

**OPTIMIZATION INVOLVED IN RSM MODEL BY USING  
TRANSESTERIFICATION REACTION OF WASTE  
COOKING OIL FROM GRAPHENE OXIDE  
NANOCATALYST(CHARCOAL)**

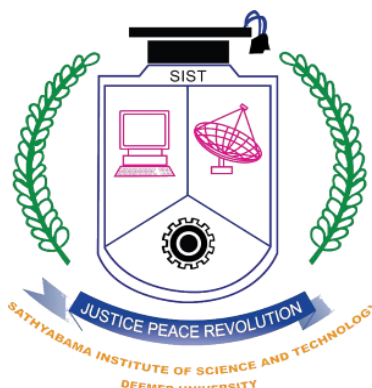
**PROJECT WORK (PHASE-II)**

Submitted in partial fulfilment of the requirements for the award of

Master of Technology degree in biotechnology

by

**NIRMAL KUMAR G (41810012)**



**DEPARTMENT OF BIOTECHNOLOGY**

**SCHOOL OF BIO AND CHEMICAL ENGINEERING**

**SATHYABAMA**

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

Accredited with Grade "A" by NAAC

JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119

**(MAY 2023)**



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**BONAFIDE CERTIFICATE**

This is to certify that this Review Report is the bonafide work of Nirmal Kumar G (41810012), who carried out the project entitled "**OPTIMIZATION INVOLVED IN RSM MODEL BY USING TRANSESTERIFICATION REACTION OF WASTE COOKING OIL ALONG WITH GRAPHENE OXIDE NANOCATALYST(CHARCOAL)**" under our supervision from January 2023 to April 2023

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## DECLARATION

I NIRMAL KUMAR G hereby declare that the Project entitled “**OPTIMIZATION INVOLVED IN RSM MODEL BY USING TRANSESTERIFICATION REACTION OF WASTE COOKING OIL ALONG WITH GRAPHENE OXIDE NANOCATALYST(CHARCOAL)**” is submitted in Partial fulfilment of the requirement for the award of Master of Technology degree in **Biotechnology**.

A handwritten signature in black ink, appearing to read 'G. D. Kumar', is written over a faint, light blue horizontal line.

**DATE: 05/05/2023**

**SIGNATURE OF CANDIDATE**

**PLACE: Chennai**

## **ACKNOWLEDGEMENT**

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## ABSTRACT

In this study, Graphene Oxide was derived from **charcoal with Ferrocene** and activated with NaOH to act as a heterogeneous base catalyst for transesterification of waste cooking oil to biodiesel. The catalyst was characterized by means of **FT-IR, XRD, HRTEM-EDX and UV VIS techniques**. **Box–Behnken design** optimization was carried out to study the complex interaction between reaction parameters. Catalyst concentration, methanol to oil molar ratio, and reaction time were varied from **1–3wt%, 3:1–4.5:1, and 60-90 min**, to obtain the maximum biodiesel conversion. Reaction parameters with the combination of **3 wt%** catalyst concentration, 90 min reaction time, 4.5:1 methanol/ethanol to oil molar ratio, and 60°C temperature led to the best yield of **62.5%** due to saponification reaction happens and becomes soapy and waxy content. The RSM Based BBD did 27 experimental runs with 4 factors 2 levels and we found that biodiesel yield is slightly decreased compared to maximum yield. **ANOVA Two Way Factorial** did the statistical analysis. **Gas chromatography (GC)** analysis disclosed **Hexadecenoic Acid Methyl Ester (25.57%)** and **Hexadecenoic Acid Ethyl Ester (12.94%)** to be the major composition of the synthesized biodiesel. Physicochemical properties of the biodiesel, such as **density (0.881g/cc)**, **Kinematic Viscosity @ 40°C (4.29 cSt)** **acid value (1.57mg NaOH/g)** for oil, **pour point (-1°C)**, **Copper Corrosion Strip @ 60°C(1a)** **Calorific Value (7375.02 Cal/g)** **Moisture Content (0.11%)** and **Cloud Point (5°C)** were measured and found to be in compliance with the standards. The minimum yield coming from a quite low catalyst concentration and high methanol/ethanol to oil molar ratio is phenomenal.

**Keywords:** GO FTIR UV VIS XRD HRTEM EDX ANOVA GC

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## **LIST OF ABBREVIATIONS**

**NO<sub>x</sub> – Nitric Oxides**

**UHC- Total Unburned Hydro Carbon**

**ANOVA – Analysis of Variance**

**GO – Graphene Oxide**

**CN – Cetane Number**

**BB – Box Behnken**

**WCO – Waste Cooking Oil**

# CHAPTER 1

## INTRODUCTION

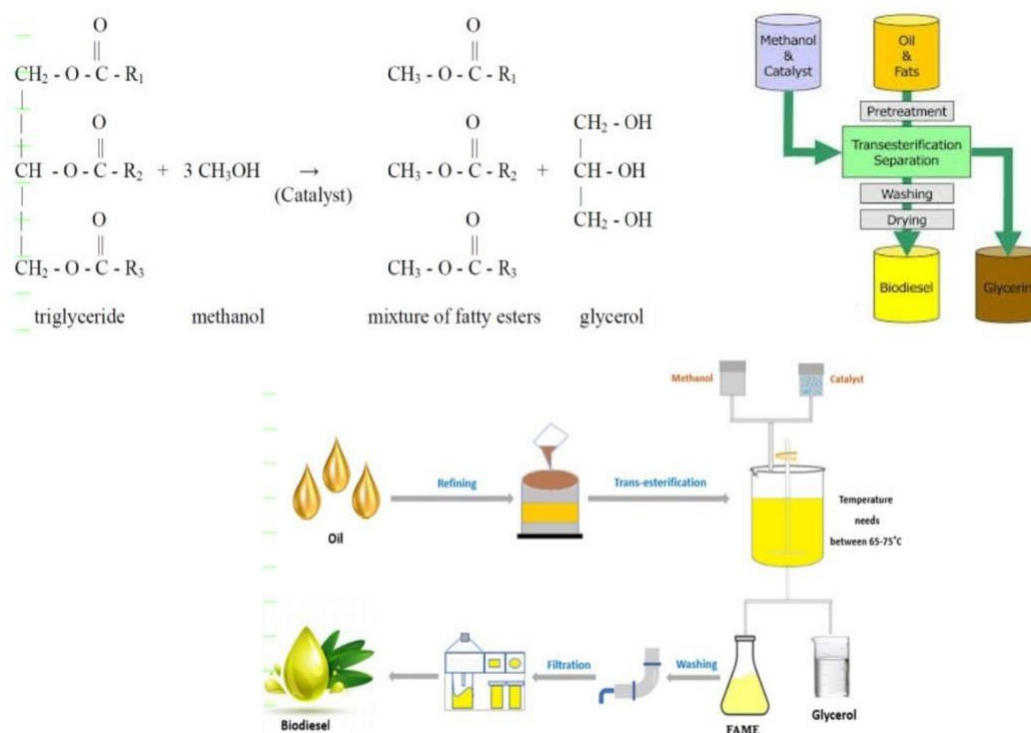
In the recent years, the petroleum will drain after 20-30 years and the crisis will rise and many eminent scientists suggested that Biofuel will be the best and replacement of fossil fuels and we are going to talk about the Biodiesel. The Diesel was coined by “**Rudolf Diesel**” and he did the Experiment of Peanut Oil at Paris Exposition Biodiesel is the best source of Biomass from Plants/Animals Algae (Microalgae) etc. which will be treated by chemical process and increases the quality of ignition and Cetane number. On contrary to expectations, the renewable source will gain 40-60% in 2030-2040 and diminishes the GHG (Green House Gases) by 60-70%. It is LCFA (Long Chain Fatty Acid) Alkyl Mono Esters contains less than 12% Oxygen (O<sub>2</sub>) reduces various emissions such as **UHC SO<sub>x</sub> Smoke PM and CO<sub>2</sub>** [1,2,3,4].



