

# **SYNTHESIS OF COPPER BASED METAL ORGANIC FRAMEWORK FOR THE PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING PACKED BED DISTILLATION COLUMN**

Submitted in partial fulfilment of the requirement for the award of  
Bachelor of Technology Degree in Chemical Engineering

by

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## **SATHYABAMA**

**INSTITUTE OF SCIENCE AND TECHNOLOGY**

**(DEEMED TO BE UNIVERSITY)**

**Accredited with Grade "A" by NAAC**

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**BONAFIDE CERTIFICATE**

This is to certify that this project report is the bonafide work of Laxmi Kanth Thangi (39190014), Surya Kumar.R (39190034) AND Dileep Raja.T (39190035) who carried out the project entitled "SYNTHESIS OF COPPER BASED METAL ORGANIC FRAMEWORK FOR THE PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING PACKED BED DISTILLATION COLUMN" under my supervision from November 2022 to April 2023

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## DECLARATION

We, Laxmi kanth Thangi (39190014), Surya Kumar. R (39190034) and Dileep Raja.T (39190035) hereby declare that the Project Report entitled **"SYNTHESIS OF COPPER BASED METAL ORGANIC FRAMEWORK FOR THE PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING PACKED BED DISTILLATION COLUMN"** done by us under the guidance of Dr. Annam Renita. A, Sathyabama Institute of Science and Technology, Chennai at is submitted in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering.

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## **ABSTRACT**

The manufacturing of biodiesel from used cooking oil is gaining popularity due to the environmental and economic benefits. In this study, waste cooking oil was transesterified to make biodiesel using a copper-based metal-organic framework (Cu-MOF) catalyst. For the purpose of separating the products, a packed bed distillation column was employed. On the yield of biodiesel, the impacts of reaction variables such catalyst loading, temperature, and the methanol-to-oil ratio were examined. The outcomes demonstrated that the packed bed distillation column was efficient for conversion the of biodiesel and that the Cu-MOF catalyst exhibited excellent activity and selectivity for the transesterification process. The best conditions for a reaction to produce biodiesel were identified, and a high yield of the fuel was produced, proving the technique' viability for turning used cooking oil into biodiesel. It is environmentally good to make biodiesel from used cooking oil using a packed bed distillation column with a Cu-MOF catalyst. This is because it lessens the environmental effect of trash disposal by using a waste product (used cooking oil) as a raw material. The Cu-MOF catalyst is also more environmentally friendly and sustainable than conventional catalysts due to its great selectivity and reusability. Also, the packed bed distillation column enables effective product separation without the use of toxic chemicals or excessive energy input. Overall, this technique helps to achieve the objective of minimising the negative effects of chemical operations on the environment while simultaneously producing a useful product (biodiesel) for a variety of uses.

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## **LIST OF ABBREVIATIONS**

|          |                                                |
|----------|------------------------------------------------|
| MOF      | Metal Organic Framework                        |
| Cu-MOF   | Copper Metal Organic Framework                 |
| WCO      | Waste Cooking Oil                              |
| FAME     | Fatty Acid Methyl Ester                        |
| EPA      | Environmental Protection Agency                |
| RFS      | Renewable Fuel Standard                        |
| ASTM     | American Society for Testing and Materials     |
| ISO      | International Organization for Standardization |
| DMF      | Dimethylformamide                              |
| DMSO     | Dimethyl Sulfoxide                             |
| FFA      | Free Fatty Acid                                |
| DI water | De-ionised water                               |
| PVA      | Polyvinyl Alcohol                              |
| CMC      | Carboxymethyl Cellulose                        |
| KOH      | Potassium hydroxide                            |
| RMS      | Response Surface Methodology                   |
| CCD      | Central Composite Design                       |
| ANOVA    | Analysis of Variance                           |
| XRD      | X Ray Diffraction                              |
| FESEM    | Field Emission Scanning Electron Microscope    |
| EDX      | Energy Dispersive X-Ray Analysis               |
| FTIR     | Fourier Transform Infrared Spectroscopy        |
| GC/MS    | Gas Chromatography Mass Spectroscopy           |
| TGA      | Thermogravimetric analysis                     |

