr. MICHAEL RAHUL SOOSAI, Sathyabama Institute of Science and Technology is submitted in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering.

DATE: 5-4-2024

PLACE: CHENNAI

 
SIGNATURE OF THE CANDIDATES

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ABSTRACT

The high demand for fossil fuels has grown, and the burning of diesel produces pollution to the environment. The emission of nitrogen oxides (NO_x) causes the formation of ground level zone, which includes smog and acid rain, which causes skin illness and respiratory problems in humans. To address these issues, biodiesel was created utilizing *spirulina* oil, and three separate catalysts were created to accelerate the process. One of the catalysts, CaO, is recovered from demolition debris and aids in waste reduction and waste management. It acts as a catalyst in the transesterification process. Cobalt chloride hexahydrate is one of the catalyst used to speed up reaction which helps to breakdown the triglycerides into biodiesel. Zeolite is a three-dimensional lattice structure composed of silica and alumina, which offer porous and active sites in zeolite production. These active sites are known as acidic sites, which results in an acidic catalytic reaction and helps in the breaking of ester bonds in triglycerides and the conversion of biodiesel. Because of the active sites in zeolite, the other two compounds, CaO and CoCl₂, may be readily doped and synthesised as catalysts. In this process, the *spirulina* is cultivated, then dried, and oil is extracted for the production of biodiesel. The transesterification method is involved in the production of biodiesel using *spirulina* microalgae. The optimisation technique is involved, and a better ratio is used for biodiesel production, which confirms a 1:12 ratio of lipids or oil microalgae to methanol and 4.5 wt% of catalyst, which is 3.09 g. The process is completed in a round bottom flask using a stirrer for 120 min, then transferred to a separation funnel and kept for a minimum of 12 h for the separation of glycerol and biodiesel, then it was subjected to a gas chromatography test and FTIR test. Then, by adjusting the time length, the yield was increased to 81% by running the reaction for 120 min at 60°C, and parameters such as density (0.863 g/cc), flash point (18°C), and fire point of biodiesel (166°C) were discovered, which are very important for engine ignition quality. This technology reduces the negative environmental impact of chemical operations while producing biodiesel for various uses.

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CHAPTER 1

INTRODUCTION

1.1 BIODIESEL

Biodiesel is a renewable alternative fuel manufactured from organic ingredients, most often vegetable oils or animal fats. Transesterification, which includes chemically turning these feedstocks into biodiesel and glycerin, is used to create it. Biodiesel may be used in diesel engines to replace normal diesel fuel without requiring substantial changes.

One of the primary benefits of biodiesel is that it emits less greenhouse gas than fossil fuel. It has a smaller carbon footprint because the carbon dioxide emitted during biodiesel combustion is countered by the carbon dioxide absorbed during feedstock plant development. Furthermore, biodiesel emits less hazardous pollutants, such as sulphur and particulate matter, resulting in better air quality.

Biodiesel may be made from a variety of feedstocks, such as soybean oil, canola oil, palm oil, *spirulina* oil and spent cooking oil. The feedstock used can have an influence on the sustainability and environmental impact of biodiesel manufacturing. Sustainable practises and responsible sourcing are required to ensure that biodiesel has a beneficial environmental impact.

Overall, biodiesel appears to be a potential alternative for lowering transportation's environmental effect and reducing reliance on fossil fuels.

1.2 CATALYST

Catalysts can be categorized into various types based on their nature, mechanism, and application. Here are some common types of catalysts:

catalysts are essential in the biodiesel synthesis process because they facilitate the complex chemical reactions that turn raw materials into high-grade fuel. In this field, homogeneous catalysts—such as potassium hydroxide (KOH) and sodium hydroxide (NaOH)—are mainstays. They use their strong basic qualities to speed up the

transesterification process Solid base catalysts like calcium oxide (CaO) and barium oxide (BaO) are examples of heterogeneous catalysts, which offer an alternative paradigm. These solid catalysts provide streamlined separation procedures and have the potential to cut waste because they function in different phases from the reactants. Lipases are particularly well-suited for the generation of high-quality biodiesel or for the management of fragile feedstocks because they catalyze transesterification processes with elegance and exhibit extraordinary specificity and environmental compatibility. Acid catalysts, such as sulfuric acid (H₂SO₄), have found a place in acid-catalyzed transesterification processes and are useful in the processing of feedstocks that are of lesser quality

1.3 THE SELECTION OF A HETEROGENEOUS CATALYST

The use of heterogeneous catalysts in biodiesel production offers several advantages:

- **Catalyst Separation:** Heterogeneous catalysts are typically solid and can be easily separated from the biodiesel and glycerol phases after the reaction. This simplifies the purification process, reducing the need for additional separation steps and making the production process more efficient.
- **Catalyst Recycling:** Many heterogeneous catalysts can be reused multiple times, reducing the overall cost of catalyst procurement and disposal. This recyclability is environmentally friendly and cost-effective.
- **Reduced Environmental Impact:** The ease of catalyst separation and recycling leads to less waste generation, minimizing the environmental footprint of biodiesel production. It also aligns with sustainability goals by reducing the consumption of catalyst materials.
- **Increased Safety:** Heterogeneous catalysts are often safer to handle compared to highly caustic homogeneous catalysts like sodium hydroxide (NaOH) or potassium hydroxide (KOH). This improves safety for workers involved in the production process.
- **Flexibility:** Heterogeneous catalysts offer flexibility in terms of the choice of catalyst material. Various solid acid catalysts, metal catalysts, and supported catalysts are available, allowing producers to select a catalyst that suits their

specific feedstock and process conditions.

- **Scalability:** Heterogeneous catalysts are well-suited for large-scale biodiesel production due to their ease of handling, separation, and recyclability. This makes them practical for industrial-scale operations.
- **Fewer Byproducts:** The use of heterogeneous catalysts often results in fewer side reactions and fewer undesirable byproducts, leading to higher biodiesel yields and product quality.
- **In summary,** heterogeneous catalysts are favored in biodiesel production because they simplify the separation process, enable catalyst recycling, reduce environmental impact, enhance safety, and provide flexibility for both small-scale and large-scale operations. These advantages contribute to more efficient and sustainable biodiesel production processes.

1.4 ADVANTAGE OF CATALYST

Doping zeolite, calcium oxide, and cobalt chloride as a single catalyst can result in a multifunctional catalyst with distinctive features and capabilities. The specific outcomes of such doping are determined by the catalyst composition, the dopants utilised, and the catalytic processes planned. Here are some examples of possible results and applications:

Catalytic Performance Enhancement:

Doping can improve the combined catalyst's total catalytic activity. Doping calcium oxide with cobalt chloride and zeolite, for example, might result in enhanced transesterification rates, greater biodiesel yields, and shorter reaction times in biodiesel synthesis.

Versatility:

A multifunctional catalyst of this type might be versatile and adaptive, making it appropriate for a wide range of reactions in a variety of applications. Catalysts are frequently tailored by researchers to satisfy the demands of certain industries or processes.

Selectivity Enhancement:

Doping with different elements can influence the selectivity of the catalyst, making it more suitable for specific chemical reactions. This could be beneficial in processes

where multiple reactions are competing, and selectivity is crucial.

Effects of Synergy:

The combination of zeolite, calcium oxide, and cobalt chloride may lead to synergistic effects, where the catalyst's overall performance is greater than the sum of its individual components. Synergies could result in improved catalytic activity, stability, and selectivity.

1.4.1 CaO



Fig 1.1: Calcium oxide

Calcium oxide also acts as an alkali-neutralizing agent, helping to neutralize any residual acidic compounds present in the feedstock oil. This is essential because the presence of acids can lead to undesirable side reactions and catalyst deactivation.

Calcium oxide is advantageous as a solid catalyst because it can be easily separated from the reaction mixture once the transesterification process is completed. Calcium oxide is cost-effective and readily available, making it an attractive option for small-scale biodiesel production operations.

1.5.2 Zeolite



Fig 1.2: Zeolite

Zeolite's porous structure allows it to adsorb impurities and water from the feedstock oil. This is crucial because water and impurities can negatively affect the biodiesel production process and reduce the quality of the final product. Zeolite helps improve the purity of the oil feedstock. Zeolite can be regenerated and reused multiple times and considered as a cost-effective choice for biodiesel production. Zeolite is eco-friendly towards the environment because they are solids and they won't generate waste byproducts during biodiesel production.

1.5.3 CoCl_2



Fig 1.3: Cobalt Chloride (II) hexahydrate

One advantage of cobalt chloride (II) hexahydrate is its ability to operate under milder reaction conditions compared to some other catalysts. This can lead to improved

energy efficiency and better control of the reaction. Typically, this is doped with other metal catalysts to improve the hydrogenation process in the synthesis of biodiesel rather than being used as a single compound catalyst.

1.5 TRANSESTERIFICATION

The transesterification process is a chemical reaction typically employed in biodiesel production to convert triglycerides present in vegetable oils or animal fats to fatty acid methyl esters (FAME), which are the major components of biodiesel.

The triglycerides present in the lipids react with catalysts, and methanol (alcohol) leads to the production of biodiesel and glycerol. This reaction takes place between 50°C and 70°C by using agitation to ensure the proper mixing of components to react.

After the reaction is completed, the mixture is allowed to separate, with glycerol at the bottom due to its high density and biodiesel at the top due to its lower density.

By using the transesterification process, the production of biodiesel can be economical and time-consuming, which also provides improved performance and a high cetane number. Although biodiesel emits fewer pollutants compared to diesel, it also generates pollutants during production, particularly if it is from non-renewable sources, which leads to environmental impact. Overproduction of glycerol sometimes leads to environmental waste management issues.

1.6 *SPIRULLINA* OIL – BLUE – GREEN ALGAE

- Renewable Resources: *Spirulina* is way faster and easier to grow in a variety of settings, which acts as a renewable source for biodiesel production.
- Oil content: *Spirulina* has a high oil content, which is approximately 5–10% of its dry weight, which is effective in making biodiesel.
- Reduced carbon: Diesel, which is made from *spirulina*, will emit less carbon, which leads to pollution management.
- Biodegradable: It is also a naturally degradable environment, which creates less impact on society.
- Nutrient recycling: Growing *spirulina* for oil production acts as a recycler of nutrients because it utilizes waste water and carbon dioxide, which are released

from industries and also from the environment.

- Overall, using *spirulina* oil gives economic, environmental, and social benefits, helping to promote less energy production and reduce dependence on fossil fuels.
- *Spirulina* may be produced in a variety of ecosystems, includes freshwater, brackish water, and wastewater, as well as under controlled circumstances in photobioreactors, making it adaptable to varied growth methods and locales.

1.7 METHANOL

Methanol reacts strongly with triglycerides, which are the primary components of vegetable oil, animal fats, and microalgae, which allows faster conversion to biodiesel production through the transesterification process. Methanol is reacted with a wide range of catalysts, mostly in transesterification reactions, which provides higher flexibility in catalyst selection and optimization processes. The use of methanol in biodiesel manufacturing mostly leads to a reduction in undesirable byproducts or side reactions; by doing so, it helps to increase the purity and quality of the end product. The biodiesel produced by the use of methanol, which contributes to a reduction in greenhouse gases compared to petroleum diesel, offers environmental benefits. The chemical formula for methanol is CH_3OH .

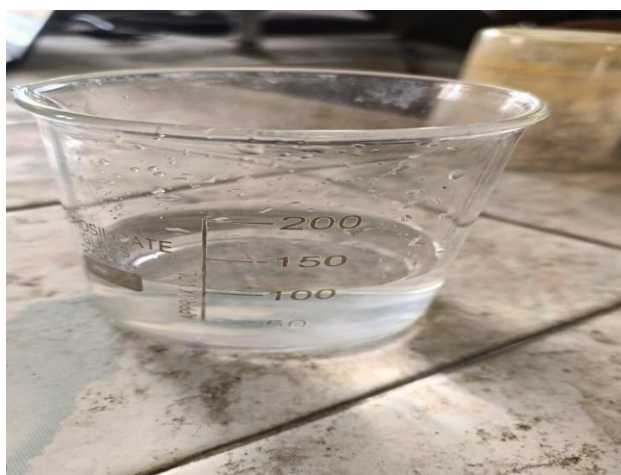


Fig 1.4: Methanol

CHAPTER 2

LITREATURE SURVEY

Sc.angulo et al. (2008) - Based on a variety of analytical techniques, this study proposes a methodology for the classification of recycled aggregates made from construction and demolition (C&D) debris. Particle size has had a greater impact on the chemical contents of mixed C&D aggregate samples than visual classification. The porous cement paste concentration in C&D aggregates is around 19.3% (w/w). This percentage, however, is much lower than the 43% found in C&D powders (0.15 mm).

Mazlan et al. (2020) - In view of their lesser impact on the environment, and simplified production and purification processes, solid base catalysts are preferred. Increasing the stability and activity of solid base catalysts remains problematic. Because of their high surface area, enhanced stability, and tunable basicity, basic zeolites, particularly two-dimensional zeolites, have emerged as appealing solid basic catalysts for triglyceride transesterification. The review demonstrates that the synthesis, characterization and catalytic performance of Zeolite Basics for TG transesterification has recently improved. The problems of basic zeolites and their development potential for biodiesel synthesis via transesterification are also emphasized.

I.lawan et al. 2020 Zeolite Material was employed as a catalytic support for calcium oxide, which was generated from discarded chicken eggshells (ES). The ultrasound-assisted approach got accustomed to create the ZM-supported calcium oxide catalyst (xCaO/ZM). The impact of several concentrations of dispersed calcium oxide ($x = 5-20$ wt%) on Zeolite and thermal treatment at various temperatures was investigated. The existence of strong active sites in a well-defined pore network indicated the presence of strong active sites suitable for the reactions of bulky chemical molecules such as triacylglycerols (TAGs).

Reza nazarifer et al. (2014) The outcome of utilizing a cobalt catalyst based on zeolite and comparing it to direct pyrolysis of *Spirulina* microalgae was explored. The study's zeolite base was HZSM-5 zeolite produced from Zeolite with a Si/Al ratio of 40. In Accordance with the manufacturer, the specific surface of zeolite was analyzed, with a pore size of 5.5 and a crystallinity of 98%. A moist incubation approach were utilized

to manufacture a cobalt metal catalyst. To do this, appropriate volumes of cobalt (II) chloride hexahydrate were mixed with the HZSM-5 base solution, and the sample was agitated on a magnetic plate (40 rpm, 25°C, 4 h) to ensure that the active metal was adsorbed to the base. Following that, the samples were dried in an oven (80°C, 18 h) and then calcinated in a furnace with a heating element.

Al Dawody et al. (2020) A process for manufacturing biodiesel from the algae *Spirulina* maximum was developed in this study, and the best operating conditions for the processes were discovered. Alkaline transesterification was used to maximize biodiesel production (86.2%), and the optimal conditions were found to be molar ratio 9:2, temperature 70°C, and mixing intensity 650 rpm. The biodiesel was tested according to ASTM standards, and the results were within permissible limits.

Mariam Murad et al. (2020) The current work sought to extract oil from *spirulina* microalgae and convert it to biodiesel via a transesterification process. diverse samples are taken from diverse sites. The transesterification method is used to create biodiesel fuel from *spirulina* microalgae oil, which was then utilized in diesel engines as an alternative fuel. Methanol and sodium hydroxide were utilized as base catalysts to reduce the raw oil's free fatty Acid concentration. The transesterification reaction is carried out at a molar ratio of (1:6) oil to methanol. The liquid is then put within the separating funnel for 12 h to separate the glycerin.

Yano Surya pradana et al. (2020) - The study says that single-stage simultaneous extraction, transesterification of *spirulina*, and using palm oil as a co-solvent of methanol reduce the number of unsaturated common fatty acid components in biodiesel. The effects of methanol-palm oil molar ratio, palm oil microalgae weight ratio, & temperature on biodiesel yield were investigated. The results showed that the best biodiesel yield was 85.28% (99.01% of the partial biodiesel yield from palm). Oil and 16.69% of the partial biodiesel yield from dry microalgae), obtained at a methanol-palm oil molar ratio of 10:1, a palm oil-microalgae weight ratio of 5:1, and at a temperature of 60°C.

Vasanth Ramasamy et al. (2013)-The extracts were analysed using gas chromatography coupled with a mass spectrophotometer (GC-MS). The dried *Spirulina* material was acquired from companies and extracted with polar solvents (ethanol and dichloromethane) and non-polar solvents (hexane). The solvent extracts

were analyzed by GC-MS on a DB-5 capillary column. GC-MS analysis revealed that the extract contains mainly fatty acid components.

Sarpal et al. (2016) - NMR was utilized to analyze the components of algal oils, including neutral (single, di, and glycerol; free fatty acids) and polar (glyceroglyco/phospho) lipids, as well as their fatty acid profile, including poly unsaturated fatty acids and GC-MS methods to investigate the biodiesel potential. Algal oils were extracted using ultrasonic solvents from lab-grown microalgal biomasses. The study found that media (modified RM6, F/2, WC), microalgae species/strains (*Chlorella vulgaris*, *Spirulina platensis*, and *Tetraselmis affchuii*), and cultivation system shape (Erlenmeyer flask, polythene tubular, or round container) all had an impact on biomass and neutral lipid productivity, as well as the quality and composition of saturated and unsaturated fatty acids.

K.Attia et al. (2014) - This study analyses the effect of reaction variables that have a significant impact on the cost of producing biodiesel from non-edible *Spirulina-Platensis* microalgae lipids using the acid-catalyzed in situ transesterification process. Experiments were designed to see how changes in the volume of reacting methanol, acid catalyst concentration, duration, temperature, and stirring affected biodiesel yield. The total lipid content of *Spirulina platensis* microalgae was found to be biomass. The weight of the byproduct glycerol was utilized to estimate the percentage yield conversion of microalgae oil biodiesel.

Tadios et al. (2019) - Biodiesel manufacturing from waste cooking oil (WCO) offers an alternative energy source for creating liquid fuels from biomass for a variety of applications. Biodiesel generation through the recycling of WCO and methanol in the presence of a calcium oxide (CaO) nano-catalyst has various advantages, including economic, environmental, and waste management. CaO nano-catalyst was manufactured using thermal decomposition and calcined at 500°C. It was then characterized using XRD and SEM techniques. The XRD measurements showed nano-scale crystal sizes with great purity, with an average particle size of around 29 nm. The SEM pictures showed the morphology of irregular forms and the porous structure of the produced nanocatalysts.

Bipul et al. (2018) - Biodiesel is considered an environmentally benign, biodegradable, non-toxic, and carbon-neutral fuel. It is derived from edible and non-edible oil feedstocks, as well as other triglyceride sources. Biodiesel production is determined by the availability of a specific feedstock and the cost of the necessary raw materials. Biodiesel is primarily created using the transesterification process with an appropriate catalyst, ideally a heterogeneous catalyst, which is more advantageous in terms of reusability, recovery, product purity, and production cost. Several reactors are being designed to create cost-effective biodiesel at the commercial level. The most recent trend in biodiesel synthesis is the use of machine learning (ML) techniques to optimize the process parameters.

Tesfa et al. (2010) - Biodiesel is a possible non-toxic, biodegradable alternative fuel for transportation. Nonetheless, biodiesel's increased viscosity and density cause some serious difficulties when utilized in an unaltered engine. Keeping this in mind, this research has been directed toward two goals. The initial goal is to determine how temperature affects density and viscosity in a range of biodiesels, as well as to build a relationship between density and viscosity for different biodiesels. The second goal is to explore and quantify the impacts of density and viscosity of biodiesels and their mixes on various components of the engine fuel delivery system, such as the fuel pump, fuel filters, and fuel injector.

Canacki et al. (2007) - Waste cooking oils, restaurant grease, and animal fats are potential biodiesel feedstocks. These low-cost feedstocks account for one-third of total fats and oils produced in the United States, although they are currently used mostly for industrial purposes and animal feed. Feedstock qualities are critical throughout the early stages of research and manufacturing. Free fatty acids and moisture hinder transesterification efficiency when turning these feedstocks into biodiesel. As a result, this study was done to investigate the levels of these pollutants in feedstock samples from a rendering factory. Free fatty acid levels ranged from 0.7% to 41.8%, and moisture from 0.01% to 55.38%.

Zhou et al. (2013) - Algae biodiesel is a potential but costly alternative fuel to petroleum diesel. To overcome cost constraints, extensive cost evaluations are required. According to a decade-old cost analysis by the U.S. National Renewable

Energy Laboratory, algal biodiesel costs between \$0.53-0.85/L (2012 USD values). However, the costs of land and transesterification were only loosely approximated. This study included an updated complete techno-economic analysis with streamlined processes and improved cost estimates. The updated algal biodiesel costs were calculated using the most recent process improvements, vendor quotations, government databases, and other relevant data sources, and the final biodiesel costs may vary.

Ghiaci et al. (2010) - Biodiesel was created by transesterifying canola oil with methanol in the presence of strongly Brønsted acidic ionic liquids based on 1-benzyl-1H-benzimidazole. The influence of reaction temperature, type and amount of catalyst, molar ratio, and reaction time were examined. Under the optimized reaction conditions, the 4B ionic liquid has the maximum catalytic activity and recyclability. Thus, this ionic liquid is capable of catalyzing the transesterification of canola oil to its methyl esters in 5 h with yields of more than 95%.