**Figure 1.1 Biodiesel and its compounds, Diesel founder Rudolf Diesel (Below)**

Biodiesel is nontoxic nondegradable and have certain good advantages such as low aromatics and viscosities but the shortcomings are balance between the Level of Saturation and Properties of Cold Flow [5,6]. The Eminent scientists predicted that the Availability of Fossil fuels will be gone by **2040-2060** due to usages by 10000

times faster than natural production simultaneously demand of world energy will rise up to 30TW. In 2030, B5 biodiesel blend will remain in India [7]. According to Global air quality reports 2022-23, India ranked 8th place among the most polluted countries in the world and its capital 'New Delhi' ranks 2nd in most polluted cities in



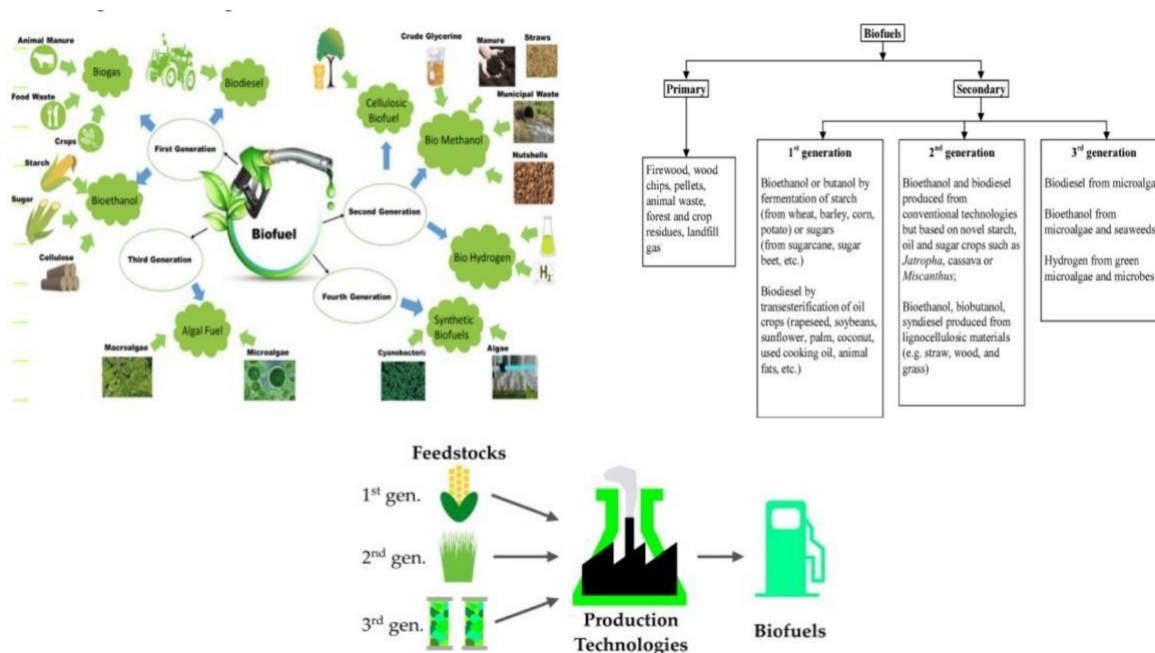
**Figure 1.2 Transesterification Process and its Reactions**

India. The viscous ranges between 10-20 times more than petroleum-based diesel and there is slight increase in **NOx emission**. Various techniques such as **Direct use, Blending, Micro emulsion, Pyrolysis and Transesterification** and to compare all techniques, Transesterification will be the best process for Biodiesel Production due to low cost and reduces longer times and Physio-chemical characteristics [8].

More scientists did the different sources and found that Algae and WCO/WFO [Waste Cooking/Frying Oil] will be the best sources for producing biodiesel. WCO/WFO is mainly used in the world especially USA, they did the project called Mc Diesel taken from Mc Donald Restaurants and have enormous amounts of triglycerides and components such as fats, proteins compared to other sources of oil. They use either in direct way or chemically modified way (Transesterification) [9]. In 2022, the biodiesel feedstock's-based Vegetable oils are 137 trillion Btu and

Losses and Co-solvents are 3 trillion Btu. The data which collected the information for consumption was 1710 MMgl [Million U.S. Gallon], 24,643 Mbbl [Thousand barrels] and 218 trillion Btu [10]. Transesterification is otherwise known as alcoholysis and is coined by “**Duff and Patrick**” and the performance was good and improves the quality. Advantages are diminishing viscosity such as Fats and Oils [6]. The process was done in large scale production to diminish the minimal cost. The **Alkyl Mono ester [Methyl or Ethyl or Propyl]** are known as biomass of biodiesel and the by-product is glycerol [22].

First generation is known as conventional and the cons are market impact and food security and so second generation can solve competition for food and feedstock [21]. In situ transesterification was the best one to check purity and yield [23]. Purity is testing % of ME and yield is to check phase over oil. However, they have certain advantages such as Cetane number and plug point, none can study this type [24].



**Figure 1.3 Generations of Biodiesel and its types**

Most catalysts may choose depends upon properties and acid, base and non-catalyst are preferably used [25]. There are small shortcomings which are NO<sub>x</sub> slightly increase [21,22] and decrease in depletion of ozone, SO<sub>2</sub>, PM, UHC and CO

[23,25,22].In this Experiment We will discuss the Waste Cooking Oil as the source for Biodiesel Production.[11] finds the Sulfonated carbon microspheres catalysts with and without waste cooking oil gives yield at 96.5% and 89.6% along with reaction temperature and time at **110°C at 120 min** and for catalyst loading will be calculated as 10wt%. Due to sulfonic acid leaching, stability of catalytic should be improved.[98] In India at 2003, the government has started a project called national Biodiesel Mission for Jatropha curcas plantation involved and to produced at 20% from 2011-2012 but the shortcomings are lack of financial support technology and institutional support. Biodiesel produced by India in 2018 at 185 million Litres which contains UCO Animal fats and industrial oil (Non edible) the consumption for petroleum-based diesel was 102079 Litres. The values are decreased to 80mg and 4.5mg/km for BS6 vehicles. Previous papers studies that Graphene Oxide will be the best one for catalysts because which has non-toxic, high yield and low cost [14]. GO coated tanks were used for Biodiesel production (Chilkoor et al,2017) and GO can be used for medical packaging to extend lifespan [19]. The pros for this principal are in reducing the number of experimental runs required to generate sufficient information for a statistically acceptable result. RSM did the successfully done in different feedstocks of biodiesel [18]. The Present work focuses on optimisation of Biodiesel and ANOVA analysis by using waste cooking oil as a source and GO(Charcoal) as Nano catalyst and Characteristics as well as analysis.

## CHAPTER 2

### REVIEW LITERATURE

Mythili R et al studied about the Jatropha and Castor oil by using Methanol [40%] and NaOH at 600rpm and yield from jatropha and castor were 76 and 27% [32].

Malani R.S et al [2020] received about non edible and waste fish oil mixture for BP by adding KOH catalyst and the agitation speed takes at 600rpm and yield would be 95.2%wt and purity will be 97.66% [33].

Leung and Guo [26] did the experiment of pure canola oil and UFO [Used Frying Oil] to check these parameters. It shows that UFO has more viscous than pure canola oil but low ester content and yield were obtained at 94% and 87.5%. If the level of alcohol increases, it will not increase in yield and it may affect alcohol recovery cost.