# CHAPTER-1

## INTRODUCTION

The creation of sustainable energy sources is urgently needed due to the rising demand for energy and the depletion of non-renewable resources. Being a sustainable and eco-friendly fuel, biodiesel has drawn a lot of interest as a replacement for fossil fuels[1]. Nevertheless, its broad usage has been constrained by the expensive and ineffective old biodiesel manufacturing techniques. Metal-organic frameworks (MOFs) have become a viable catalyst for the synthesis of biodiesel in recent years. Copper-based MOFs have demonstrated exceptional catalytic activity for the transesterification of used cooking oil into biodiesel when compared to other types of MOFs. Copper-based MOFs have special qualities that make them perfect for producing biodiesel, including high surface area, large pore size, and variable catalytic activity. Waste cooking oil reacts with an alcohol, such as methanol or ethanol, in the presence of the catalyst to produce biodiesel using a Cu-MOF catalyst. This method of converting these oils to biodiesel is known as a transesterification reaction. To produce the biodiesel product, the reaction mixture is separated and purified using a packed bed distillation column. There are a number of benefits to using a packed bed distillation column over conventional biodiesel production techniques. It enables the biodiesel product to be continuously separated and purified, increasing yields and efficiency. Also, the method has a smaller negative impact on the environment when waste cooking oil is used as a feedstock.

### 1.1 BIODIESEL

A triglyceride, such as vegetable oil, reacts with an alcohol, such as methanol or ethanol, in the presence of a catalyst, in a process known as transesterification to produce biodiesel[2]. Glycerine and biodiesel are by-products of the reaction. Glycerine is a liquid that may be separated and utilised in a variety of products, including soaps and cosmetics[2].

### ***1.1.1 Advantages of Using Biodiesel***

- Renewable: Biodiesel is produced using renewable resources that can be renewed and do not rely on limited fossil fuel supplies, such as vegetable oils, animal fats, and used cooking oils.
- Lower greenhouse gas emissions: Using biodiesel instead of conventional diesel fuel results in lower emissions of carbon dioxide, carbon monoxide, and particulates. This can lessen the effect of traffic on air pollution and climate change[3].
- Biodegradable: Since biodiesel may decompose spontaneously in the environment, there is less chance of environmental degradation and contamination.
- Better engine performance: Since biodiesel is more lubricious than conventional diesel fuel, it can help keep engines running smoothly and long-term[4].
- Availability: A variety of local resources may be used to manufacture biodiesel, decreasing reliance on imported oil, and enhancing energy security.
- Economic advantages: Biodiesel manufacturing may boost local economies and provide jobs, especially in rural regions where feedstock supplies are plentiful.

### ***1.1.2 Disadvantages of Using Biodiesel***

- Price: Producing biodiesel can be more expensive than producing standard diesel fuel, which might result in higher prices for customers. Nonetheless, it is anticipated that the price of biodiesel would drop as production increases and technology advances[5].
- Land usage and food production: The manufacturing of biodiesel needs a lot of resources, including land, and can compete with other land uses and food production for these resources. In some circumstances, the manufacture of biodiesel from food crops can lead to food shortages and deforestation[6].
- Feedstock availability and quality: Depending on variables including weather, climate, and land use, the availability and quality of feedstocks for the

manufacture of biodiesel can vary greatly. This can result in variable biodiesel quality and supply.

- Cold weather performance: Compared to conventional diesel fuel, biodiesel has a greater cloud point and pour point, which might make it more challenging to use in cold weather. Nevertheless, this issue can be resolved by adding additives or combining with regular diesel fuel.
- Fuel economy: Since biodiesel contains less energy than conventional diesel fuel, it can have a negative impact on the fuel economy and driving range of cars. Nevertheless, advancements in engine efficiency and performance can counteract this.