CHAPTER 3

AIM AND SCOPE

3.1 AIM

- To establish a sustainable and an eco-friendly method for synthesis biodiesel.
- To synthesis a Catalyst to speed up the reaction time then better yield of biodiesel.
- To synthesis Calcium oxide from demolition debris which acts as waste management.
- To integrate the synthesized CaO with zeolite then further the complex is incorporated with CoCl_2 to form catalyst.
- To extract oil from *spirulina* or blue-green algae and further use it for biodiesel production.
- Then it is subjected to a transesterification process with methanol and oil to produce biodiesel
- Then the biodiesel is water washed, and the byproducts(glycerol) are removed.

3.2 SCOPE

- Waste management - CaO extracted from demolition debris for catalyst integration.
- *Spirulina* is an algae that may be cultivated even in home and can also be cultivated in large scale
- biodiesel is safer to use and less harmful compared to fossil fuels in terms of emission
- Usage of biodiesel maintains Low rate of greenhouse gases (CO , HC , CO_2 , NO_x) generation
- The crude glycerol is produced as a byproduct during biodiesel production which can be utilized as lubricants
- The use of biodiesel in diesel engines doesn't requires many alterations.

CHAPTER 4

MATERIALS AND METHODOLOGY

4.1.1. MATERIALS REQUIRED

- Calcium oxide (CaO) extracted from demolition debris
- Zeolite
- Cobalt (II) chloride hexahydrate
- Distilled water
- Methanol
- *Spirulina* oil
- 0.1N NaOH solution.
- 10g oil (expected acid value {1-4}).
- 50ml ethanol.
- Phenolphthalein indicator.

4.1.2 APPARATUS REQUIRED

- Beaker
- Magnetic stirrer
- Ultrasonicator
- Muffle furnace
- Spatula
- Hot air oven
- Thermometer
- Round bottom flask
- Condenser
- Filter paper
- Separation funnel

4.2 METHODOLOGY

4.2.1 Preparation of CaO from Demolition Debris

- Crush the demolition debris into smaller pieces if necessary in order to improve the surface area for efficient extraction.
- Insert the crushed debris into the furnace: Make sure there is enough ventilation for the fuel to burn.
- Whether vital to improve the furnace to between 900 and 1,000°C (1,652-1,832°F). This temperature range is enough to breakdown calcium carbonate thermally into calcium oxide & carbon dioxide.
- Calcium carbonate (CaCO_3) $\rightarrow$ CaO (calcium oxide) + CO_2 (carbon dioxide)



Fig 4.1: Hot air oven



Fig 4.2: Muffle Furnace

- Collect the Calciumoxide. CaO will be formed as the demolition debris heats up. Collect the CaO as it forms in a crucible or container.

- After gathering enough calcium oxide, switch off the furnace and let the CaO to cool until it reaches room temperature.



Fig 4.3: Magnetic stirrer

- Transfer the extracted calcium oxide to an appropriate storage container to be kept. CaO should be maintained in a dry atmosphere to reduce moisture absorption since it reacts with water fast to form calcium hydroxide (Ca(OH)_2).

4.2.2 Doping of Calcium oxide and zeolite



Fig 4.4: Ultra sonicator

- Zeolite was incorporated to calcium oxide (CaO) by the impregnation method of doping. Zeolite and calcium oxide were weighed in this method at a 1:1 ratio (10g each).
- Fill a beaker with 200 ml of distilled water next. Start the magnetic stirrer at a set temperature 80°C and speed of 100 rpm, add 10 g of zeolite and 10 g of calcium oxide, and continue stirring for 2h or until the calcium oxide is

completely attached to the active sites of the zeolite. Then, turn the stirrer off. The beaker was placed in the ultrasonicator, which was



Fig 4.5: Muffle furnace

- Operating for 15 min at 40°C, to achieve the strong binding of zeolite and calcium oxide.
- After that, the water was transferred into a Petri plate and filtered using filter papers. The sample was positioned in a oven set at 125°C for three hours to completely dry it out. The material was then transferred to a sealed pot so that no air could enter. After the closed pot was placed inside the muffle furnace, the process of calcination was carried out there for four hours at a temperature of 600°C. After that, the sample was removed from the pot.

4.2.3 Incorporation of Synthesized complex with CoCl_2



Fig 4.6: Magnetic stirrer with sample

- Final catalyst was achieved by doping the synthesized Zeolite and calcium oxide with Cobalt (II) chloride hexahydrate, in this process doped sample

(zeolite and calcium oxide) and Cobalt (II) chloride was weighed about 1:1 ratio of 10g



Fig 4.7: Sample after filtration

- Distilled water which was 200 ml then added to the beaker, and a magnetic stirrer was set to operate at 80°C and 100 rpm. After a few min, weighed doped sample (CaO and zeolite) were added to the beaker, and the stirring was continued for another few min. Next, weighed cobalt (II) chloride hexahydrate was added, and the mixture was continued for two hours to create a strong bond between



Fig 4.8: Muffle furnace

- After using the ultrasonicator, the sample's water was filtered out using filter paper, transferred to a Petri plate dish, and then kept in a hot air oven at 125°C for three hours to completely remove the sample's water molecules and create a dry sample. The sample was set up in a sealed container for the calcination process, in which no air should pass, and the sealed container was then placed inside a muffle furnace and heated to 400°C for three hours and thirty min. After the calcination process, the sample was removed, and the catalyst was sent for characterization to determine the catalyst's nature



Fig 4.9: Obtained end catalyst

4.2.4 Catalyst characterization

A form of porous material is formed by doped catalyst that contains three chemical compounds. It is necessary of understanding the characteristics of catalyst so can maximize the performance Fourier Transform Infrared Spectroscopy (FTIR) is a method used to analyze the functional group present in the doped catalyst of CoCl_2 , CaO and zeolite it is analyzed by equipment called FTIR spectrometer . To analyses this the catalyst sample is kept in spectroscopy at vacuum then the infrared light is passed through the sample then the wavelength was calculated by absorption of Infrared rays by sample. Each peak in spectrum depends on specific vibration on the bond with molecules. The condition to analyses is to keep the optics clean so no other air particles interact FESEM WITH EDX: The shape and particle size of the compounds or porous material is analyzed using field emission scanning electron microscopy. The sample is kept in vacuum then electron beam is accelerated using high voltage and passed through the electromagnetic lenses then the beam strike with

atoms in the material and after interaction various signals are emitted .It is achieved in ultra-high vacuum condition X-Ray diffraction is the method that is used to analyze whether the prepared catalyst is in crystalline state or amorphous state .The x-ray (monochromatic ray) is passed through the sample and it is interacts with atoms of crystal lattice and it is depends on periodic arrangement . The angle is calculated using Bragg's law ($n = 2d \sin \theta$), the sampling is scanned using 2θ and its range from 10° to 60° .The wavelength of Co(II) complex is $1.54\text{\AA}$.

4.2.5 Method to cultivate *Spirulina*

- To develop, *spirulina* algae make a growth medium from nutrients in water. For best growth, *spirulina* requires an alkaline environment.



Fig 4.10: *Spirulina*

- Then, to maximise exposure to sunlight, we used a large, shallow container with a large surface area.
- Then introduce a live *spirulina* culture in a prepared growth medium.

- To grow a *spirulina*, temperature is maintained between 30 and 35°C, and pH is to be maintained between 8 and 11.



Fig 4.11: Spirulina harvesting

- Then stir a water container 2-3 times a week. It takes 10–14 days to grow a *spirulina*.
- Adjust the lighting if the *spirulina* looks yellow or olive green.
- Clean the tank and remove any white or yellow *spirulina* clumps

4.2.6 Harvesting the *spirulina*



Fig 4.12: Spirulina processing

- Scoop out the *spirulina* when the pH stays at 10 for 24h
- Filter and rinse your *spirulina* through a fine strainer cloth.

4.2.7 .Extraction of oil

Mechanical extraction: In this method, the *spirulina* or blue-green algae is extracted using mechanical equipment a screw press, and then, for further purity, it is heated or refined, in which water molecules are removed.

4.2.8. DETERMINATION OF ACID VALUE

The acid value of an oil is a measure of its free fatty acid composition. It is an important factor in determining the quality and reliability of oils. A higher acid value in oil indicates poor quality due to the increase in free fatty acids in lipids or oil, which will reduce the shelf life of oil. Monitoring acid values during the process helps in production with consistent quality; it also helps in controlling factors like temperature, processing content, and moisture content. Oil with a low acid value helps to have better stability.

Procedure

- Ethanol is neutralized with NaOH solution with phenolphthalein indicator.
- Neutralized ethanol is added to the flask contain oil and heated (until the sample gets dissolves completely).



Fig 4.13: Acid value determination

4.2.9 Determination of Saponification Value

Procedure

In this experiment, a sample of 5g of oil is measured and mixed with 50 ml of 4% ethanolic KOH solution, while another sample consists of only 50 ml of 4% KOH solution. These samples are then heated separately on two different heating plates, with distillation columns connected to each sample. The heating process continues for 30 min until the ethanol begins to condense. It's crucial to observe that the oil sample doesn't form two layers during heating, ensuring proper mixing and reaction. Following this, titration is initiated using 0.5 N of HCl for each sample separately, with the burette values being noted throughout the process. This experimental setup allows for the determination of the acid value of the oil sample, providing valuable insights into its quality and composition. Ensure a sample of 5g of oil and mix it with 50 ml of 4% ethanolic KOH

$$\text{Saponification value} = (28.05 * (v_b - v_s))/w_s$$

Molecular wt. of oil

$$\text{Molecular wt. of oil} = (56.1 * 1000 * 3)/(s.v - a.v)$$

4.2.11 Transesterification

- The method involved in this process is transesterification, in which oil to methanol is taken in different ratios and the catalyst weighed in different weight percentages.



Fig 4.14: Oil preheating

- By the optimization technique, it is confirmed that the ratio is 1:12 with a temperature of 60°C and run hours of 120 min.

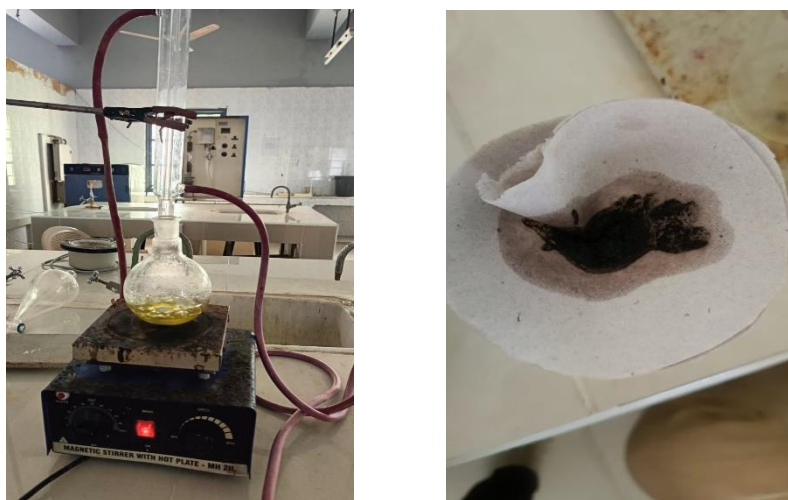


Fig 4.15: Transesterification

- By the preferred perfect ratio, the oil is taken as 50 ml and the methanol is taken as 31.69 ml, weight of the catalyst is 4.5wt% points, so it is 3.51 g.



Fig 4.16: Separating funnel

- The weighed catalyst is mixed with measured methanol and agitated, which ensures perfect mixing. Then the oil is heated to remove water molecules.



Fig 4.17: Glycerol

- The round bottom setup is done with a stirrer, then the oil and mixed solution of methanol are started to run for 120 min at a temperature of 60°C.

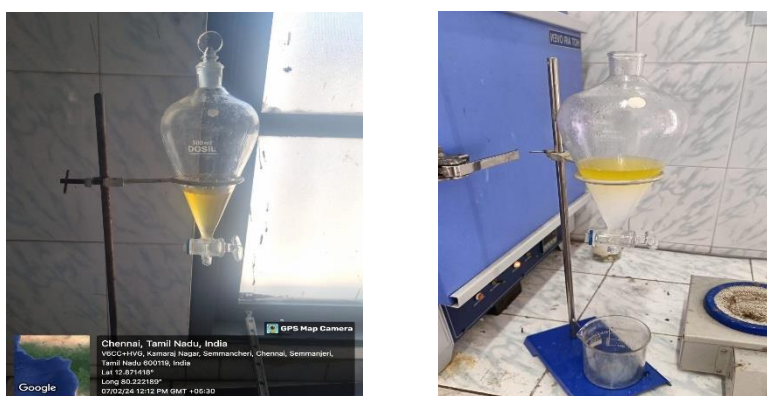


Fig 4.18: Water washing

- Then, after the reaction is done, the catalyst is separated and the biodiesel is transferred to the separation funnel, in which glycerol forms at the bottom and biodiesel comes at the top of the glycerol due to its low density.



Fig 4.19: Bio diesel

- Then the glycerol is separated, further diesel is water washed to remove impurities, and then the produced biodiesel is subjected to further tests to ensure methyl ester formation.

$$\text{Yield} = (\text{Mass of diesel} / \text{Mass of oil}) * 100$$

4.2.13 Bio diesel characterization

Analyzing characterization of biodiesel is necessary to find the applicability and quality as a fuel, such as density, viscosity, pour point, flash point and cloud point. Gas chromatography Mass spectroscopy (GC-MS) is used to analyze the compounds present in acid such as saturated or unsaturated fatty acid .It is performed by taking a sample of biodiesel and mixing it with solvent (hexane) which has low boiling point then allowed to vaporize and the gas is sent to long column of stationary phase where some compounds interacts in that phase and helium acts as carrier gas which allows to flow the gas through the phase at different rates .Then it's sent to mass analyzer where it's separated based on mass to charge ratio (m/z) .Then the acid compounds are found by intensity of peaks .It is done by quadrupole mass spectrometer.

CHAPTER 5 RESULTS AND DISCUSSION

5.1 CHARACTERISATION

5.1.1 FTIR

Table no. 5.1 Catalyst FTIR analysis

CaO	Zeolite	Catalyst	Compounds
3640.95	3690.12	3366.14	-
2367.19	2357.55	2361.41	CaO
1407.78	1633.41	1636.3	Zeo
1145.51	1392.35	1414.53	CaO
948.806	911.201	984.482	CoCl ₂
875.524	789.707	871.667	CaO
709.676	684.606	658.571	CoCl ₂
507.187	530.328	554.434	Zeo

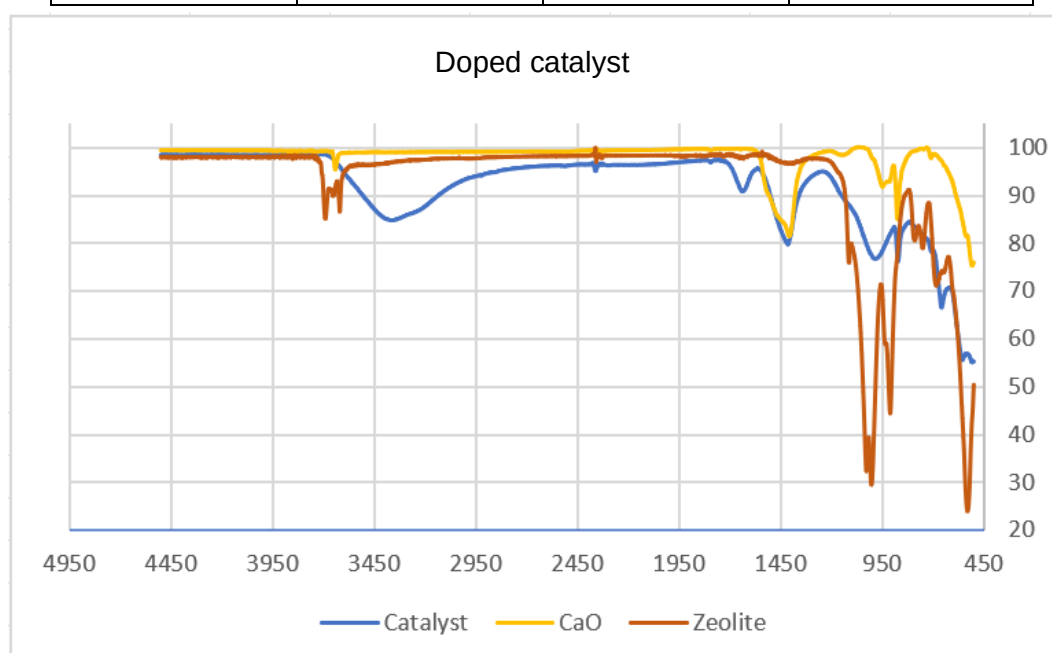


Fig 5.1: Doped catalyst FTIR results

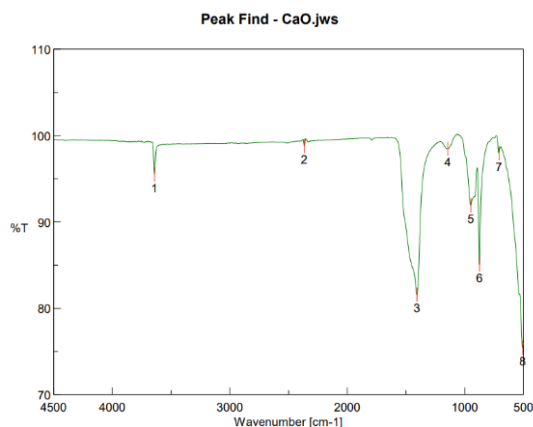


Fig 5.2: FTIR – CaO

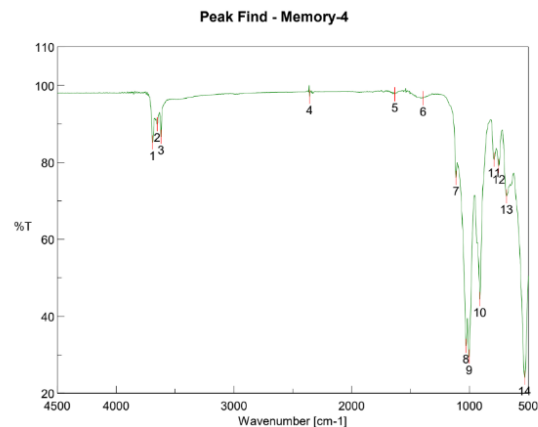


Fig 5.3: FTIR – Zeolite

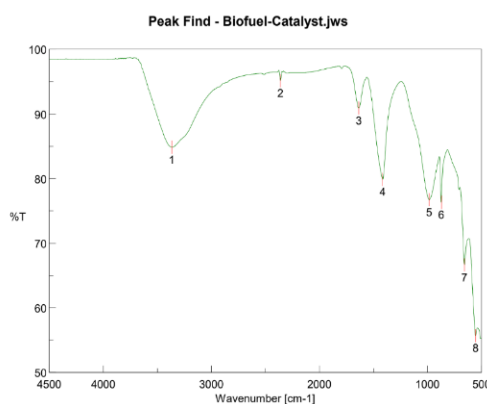


Fig 5.4: FTIR -catalyst

The peak level in the graph (Fig : c.1) at 1414.53 cm^{-1} and 2361.41 cm^{-1} shows the appearance of Calcium oxide, which is a feature of the C-O bond and demonstrates a bond between the oxygen atom of carbonate and the calcium atom.

According to FTIR spectrum in the graph the peak level at 1636.3 cm^{-1} and 554.53 cm^{-1} indicates the occurrence of zeolite SiO_4 and other three peaks 1392.53 cm^{-1} , 911.201 cm^{-1} and 789.707 cm^{-1} shows the vibration of Si -O - Al then the last peak 3690.12 cm^{-1} shows the O-H bond caused by absorbed water.