[64] Niju S et al [2016] analysed two images of SEM such as WBCS-900-600 [width: 53.9 to 62.6nm] and WBCS 900 [width: 1.71 to 2.42 pm] and it shows that there is high surface area between grains and aggregates. WBCS-900 generates CaO NP due to hydration and dehydration subsequent.

[66] did the BP from Jatropha curcas oil by using Bi<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> as the catalyst and According to the findings, adding Bi<sub>2</sub>O<sub>3</sub> improved the catalysts acid resistance. The intensity of the XRD peaks changes as the bismuth loading is increased, whereas La<sub>2</sub>O<sub>3</sub> intensity decreases. The basicity of the catalysts agreed with the peak's intensity, which showed a drop in La<sub>2</sub>O<sub>3</sub> peak intensity and an increase in the quantity of CO<sub>2</sub> that it absorbed overall.

[70] Absorption bands with absorbance maxima at roughly 232, 270, and 280 nm are visible in the spectral curves of BD samples. The C-C bond of the conjugated PUFA long carbon chain and the carbonyl groups (C=O), which also contribute to conjugation, are primarily responsible for the m,m\* transitions that cause the

absorbance maximum to be detected at about 230 nm. The spectral data of alkyl compounds with very little to no conjugation are similarly impacted by these groups. The peaks at 270 and 280 nm are characteristic of carbonyl-containing short-chain aliphatic molecules, such as free fatty acids, alkyl esters, aldehydes, and ketones.

[14] did the Pt Nanocatalyst on RGO for Cellulose/Cellobiose conversion to Sorbitol and the optimum for particle size would be 3.6nm and yield of 91.5% from sorbitol

[18] noted sulfonated Graphene at chemical exfoliation and functionalization which methanol/oil ratio will be noted as 20:1 and time and temperature of reaction will be 14hrs and 100°C.

[13] did the UCO biodiesel production by using eggshells of ostrich and eggshell based CaO as base heterogeneous catalyst. The characteristics of catalyst were noted by BET CO<sub>2</sub>-TPD TGA SEM XRD FTIR etc. and effects of parameters such as reaction of temperature (65°C) and time (120 min), methanol: oil ratio (12:1 M), catalyst reusability (1.5wt% and 5 times reusable), speed and concentration were noted. The ostrich eggshell based CaO catalyst have more surface area, basicity was high and particle size is small. Biodiesel yield were calculated as 96% and 94%.

[12] did the in-situ biodiesel production by using castor seeds with RSM based CCD design which Methanol: Oil ratio(v/w) calculated as 7.47, reaction temperature (44°C) and time (29.48 min) would be calculated along with KOH catalyst (1.7%). The R<sup>2</sup> and adj R<sup>2</sup>(0.974 and 0.951) were calculated based on regression equation for model and it shows suitable for good.

[9] says that Heterogeneous Base Catalysts have more advantages than Homogeneous Base catalysts due to economically and environmentally friendly operation as well as cheaper and safer. It can solve errors by using Simple filtration w/o solvent use and regenerates easily.

S Sathish et al did the biodiesel production about *Azolla filiculoides* by using GO Nanocatalyst from agro and results was good when temperatures are changes between 60 and 65°C with Oil :Methanol ratio 1:9 and catalyst 2% by weight[10].

Shehabaldin Rezaldia et al did the WCO (acidic) biodiesel production using Strontium-TiO<sub>2</sub> doped magnetic GO based Fe<sub>3</sub>O<sub>4</sub> results shows that the catalytic effectiveness was greater than 90% and separation was ease with Oil Methanol ratio was 10:1 within 3hrs at 10%wt catalysis [12].

## CHAPTER 3

### AIM AND OBJECTIVES

#### 3.1 AIM

To Check the Characteristics analysis of Nano Catalyst (GO) from Charcoal source for Biodiesel Production through Transesterification Process and then optimize through RSM Model with Statistical Analysis.

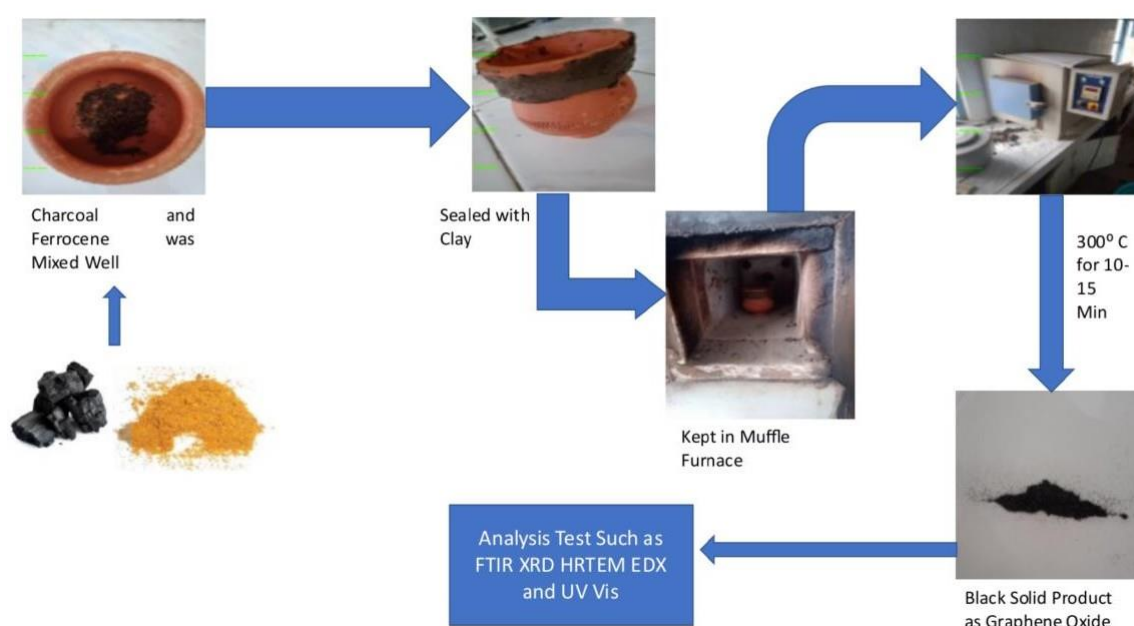
#### 3.2 OBJECTIVES

1. To synthesize Graphene Oxide (GO) from Charcoal and then analyse through **FTIR-ATR XRD HRTEM with EDX UV Vis Spectroscopy**
2. To Work Transesterification Process from WCO (Fish Fry) along with Alcohol and Catalyst and then measure **Reaction Time, Oil: Methanol Ratio, Yield (%) Catalyst Concentration(%wt)**, with GC-MS Analysis for Ester compound present.
3. To optimize **RSM Model** through Software.
4. ANOVA Table for Statistical Analysis through two way factorial

## CHAPTER 4

### MATERIALS AND METHODS

**4.1 Synthesis of Graphene Oxide (GO):** I followed Somanathan T et al method for GO synthesis. Take 5:1 ratio of Charcoal(0.5gm) and Ferrocene(0.1gm), mixed well and poured in Mud pot sealed with clay. Keep it in Muffle Furnace at 300°C for 10-15 minutes under atmospheric conditions. After the black solid was produced and collected at Room temperature. The Black Solid product was subjected to further analysis such as FTIR XRD HRTEM-EDX and UV Vis Spectroscopy etc.



**Figure 4.1 Graphene Oxide Synthesis Through Charcoal (Somanathan T et al 2015)**

**4.2 WCO Purification & Free Fatty Acid Content and Acid value Measurement:** WCO must be added with GO Nano Catalyst and heated well at **100°C for 20 minutes**. Then keep it at 10 hrs after purified with filter paper for removing any impurities present in oil. Take conical flask and add 5ml of purified oil with 25ml of Isopropyl Alcohol, heated at 5 mins. After heating, add phenolphthalein(indicator) and then NaOH was filled in Burette glass add dropwise and measured. If the value is lesser than 4, it would be ready to use transesterification.