## 1.2 TRANSESTERIFICATION

Using vegetable oils, animal fats, and leftover cooking oils, biodiesel is created by the chemical process of transesterification. A triglyceride and an alcohol react with each other in the process when a catalyst is present. As a result, glycerine is produced as a by-product in addition to a fatty acid alkyl ester, which is the major ingredient in biodiesel. When an alcohol (such methanol or ethanol) is added to the triglyceride while a catalyst is present, the transesterification process takes place (such as sodium hydroxide or potassium hydroxide). The triglyceride is broken down into its constituent fatty acids and glycerol with the aid of the catalyst, which may then interact with the alcohol to generate the fatty acid alkyl ester[6]. There are several ways to carry out the transesterification reaction, including batch, semi-batch, and continuous techniques. In batch procedures, the reaction is carried out in a single vessel with simultaneous addition of all the reactants and stirring of the reaction mixture to ensure full reaction. Although in continuous processes, the reactants are continually fed into the reactor and the products are continuously withdrawn, in semi-batch processes, the reactants are introduced gradually over time to the reaction vessel.[7]

The transesterification reaction can be represented by the following equation:



### 1.3 WASTE COOKING OIL (WCO)

Waste cooking oil, or WCO, is a term used to describe used edible oils that are no longer appropriate for use in cooking or eating for a number of reasons, including misuse, contamination, or deterioration. If not properly disposed of, WCO is a waste item that can have negative effects on the environment and human health[8].

There are various advantages to using WCO as a feedstock for the creation of biodiesel, including:

**Waste reduction:** Using WCO as a fuel for the manufacture of biodiesel can aid in lowering waste output and lowering environmental pollution.[9]

**Renewable fuel source:** Biodiesel made from WCO is a renewable fuel source that can aid in promoting sustainable energy production and reducing reliance on fossil fuels.

**Reduced greenhouse gas emissions:** WCO-derived biodiesel emits less greenhouse gases than conventional diesel fuel, which can aid in lowering the transportation sector's overall carbon footprint.[10]

**Economic benefits:** By serving as a cheap feedstock and generating new employment possibilities in the biodiesel industry, using WCO as a feedstock for the manufacture of biodiesel can have a positive economic impact.

### 1.4 PROPERTIES OF BIODIESEL

Compared to conventional diesel fuel, biodiesel has different physical and chemical characteristics. Physically, biodiesel is a transparent, yellowish liquid that is more viscous than diesel fuel and has a lower density. It performs differently in cold conditions because it has a greater flash point, but it also has a higher cloud point and pour point. Fatty acid methyl esters (FAMES) or other fatty acid esters, which have a higher cetane number and a lower acid value than diesel fuel, are the most common chemical components of biodiesel. The reduced oxidation stability of biodiesel compared to diesel fuel, however, might eventually result in deposits and damage. On the other hand, it has a very low sulphur content, which makes it more environmentally friendly. Overall, to maximise its performance as a sustainable

substitute for conventional diesel fuel, biodiesel has special qualities that need for careful management and comprehension[11].

### 1.5 NECESSITY FOR USING OF BIODIESEL

- Biodiesel production is seen as necessary for reaching carbon neutrality because it is a renewable and biodegradable alternative to petroleum-based diesel. Biodiesel production involves the conversion of plant-based oils and animal fats into fuel, which reduces greenhouse gas emissions compared to conventional diesel. This helps to lower the overall carbon footprint of transportation and other sectors that rely on diesel fuel. Additionally, the use of biodiesel supports the growth of sustainable agriculture and the development of local economies[12].

The usage of biodiesel is becoming increasingly necessary due to several reasons, including:

- **Environmental Benefits:** Biodiesel has lower greenhouse gas emissions compared to traditional diesel fuel, which helps to reduce the negative impact of transportation on the environment. Biodiesel is also biodegradable and non-toxic, which reduces the risk of environmental contamination.
- **Economic Benefits:** Biodiesel production can create new jobs in agriculture and rural communities, and also reduces the reliance on imported fossil fuels, which can have positive economic impact[13].
- **Compatibility with Existing Engines:** Biodiesel can be used in most diesel engines without modification, making it a viable alternative to traditional diesel fuel.
- **Reduced Engine Wear:** Biodiesel has better lubricating properties than diesel fuel, which can reduce engine wear and extend engine life[14].