Then the last Spectrum in the graph the peak level at 984 and 658 indicates the emergence of CoCl_2 and therefore adding compound like Co doesn't cause any notable changes

5.1.2 EDAX

Synthesized catalyst

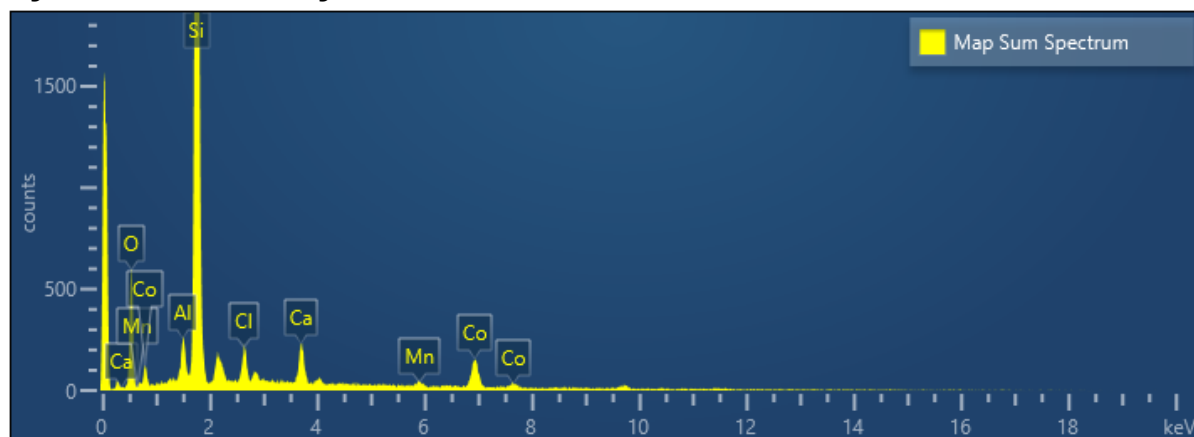


Fig 5.5: EDAX of catalyst

Table no.5.2 EDAX

Map Sum Spectrum Element	Line Type	Weight %	Weight % Sigma	Atomic %
O	K series	30.68	0.59	46.44
Al	K series	2.15	0.13	1.93
Si	K series	49.50	0.51	42.68
Cl	K series	3.17	0.16	2.17
Ca	K series	4.07	0.17	2.46
Mn	K series	1.09	0.19	0.48
Co	K series	9.34	0.37	3.84
Total		100.00		100.00

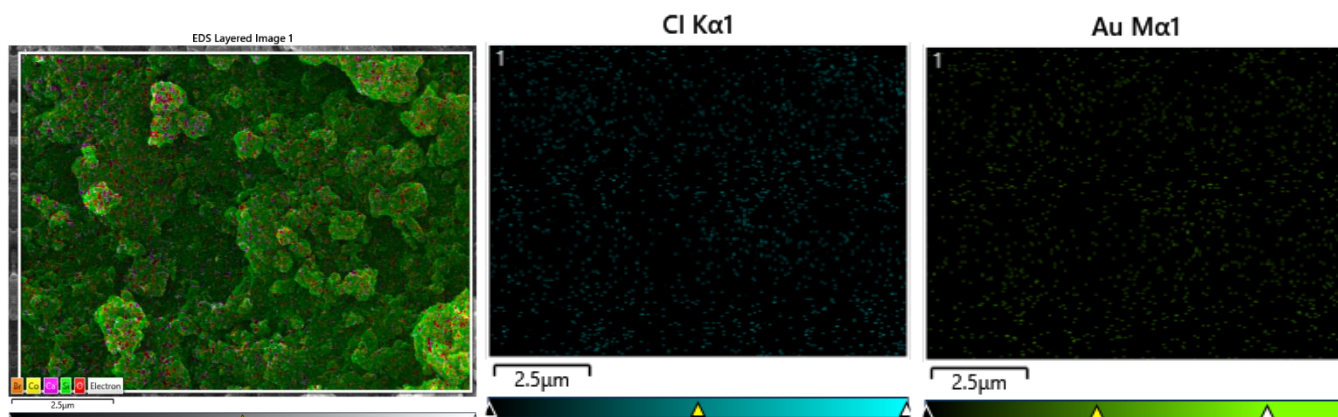


Fig 5.6: EDS colour graph

EDX analysis measures a sample's elemental composition by analyzing the X-rays it releases after being exposed to high-energy electrons or X-rays. This method is commonly employed with scanning electron microscopy and is widely used in materials science, biology, and geology.

The appearance of Calcium (Ca), Oxygen (O), Cobalt (Co), Chloride (Cl), Silica (Si), Manganese (Mn) and aluminium (Al) at different peaks in EDS analysis shows the usage of three distinct compounds in synthesized catalyst.

From the above graph it's analyzed that the silica present in the catalyst has high counts compared to other compounds and also analyzed that all the compounds present are in the k series line type, then their weight % also verified among that silica has highest which is 49.50% and followed by oxygen 30.68 then least is manganese which is 1.09 weight %.

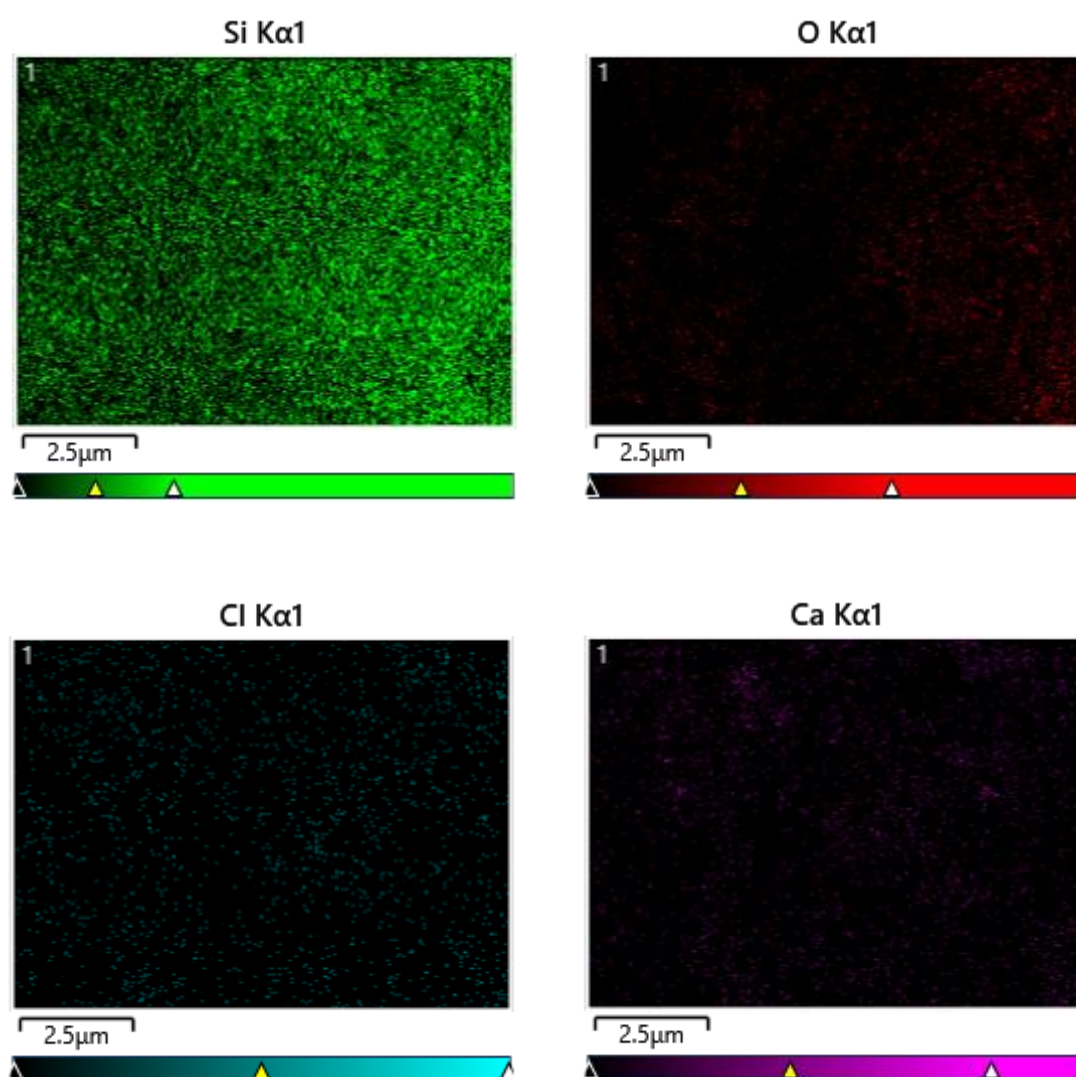


Fig 5.7: EDS colour graph

5.1.3 FESEM

Synthesized catalyst

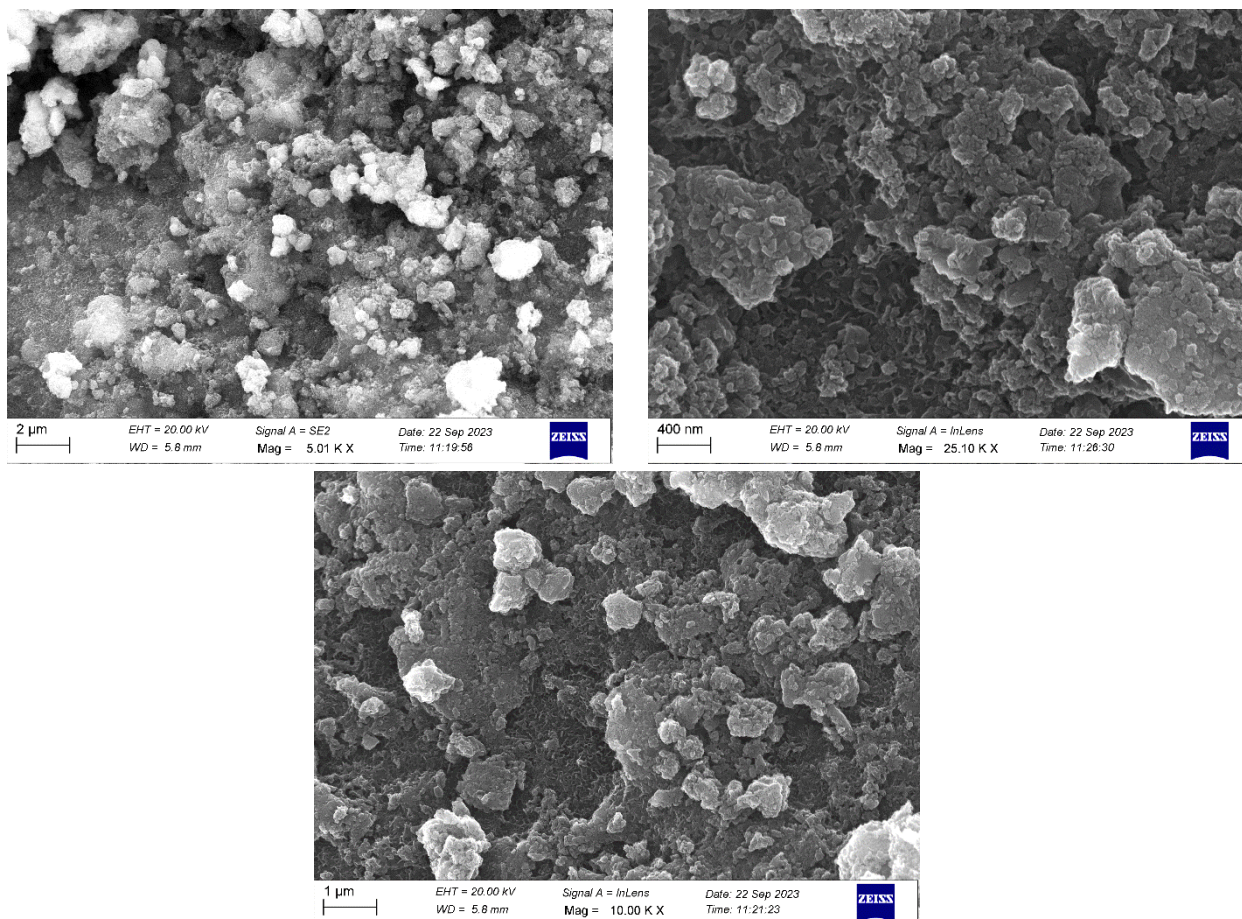


Fig 5.8: FESEM of catalyst

The FESEM analysis of synthesized catalyst which consists of doped (Calcium oxide, zeolite and Cobalt(II) chloride hexahydrate), The FESEM analysis in the above picture shows the heterogeneous structure of catalyst.

Field Emission Scanning Electron Microscopy (FESEM) is used to find the size, shape, and distribution of catalyst particles because of their catalytic activity and selectivity.

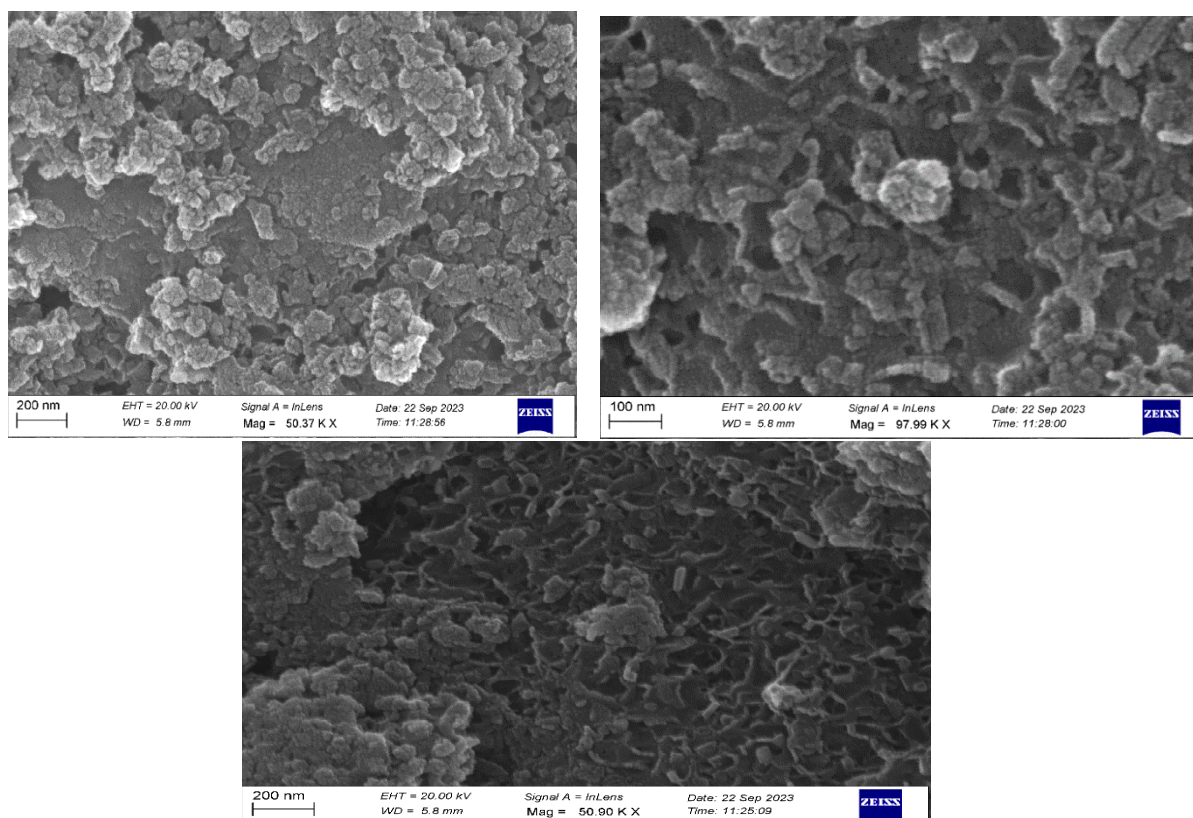


Fig 5.9: FESEM of catalyst

Catalysts with a higher surface area are more active compared to those with a smaller surface area. This is because the higher surface area of the particle gives more sites for reactant molecules to absorb and attract.

By the above Field emission scanning electron microscopy images, it analyzed that the pores sizes of compounds in which they are analyzed at different magnifications. At mag 5.01 k X it is noted that the pore size is 2 μm and at 25.1 K X mag the pore is detected as 400 nm. By this it is confirmed that increasing a magnification range increases the pore view of compound.

5.1.4 XRD

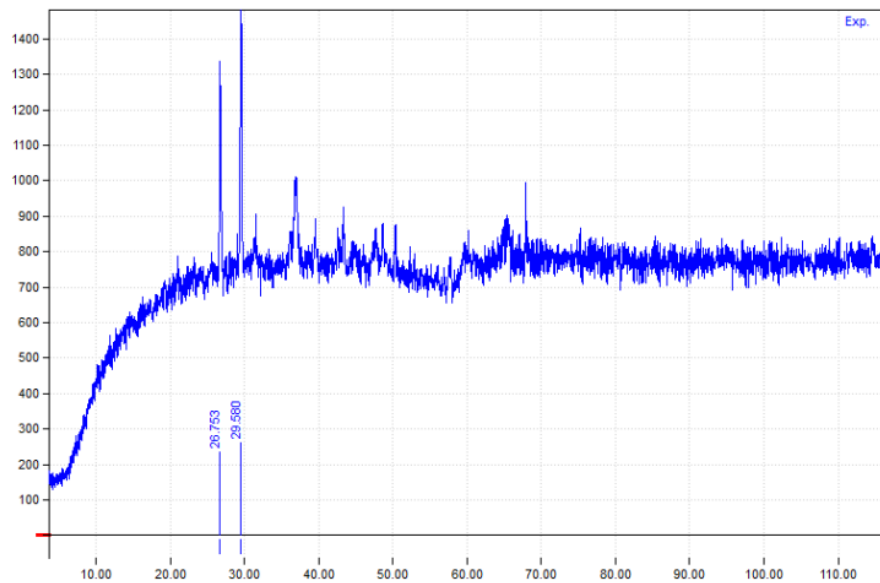


Fig 5.10: XRD of catalyst

Peak List

No.	2theta [°]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM
1	26.75	3.3295	816.15	235.62	0.2657
2	29.58	3.0174	1000.00	262.09	0.2412

Integrated Profile Areas

Based on calculated profile

Profile area	Counts	Amount
Overall diffraction profile	2798666	100.00%
Background radiation	2533361	90.52%
Diffraction peaks	265305	9.48%
Peak area belonging to selected phases	0	0.00%
Unidentified peak area	265305	9.48%

Peak Residuals

Peak data	Counts	Amount
Overall peak intensity	498	100.00%
Peak intensity belonging to selected phases	348	70.00%
Unidentified peak intensity	149	30.00%

One of the primary advantages of XRD analysis is its capacity to distinguish between different crystal forms and identify unknown substances. XRD analysis can provide quantitative information on the proportion of each phase in a sample. From the above graph of x-ray diffraction it is analyzed that at $2[\theta^\circ]$ 26.75 and 29.58 shows the increase in number of counts and intense peak which is 1400 and 1300 counts. And also analyzed that overall peak intensity has 498 counts in which 348 counts belongs to selected phase and 149 counts belongs to unidentified peak intensity.

5.1.5. Post studies of catalyst (FTIR)

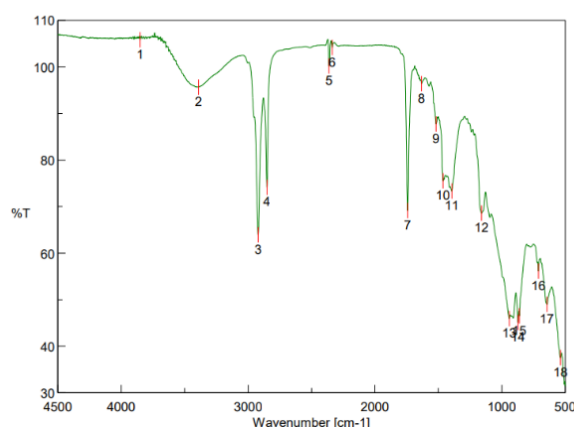


Fig 5.11: FTIR of catalyst post studies

The supplied FTIR spectrum offers important information about the sample's molecular composition. The signal at 2920.66 cm^{-1} corresponds to O-H stretching, indicating the presence of absorbed water and perhaps oxygen from calcium oxide (CaO) in the sample. This peak represents the interaction of water molecules with the material, which is important for understanding its stability and reactivity. Furthermore, the signal at 1742 cm^{-1} indicates C-O stretching, implying the presence of ester linkages, most likely originated from triglycerides in the biofuel. This verifies the presence of ester, an important component in biodiesel manufacturing. Furthermore, the peak at 1463 cm^{-1} indicates O-H stretching of a molecule, which could be due to residual moisture or hydroxyl groups in the sample.

5.1.6. Post studies of catalyst (EDAX)

Post-EDAX investigations of catalyst testing are useful for determining the catalyst's elemental composition after it has undergone reactions. These studies can provide light on changes in catalyst composition, detect potential catalyst deactivation or poisoning, and help optimize catalyst performance. And also used to find whether any compounds are mixed during transportation process. In this given post studies graph it is analyzed that all the compounds are similar has before reaction but there is slight change in counts of compounds. Calcium has large number in counts in after studies compared to before studies and all the compounds present in after studies are in k series line type and carbon has large number in weight percentage which is 42.15% and followed by oxygen 24.59 % and least is manganese which is 1.19 %. But silica has large decrease in weight % compared to before studies.