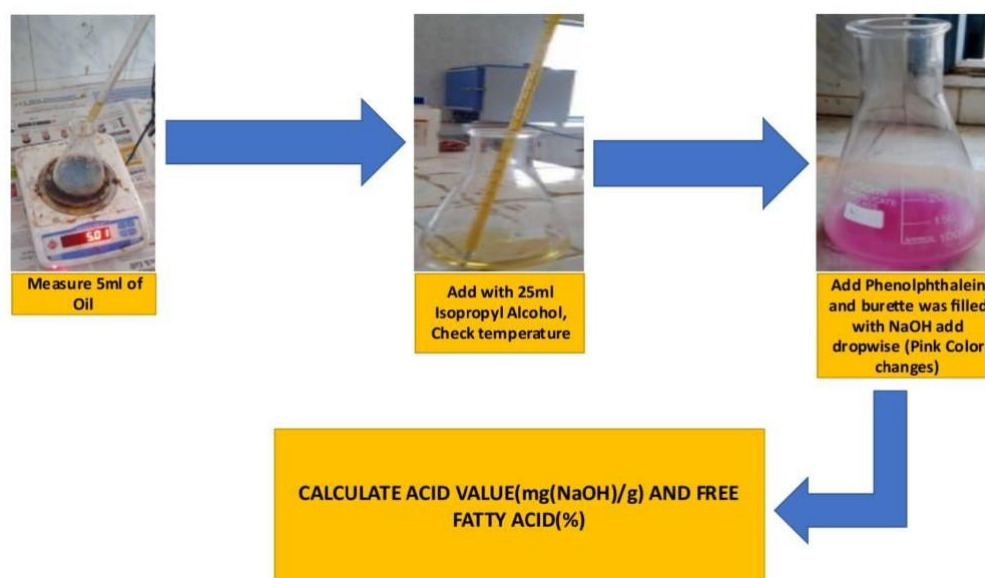
$$\text{Acid Value(mg/g)} = \frac{V_{\text{NaOH}} \times \text{MW of NaOH} \times N_{\text{NaOH}}}{\text{Weight of Sample (Oil)}}$$

$$= \frac{1.8\text{ml} \times 28.2 \times 0.1\text{N}}{5\text{ml}} = 1.57\text{mg/g}$$

**Free Fatty Acid (%) = Acid Value x Mol wt of Decanoic acid/Mol wt of NaOH  
x 100/1000**

$$= 1.57 \times 172.268/28.2 \times 1/10$$

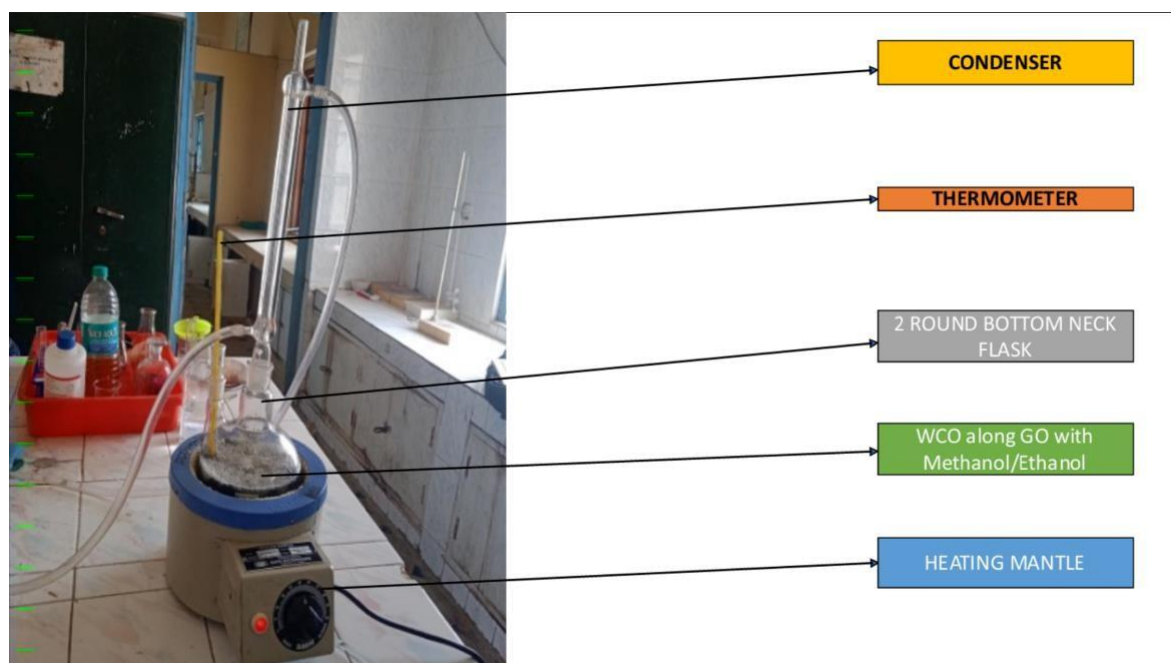
$$= 9.59/10 \rightarrow 0.96\%$$



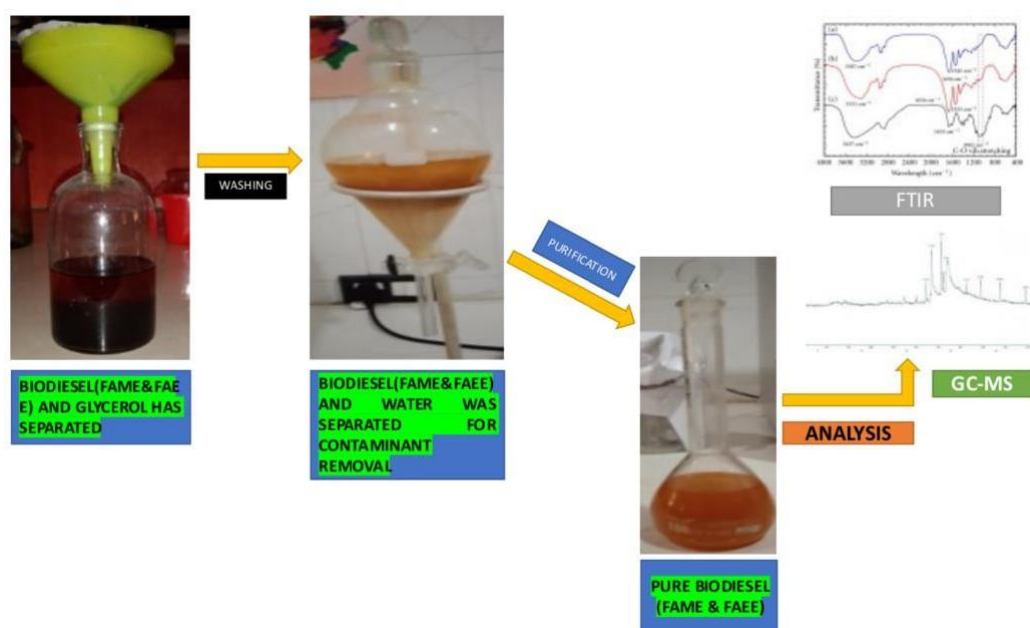
**Figure 4.2 Acid value and Free Fatty Acid Calculation**

**4.3 Biodiesel Production through Transesterification Process:** Take 2 Round Bottom Neck along with condenser tube, fixed it and connect water in inlet and put tube in outlet for water flowing. Oil collected from Satyabhama Mess Godown and then purified to remove impurities. Measure 300ml of WCO (Fish Fry) and 100ml of both Methanol and Ethanol (each 50 ml) mixed with 5gm of NaOH (Sodium Hydroxide), pour it in Round Bottom Flask and fixed with thermometer. The Reaction will be done for 1 to 2 hours at 50 - 60°C under Heating Mantle. After the reaction completed, Biodiesel (Upper Phase) and Glycerol (Lower Phase) will be separated based on density. Next, the upper phase of biodiesel (FAME&FAEE) will be washed with D.H<sub>2</sub>O for removing impurities and the washed biodiesel heated at 100°C for 5-10 min to remove water and methanol contents. Measure and Calculate Effects of Reaction Parameters such as Reaction Time Catalyst Concentration and Alcohol (Meth and Eth): Oil Ratio for plotting the graph.

$$\text{Biodiesel Yield (\%)} = \frac{\text{Weight of Biodiesel}}{\text{Weight of Oil}} \times 100$$



**Figure 4.3 Transesterification Reaction Setup**



**Figure 4.4 Separation and Purification of Biodiesel (FAME & FAEE)**

**4.3.1 Biodiesel Characteristics:** The Biodiesel was analysed by using Gas Chromatography Mass Spectrometry for finding Organic Compounds.