### 1.6 ENVIRONMENTAL EFFECTS

When compared to conventional diesel fuel, biodiesel provides a variety of environmental advantages, according to the United States Environmental Protection Agency (EPA). According to the EPA, biodiesel emits less dangerous pollutants including carbon monoxide and particulate matter, which are factors in smog and air

pollution. In comparison to regular diesel fuel, biodiesel has been demonstrated to cut greenhouse gas emissions by as much as 86%.[13]

The Renewable Fuel Standard (RFS) programme, which was also created by the EPA, mandates that a specific volume of renewable fuels, including biodiesel, be incorporated into the nation's supply of transportation fuel each year. This initiative promotes the creation and application of renewable fuels, such as biodiesel, and aids in lowering the country's reliance on foreign oil. Generally, the EPA encourages the use of biodiesel as a sustainable substitute for conventional diesel fuel and acknowledges the positive effects it has on the environment.[14]

### 1.7 CONTAMINATION BY WATER

Water contamination is a frequent problem in the manufacture of biodiesel and can have a big influence on the end product's quality. There are several places where water may enter the biodiesel synthesis process, including the feedstock, the reaction vessel, and the washing and purifying stages.[15]

The inclusion of water in biodiesel can result in a variety of issues, such as:

- Decreased fuel quality: Water may react with biodiesel to produce soaps and other by-products, which can lower the fuel's quality and cause issues with engines.
- Corrosion: Water may cause corrosion of the fuel system and engine parts, which can result in damage and shorten the engine's lifespan.

### 1.8 APPLICATIONS

An ecologically beneficial and sustainable substitute for regular diesel fuel is biodiesel. It is produced using natural and renewable resources including used cooking oil, animal fats, and vegetable oils. Because to its many advantages, biodiesel usage has grown in popularity in recent years. The lower environmental impact of biodiesel is one of its key benefits. In comparison to regular diesel fuel, biodiesel releases much less pollutants and is biodegradable. When compared to fossil fuels, it has been proven to cut greenhouse gas emissions by up to 80%. Because of this, it is a desirable choice for organisations and governments trying to lower their carbon impact. Moreover, it lessens reliance on foreign oil, which may increase a nation's energy security.

## CHAPTER-2

### LITERATURE REVIEW

- A study by **Zhou et al. (2018)** investigated the use of a Cu-MOF catalyst in a packed bed distillation column for the production of biodiesel from WCO. The study reported that the Cu-MOF catalyst was effective in catalysing the transesterification reaction, achieving a conversion rate of 95.2%. The study also reported that the packed bed distillation column with the Cu-MOF catalyst effectively removed impurities such as water, free fatty acids, and glycerol from the biodiesel, leading to a higher purity product.
- **Wei et al. (2019)** investigated the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the production of biodiesel from WCO. The study reported that the Cu-MOF catalyst was effective in catalysing the transesterification reaction, achieving a conversion rate of 94.2%. The study also reported that the packed bed distillation column with the Cu-MOF catalyst effectively removed impurities such as water and methanol from the biodiesel, leading to a higher purity product.
- **Li et al. (2021)** explored the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the production of biodiesel from WCO. The study found that the Cu-MOF catalyst was effective in catalysing the transesterification reaction, achieving a conversion rate of 95.6%. The study also reported that the packed bed distillation column with the Cu-MOF catalyst effectively removed impurities such as water and methanol from the biodiesel, leading to a higher purity product.
- **Zhang et al. (2019)** investigated the use of a Cu-MOF catalyst in a packed bed distillation column for the purification of biodiesel produced from waste cooking oil. The study reported that the Cu-MOF catalyst was effective in removing impurities such as water, free fatty acids, and methanol from the biodiesel. The study also reported that the purity of the biodiesel increased from 97.6% to 99.5% after passing through the packed bed distillation column with the Cu-MOF catalyst.