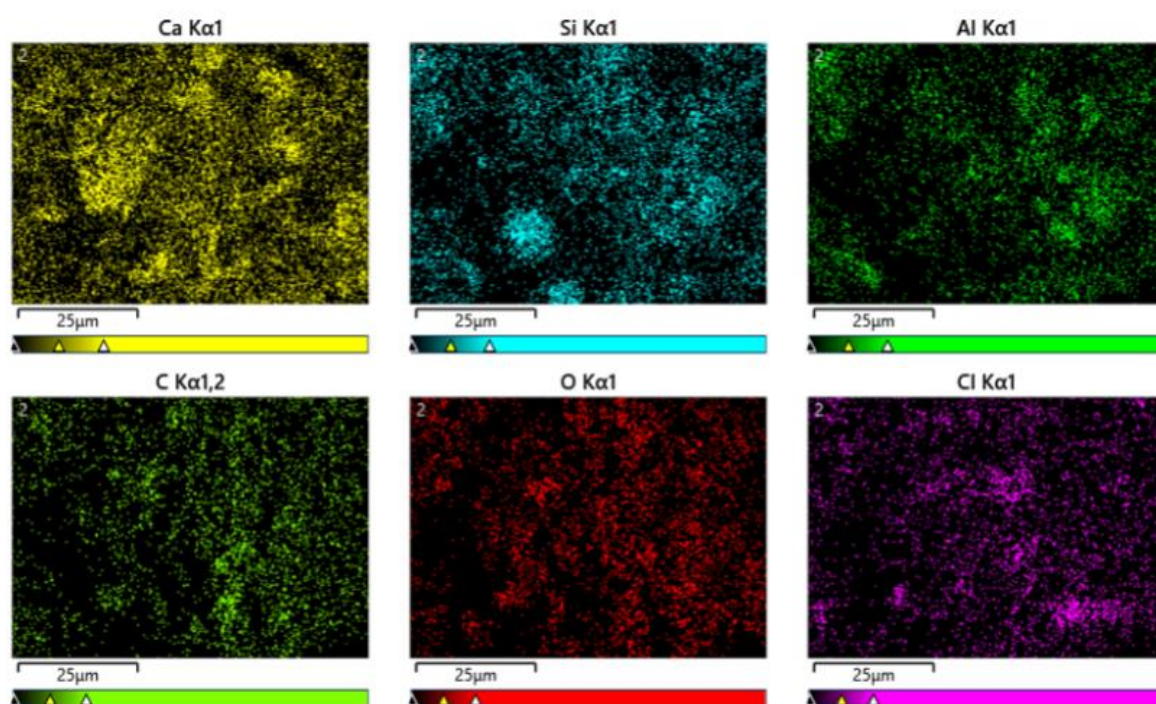


Fig 5.12: EDS post colour graph

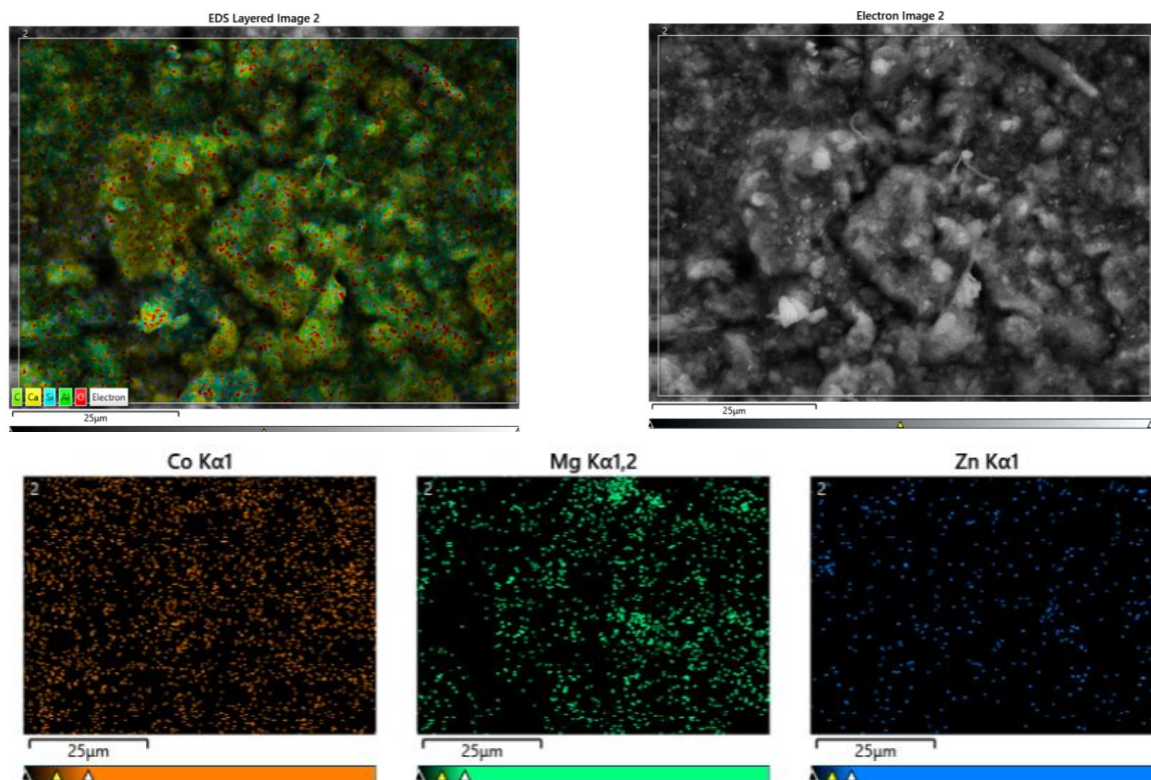


Fig 5.13 EDS post colour graph

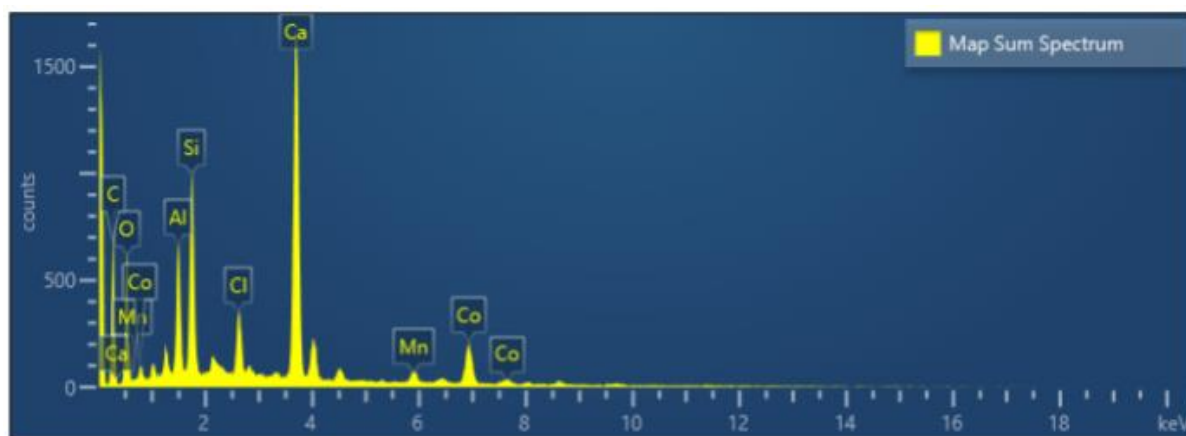


Fig 5.14 EDAX of post catalyst

Table no.5.3 EDAX of post catalyst

Map Sum Spectrum Element	Line Type	Weight %	Weight % Sigma	Atomic %
C	K series	42.15	0.79	59.24
O	K series	24.59	0.60	25.94
Al	K series	3.61	0.11	2.26
Si	K series	5.09	0.12	3.06
Cl	K series	2.02	0.08	0.96
Ca	K series	15.21	0.26	6.41
Mn	K series	1.19	0.11	0.37
Co	K series	6.12	0.22	1.75
Total		100.00		100.00

5.1.7. Post studies of catalyst (FESEM)

The below images demonstrate the post-FESEM studies for catalysts. The necessity of this post-study is to analyse whether the pores or active sites of the catalyst got enclosed, and it's confirmed that the pores or surface of the catalyst got lit up due to the reaction between methanol and *spirulina* oil, which ensures that the catalyst is involved in the reaction, is filtered, and can further be used for other reactions. By this above Field emission scanning electron microscopy (FESEM) image it is analyzed that the pore size of compound is 10 μm when it's seen at 1.00 K X magnification and also analyzed same pore size at 1.50 K X mag. Then at 2.0 K X mag it is noted 5 μm pore size of compound.

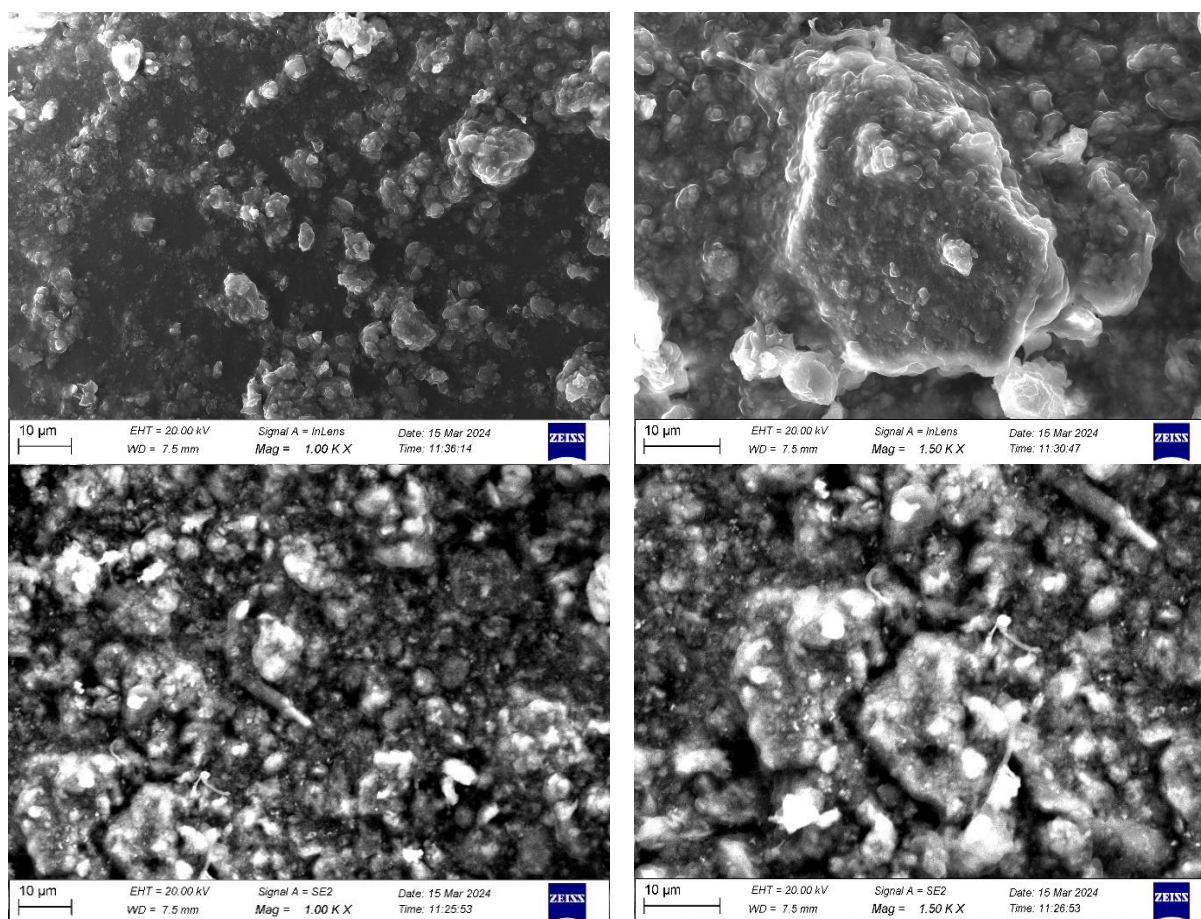


Fig 5.15 FESEM of catalyst Post studies

5.1.8. GC/MS- Gas Chromatography/ Mass Spectrometry of *spirulina* oil

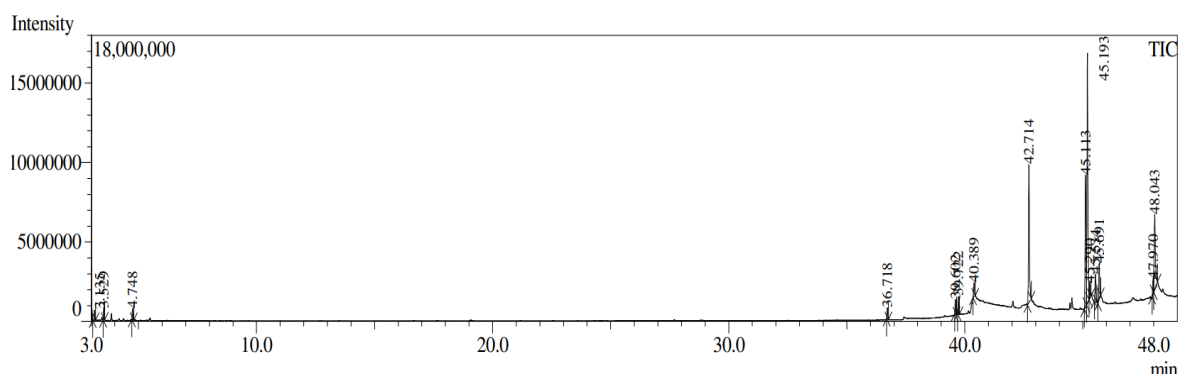


Fig 5.16 GC/MS spirulina oil graph

Table no.5.4.GC/MS spirulina oil Peak Report

Peak Report TIC				
Peak#	R.Time	Area	Area%	Name
1	3.135	1315338	0.97	BENZENE, 1,2-DIMETHYL-
2	3.529	1426987	1.05	Pentane, 3-ethyl-2,4-dimethyl-
3	4.748	1535254	1.13	3-HEXEN-2-ONE
4	36.718	1493777	1.10	Hexadecanoic acid
5	39.602	1975650	1.45	9,12-Octadecadienoic acid (Z,Z)-, methyl est
6	39.722	2308153	1.70	9-Octadecenoic acid
7	40.389	2287166	1.68	9-Octadecenoic acid, (E)-
8	42.714	24785754	18.21	Glycidol stearate
9	45.113	22217853	16.32	ETHYL (9Z,12Z)-9,12-OCTADECADIENO
10	45.193	43972639	32.30	9-Octadecenoic acid, 1,2,3-propanetriyl ester
11	45.290	2472176	1.82	14-METHYL-8-HEXADECYN-1-OL #
12	45.534	4519182	3.32	Glycidol stearate
13	45.691	5883606	4.32	HEXADECANOIC ACID, 2-HYDROXY-1-
14	47.970	2526992	1.86	9,12-OCTADECADIENOIC ACID (Z,Z)-, 2
15	48.043	17422284	12.80	9-Octadecenoic acid (Z)-, 2,3-dihydroxyprop
		136142811	100.00	

GCMS stands for gas chromatography. Mass spectroscopy, which is used to find unique components present in the compounds. The above result for *spirulina* oil demonstrates the presence of octadecadienoic acid and hexadecenoic acid.

By the above table it is noted that octadecadienoic acid which is also called as Linolelaidic acid and Hexadecenoic acid (palmitic acid) is an unsaturated fatty acids because in linolelaidic acid it contains two double bonds in its carbon chain. Its structure consists of a carboxylic acid group (COOH) at one end and an 18-carbon chain with two double bonds at positions 9 and 12 .If the fatty acid contains one or more double bond in carbon chain it is said to be unsaturated fatty acid and also noted that highest of 32.30% octadecadienoic acid and lowest is 1.10% Hexadecenoic acid then 0.97% of benzene.

5.1.9. Transesterification result

After an examination of the characteristics of oil and the fatty acids it contains, a transesterification reaction occurs. Different ratios of oil and methanol are used in this reaction, and the catalyst is weighed in accordance with those ratios. Variable ratios are experimented and it is confirmed that 1:12 ratio of oil to methanol with the temperature of 60°C and run time of 90 min. The round bottom flask is set up in the magnetic stirrer then the oil is heated then the weighed methanol and catalyst is mixed as a sample. It is mixed with heated oil and started to run for 90 min until the reaction takes place. For further better yield, time parameter is varied and analyzed. After the analysis biodiesel sample is transferred to separation funnel to remove glycerol from biodiesel after removal of glycerol diesel is waterwashed to remove impurities and subjected to diesel analysis tests

$$\text{Saponification value} = ((28.05 * (60.2 - 19.3))/5.2$$

$$\text{Saponification value} = 256$$

$$\text{Molecular wt. of oil} = 168300/254.94$$

$$\text{Molecular wt. of oil} = 660.15$$

Biodiesel calculation

$$\text{Molecular weight of oil} = 660.15 \text{ g/mol}$$

$$\text{Molecular weight of methanol} = 32.04 \text{ g/mol}$$

$$\text{Density of oil} = 0.863 \text{ g/cc}$$

$$\text{Density of methanol} = 0.792 \text{ g/cc}$$

$$1 \text{ mol of fatty acid} = 12 \text{ mol of methanol}$$

$$1 \text{ mol} * 660.16 \text{ g/mol} = 12 \text{ mol} * 32 \text{ g/mol}$$

$$660.16 \text{ g} / 0.863 \text{ g/ml} = 384 \text{ g} / 0.792 \text{ g/ml}$$

$$764.7 = 484.84$$

$$50 \text{ ml oil} = 31.69 \text{ ml methanol}$$

$$\text{Mass of oil} = 50 * 0.863 = 43.15$$

$$\text{Mass of methanol} = 31.69 * 0.792 = 12.55$$

$$\text{Total mass} = 68.249$$

$$\text{Catalyst} = (5 * 68.249) / 100 = 3.4 \text{ g}$$

$$\text{Yield \%} = (40.5 / 50) * 100 = 81\%$$

5.1.10. One variable at a time Optimization

One variable at a time (OVAT) optimization is a method used in experimental design and optimization processes. In OVAT, each variable is altered individually while keeping all other variables constant, and the impact of each variable on the system's performance or output is observed. This method allows for a systematic examination of how changes in each variable affect the overall outcome, helping to understand the individual contributions of each variable and identify the optimal values for them.

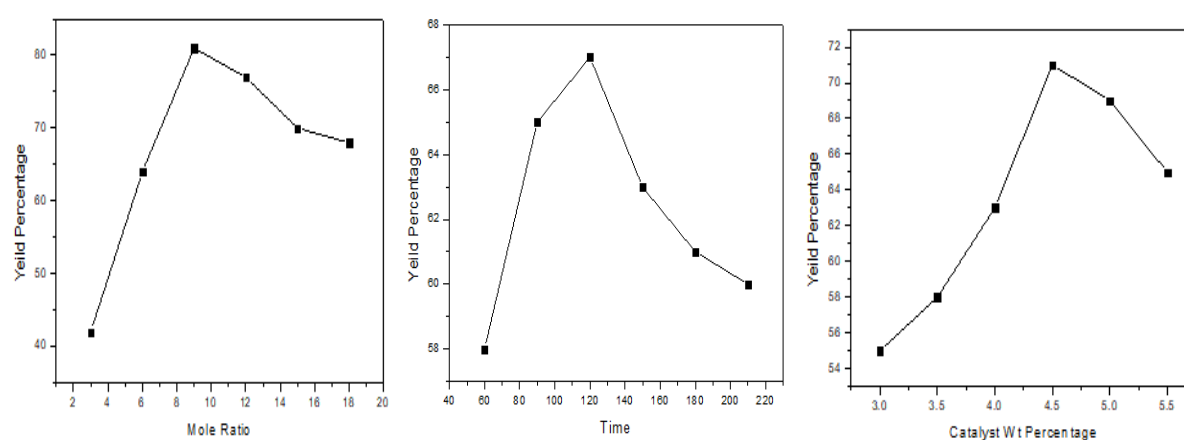


Figure 5.17 OVAT Optimization image

From the above graph it is noted the best yield which attained during one variable change in parameter. The graph denotes that experimental change in mole ratio and calculated the better yield and it is noted that ratio at 1:12 gives the better yield of 81% and there's a decrease in yield while increase ratio. Then also noted the next variable change in time to yield and analyzed the better yield at run time of 120 min and next parameter change has catalyst wt% in which there as analysis for change in catalyst wt% to yield and also noted that better yield at 4.5 wt%. Finally, the experimental graph concludes that the biodiesel production in 1:12 ratio at 60°C and run time of 120 min with the catalyst of 4wt% gives the better yield of 81% and there's a decrease in yield at different ratios.