**4.3.2 Biodiesel Properties:** The Properties of Biodiesel sample has done according to the ASTM (American Standard Testing and Method) such as Density, Kinematic Viscosity at 40°C, Calorific Value, Copper Corrosion Strip at 60°C, Moisture Content (%), Cloud and Pour Point(°C).

#### 4.4 Experimental Design and Statistical Analysis

BBD (Box Behnken Design) was utilized to gain insight into the interaction of transesterification reaction's process parameters leading to biodiesel conversion. The impact of three reaction variables (A) Catalyst concentration (wt%), (B) Alcohol (Methanol and Ethanol) to oil ratio and (C) Reaction Time (min) on the response transesterification conversion was evaluated through regression and graphical analysis.

**Table 4.1 Selected Variables and Coded Levels Uses in BBD**

| Variables                    | Symbol | Code Levels |    |
|------------------------------|--------|-------------|----|
|                              |        | -1          | +1 |
| Catalyst Concentration (%wt) | A      | 1           | 5  |
| Alcohol: Oil Ratio           | B      | 3           | 6  |
| Reaction Time(min)           | C      | 1           | 2  |

Analysis of Variance (ANOVA) may be used for experimental study and measurement runs. Here we use 2 Factorial ANOVA for the influence of two different categorical independent variables on one continuous dependent variable. The two-way ANOVA not only aims at assessing the main effect of each independent variable but also if there is any interaction between them.

$$Y_{\text{Biodiesel Conversion (\%)}} = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i,j=1}^n \beta_{ij} X_{ij}$$

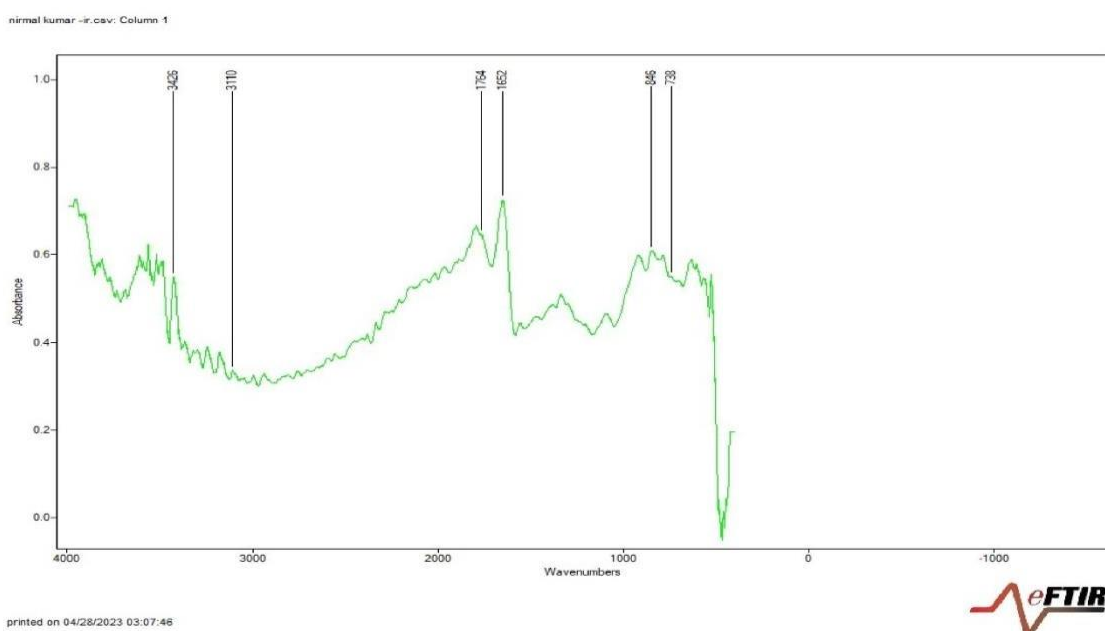
## CHAPTER 5

### RESULTS AND DISCUSSIONS

#### 5.1 Characteristics of Catalyst of GO

##### FTIR ATR Analysis

The FTIR ATR of Graphene Oxide has been analysed and various peaks are came. The broad band at **3426 cm<sup>-1</sup>** and **3110 cm<sup>-1</sup>** can be attributed to "O–H stretching" at Alcohols and Carboxylic Acids. The anhydrides found the peak at **1764 cm<sup>-1</sup>** responsible for "C=O Stretching". The strong absorption band at **1652 cm<sup>-1</sup>** is responsible for "C=C stretching"(isolated). On the other hand, the presence of bands at **738 cm<sup>-1</sup>** and **846 cm<sup>-1</sup>** can be attributed to C-H bend(ortho) as aromatics and C–H stretching respectively[



**Figure 5.1 FTIR ATR of Graphene Oxide**

## XRD Analysis

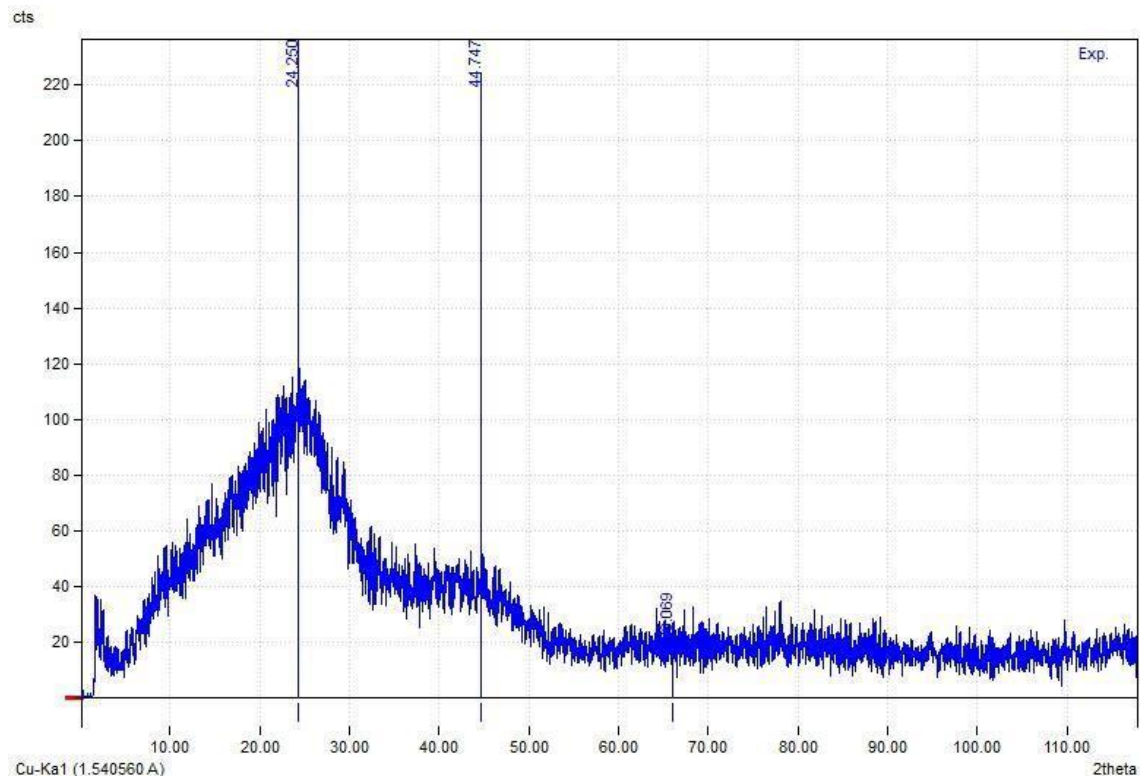
Broad diffraction peaks at  $2\theta=24.25^\circ$ ,  $2\theta=44.47^\circ$  and  $2\theta = 66.07^\circ$  for GO sample relate to typical amorphous carbon and can be indexed to **C (120)** **C (052)** and **C (035)** planes, respectively, of the hexagonal graphene structure. According to Braggs Law,