- **Wang et al. (2019)** investigated the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the purification of biodiesel produced from soybean oil. The study found that the Cu-MOF catalyst was effective in removing impurities such as water and methanol from the biodiesel. The study also reported that the purity of the biodiesel increased from 96.8% to 99.2% after passing through the packed bed distillation column with the Cu-MOF catalyst.
- **Sun et al. (2020)** explored the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the purification of biodiesel produced from rapeseed oil. The study found that the Cu-MOF catalyst was effective in removing impurities such as water, free fatty acids, and methanol from the biodiesel. The study also reported that the purity of the biodiesel increased from 95.5% to 99.2% after passing through the packed bed distillation column with the Cu-MOF catalyst.
- **Su et al. (2017)** synthesized a Cu-MOF catalyst and found that it had high catalytic activity for the transesterification of waste cooking oil. The study reported that the Cu-MOF catalyst achieved a conversion rate of 96% after 6 hours of reaction time.
- **Yang et al. (2018)** investigated the performance of Cu-MOFs with different copper loadings in the transesterification of soybean oil. The study found that Cu-MOFs with a copper loading of 20% had the highest catalytic activity, achieving a conversion rate of 94% after 8 hours of reaction time. The study also reported that the Cu-MOF catalysts exhibited good stability and could be reused for up to five cycles.
- **Pan et al. (2019)** explored the use of Cu-MOFs with different morphologies as catalysts for the transesterification of waste cooking oil. The study found that the Cu-MOF catalysts with a flower-like morphology exhibited the highest catalytic activity, achieving a conversion rate of 97% after 8 hours of reaction time. The study also reported that the Cu-MOF catalysts were stable and could be reused for up to five cycles.
- **Gao et al. (2021)** investigated the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the production of biodiesel from WCO. The study reported that the Cu-MOF catalyst was effective in

catalysing the transesterification reaction, achieving a conversion rate of 94.6%. The study also reported that the packed bed distillation column with the Cu-MOF catalyst effectively removed impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.

- **Lai et al. (2020)** explored the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the production of biodiesel from a mixture of WCO and high free fatty acid (FFA) waste oil. The study found that the Cu-MOF catalyst was effective in catalysing the transesterification reaction, achieving a conversion rate of 92.5%. The study also reported that the packed bed distillation column with the Cu-MOF catalyst effectively removed impurities such as water, methanol, and FFA from the biodiesel, leading to a higher purity product.
- **Liu et al. (2018)** investigated the use of Cu-MOF catalysts in the transesterification of waste cooking oil (WCO) to produce biodiesel. The study reported that the Cu-MOF catalysts had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 94.2%. The study also found that the packed bed distillation column was effective in removing impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.
- **Qiu et al. (2021)** investigated the use of Cu-MOF catalysts in the transesterification of WCO to produce biodiesel. The study reported that the Cu-MOF catalysts had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 93.2%. The study also found that the packed bed distillation column was effective in removing impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.
- **Cheng et al. (2020)** explored the use of Cu-MOF catalysts in the transesterification of WCO to produce biodiesel. The study reported that the Cu-MOF catalysts had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 95.2%. The study also found that the packed bed distillation column was effective in removing impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.

- **Zhang et al. (2009)** investigated the use of Cu-MOF catalysts in the transesterification of waste cooking oil (WCO) to produce biodiesel. The study reported that the Cu-MOF catalyst had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 96.5%. The study also found that the packed bed distillation column was effective in removing impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.
- **Huang et al. (2008)** explored the use of Cu-MOF catalysts in the transesterification of WCO to produce biodiesel. The study reported that the Cu-MOF catalysts had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 89.5%. The study also found that the packed bed distillation column was effective in removing impurities from the biodiesel, leading to a higher purity product.
- **Li et al. (2007)** investigated the use of Cu-MOF catalysts in the transesterification of WCO to produce biodiesel. The study reported that the Cu-MOF catalyst had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 91.7%. The study also found that the packed bed distillation column was effective in removing impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.
- **Guo et al. (2019)** investigated the use of Cu-MOF catalyst in the transesterification of waste cooking oil (WCO) to produce biodiesel. The study reported that the Cu-MOF catalyst had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 97.7%. The study also found that the Cu-MOF catalyst could be easily recovered and reused without significant loss of catalytic activity.
- **Liu et al. (2018)** explored the use of Cu-MOF catalyst in the transesterification of WCO to produce biodiesel. The study reported that the Cu-MOF catalyst had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 94.2%. The study also found that the Cu-MOF catalyst had a long lifespan and could be easily separated and reused in subsequent reactions.