5.1.11. GC/MS- Gas Chromatography/ Mass Spectrometry(bio diesel)

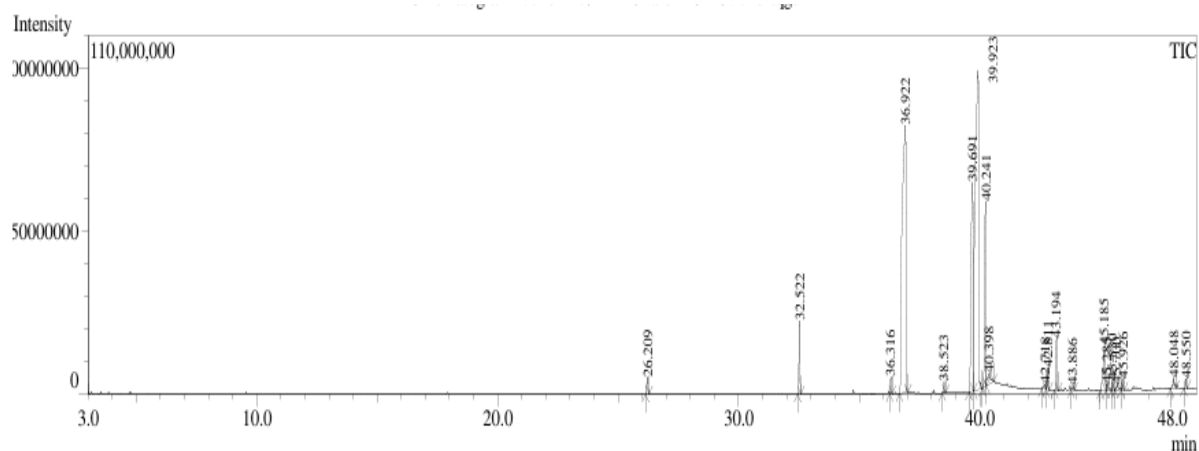


Fig 5.18 GC/MS spirulina diesel graph

Table no.5.6.GC/MS spirulina diesel Peak Report

Peak Report TIC				
Peak#	R.Time	Area	Area%	Name
1	26.209	17270664	0.62	DODECANOIC ACID, METHYL ESTER
2	32.522	61434727	2.20	TETRADECANOIC ACID, METHYL ESTER
3	36.316	12584832	0.45	9-HEXADECENOIC ACID, METHYL ESTER
4	36.922	824157726	29.56	HEXADECANOIC ACID, METHYL ESTER
5	38.523	8082331	0.29	Heptadecanoic acid, methyl ester
6	39.691	443381575	15.90	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
7	39.923	971907492	34.86	9-OCTADECENOIC ACID, METHYL ESTER
8	40.241	212799307	7.63	Methyl stearate
9	40.398	30576298	1.10	6-Octadecenoic acid, (Z)-
10	42.718	9330439	0.33	Glycidol stearate
11	42.811	16524603	0.59	cis-11-Eicosenoic acid, methyl ester
12	43.194	38642165	1.39	EICOSANOIC ACID, METHYL ESTER
13	43.886	4832219	0.17	NAPHTHALENE, DECAHYDRO-1,6-DIMETHYL
14	45.185	75325777	2.70	9-Octadecenoic acid, 1,2,3-propanetriyl ester
15	45.285	10314218	0.37	BICYCLO[10.1.0]TRIDEC-1-ENE
16	45.530	9145661	0.33	Glycidol stearate
17	45.700	8598622	0.31	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)
18	45.926	8382690	0.30	DOCOSANOIC ACID, METHYL ESTER
19	48.048	16633043	0.60	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester
20	48.550	8254086	0.30	TETRACOSANOIC ACID, METHYL ESTER
		2788178475	100.00	

The above table and peaks present in the graph demonstrate the presence of methyl ester, which is the main component of biodiesel, and confirm whether the oil is converted into biodiesel, which is attained by the transesterification process. The acids present in the biodiesel also confirm the presence of *spirulina* compounds. From the table and graph it is also analyzed that the presence of both saturated and unsaturated

fatty acids .Tetra decanoic acid and Heptadecanoic acid are saturated fatty acids because they doesn't contain double bond in carbon chain in which Heptadecanoic has 0.29% and Tetra decanoic acid has 2.20% .Then also analyzed unsaturated fatty acids such as Hexadecenoic and octadecadienoic acid because they contains double bonds in their carbon chain in which octadecadienoic acid has 34.86% which is highest and Hexadecenoic acid has 29.56 %which is second highest. By this analysis it is confirmed unsaturated acids are in large amount compared to saturated fatty acid.

5.1.12.Bio diesel (FTIR)

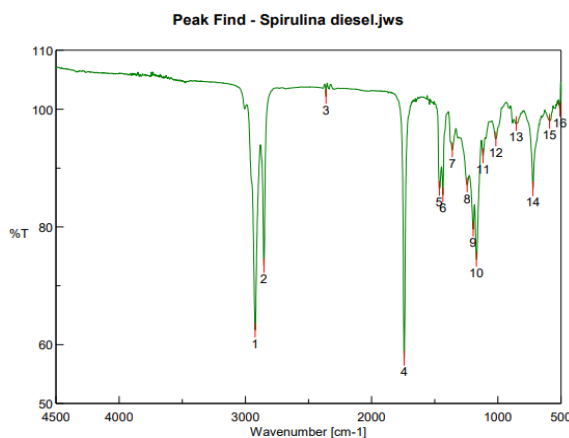


Fig 5.19 FTIR of biodiesel

The spectrum analysis offers important information about the biofuel sample's composition. The peak at 1742.37 cm^{-1} indicates the presence of ester, a critical component in biofuels that is primarily produced from triglycerides via transesterification. This peak confirms the esterification reaction that takes place during biodiesel manufacturing. Furthermore, the peak at 1117.55 cm^{-1} indicates the C-O stretching property of tertiary alcohol, which may be present as impurities or

byproducts during the biofuel production process. The signal at 1435.74 cm^{-1} corresponds to O-H bonding, which is most likely due to residual moisture content or hydroxyl groups in the source material. Furthermore, the identification of C-O stretching at 1169.62 cm^{-1} confirms the presence of ester bonds in the sample. Overall, the spectrum analysis provides useful insights into the biofuel's chemical composition, revealing the presence of ester as the primary component, as well as other functional groups that may influence its characteristics and performance as a renewable energy source.

5.1.13. Properties of bio diesel

Table no.5.7. Properties of bio diesel

S.No	Parameters	Results
1	Density (g/cc)	0.863
2	Kinematic Viscosity @40 °C (cSt)	4.5
3	Flash point by PMCC method (°C)	178
4	Fire point by PMCC method (°C)	166
5	Calorific value (Cal/g)	10,915.26
6	Pour point (°C)	-5

Density:

Density is a major factor in biodiesel's combustion characteristics, such as ignition quality and emission. If it has a deviation from expected density values, which indicates impurities or changes in the production process. By the above test it is confirmed that the density of synthesized biodiesel is 0.863 g/cc . Mostly biodiesel density ranges between 0.86-0.88 g/cc based on process and feedstocks.

Kinematic viscosity:

Basically, viscosity means resistance to flow. The kinematic viscosity of the diesel shows the flow behavior, in which a higher value results in more resistance to flow, which impacts the fuel injection system, and it's also influenced by the lubricating properties of the engine. Proper lubrication is required for the longevity of the engine. Kinematic viscosity values range between 3.5 and 5 centistokes. By the above test the kinematic viscosity is 4.5 cst which confirms the better flow of biodiesel.

Flash point:

The flash point is the temperature at which the liquid or fuel starts to form vapor to get flame. This point is necessary to handle, transport, and store fuel and follow the safety measures according to it, and if biodiesel blends with a lower flash, then it has higher flammability. The attained flash point of produced biodiesel is 178°C.

Fire point:

Fire points are those followed by flash points in which fuel starts to ignite and define how long the ignition of fuel lasts. Basically, the fire point ranges between 130°C and 180°C, depending on the blend and composition used. This is also used for safety measures. The fire point of our biodiesel is 166°C which lies in the range of fire point mentioned.

Calorific value:

The calorific value is important to find the amount of energy exerted during the combustion of fuel; it also depends on the fuel feedstock, purity, and composition used for biodiesel. The calorific value ranges from 128000 to 135000 cal/g.

Pour point:

Pour point is the lowest temperature at which the fuel or biodiesel starts to pour or become cloudy, so the diesel starts to transition from a free-flowing state to a solid state. This is the initial stage of the cloud point, followed by the freezing point. Pour point is important to note whether the fuel can withstand and flow at low temperatures; it ranges from -12°C to -3°C for biodiesel.

CHAPTER 6

SUMMARY AND CONCLUSION

A catalyst doped with cobalt chloride hexahydrate, zeolite, and calcium oxide was examined as a possible catalyst for biodiesel generation from *spirulina* oil. Zeolite catalysts are a type of porous material with variable pore size, making them ideal candidates for catalytic applications due to their high surface area. Based on the available studies, the synthesized catalyst for biodiesel production has produced promising results. The doped catalyst demonstrated significant catalytic activity and selectivity for the transesterification reaction, which is the primary step in biodiesel generation. The use of a doped catalyst (cobalt chloride hexahydrate, zeolite, and calcium oxide) has resulted in better biodiesel yields than other catalysts. The *spirulina* oil is heated and transferred to a round bottom flask. The catalyst is then weighed and blended with methanol before being added to the oil in a round bottom flask. The setup is then completed in a magnetic stirrer, and the transesterification reaction begins. Glycerol and biodiesel are separated and delivered to a separation funnel, making it easy to remove glycerol from biodiesel because of its high density. The diesel is then water washed to eliminate any remaining contaminants. This procedure has been found to be effective in producing large yields of biodiesel from *spirulina* oil. The synthesized biodiesel is then subjected to an FTIR test to determine the functional and organic groups present, followed by a GC-MS analysis to determine whether the oil has been converted into biodiesel and to determine the amount of saturated and unsaturated fatty acids present in the diesel, which can be useful for engine ignition quality and properties tests such as density, pour point, fire point, and flash point. By this process and test's we are concluded that *spirulina* oil can be converted into biodiesel and can be called up for future work.

REFERENCE

- Arman Arefin Md, Fazlur Rashid, Amirul Islam,” A review of biofuel production from floating aquatic plants: an emerging source of biorenewable energy”,102,(2021) 210-256
- Angulo.S.C ,John,H.Khan Chemical Mineralogical characterization of C&D waste recycled aggregates from Sao Paulo,Waste Management ,29,(2020) 721-730.
- Canakci, M. . The potential of restaurant waste lipids as biodiesel feedstocks. Bioresour,14,(2005) 620-696
- Costa CR,Claudia MLL Teixeira Investigation of Biodiesel Potential of Biomasses of Microalgae Chlorella, *Spirulina* and Tetraselmis by NMR and GC-MS Techniques Sarpal AS1 ,1,(2016) 30-60
- Diwani.G.I Catalytic pyrolysis-GC/MS of *Spirulina*: Evaluation of a highly proteinaceous biomass source for production of fuels and chemicals Fuel 179 (2016) 124–134
- Guoju Yang and Jihong Yu. Advancements in Basic zeolite for biodiesel production via transesterification 3,(2023) . 438-451.
- Hasheminejad, M., Tabatabaei, M., Mansourpanah, Y., Khatami far, M., and Javani, A. (2011). Upstream and downstream strategies to economize biodiesel production. Bioresource Technol. 102,(2010) 461–468.
- Nagarajan, S., Chou, S. K., Cao, S., Wu, C., and Zhou, Z. (2013). An updated comprehensive techno-economic analysis of algae biodiesel. Bioresource Technol. 145, (2014) 150-166.
- Mariam Emad Murad,Mohamed F. Al-Dawody. Biodiesel production from *spirulina* microalgae 2020. Material Science and engineering 928 ,(2020) 329-350
- Mohammad Reza Nazarifer. Cobalt (II) Chloride hexahydrate as an efficient and inexpensive catalyst for preparation of Biscoumarin derivatives. Advances in Chemistry,232,(2014) 64-73
- RahmanM.A,Aziz,Rami Ali Al-khulaidi,Nazmus Sakib,Maidul Islam. Biodiesel production from microalgae *spirulina* maxima by two step process 2017. Journal of Radiation Research and Applied science 10,(2017) 140-147.

- Raza Hematkhah, Nasrollah Majidian, Ahmad Hallajisani, Mohammad Samipoorgiri. Investigation of catalytic pyrolysis of *spirulina* for biodiesel production .Arabain journal of Chemistry ,16,(2023) 2-15 .
- Shimi.H.I ,Nahed K.Attia ,S.T.El-Sheltawy , Production from *Spirulina*-Platensis Microalgae by In-Situ Transesterification Process,193,(2014) 1-13.
- Stefan M.Pavlovic ,Dalibor M.Marinkovic,Milan D kostic ,Davor R.Loncarevic .The chicken eggshell calcium oxide ultrasonically dispersed over lignite coal fly ash based cancrinite zeolite support as a catalyst for Biodiesel production 0. Fuel, 289,(2018) 118-130.
- Sujata Brahma a, Biswajit Nath a b, Bidangshri Basumatary a, Bipul Das c, Pankaj Saikia d Biodiesel production from mixed oils: A sustainable approach towards industrial biofuel production .Fuel,60(2020) 284-305.
- Tabatabaei, M., Aghbashlo, M., Dehghani, M., Panahi, H. K. S., Mollahosseini, A. Reactor technologies for biodiesel production and processing: a review. Progress Energy Combust,36,(2019) 1-20
- Tesfayo.k,MamoOptimized Biodiesel Production from Waste Cooking Oil (WCO) using Calcium Oxide (CaO) Nano-catalystTadesse Anbessie Degfie,Tadios.article ,60,(2013) 222-229
- Tesfa, B., Mishra, R., Gu, F., and Powles, N. (2010). Prediction models for density and viscosity of biodiesel and their effects on fuel supply system in CI engines. Renew. Energy 35,(2010) 2752–2760.
- Yano Surya Pradana, Resti Nurmala Dewi, Kanadya Di Livia,Advancing biodiesel production from microalgae *Spirulina* sp. by a simultaneous extraction–transesterification process using palm oil as a co-solvent of methanolchem,21(2013) 1075-1087
- Ullah, Z., Khan, A. S., Muhammad, N., Ullah, R., Alqahtani, A. S., Shah, S. N., et al . A review on ionic liquids as perspective catalysts in transesterification of different feedstock oil into biodiesel, 266,(2018) 673–686.

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CHAPTER 1

INTRODUCTION

1.1 BIODIESEL

Biodiesel is a renewable alternative fuel manufactured from organic ingredients, most often vegetable oils or animal fats. Transesterification, which includes chemically turning these feedstocks into biodiesel and glycerin, is used to create it. Biodiesel may be used in diesel engines to replace normal diesel fuel without requiring substantial changes.

One of the primary benefits of biodiesel is that it emits less greenhouse gas than fossil fuel. It has a smaller carbon footprint because the carbon dioxide emitted during biodiesel combustion is countered by the carbon dioxide absorbed during feedstock plant development. Furthermore, biodiesel emits less hazardous pollutants, such as sulphur and particulate matter, resulting in better air quality.

Biodiesel may be made from a variety of feedstocks, such as soybean oil, canola oil, palm oil, spirulina oil and spent cooking oil. The feedstock used can have an influence on the sustainability and environmental impact of biodiesel manufacturing. Sustainable practises and responsible sourcing are required to ensure that biodiesel has a beneficial environmental impact.

Overall, biodiesel appears to be a potential alternative for lowering transportation's environmental effect and reducing reliance on fossil fuels.

1.2 CATALYST

Catalysts can be categorized into various types based on their nature, mechanism, and application. Here are some common types of catalysts:

catalysts are essential in the biodiesel synthesis process because they facilitate the complex chemical reactions that turn raw materials into high-grade fuel. In this field, homogeneous catalysts—such as potassium hydroxide (KOH) and sodium hydroxide

(NaOH)—are mainstays. They use their strong basic qualities to speed up the transesterification process. Solid base catalysts like calcium oxide (CaO) and barium oxide (BaO) are examples of heterogeneous catalysts, which offer an alternative paradigm. These solid catalysts provide streamlined separation procedures and have the potential to cut waste because they function in different phases from the reactants. Lipases are particularly well-suited for the generation of high-quality biodiesel or for the management of fragile feedstocks because they catalyze transesterification processes with elegance and exhibit extraordinary specificity and environmental compatibility. Acid catalysts, such as sulfuric acid (H₂SO₄), have found a place in acid-catalyzed transesterification processes and are useful in the processing of feedstocks that are of lesser quality.

1.3 THE SELECTION OF A HETEROGENEOUS CATALYST

The use of heterogeneous catalysts in biodiesel production offers several advantages:

- **Catalyst Separation:** Heterogeneous catalysts are typically solid and can be easily separated from the biodiesel and glycerol phases after the reaction. This simplifies the purification process, reducing the need for additional separation steps and making the production process more efficient.
- **Catalyst Recycling:** Many heterogeneous catalysts can be reused multiple times, reducing the overall cost of catalyst procurement and disposal. This recyclability is environmentally friendly and cost-effective.
- **Reduced Environmental Impact:** The ease of catalyst separation and recycling leads to less waste generation, minimizing the environmental footprint of biodiesel production. It also aligns with sustainability goals by reducing the consumption of catalyst materials.
- **Increased Safety:** Heterogeneous catalysts are often safer to handle compared to highly caustic homogeneous catalysts like sodium hydroxide (NaOH) or potassium hydroxide (KOH). This improves safety for workers involved in the production process.
- **Flexibility:** Heterogeneous catalysts offer flexibility in terms of the choice of catalyst material. Various solid acid catalysts, metal catalysts, and supported

catalysts are available, allowing producers to select a catalyst that suits their specific feedstock and process conditions.

- Scalability: Heterogeneous catalysts are well-suited for large-scale biodiesel production due to their ease of handling, separation, and recyclability. This makes them practical for industrial-scale operations.
- Fewer Byproducts: The use of heterogeneous catalysts often results in fewer side reactions and fewer undesirable byproducts, leading to higher biodiesel yields and product quality.
- In summary, heterogeneous catalysts are favored in biodiesel production because they simplify the separation process, enable catalyst recycling, reduce environmental impact, enhance safety, and provide flexibility for both small-scale and large-scale operations. These advantages contribute to more efficient and sustainable biodiesel production processes.

1.4 ADVANTAGE OF CATALYST

Doping zeolite, calcium oxide, and cobalt chloride as a single catalyst can result in a multifunctional catalyst with distinctive features and capabilities. The specific outcomes of such doping are determined by the catalyst composition, the dopants utilised, and the catalytic processes planned. Here are some examples of possible results and applications:

Catalytic Performance Enhancement:

Doping can improve the combined catalyst's total catalytic activity. Doping calcium oxide with cobalt chloride and zeolite, for example, might result in enhanced transesterification rates, greater biodiesel yields, and shorter reaction times in biodiesel synthesis.

Versatility:

A multifunctional catalyst of this type might be versatile and adaptive, making it appropriate for a wide range of reactions in a variety of applications. Catalysts are frequently tailored by researchers to satisfy the demands of certain industries or processes.

Selectivity Enhancement:

Doping with different elements can influence the selectivity of the catalyst, making it

more suitable for specific chemical reactions. This could be beneficial in processes where multiple reactions are competing, and selectivity is crucial.

Effects of Synergy:

The combination of zeolite, calcium oxide, and cobalt chloride may lead to synergistic effects, where the catalyst's overall performance is greater than the sum of its individual components. Synergies could result in improved catalytic activity, stability, and selectivity.

1.4.1 CaO



Fig1.1 : Calcium oxide

Calcium oxide also acts as an alkali-neutralizing agent, helping to neutralize any residual acidic compounds present in the feedstock oil. This is essential because the presence of acids can lead to undesirable side reactions and catalyst deactivation.

Calcium oxide is advantageous as a solid catalyst because it can be easily separated from the reaction mixture once the transesterification process is completed. Calcium oxide is cost-effective and readily available, making it an attractive option for small-scale biodiesel production operations.

1.5.2 Zeolite

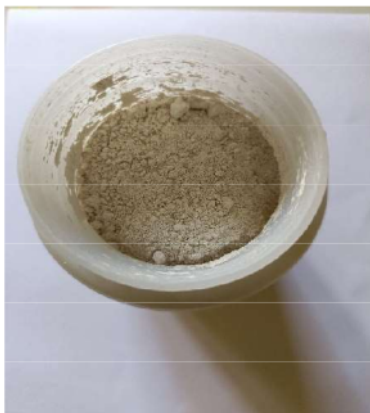


Fig1.2 : Zeolite

Zeolite's porous structure allows it to adsorb impurities and water from the feedstock oil. This is crucial because water and impurities can negatively affect the biodiesel production process and reduce the quality of the final product. Zeolite helps improve the purity of the oil feedstock. Zeolite can be regenerated and reused multiple times and considered as a cost-effective choice for biodiesel production. Zeolite is eco-friendly towards the environment because they are solids and they won't generate waste byproducts during biodiesel production.

1.5.3 CoCl_2



Fig1.3 : Cobalt Chloride (II) hexahydrate

One advantage of cobalt chloride (II) hexahydrate is its ability to operate under milder reaction conditions compared to some other catalysts. This can lead to improved energy efficiency and better control of the reaction. Typically, this is doped with other metal catalysts to improve the hydrogenation process in the synthesis of biodiesel rather than being used as a single compound catalyst.

1.5 TRANSESTERIFICATION

The transesterification process is a chemical reaction typically employed in biodiesel production to convert triglycerides present in vegetable oils or animal fats to fatty acid methyl esters (FAME), which are the major components of biodiesel.

The triglycerides present in the lipids react with catalysts, and methanol (alcohol) leads to the production of biodiesel and glycerol. This reaction takes place between 50°C and 70°C by using agitation to ensure the proper mixing of components to react.

After the reaction is completed, the mixture is allowed to separate, with glycerol at the bottom due to its high density and biodiesel at the top due to its lower density.

By using the transesterification process, the production of biodiesel can be economical and time-consuming, which also provides improved performance and a high cetane number. Although biodiesel emits fewer pollutants compared to diesel, it also generates pollutants during production, particularly if it is from non-renewable sources, which leads to environmental impact. Overproduction of glycerol sometimes leads to environmental waste management issues.