$$n\lambda = 2d \sin\theta$$

$$\lambda = 2(3.6672) \sin (24.25^\circ) \lambda$$

$$= 3.01\text{\AA}$$

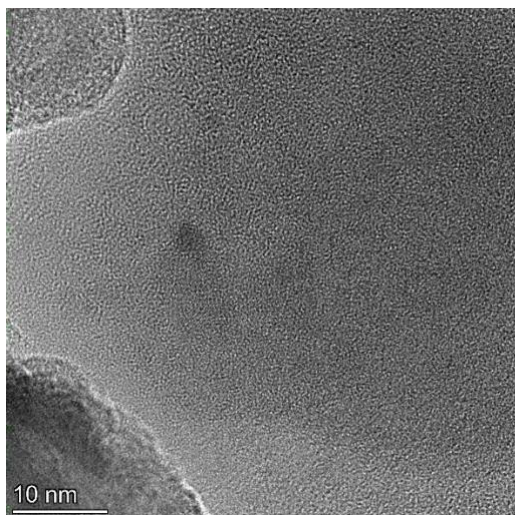
It would be confirmed that GO is present and did oxidise due to degree of freedom[



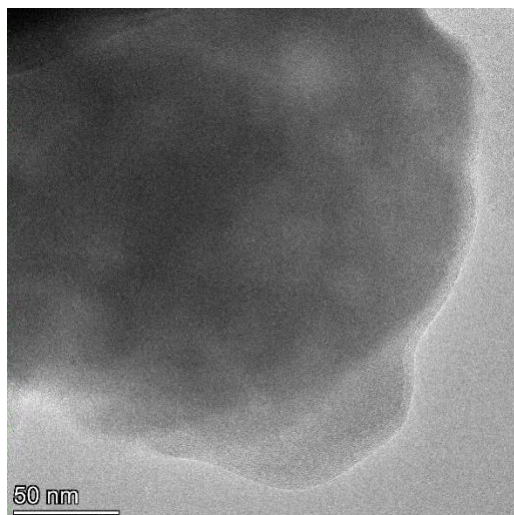
**Figure 5.2 XRD of Graphene Oxide (GO)**

## HRTEM EDX

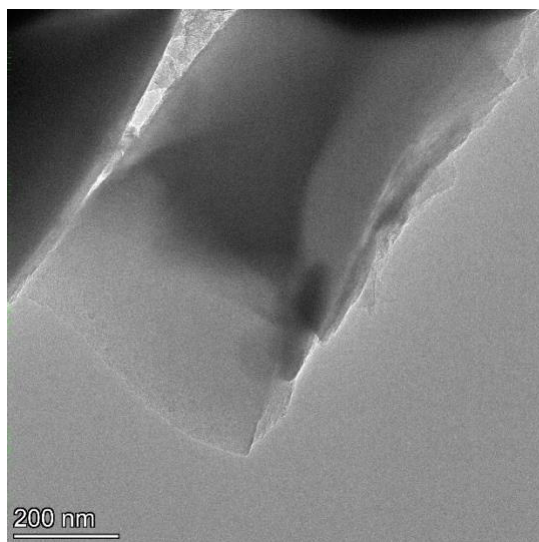
HRTEM OF Graphene Oxide (GO) has been analysed and 5.3(a) It was minimal extent of Porosity measured at 10nm and 5.3(b) GO measured at 50nm, surface has been founded that minimum content of ferrocene that was stacked one other [30,31,32,33,35,34,36,37]



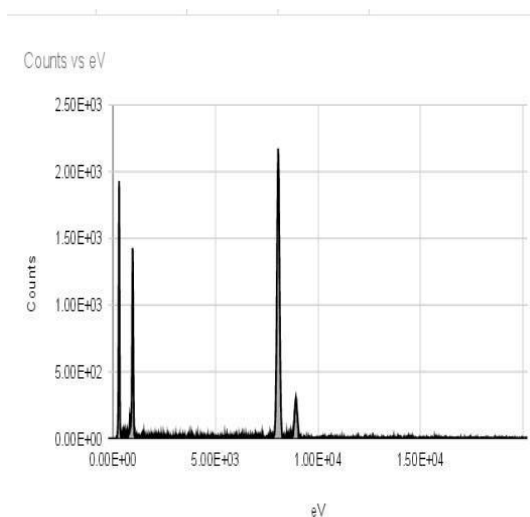
**5.3(a) 10nm of GO**



**5.3(b) 50nm of GO**



**5.3(c) Flakes of GO**



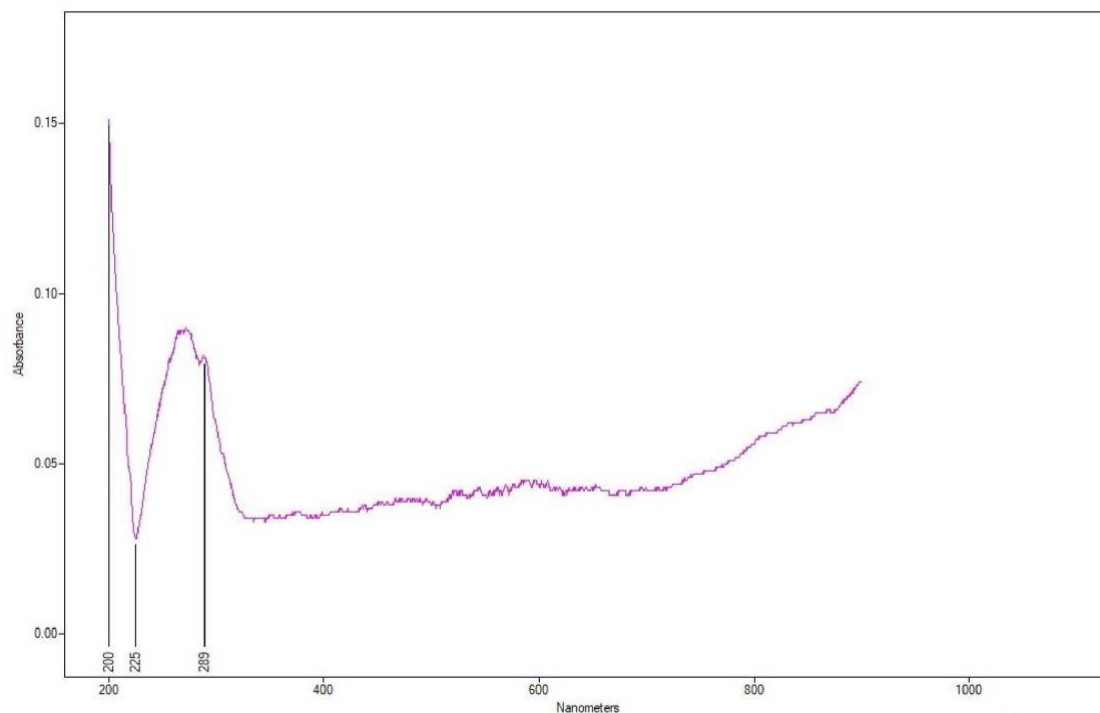
**5.3(c) GO EDX SPECTRUM**

The EDX spectra and corresponding HRTEM images of Graphene Oxide (GO) are shown in Fig 5.3(c) and EDX spectrum of GO has shown the presence of C (46.31%), O (51.21%) Fe (1.12%) and H (1.36%)[38,26,27,28,29]