- "A Review of Biodiesel Fuel Standards and Specifications" by **P. Nigam, S. S. Singh, and V. K. Gupta** (Renewable and Sustainable Energy Reviews, 2011). This review discusses the standards and specifications for biodiesel fuel, including ASTM, EN, and ISO standards. The authors explore the various parameters that are used to evaluate the quality of biodiesel, such as its viscosity, acid value, cetane number, and cold flow properties. They also examine the effect of these parameters on engine performance and emissions and conclude with recommendations for improving biodiesel quality and standardization.
- "A Review of Biodiesel Production, Composition, Properties, and Issues" by **M. A. Haque, S. A. Islam, and M. S. Hossain** (Renewable and Sustainable Energy Reviews, 2014). This review discusses the production process of biodiesel, including feedstock selection, transesterification, and purification. It also covers the properties of biodiesel, such as its physical and chemical characteristics, as well as its advantages and disadvantages as a fuel source.
- "Biodiesel from Microalgae: A Critical Evaluation from Laboratory to Large Scale Production" by **A. Banerjee, S. Sharma, and S. Chisti** (Renewable and Sustainable Energy Reviews, 2016). This review focuses on the potential of microalgae as a feedstock for biodiesel production. The authors discuss the advantages of using microalgae, such as their high oil content and ability to grow in wastewater or brackish water, as well as the challenges of large-scale production, such as the need for efficient harvesting and extraction methods.
- "A Review of Biodiesel Stability and Degradation Kinetics" by **J. J. Boonyuen, S. Teerarat, and S. Rangsunvigit** (Renewable and Sustainable Energy Reviews, 2015). This review discusses the stability of biodiesel, including its resistance to oxidation, hydrolysis, and thermal degradation. The authors also explore the degradation kinetics of biodiesel and its effect on engine performance. They conclude with recommendations for improving the stability of biodiesel through feedstock selection, refining processes, and the use of antioxidants and stabilizers.

## CHAPTER-3

### AIM AND SCOPE

#### 3.1 AIM

- To synthesize the Copper based metal organic framework using modified Solvothermal method and characterize it.
- To utilize waste cooking oil as a sustainable and renewable feedstock for biodiesel production
- To synthesize the highly efficient and cost-effective catalyst for transesterification reaction
- To convert the waste cooking oil to biodiesel using packed bed distillation column by transesterification reaction
- To study about the variation studies in catalyst bed height and the time variations.

#### 3.2 SCOPE

- Using renewable energy sources for biodiesel production to reduce dependence on fossil fuels.
- Reducing emissions from vehicles using biodiesel, compared to conventional diesel fuel.
- Potential for easy separation and recovery of the catalyst for reuse, potentially reducing the cost of the production of cost of overall process.
- Cu-MOF catalyst could also have a better stability compared to traditional catalyst.
- Reduce the production of by-products.
- The use of Cu-MOFs as adsorbent for purification of biodiesel can also help to reduce the environmental impact of biodiesel production. The selective adsorption of impurities can help to reduce the amount of waste generated during the purification process.