1.6 SPIRULLINA OIL – BLUE – GREEN ALGAE

- Renewable Resources: *Spirulina* is way faster and easier to grow in a variety of settings, which acts as a renewable source for biodiesel production.
- Oil content: *Spirulina* has a high oil content, which is approximately 5–10% of its dry weight, which is effective in making biodiesel.
- Reduced carbon: Diesel, which is made from *spirulina*, will emit less carbon, which leads to pollution management.
- Biodegradable: It is also a naturally degradable environment, which creates less impact on society.

- Nutrient recycling: Growing *spirulina* for oil production acts as a recycler of nutrients because it utilizes waste water and carbon dioxide, which are released from industries and also from the environment.
- Overall, using *spirulina* oil gives economic, environmental, and social benefits, helping to promote less energy production and reduce dependence on fossil fuels.
- *Spirulina* may be produced in a variety of ecosystems, includes freshwater, brackish water, and wastewater, as well as under controlled circumstances in photobioreactors, making it adaptable to varied growth methods and locales.

1.7 METHANOL

Methanol reacts strongly with triglycerides, which are the primary components of vegetable oil, animal fats, and microalgae, which allows faster conversion to biodiesel production through the transesterification process. Methanol is reacted with a wide range of catalysts, mostly in transesterification reactions, which provides higher flexibility in catalyst selection and optimization processes. The use of methanol in biodiesel manufacturing mostly leads to a reduction in undesirable byproducts or side reactions; by doing so, it helps to increase the purity and quality of the end product. The biodiesel produced by the use of methanol, which contributes to a reduction in greenhouse gases compared to petroleum diesel, offers environmental benefits. The chemical formula for methanol is CH_3OH .



Fig1.4 : Methanol

CHAPTER 2

LITREATURE SURVEY

Sc.angulo et al. (2008) - Based on a variety of analytical techniques, this study proposes a methodology for the classification of recycled aggregates made from construction and demolition (C&D) debris. Particle size has had a greater impact on the chemical contents of mixed C&D aggregate samples than visual classification. The porous cement paste concentration in C&D aggregates is around 19.3% (w/w). This percentage, however, is much lower than the 43% found in C&D powders (0.15 mm).

Mazlan et al. (2020) - In view of their lesser impact on the environment, and simplified production and purification processes, solid base catalysts are preferred. Increasing the stability and activity of solid base catalysts remains problematic. Because of their high surface area, enhanced stability, and tunable basicity, basic zeolites, particularly two-dimensional zeolites, have emerged as appealing solid basic catalysts for triglyceride transesterification. The review demonstrates that the synthesis, characterization and catalytic performance of Zeolite Basics for TG transesterification has recently improved. The problems of basic zeolites and their development potential for biodiesel synthesis via transesterification are also emphasized.

I.lawan et al. 2020 Zeolite Material was employed as a catalytic support for calcium oxide, which was generated from discarded chicken eggshells (ES). The ultrasound-assisted approach got accustomed to create the ZM-supported calcium oxide catalyst (xCaO/ZM). The impact of several concentrations of dispersed calcium oxide (x = 5-20 wt%) on Zeolite and thermal treatment at various temperatures (450-600 C) was investigated. The existence of strong active sites in a well-defined pore network indicated the presence of strong active sites suitable for the reactions of bulky chemical molecules such as triacylglycerols (TAGs).

Reza nazarifer et al. (2014) The outcome of utilizing a cobalt catalyst based on zeolite and comparing it to direct pyrolysis of *Spirulina* microalgae was explored. The study's zeolite base was HZSM-5 zeolite produced from Zeolite with a Si/Al ratio of 40. In Accordance with the manufacturer, the specific surface of zeolite was analyzed, with a pore size of 5.5 and a crystallinity of 98%. A moist incubation approach were utilized to manufacture a cobalt metal catalyst. To do this, appropriate volumes of cobalt (II)

chloride hexahydrate were mixed with the HZSM-5 base solution, and the sample was agitated on a magnetic plate (40 rpm, 25°C, 4 h) to ensure that the active metal was adsorbed to the base. Following that, the samples were dried in an oven (80°C, 18 h) and then calculated in a furnace with a heating element.

Bipul et al. (2018) - Biodiesel is considered an environmentally benign, biodegradable, non-toxic, and carbon-neutral fuel. It is derived from edible and non-edible oil feedstocks, as well as other triglyceride sources. Biodiesel production is determined by the availability of a specific feedstock and the cost of the necessary raw materials. Biodiesel is primarily created using the transesterification process with an appropriate catalyst, ideally a heterogeneous catalyst, which is more advantageous in terms of reusability, recovery, product purity, and production cost. Several reactors are being designed to create cost-effective biodiesel at the commercial level. The most recent trend in biodiesel synthesis is the use of machine learning (ML) techniques to optimize the process parameters.

Tesfa et al. (2010) - Biodiesel is a possible non-toxic, biodegradable alternative fuel for transportation. Nonetheless, biodiesel's increased viscosity and density cause some serious difficulties when utilized in an unaltered engine. Keeping this in mind, this research has been directed toward two goals. The initial goal is to determine how temperature affects density and viscosity in a range of biodiesels, as well as to build a relationship between density and viscosity for different biodiesels. The second goal is to explore and quantify the impacts of density and viscosity of biodiesels and their mixes on various components of the engine fuel delivery system, such as the fuel pump, fuel filters, and fuel injector.

Canacki et al. (2007) - Waste cooking oils, restaurant grease, and animal fats are potential biodiesel feedstocks. These low-cost feedstocks account for one-third of total fats and oils produced in the United States, although they are currently used mostly for industrial purposes and animal feed. Feedstock qualities are critical throughout the early stages of research and manufacturing. Free fatty acids and moisture hinder transesterification efficiency when turning these feedstocks into biodiesel. As a result, this study was done to investigate the levels of these pollutants in feedstock samples from a rendering factory. Free fatty acid levels ranged from 0.7% to 41.8%, and moisture from 0.01% to 55.38%.

Zhou et al. (2013) - ²Algae biodiesel is a potential but costly alternative fuel to petroleum diesel. To overcome cost constraints, extensive cost evaluations are required. According to a decade-old cost analysis by the U.S. National Renewable Energy Laboratory, algal biodiesel costs between \$0.53-0.85/L (2012 USD values). ²However, the costs of land and transesterification were only loosely approximated. ²This study included an updated complete techno-economic analysis with streamlined processes and improved cost estimates. The updated algal biodiesel costs were calculated using the most recent process improvements, vendor quotations, government databases, and other relevant data sources, and the final biodiesel costs may vary.

Ghiaci et al. (2010) - Biodiesel was created by transesterifying ³canola oil with methanol in the presence of strongly Brønsted acidic ionic liquids based on 1-benzyl-1H-benzimidazole. The influence of reaction temperature, type and amount of catalyst, molar ratio, and reaction time were examined. Under the optimized reaction conditions, the 4B ionic liquid has the maximum catalytic activity and recyclability. ³Thus, this ionic liquid is capable of catalyzing the transesterification of canola oil to its methyl esters in 5 h with yields of more than 95%.

CHAPTER 3

AIM AND SCOPE

3.1 AIM

- To establish a sustainable and an eco-friendly method for synthesis biodiesel.
- To synthesis a Catalyst ²⁴ to speed up the reaction time then better yield of biodiesel.
- To synthesis Calcium oxide from demolition debris which acts as waste management.
- To integrate the synthesized CaO with zeolite then further the complex is incorporated with CoCl_2 to form catalyst.
- To extract oil from *spirulina* or blue-green algae and further use it for biodiesel production.
- Then it is subjected to a transesterification process with methanol and oil to produce biodiesel
- Then the biodiesel is water washed, and the byproducts(glycerol) are removed.

3.2 SCOPE

- Waste management - CaO extracted from demolition debris for catalyst integration.
- *Spirulina* is an algae that may be cultivated even in home and can also be cultivated in large scale
- biodiesel is safer to use and less harmful ²² compared to fossil fuels in terms of emission

- Usage of biodiesel maintains Low rate of greenhouse gases (CO,HC,CO₂,NO_x) generation
- The crude glycerol is produced as a byproduct during biodiesel production which can be utilized as lubricants
- The use of biodiesel in diesel engines doesn't requires many alterations.

CHAPTER 4

MATERIALS AND METHODOLOGY

4.1.1. MATERAILS REQUIRED

- Calcium oxide (CaO) extracted from demolition debris
- Zeolite
- Cobalt (II) chloride hexahydrate
- Distilled water
- Methanol
- *Spirulina* oil
- 0.1N NaOH solution.
- 10g oil (expected acid value {1-4}).
- 50ml ethanol.
- Phenolphthalein indicator.

4.1.2 APPARATUS REQUIRED

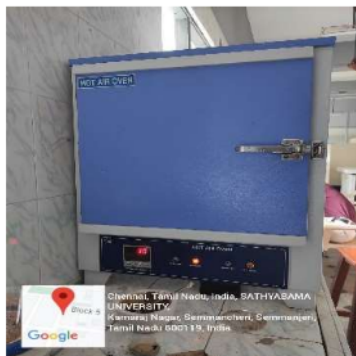
- Beaker
- Magnetic stirrer
- Ultrasonicator
- Muffle furnace
- Spatula
- Hot air oven
- Thermometer
- Round bottom flask
- Condenser

- Filter paper
- Separation funnel

4.2 METHODOLOGY

4.2.1 Preparation of CaO from Demolition Debris

- Crush the demolition debris into smaller pieces if necessary in order to improve the surface area for efficient extraction.
- Insert the crushed debris into the furnace: Make sure there is enough ventilation



for the fuel to burn.

- Whether vital to improve the furnace to between 900 and 1,000°C (1,652-1,832°F). This temperature range is enough to breakdown calcium carbonate thermally into calcium oxide & carbon dioxide.
- Calcium carbonate (CaCO_3) $\rightarrow$ CaO (calcium oxide) + CO_2 (carbon dioxide)

Fig4.1 : Hot air oven



Fig4.2 : Muffle Furnace

- Collect the Calciumoxide. CaO will be formed as the demolition debris heats up. Collect the CaO as it forms in a crucible or container.
- After gathering enough calcium oxide, switch off the furnace and let the CaO to cool until it reaches room temperature.



Fig4.3: Magnetic stirrer

- Transfer the extracted calcium oxide to an appropriate storage container to be kept. CaO should be maintained in a dry atmosphere to reduce moisture absorption since it reacts with water fast to form calcium hydroxide ($\text{Ca}(\text{OH})_2$).

4.2.2 Doping of Calcium oxide and zeolite



Fig4.4 : Ultra sonicator

- Zeolite was incorporated to calcium oxide (CaO) by the impregnation method of doping. Zeolite and calcium oxide were weighed in this method at a 1:1 ratio (10g each).

- Fill a beaker with 200 ml of distilled water next. Start the magnetic stirrer at a set temperature 80°C and speed of 100 rpm, add 10 g of zeolite and 10 g of calcium oxide, and continue stirring for 2h or until the calcium oxide is



completely attached to the active sites of the zeolite. Then, turn the stirrer off. The beaker was placed in the ultrasonicator, which was

Fig4.5: Muffle furnace

- Operating for 15 min at 40°C, to achieve the strong binding of zeolite and calcium oxide.
- After that, the water was transferred into a Petri plate and filtered using filter papers. The sample was positioned in a oven set at 125°C for three hours to completely dry it out. The material was then transferred to a sealed pot so that no air could enter. After the closed pot was placed inside the muffle furnace, the process of calcination was carried out there for four hours at a temperature of 600°C. After that, the sample was removed from the pot.

4.2.3 Incorporation of Synthesized complex with CoCl_2



Fig4.6 : Magnetic stirrer with sample

- Final catalyst was achieved by doping the synthesized Zeolite and calcium oxide with Cobalt (II) chloride hexahydrate ,in this process doped sample (zeolite and calcium oxide) and Cobalt (II) chloride was weighed about 1:1 ratio of 10g



Fig4.7 : Sample after filtration

- Distilled water which was 200 ml then added to the beaker, and a magnetic stirrer was set to operate at 80°C and 100 rpm. After a few minutes, weighed doped sample (CaO and zeolite) were added to the beaker, and the stirring was continued for another few minutes. Next, weighed cobalt (II) chloride hexahydrate was added, and the mixture was continued for two hours to create a strong bond between



Fig4.8 : Muffle furnace

- After using the ultrasonicator, the sample's water was filtered out using filter paper, transferred to a Petri plate dish, and then kept in a hot air oven at 125°C for three hours to completely remove the sample's water molecules and create a dry sample. The sample was set up in a sealed container for the calcination process, in which no air should pass, and the sealed container was then placed inside a muffle furnace and heated to 400°C for three hours and thirty minutes. After the calcination process, the sample was removed, and the catalyst was sent for characterization to determine the catalyst's nature



Fig4.9 : Obtained end catalyst

4.2.4 Catalyst characterization

A form of porous material is formed by doped catalyst that contains three chemical compounds. It is necessary of understanding the characteristics of catalyst so can maximize the performance. Fourier Transform Infrared Spectroscopy (FTIR) is a method used to analyze the functional group present in the doped catalyst of CoCl_2 , CaO and zeolite it is analyzed by equipment called FTIR spectrometer. To analyses this the catalyst sample is kept in spectroscopy at vacuum then the infrared light is passed through the sample then the wavelength was calculated by absorption of Infrared rays by sample. Each peak in spectrum depends on specific vibration on the bond with molecules. The condition to analyses is to keep the optics clean so no other air particles interact. FESEM WITH EDX: The shape and particle size of the compounds or porous material is analyzed using field emission scanning electron microscopy. The sample is kept in vacuum then electron beam is accelerated using

high voltage and passed through the electromagnetic lenses then the beam strike with atoms in the material and after interaction various signals are emitted .It is achieved in ultra-high vacuum condition X-Ray diffraction is the method that is used to analyze whether the prepared catalyst is in crystalline state or amorphous state .The x-ray (monochromatic ray) is passed through the sample and it is interacts with atoms of crystal lattice and it is depends on periodic arrangement . The angle is calculated using Bragg's law ($n = 2d \sin \theta$), the sampling is scanned using 2θ and its range from 10°C to 60°C .The wavelength of Co(II) complex is $1.54\text{\AA}$.

4.2.5 Method to cultivate *Spirulina*

- To develop, *spirulina* algae make a growth medium from nutrients in water. For best growth, *spirulina* requires an alkaline environment.



Fig4.10 : *Spirulina*

- Then, to maximise exposure to sunlight, we used a large, shallow container with a large surface area.
- Then introduce a live *spirulina* culture in a prepared growth medium.

- To grow a *spirulina*, temperature is maintained between 30 and 35°C, and pH is to be maintained between 8 and 11.



Fig4.11: Spirulina harvesting

- Then stir a water container 2-3 times a week. It takes 10–14 days to grow a *spirulina*.
- Adjust the lighting if the *spirulina* looks yellow or olive green.
- Clean the tank and remove any white or yellow *spirulina* clumps

4.2.6 Harvesting the *spirulina*



Fig4.12 : Spirulina processing

- Scoop out the *spirulina* when the pH stays at 10 for 24hr.
- Filter and rinse your *spirulina* through a fine strainer cloth.

4.2.7 .Extraction of oil

Mechanical extraction: In this method, the *spirulina* or blue-green algae is extracted using mechanical equipment a screw press, and then, for further purity, it is heated or refined, in which water molecules are removed.

4.2.8. DETERMINATION OF ACID VALUE

¹¹ The acid value of an oil is a measure of its free fatty acid composition. It is an important factor in determining the quality and reliability of oils. A higher acid value in oil indicates poor quality due to the increase in free fatty acids in lipids or oil, which will reduce the shelf life of oil. Monitoring acid values during the process helps in production with consistent quality; it also helps in controlling factors like temperature, processing content, and moisture content. Oil with a low acid value helps to have better stability.

Procedure

- Ethanol is neutralized with NaOH solution with phenolphthalein indicator.
- Neutralized ethanol is added to the flask contain oil and heated (until the sample gets dissolves completely).



Fig4.13 : Acid value determination

- Titration by adding few drops of indicator with NaOH solution.

$$(40.01 \times 0.1 \times 2.5) / 10 = 1.0025$$

$$\text{Acid value of oil} = 1.0025$$

$$\text{Free fatty acid value of oil} = 0.5$$

4.2.9 Determination of Saponification Value

Procedure

In this experiment, a sample of 5g of oil is measured and mixed with 50 ml of 4% ethanolic KOH solution, while another sample consists of only 50 ml of 4% KOH solution. These samples are then heated separately on two different heating plates, with distillation columns connected to each sample. The heating process continues for 30 minutes until the ethanol begins to condense. It's crucial to observe that the oil sample doesn't form two layers during heating, ensuring proper mixing and reaction. Following this, titration is initiated using 0.5 N of HCl for each sample separately, with the burette values being noted throughout the process. This experimental setup allows for the determination of the acid value of the oil sample, providing valuable insights into its quality and composition. Ensure a sample of 5g of oil and mix it with 50 ml of 4% ethanolic KOH

$$\text{Saponification value} = (28.05 * (vb - vs))/ws$$

Molecular wt. of oil

$$\text{Molecular wt. of oil} = (56.1 * 1000 * 3)/(s.v - a.v)$$

4.2.11 Transesterification

- The method involved in this process is transesterification, in which oil to methanol is taken in different ratios and the catalyst weighed in different weight percentages.



Fig4.14 : Oil preheating

- By the optimization technique, it is confirmed that the ratio is 1:12 with a temperature of 60°C and run hours of 90 min.



Fig4.15 : Transesterification

- By the preferred perfect ratio, the oil is taken as 50 ml and the methanol is taken as 31.69 ml, and the weight of the catalyst is 5% points, so it is 3.51 g.



Fig4.16 : Separating funnel

- The weighed catalyst is mixed with measured methanol and agitated, which ensures perfect mixing. Then the oil is heated to remove water molecules.



Fig4.17 : Glycerol

- The round bottom setup is done with a stirrer, then the oil and mixed solution of methanol are started to run for 90 min at a temperature of 60°C.

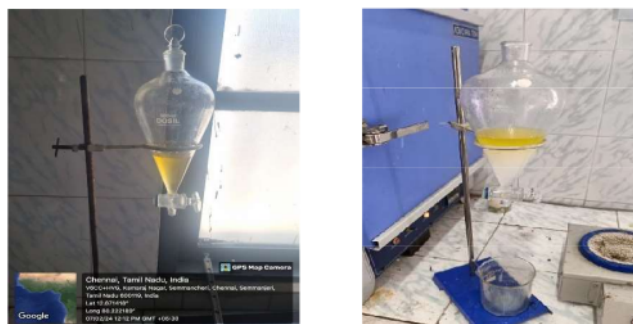


Fig4.18 : Water washing

- Then, after the reaction is done, the catalyst is separated and the biodiesel is transferred to the separation funnel, in which glycerol forms at the bottom and biodiesel comes at the top of the glycerol due to its low density.



Fig4.19 : Bio diesel

- Then the glycerol is separated, further diesel is water washed to remove impurities, and then the produced biodiesel is subjected to further tests to ensure methyl ester formation.

$$\text{Yield} = (\text{Mass of diesel} / \text{Mass of oil}) * 100$$

4.2.13 Bio diesel characterization

Analyzing characterization of biodiesel is necessary to find the applicability and quality as a fuel, such as density, viscosity, pour point, flash point and cloud point. Gas chromatography Mass spectroscopy (GC-MS) is used to analyze the compounds present in acid such as saturated or unsaturated fatty acid. It is performed by taking a sample of biodiesel and mixing it with solvent (hexane) which has low boiling point then allowed to vaporize and the gas is sent to long column of stationary phase where some compounds interacts in that phase and helium acts as carrier gas which allows to flow the gas through the phase at different rates. Then it's sent to mass analyzer where it's separated based on mass to charge ratio (m/z). Then the acid compounds are found by intensity of peaks. It is done by quadrupole mass spectrometer.