## UV VIS Spectroscopy

The Sample has been done with the solvent of n-Hexane which can read till 329nm. UV- Vis spectra of GO(Charcoal) are shown in Fig 5.4. The spectrum of GO (Fig 5.4) indicates a strong characteristics absorption peak at 225 nm which is arising from the aromatic C=C bonds of GO attributing to  $\pi \rightarrow \pi^*$  transitions

NIRMAL.CSV: Column 1



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[50,51,49,48,47,45,43].

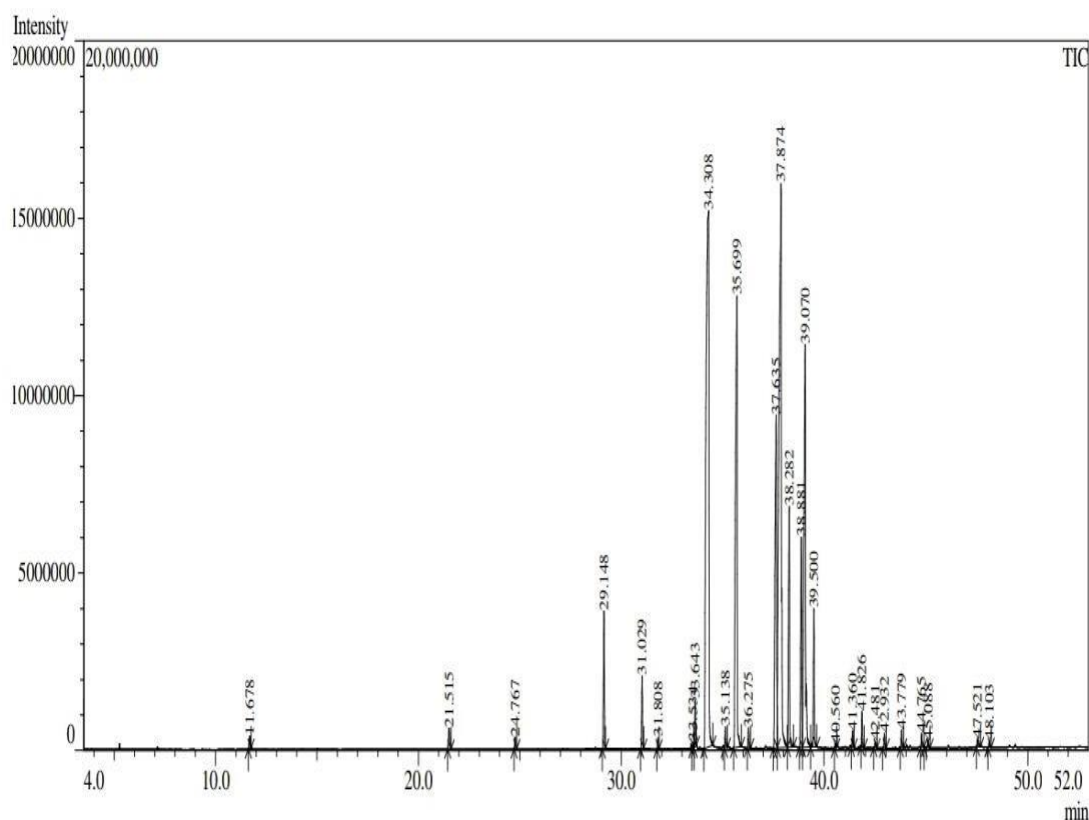
**Figure 5.4 UV VIS Spectroscopy of Graphene Oxide (GO)**

## 5.2 Biodiesel Characteristics

### Gas Chromatography – Mass Spectroscopy

The GC-MS of Biodiesel (FAME AND FAEE) analysed by using n-Hexane as solvent and detected more peaks and organic compounds. The High Peaks of 25.57 and 23.62 which has more Methyl Esters of Hexadecenoic Acid and 9-Octadecanoic Acid. Mostly Decanoic Acid

present in Biodiesel Sample which has soapy and waxy colour. Hexadecanoic Acid Ethyl Esters and 9 Octadecenoic Acid Ethyl Esters has peak values such as 12.94 and 11.38. 0.22% Ferrocene Compound is present in Biodiesel Sample which tells that there is some impurities [78,79,86,88,90,100].



**Figure 5.5 GC-MS ANALYSIS OF BIODIESEL (FAME & FAEE)**

**Table 5.1 Reports of GC-MS Analysis for Biodiesel (FAME&FAEE)**

| Peak Report TIC |        |           |        |                                                     |
|-----------------|--------|-----------|--------|-----------------------------------------------------|
| Peak#           | R.Time | Area      | Area%  | Name                                                |
| 1               | 11.678 | 1260570   | 0.22   | Ferrocene                                           |
| 2               | 21.515 | 2520054   | 0.44   | DODECANOIC ACID, METHYL ESTER                       |
| 3               | 24.767 | 1141925   | 0.20   | ETHYL TRIDECANOATE                                  |
| 4               | 29.148 | 11975912  | 2.11   | TETRADECANOIC ACID, METHYL ESTER                    |
| 5               | 31.029 | 5917917   | 1.04   | TETRADECANOIC ACID, ETHYL ESTER                     |
| 6               | 31.808 | 851052    | 0.15   | PENTADECANOIC ACID, METHYL ESTER                    |
| 7               | 33.534 | 383838    | 0.07   | 9-HEXADECENOIC ACID, METHYL ESTER                   |
| 8               | 33.643 | 3817034   | 0.67   | 9-OCTADECENOIC ACID (Z)-, METHYL ESTER              |
| 9               | 34.308 | 145401524 | 25.57  | HEXADECANOIC ACID, METHYL ESTER                     |
| 10              | 35.138 | 1578091   | 0.28   | Ethyl 9-hexadecenoate                               |
| 11              | 35.699 | 73558201  | 12.94  | HEXADECANOIC ACID, ETHYL ESTER                      |
| 12              | 36.275 | 1475374   | 0.26   | Heptadecanoic acid, methyl ester                    |
| 13              | 37.635 | 50092987  | 8.81   | 9,12-Octadecadienoic acid (Z,Z)-, methyl ester      |
| 14              | 37.874 | 134282304 | 23.62  | 9-OCTADECENOIC ACID, METHYL ESTER                   |
| 15              | 38.282 | 24971135  | 4.39   | Methyl stearate                                     |
| 16              | 38.881 | 21935029  | 3.86   | ETHYL (9Z,12Z)-9,12-OCTADECADIENOIC ACID            |
| 17              | 39.070 | 64683421  | 11.38  | 9-OCTADECENOIC ACID (Z)-, ETHYL ESTER               |
| 18              | 39.500 | 12089361  | 2.13   | Octadecanoic acid, ethyl ester                      |
| 19              | 40.560 | 412236    | 0.07   | cis-7,10,13,16-Docosatetraenoic acid, methyl ester  |
| 20              | 41.360 | 1343010   | 0.24   | cis-13-Eicosenoic acid, methyl ester                |
| 21              | 41.826 | 2596061   | 0.46   | EICOSANOIC ACID, METHYL ESTER                       |
| 22              | 42.481 | 520776    | 0.09   | Butyl 11-eicosenoate                                |
| 23              | 42.932 | 1106796   | 0.19   | Heptadecanoic acid, ethyl ester                     |
| 24              | 43.779 | 1350296   | 0.24   | 4,7,10,13,16,19-Docosahexaenoic acid, methyl ester  |
| 25              | 44.765 | 1266658   | 0.22   | DOCOSAHEXAENOIC ACID, 1,2,3-PROPYL ESTER            |
| 26              | 45.088 | 718364    | 0.13   | DOCOSANOIC ACID, METHYL ESTER                       |
| 27              | 47.521 | 750436    | 0.13   | 9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester |
| 28              | 48.103 | 548190    | 0.10   | TETRACOSANOIC ACID, METHYL ESTER                    |
|                 |        | 568548552 | 100.00 |                                                     |

### 5.3 Response Surface Methodology Analysis

Table 5.2 represents the experiments that were carried out following BBD matrix. The experimental data was found to be best fitted to a linear model. The relevant parameters associated with the model is presented in Table 5.3.[77,80,81,85,84].

**Table 5.2 BOX BEHNKEN DESIGN DOE FOR RSM MODEL AT BIODIESEL**

| <b>Experimental Design: Box-Behnken</b> |              |                      |                 |                 |                 |
|-----------------------------------------|--------------|----------------------|-----------------|-----------------|-----------------|
| <b>S.No</b>                             | <b>Block</b> | <b>Cat Conc(wt%)</b> | <b>MeOH:Oil</b> | <b>Time(hr)</b> | <b>Yield(%)</b> |
| 1                                       | 1            | 1                    | 3               | 1.5             | 62.5            |
| 2                                       | 1            | 5                    | 3               | 1.5             | 62.5            |
| 3                                       | 1            | 1                    | 6               | 1.5             | 62.5            |
| 4                                       | 1            | 5                    | 6               | 1.5             | 62.5            |
| 5                                       | 1            | 3                    | 4.5             | 1               | 25              |
| 6                                       | 1            | 3                    | 4.5             | 2               | 25              |
| 7                                       | 1            | 3                    | 4.5             | 1               | 100             |
| 8                                       | 1            | 3                    | 4.5             | 2               | 100             |
| 9                                       | 1            | 3                    | 4.5             | 1.5             | 62.5            |
| 10                                      | 2            | 1                    | 4.5             | 1.5             | 25              |
| 11                                      | 2            | 5                    | 4.5             | 1.5             | 25              |
| 12                                      | 2            | 1                    | 4.5             | 1.5             | 100             |
| 13                                      | 2            | 5                    | 4.5             | 1.5             | 100             |
| 14                                      | 2            | 3                    | 3               | 1               | 62.5            |
| 15                                      | 2            | 3                    | 6               | 1               | 62.5            |
| 16                                      | 2            | 3                    | 3               | 2               | 62.5            |
| 17                                      | 2            | 3                    | 6               | 2               | 62.5            |
| 18                                      | 2            | 3                    | 4.5             | 1.5             | 62.5            |
| 19                                      | 3            | 1                    | 4.5             | 1               | 62.5            |
| 20                                      | 3            | 5                    | 4.5             | 1               | 62.5            |
| 21                                      | 3            | 1                    | 4.5             | 2               | 62.5            |
| 22                                      | 3            | 5                    | 4.5             | 2               | 62.5            |
| 23                                      | 3            | 3                    | 3               | 1.5             | 25              |
| 24                                      | 3            | 3                    | 6               | 1.5             | 25              |
| 25                                      | 3            | 3                    | 3               | 1.5             | 100             |
| 26                                      | 3            | 3                    | 6               | 1.5             | 100             |
| 27                                      | 3            | 3                    | 4.5             | 1.5             | 62.5            |

## ANOVA (Analysis of Variance) Two Way Factorial

ANOVA table

| FV    | Sum Squares | Degrees Freedom | MeanSum s | F       |
|-------|-------------|-----------------|-----------|---------|
| A     | 4238.25     | 26              | 163.01    | 1.0     |
| B     | 71811.563   | 3               | 23937.188 | 146.845 |
| ERROR | 12714.75    | 78              | 163.01    |         |
| TOTAL | 88764.563   | 107             |           |         |

Critical Value F

A:  $FT(26, 78, 0.05) = 1.638$   
B:  $FT(3, 78, 0.05) = 2.722$

|   | F       | Probability (p) | Critical Value F |
|---|---------|-----------------|------------------|
| A | 1.0     | 0.479           | 1.638            |
| B | 146.845 | 0.0             | 2.722            |

B

| Column       | Samples | Sum    | Mean | Variance |
|--------------|---------|--------|------|----------|
| Cat Conc %wt | 27      | 81.0   | 3.0  | 1.846    |
| A : O        | 27      | 121.5  | 4.5  | 1.038    |
| Time(hr)     | 27      | 40.5   | 1.5  | 0.115    |
| Yield(%)     | 27      | 1687.5 | 62.5 | 649.038  |

Total Average and Total Variance

$y_{..} = 17.875$   
 $S^2 = 829.575$

**Figure 5.6 ANOVA TWO WAY FACTORIAL AND ITS ANALYSIS**

The ANOVA for the suggested linear model is shown in Table 5.2 The fitted model can be termed statistically significant at 95%(0.95).

27 Samples were tested and 4 Factors did for BBD Matrix.

The F and P value will be 1 and 0.479 for Critical Value F the values of A and B are 1.638 and 2.722.

The Reaction Time, Catalyst Concentration and Alcohol : Oil Ratio were noted as 1.5hrs, 3.0%wt and 4.5:1 Ratio which would be highest value for the sample[83,86,89,90,91].

## 5.4 Biodiesel Properties

The sample must be done in different standards such as ASTM. .In this sample, we did ASTM Standards as D6751 Testing Methods.

**Figure 5.3 Physicochemical Properties of Biodiesel and it's Properties**

| S. No | Biodiesel Properties           | Biodiesel(FAME AND FAEE) Values | ASTM Standard D6751 Methods (Ranges) | References |
|-------|--------------------------------|---------------------------------|--------------------------------------|------------|
| 1     | Density                        | 0.881 g/cc                      | ASTM D6751                           | [87] [99]  |
| 2     | Kinematic Viscosity @ 40°C     | 4.29 cSt                        | ASTM D6751                           | [82,94]    |
| 3     | Copper corrosion strip @ 60 °C | 1 a                             | ASTM D6751                           | [72] [92]  |
| 4     | Cloud Point °C                 | 5 °C                            | EN ISO 12937                         | [74] [96]  |
| 5     | Pour Point °C                  | -1 °C                           | ASTM D675                            | [71] [73]  |
| 6     | Moisture Content               | 0.11 %                          | EN ISO 12937                         | [75] [100] |
| 7     | Calorific Value                | 7375.02 Cal/g                   | ASTM D-97598                         | [76] [93]  |

## **CHAPTER 6**

### **CONCLUSION**

1. We found out that GO from Charcoal has more Carbon and Oxygen compounds present in sample detected and analyzed by FTIR UV VIS XRD AND HRTEM EDX
2. The Biodiesel Yield will be noted as 62.5% which will be decreased gradually due to the saponification of waste cooking oil(fish fry) present and has soapy, waxy content that's why it decreased.
3. Alcohol: Oil Ratio is increased from 3:1 to 4.5: 1 Reaction Time is increased from 1 to 1.5hrs and Catalyst Concentration increases from 1 to 3wt%.
4. RSM Model based BOX BEHNKEN DESIGN done 4 factor 2 level and did 27 experiments

## CHAPTER 7

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