CHAPTER 5¹² RESULTS AND DISCUSSION

5.1 CHARACTERISATION

5.1.1 FTIR

Table no. 5.1 Catalyst FTIR analysis

CaO	Zeolite	Catalyst	Compounds
3640.95	3690.12	3366.14	-
2367.19	2357.55	2361.41	CaO
1407.78	1633.41	1636.3	Zeo
1145.51	1392.35	1414.53	CaO
948.806	911.201	984.482	Cocl
875.524	789.707	871.667	CaO
709.676	684.606	658.571	Cocl
507.187	530.328	554.434	Zeo

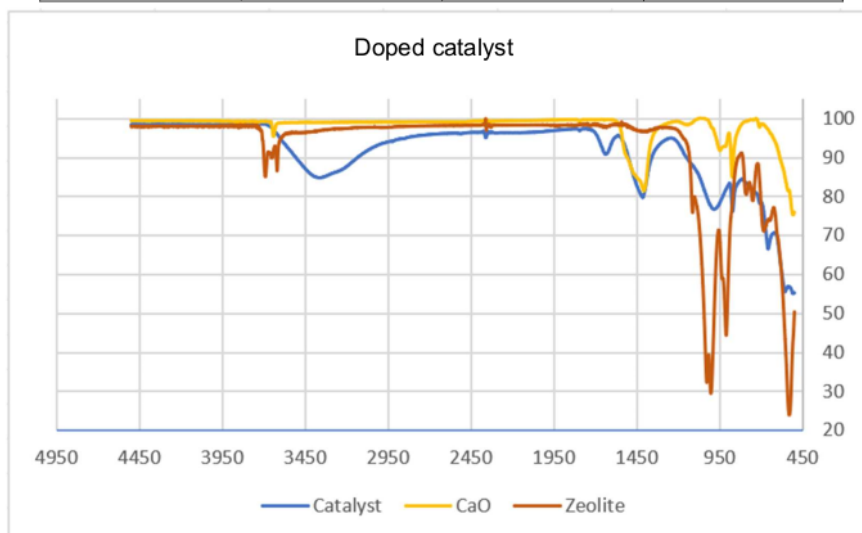


Fig5.1 : Doped catalyst FTIR results

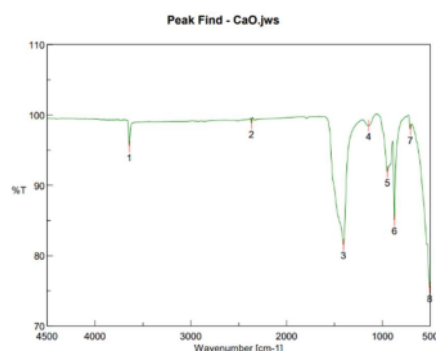


Fig5.2 : FTIR – CaO

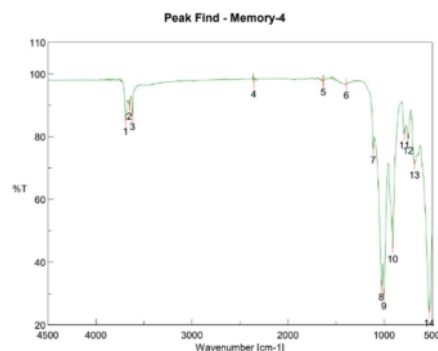


Fig5.3 : FTIR – Zeolite

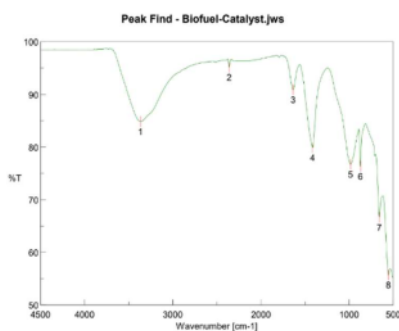


Fig5.4 : FTIR - bio catalyst

The peak level in the graph (Fig : c.1) at 1414.53 cm^{-1} and 2361.41 cm^{-1} shows the appearance of Calcium oxide, which is a feature of the C-O bond and demonstrates a bond between the oxygen atom of carbonate and the calcium atom.

According to FTIR spectrum in the graph the peak level at 1636.3 cm^{-1} and 554.53 cm^{-1} indicates the occurrence of zeolite SiO_4 and other three peaks 1392.53 cm^{-1} , 911.201 cm^{-1} and 789.707 cm^{-1} shows the vibration of Si -O - Al then the last peak 3690.12 cm^{-1} shows the O-H bond caused by absorbed water.

Then the last Spectrum in the graph the peak level at 984 and 658 indicates the emergence of CoCl_2 and therefore adding compound like Co doesn't cause any notable changes

5.1.2 EDAX

Synthesized catalyst

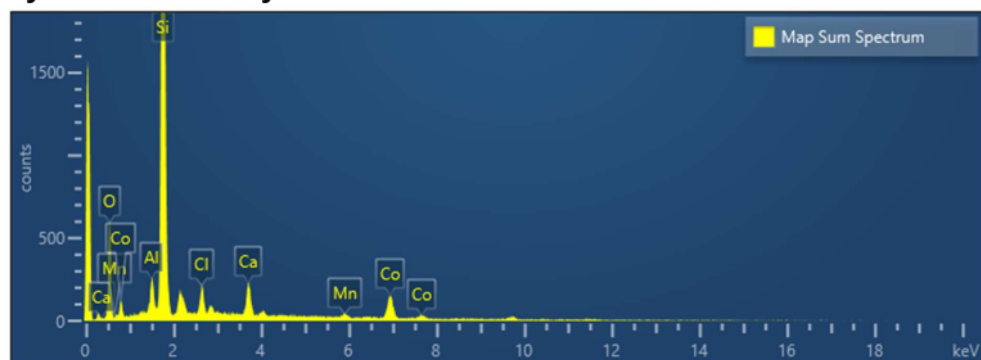


Fig5.5 : EDAX of catalyst

Table no.5.2 EDXA

Map Sum Spectrum Element	Line Type	Weight %	Weight % Sigma	Atomic %
O	K series	30.68	0.59	46.44
Al	K series	2.15	0.13	1.93
Si	K series	49.50	0.51	42.68
Cl	K series	3.17	0.16	2.17
Ca	K series	4.07	0.17	2.46
Mn	K series	1.09	0.19	0.48
Co	K series	9.34	0.37	3.84
Total		100.00		100.00

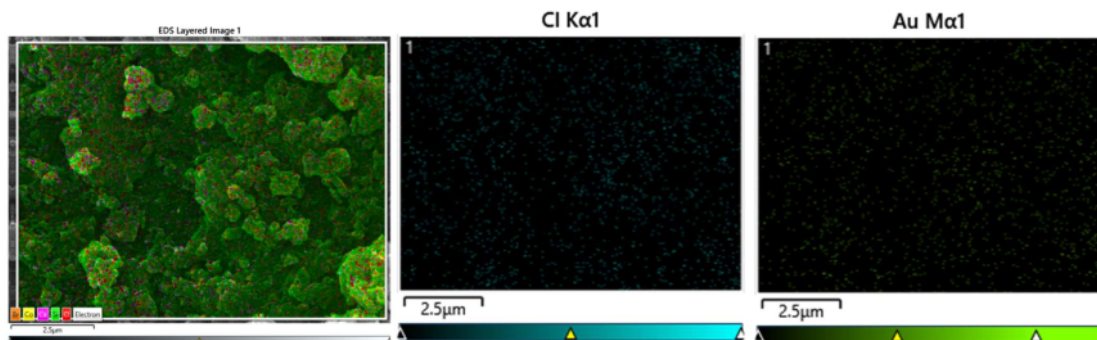


Fig5.6 : EDS colour graph

EDX analysis measures a sample's elemental composition by analyzing the X-rays it releases after being exposed to high-energy electrons or X-rays. This method is commonly employed with scanning electron microscopy and is widely used in materials science, biology, and geology.

The appearance of Calcium (Ca), Oxygen (O), Cobalt (Co), Chloride (Cl), Silica (Si), Manganese (Mn) and aluminium (Al) at different peaks in EDS analysis shows the usage of three distinct compounds in synthesized catalyst.

From the above graph it's analyzed that the silica present in the catalyst has high counts compared to other compounds and also analyzed that all the compounds present are in the k series line type, then their weight % also verified among that silica has highest which is 49.50% and followed by oxygen 30.68 then least is manganese which is 1.09 weight %.

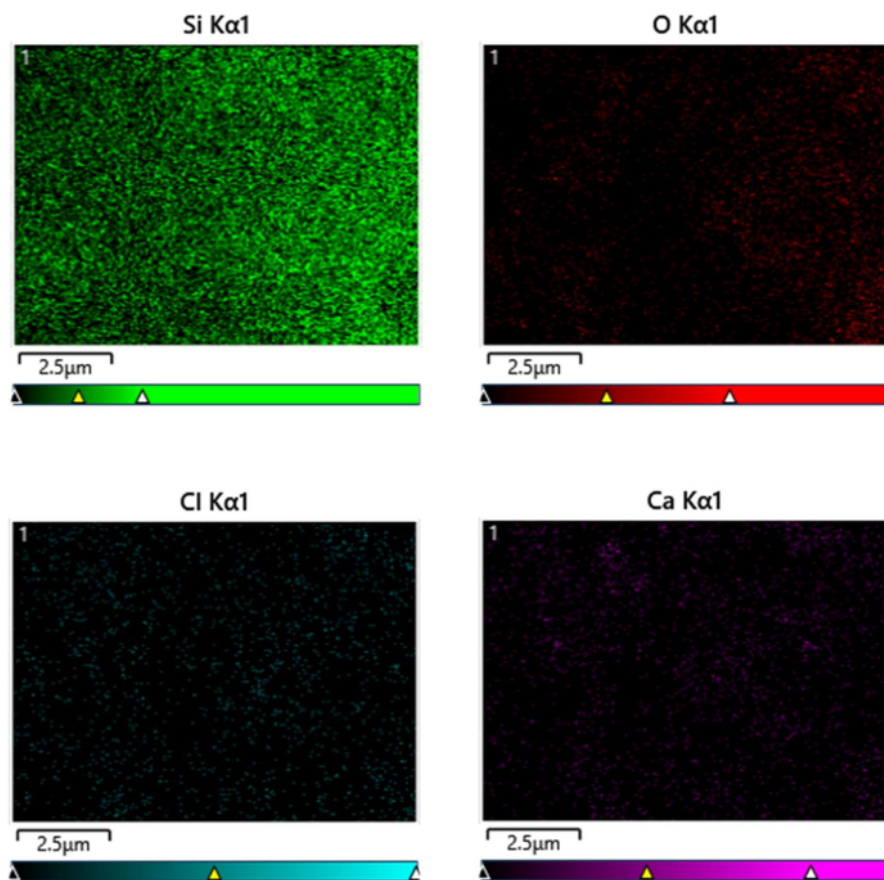


Fig5.7: EDS colour graph

5.1.3 FESEM

Synthesized catalyst

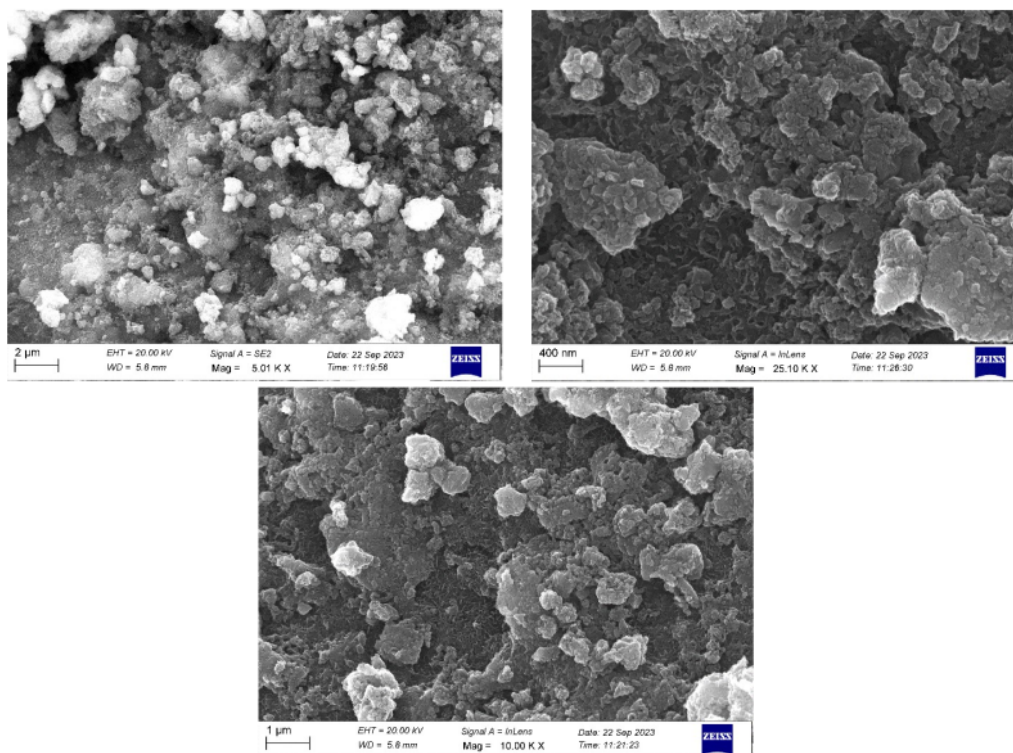


Fig5.8 : FESEM of catalyst

The FESEM analysis of synthesized catalyst which consists of doped (Calcium oxide, zeolite and Cobalt(II) chloride hexahydrate), The FESEM analysis in the above picture shows the heterogeneous structure of catalyst.

Field Emission Scanning Electron Microscopy (FESEM) is used to find the size, shape, and distribution of catalyst particles because of their catalytic activity and selectivity.

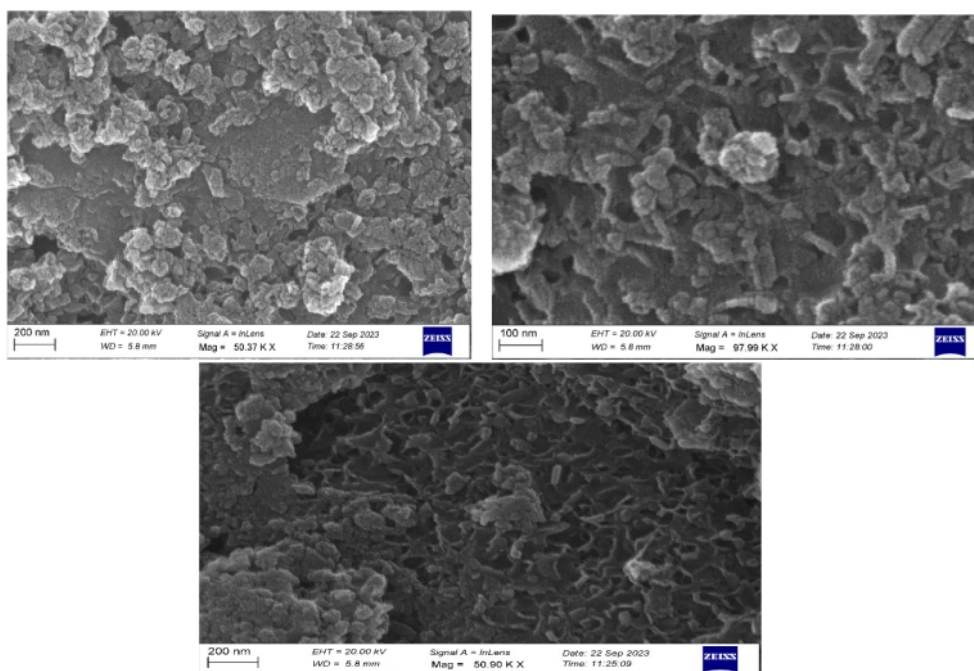


Fig5.9: FESEM of catalyst

Catalysts with a higher surface area are more active compared to those with a smaller surface area. This is because the higher surface area of the particle gives more sites for reactant molecules to absorb and attract.

By the above Field emission scanning electron microscopy images, it analyzed that the pores sizes of compounds in which they are analyzed at different magnifications. At mag 5.01 k X it is noted that the pore size is 2 μm and at 25.1 K X mag the pore is detected as 400 nm. By this it is confirmed that increasing a magnification range increases the pore view of compound.

5.1.4 XRD

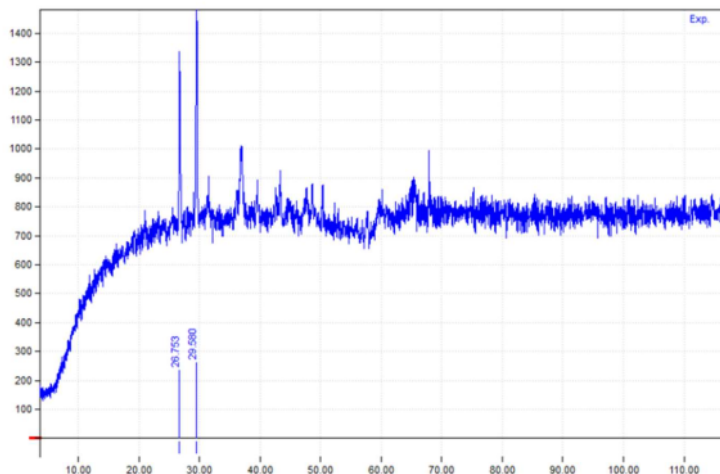


Fig5.10 : XRD of catalyst

Peak List

No.	2theta [°]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM
1	26.75	3.3295	816.15	235.62	0.2657
2	29.58	3.0174	1000.00	262.09	0.2412

Integrated Profile Areas

Based on calculated profile

Profile area	Counts	Amount
Overall diffraction profile	2798666	100.00%
Background radiation	2533361	90.52%
Diffraction peaks	265305	9.48%
Peak area belonging to selected phases	0	0.00%
Unidentified peak area	265305	9.48%

Peak Residuals

Peak data	Counts	Amount
Overall peak intensity	498	100.00%
Peak intensity belonging to selected phases	348	70.00%
Unidentified peak intensity	149	30.00%

One of the primary advantages of XRD analysis is its capacity to distinguish between different crystal forms and identify unknown substances. XRD analysis can provide quantitative information on the proportion of each phase in a sample. From the above graph of x- ray diffraction it is analyzed that at 2θ 26.75 and 29.58 shows the increase in number of counts and intense peak which is 1400 and 1300 counts And also analyzed that overall peak intensity has 498 counts in which 398 counts belongs to selected phase and 149 counts belongs to unidentified peak intensity

5.1.5. Post studies of catalyst (FTIR)

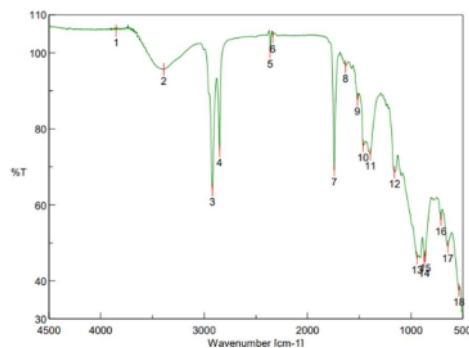


Fig5.11: FTIR of catalyst post studies

The supplied FTIR spectrum offers important information about the sample's molecular composition. The signal at 2920.66 cm^{-1} corresponds to O-H stretching, indicating the presence of absorbed water and perhaps oxygen from calcium oxide (CaO) in the sample. This peak represents the interaction of water molecules with the material, which is important for understanding its stability and reactivity. Furthermore, the signal at 1742 cm^{-1} indicates C-O stretching, implying the presence of ester linkages, most likely originated from triglycerides in the biofuel. This verifies the presence of ester, an important component in biodiesel manufacturing. Furthermore, the peak at 1463 cm^{-1} indicates O-H stretching of a molecule, which could be due to residual moisture or hydroxyl groups in the sample.

5.1.6. Post studies of catalyst (EDAX)

Post-EDAX investigations of catalyst testing are useful for determining the catalyst's elemental composition after it has undergone reactions. These studies can provide light on changes in catalyst composition, detect potential catalyst deactivation or poisoning, and help optimize catalyst performance. And also used to find whether any compounds are mixed during transportation process. In this given post studies graph it is analyzed that all the compounds are similar has before reaction but there is slight change in counts of compounds. Calcium has large number in counts in after studies compared to before studies and all the compounds present in after studies are in k series line type and carbon has large number in weight percentage which is 42.15% and followed by oxygen 24.59 % and least is manganese which is 1.19 %. But silica has large decrease in weight % compared to before studies.

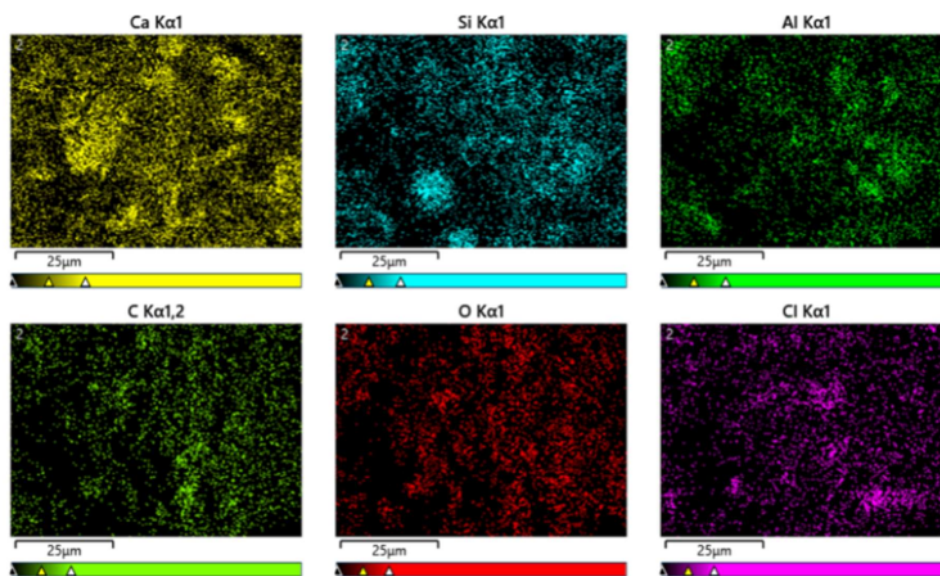


Fig5.12: EDS post colour graph

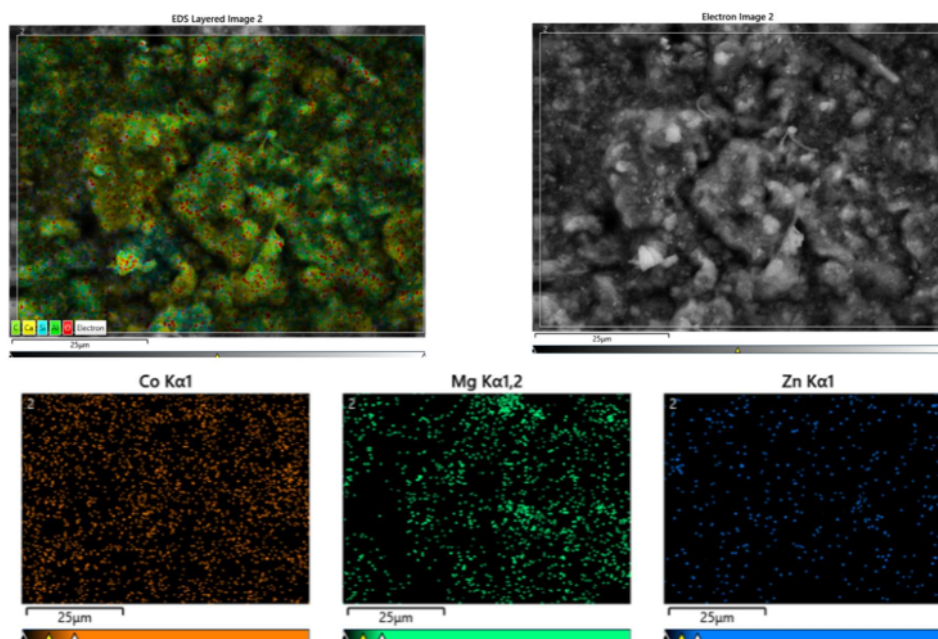


Fig5.13: EDS post colour graph

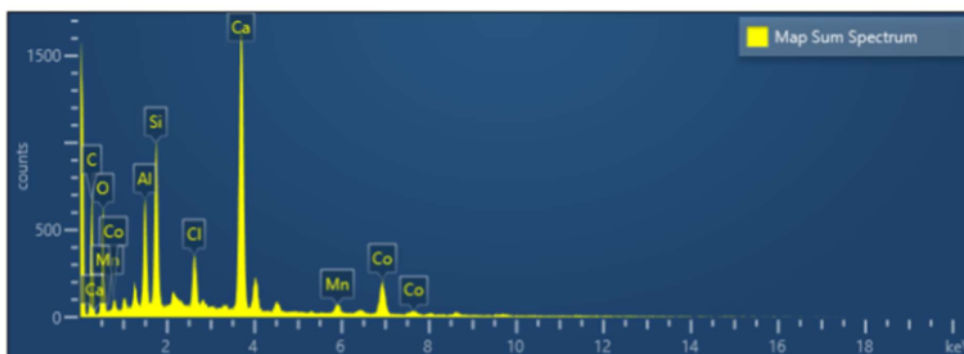


Fig5.14: EDAX of post catalyst

Table no.5.3 EDAX of post catalyst

Map Sum Spectrum Element	Line Type	Weight %	Weight % Sigma	Atomic %
C	K series	42.15	0.79	59.24
O	K series	24.59	0.60	25.94
Al	K series	3.61	0.11	2.26
Si	K series	5.09	0.12	3.06
Cl	K series	2.02	0.08	0.96
Ca	K series	15.21	0.26	6.41
Mn	K series	1.19	0.11	0.37
Co	K series	6.12	0.22	1.75
Total		100.00		100.00

5.1.7. Post studies of catalyst (FESEM)

The below images demonstrate the post-FESEM studies for catalysts. The necessity of this post-study is to analyse whether the pores or active sites of the catalyst got enclosed, and it's confirmed that the pores or surface of the catalyst got lit up due to the reaction between methanol and *spirulina* oil, which ensures that the catalyst is involved in the reaction, is filtered, and can further be used for other reactions. By this above Field emission scanning electron microscopy (FESEM) image it is analyzed that the pore size of compound is 10 μm when it's seen at 1.00 K X magnification and also analyzed same pore size at 1.50 K X mag. Then at 2.0 K X mag it is noted 5 μm pore size of compound.

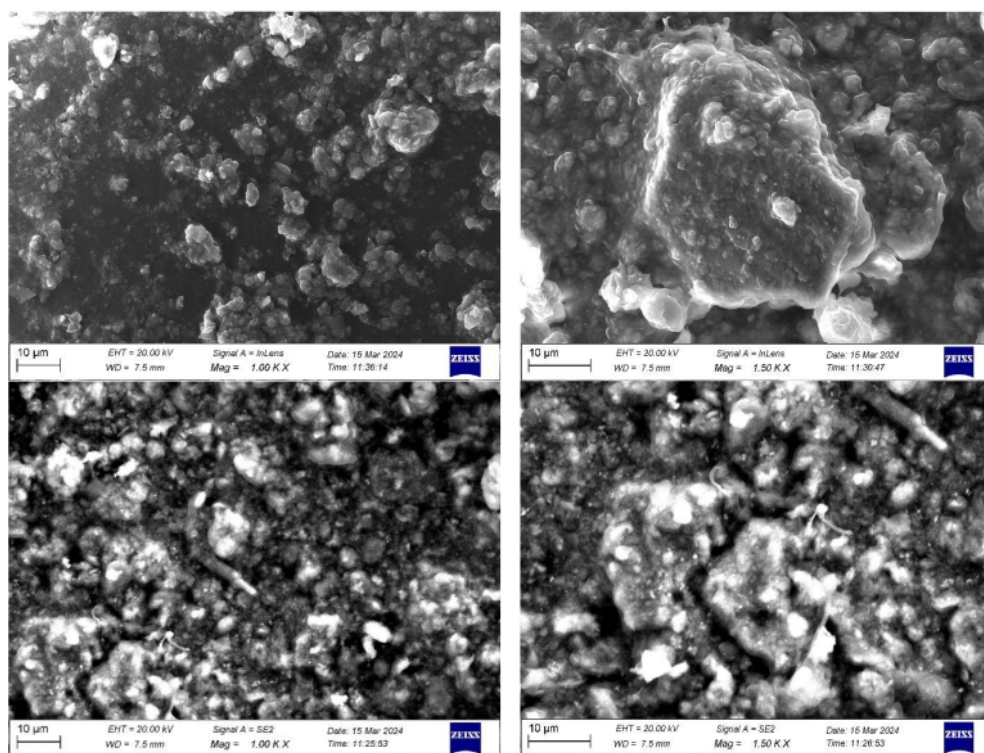


Fig5.15: FESEM of catalyst Post studies

5.1.8. GC/MS- Gas Chromatography/ Mass Spectrometry of *spirulina* oil

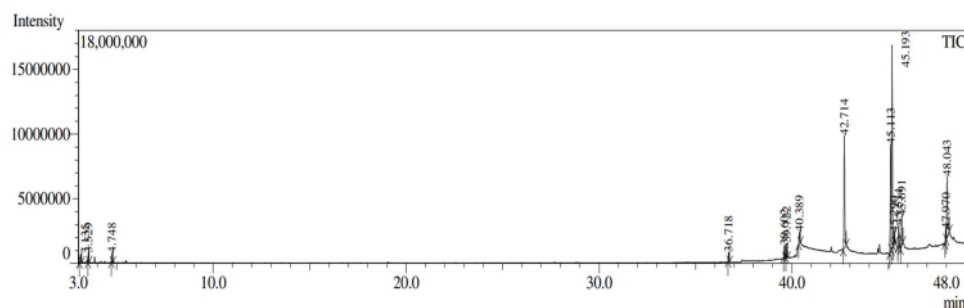


Fig5.16: GC/MS spirulina oil graph

Table no.5.4.GC/MS spirulina oil Peak Report

Peak Report TIC				
Peak#	R.Time	Area	Area%	Name
1	3.135	1315338	0.97	BENZENE, 1,2-DIMETHYL-
2	3.529	1426987	1.05	Pentane, 3-ethyl-2,4-dimethyl-
3	4.748	1535254	1.13	3-HEXEN-2-ONE
4	36.718	1493777	1.10	Hexadecanoic acid
5	39.602	1975650	1.45	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
6	39.722	2308153	1.70	9-Octadecenoic acid
7	40.389	2287166	1.68	9-Octadecenoic acid, (E)-
8	42.714	24785754	18.21	Glycidol stearate
9	45.113	22217853	16.32	ETHYL (9Z,12Z)-9,12-OCTADECADIENO
10	45.193	43972639	32.30	9-Octadecenoic acid, 1,2,3-propanetriyl ester
11	45.290	2472176	1.82	14-METHYL-8-HEXADECYN-1-OL #
12	45.534	4519182	3.32	Glycidol stearate
13	45.691	5883606	4.32	HEXADECANOIC ACID, 2-HYDROXY-1-
14	47.970	2526992	1.86	9,12-OCTADECADIENOIC ACID (Z,Z)-, 2-
15	48.043	17422284	12.80	9-Octadecenoic acid (Z)-, 2,3-dihydroxyprop
		136142811	100.00	

GCMS stands for gas chromatography. Mass spectroscopy, which is used to find unique components present in the compounds. The above result for *spirulina* oil demonstrates the presence of octadecadienoic acid and hexadecenoic acid.

By the above table it is noted that octadecadienoic acid which is also called as Linolelaidic acid and Hexadecenoic acid (palmitic acid) is an unsaturated fatty acids because in linolelaidic acid it contains two double bonds in its carbon chain. Its structure consists of a carboxylic acid group (COOH) at one end and an 18-carbon chain with two double bonds at positions 9 and 12 .If the fatty acid contains one or more double bond in carbon chain it is said to be unsaturated fatty acid and also noted that highest of 32.30% octadecadienoic acid and lowest is 1.10% Hexadecenoic acid then 0.97% of benzene.

5.1.9. Transesterification result

After an examination of the characteristics of oil and the fatty acids it contains, a transesterification reaction occurs. Different ratios of oil and methanol are used in this reaction, and the catalyst is weighed in accordance with those ratios. Variable ratio's are experimented and it is confirmed that ¹³ 1:12 ratio of oil to methanol with the temperature of 60°C and run time of 90 min. The round bottom flask is set up in the magnetic stirrer then the oil is heated then the weighed methanol and catalyst is mixed as a sample. It is mixed with heated oil and started to run for 90 min until the reaction takes place. For further better yield, time parameter is varied and analyzed. After the analysis biodiesel sample is transferred to separation funnel to remove glycerol from biodiesel after removal of glycerol diesel is waterwashed to remove impurities and subjected to diesel analysis tests

$$\text{Saponification value} = ((28.05 * (60.2 - 19.3))/5.2$$

$$\text{Saponification value} = 256$$

$$\text{Molecular wt. of oil} = 168300/254.94$$

$$\text{Molecular wt. of oil} = 660.15$$

Biodiesel calculation

$$\text{Molecular weight of oil} = 660.15 \text{ g/mol}^{\text{14}}$$

$$\text{Molecular weight of methanol} = 32.04 \text{ g/mol}$$

$$\text{Density of oil} = 0.863 \text{ g/cc}$$

$$\text{Density of methanol} = 0.792 \text{ g/cc}$$

$$1 \text{ mol of fatty acid} = 12 \text{ mol of methanol}$$

$$1 \text{ mol} * 660.16 \text{ g/mol} = 12 \text{ mol} * 32 \text{ g/mol}$$

$$660.16 \text{ g} / 0.863 \text{ g/ml} = 384 \text{ g} / 0.792 \text{ g/ml}$$

$$764.7 = 484.84$$

$$50 \text{ ml oil} = 31.69 \text{ ml methanol}$$

$$\text{Mass of oil} = 50 * 0.863 = 43.15$$

$$\text{Mass of methanol} = 31.69 * 0.792 = 12.55$$

$$\text{Total mass} = 68.249$$

$$\text{Catalyst} = (5 * 68.249) / 100 = 3.4 \text{ g}$$

$$\text{Yield \%} = (40.5 / 50) * 100 = 81\%$$

5.1.10. GC/MS- Gas Chromatography/ Mass Spectrometry(bio diesel)

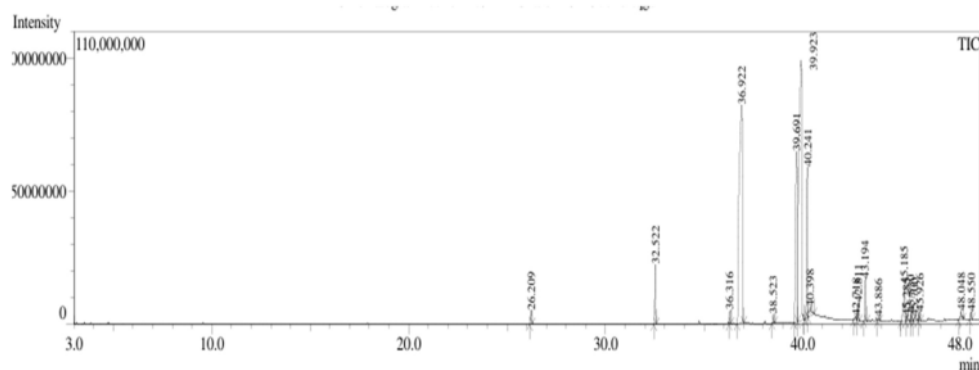


Fig5.17: GC/MS spirulina diesel graph

Table no.5.5.GC/MS spirulina diesel Peak Report

Peak Report TIC				
Peak#	R.Time	Area	Area%	Name
1	26.209	17270664	0.62	DODECANOIC ACID, METHYL ESTER
2	32.522	61434727	2.20	TETRADECANOIC ACID, METHYL ESTER
3	36.316	12584832	0.45	9-HEXADECENOIC ACID, METHYL ESTER
4	36.922	824157726	29.56	HEXADECANOIC ACID, METHYL ESTER
5	38.523	8082331	0.29	Heptadecanoic acid, methyl ester
6	39.691	443381575	15.90	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
7	39.923	971907492	34.86	9-OCTADECENOIC ACID, METHYL ESTER
8	40.241	212799307	7.63	Methyl stearate
9	40.398	30576298	1.10	6-Octadecenoic acid, (Z)-
10	42.718	9330439	0.33	Glycidol stearate
11	42.811	16524603	0.59	cis-11-Eicosenoic acid, methyl ester
12	43.194	38642165	1.39	EICOSANOIC ACID, METHYL ESTER
13	43.886	4832219	0.17	NAPHTHALENE, DECAHYDRO-1,6-DIMETHYL
14	45.185	75325777	2.70	9-Octadecenoic acid, 1,2,3-propanetriyl ester
15	45.285	10314218	0.37	BICYCLO[10.1.0]TRIDEC-1-ENE
16	45.530	9145661	0.33	Glycidol stearate
17	45.700	8598622	0.31	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)
18	45.926	8382690	0.30	DOCOSANOIC ACID, METHYL ESTER
19	48.048	16633043	0.60	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester
20	48.550	8254086	0.30	TETRACOSANOIC ACID, METHYL ESTER
		2788178475	100.00	

The above table and peaks present in the graph demonstrate the presence of methyl ester, which is the main component of biodiesel, and confirm whether the oil is converted into biodiesel, which is attained by the transesterification process. The acids

present in the biodiesel also confirm the presence of *spirulina* compounds. From the table and graph it is also analyzed that the presence of both saturated and unsaturated fatty acids. Tetra decanoic acid and Heptadecanoic acid are saturated fatty acids because they doesn't contain double bond in carbon chain in which Heptadecanoic has 0.29% and Tetra decanoic acid has 2.20% .Then also analyzed unsaturated fatty acids such as Hexadecenoic and octadecadienoic acid because they contains double bonds in their carbon chain in which octadecadienoic acid has 34.86% which is highest and Hexadecenoic acid has 29.56 %which is second highest. By this analysis it is confirmed unsaturated acids are in large amount compared to saturated fatty acid.

5.1.11.Bio diesel (FTIR)

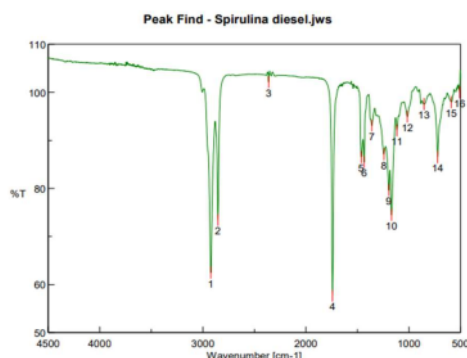


Fig5.18: FTIR of biodiesel

The spectrum analysis offers important information about the biofuel sample's composition. The peak at 1742.37 cm^{-1} indicates the presence of ester, a critical component in biofuels that is primarily produced from triglycerides via transesterification. This peak confirms the esterification reaction that takes place during biodiesel manufacturing. Furthermore, the peak at 1117.55 cm^{-1} indicates the C-O stretching property of tertiary alcohol, which may be present as impurities or byproducts during the biofuel production process. The signal at 1435.74 cm^{-1} corresponds to O-H bonding, which is most likely due to residual moisture content or hydroxyl groups in the source material. Furthermore, the identification of C-O

stretching at 1169.62 cm^{-1} confirms the presence of ester bonds in the sample. Overall, the spectrum analysis provides useful insights into the biofuel's chemical composition, revealing the presence of ester as the primary component, as well as other functional groups that may influence its characteristics and performance as a renewable energy source.

5.1.1. Properties of bio diesel

Table no.5.6. Properties of bio diesel

S.No	Parameters	Results
1	Density (g/cc)	0.863
2	Kinematic Viscosity @40 °C (cSt)	4.5
3	Flash point by PMCC method (°C)	178
4	Fire point by PMCC method (°C)	166
5	Calorific value (Cal/g)	10,915.26
6	Pour point (°C)	-5

Density:

Density is a major factor in biodiesel's combustion characteristics, such as ignition quality and emission. If it has a deviation from expected density values, which indicates impurities or changes in the production process. By the above test it is confirmed that the density of synthesized biodiesel is 0.863 g/cc . Mostly biodiesel density ranges between 0.86-0.88 g/cc based on process and feedstocks.

Kinematic viscosity:

Basically, viscosity means resistance to flow. The kinematic viscosity of the diesel shows the flow behavior, in which a higher value results in more resistance to flow,

which impacts the fuel injection system, and it's also influenced by the lubricating properties of the engine. Proper lubrication is required for the longevity of the engine. Kinematic viscosity values range between 3.5 and 5 centistokes. By the above test the kinematic viscosity is 4.5 cst which confirms the better flow of biodiesel.

Flash point:

The flash point is the temperature at which the liquid or fuel starts to form vapor to get flame. This point is necessary to handle, transport, and store fuel and follow the safety measures according to it, and if biodiesel blends with a lower flash, then it has higher flammability. The attained flash point of produced biodiesel is 178°C.

Fire point:

Fire points are those followed by flash points in which fuel starts to ignite and define how long the ignition of fuel lasts. Basically, the fire point ranges between 130°C and 180°C, depending on the blend and composition used. This is also used for safety measures. The fire point of our biodiesel is 166°C which lies in the range of fire point mentioned.

Calorific value:

The calorific value is important to find the amount of energy exerted during the combustion of fuel; it also depends on the fuel feedstock, purity, and composition used for biodiesel. The calorific value ranges from 128000 to 135000 cal/g.

Pour point:

¹⁵ Pour point is the lowest temperature at which the fuel or biodiesel starts to pour or become cloudy, so the diesel starts to transition from a free-flowing state to a solid state. This is the initial stage of the cloud point, followed by the freezing point. Pour point is important to note whether the fuel can withstand and flow at low temperatures; it ranges from -12°C to -3°C for biodiesel.

CHAPTER 6

SUMMARY AND CONCLUSION

A catalyst doped with cobalt chloride hexahydrate, zeolite, and calcium oxide was examined as a possible catalyst for biodiesel generation from *spirulina* oil. Zeolite catalysts are a type of porous material with variable pore size, making them ideal candidates for catalytic applications due to their high surface area. Based on the available studies, the synthesized catalyst for biodiesel production has produced promising results. The doped catalyst demonstrated significant catalytic activity and selectivity for the transesterification reaction, which is the primary step in biodiesel generation. The use of a doped catalyst (cobalt chloride hexahydrate, zeolite, and calcium oxide) has resulted in better biodiesel yields than other catalysts. The *spirulina* oil is heated and transferred to a round bottom flask. The catalyst is then weighed and blended with methanol before being added to the oil in a round bottom flask. The setup is then completed in a magnetic stirrer, and the transesterification reaction begins. Glycerol and biodiesel are separated and delivered to a separation funnel, making it easy to remove glycerol from biodiesel because of its high density. The diesel is then water washed to eliminate any remaining contaminants. This procedure has been found to be effective in producing large yields of biodiesel from *spirulina* oil. The synthesized biodiesel is then subjected to an FTIR test to determine the functional and organic groups present, followed by a GC-MS analysis to determine whether the oil has been converted into biodiesel and to determine the amount of saturated and unsaturated fatty acids present in the diesel, which can be useful for engine ignition quality and properties tests such as density, pour point, fire point, and flash point. By this process and test's we are concluded that *spirulina* oil can be converted into biodiesel and can be called up for future work.

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