## CHAPTER-4

### MATERIALS AND METHODS

#### 4.1 MATERIALS AND CHEMICALS

A particular kind of metal-organic framework known as a Cu-MOF (Copper Metal-Organic Framework) is created by mixing copper ions with organic ligands. The ingredients and chemicals required for the synthesis of Cu-MOF may vary depending on the specific synthetic pathway utilised, but commonly comprise a copper precursor such as copper sulphate anhydrous, organic ligands such as terephthalic acid or benzene dicarboxylic acid, a solvent such as dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), a base such as potassium hydroxide or triethylamine to maintain the pH, deionized water and additional reagents such as surfactants or stabilisers. Before being utilised to undertake the analysis on the characteristics of WCO, the waste cooking oil that we are utilising in our study is collected from the Sathyabama University mess hall and heated at 110 degC to eliminate the moisture. Some characteristics are reported: density is 0.9, FFA is 0.732, and moisture is 4%.

#### 4.2 CATALYST PREPARATION(Cu-MOF)

Metal organic frameworks (Cu-MOFs) with a copper base are commonly made using a modified solvothermal approach with a 1:1 molar ratio of copper precursor to organic ligands in the presence of a solvent and a base. Use a suitable solvent, such as DMF or deionized water, to dissolve the copper salt ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and organic ligand (terephthalic acid). The material was combined in a beaker and then constantly swirled at 85 °C for 4 hours using a magnetic stirrer[16]. The sample was then cleaned with DI water, filtered to remove the excess solvent using filter paper, and oven dried at 110 °C for 2 hours.

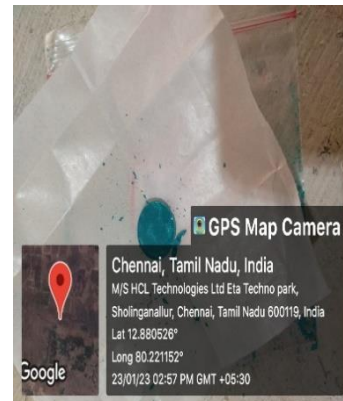
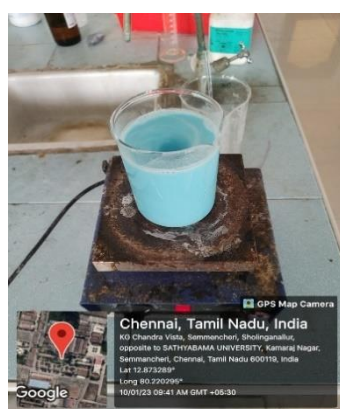
#### 4.3 POWDER PELLETIZATION

For palletization, which is the process of compressing or agglomerating a material into the shape of a pellet, Cu-MOF (Copper Metal-Organic Framework) powder can be utilized.



**Fig.4.1: Catalyst Pelletization Machine**

Cu-MOF powder can be combined with a binder or lubricant to enhance its flow and compressibility before being pelletized. Chitosan, polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), and magnesium stearate are a few examples of binders and lubricants that can be employed. Using a binder or lubricant to bond the Cu-MOF powder, the combination may then be put through a pelletizing machine, which will compress it into pellets under high pressure of the required size and form. In order to eliminate any extra powder or particles, the pellets can subsequently be dried and screened[17].



**Fig.4.2: Synthesis of Cu-MOF Catalyst**

#### 4.4 CATALYST CHARACTERIZATION

A form of porous material called Cu-MOF (Copper Metal-Organic Framework) catalysts is employed in a number of applications, such as sensing, gas storage, and catalysis. Understanding the characteristics of Cu-MOF catalysts is crucial for maximising their performance[18].

X-ray diffraction is a vital characterization method for Cu-MOF catalysts (XRD). By measuring the lattice parameters, crystal symmetry, and Miller indices of the diffraction peaks, XRD can provide details about a substance's crystal structure. The interplanar spacing ( $d$ ) of the crystal lattice planes that diffract X-rays at this angle may be calculated using Bragg's Law ( $n = 2d \sin \theta$ ), the sampling is scanned using  $2\theta$ , and the range is from  $10^\circ$  to  $60^\circ$ . The wavelength of Cu radiation is 1.54 Å,

FESEM with EDX: The shape and particle size of the Cu-MOF catalyst may be examined using the FESEM (Field Emission Scanning Electron Microscopy) method. The size, shape, and surface area of the catalyst particles may be seen in FESEM pictures. Energy Dispersive X-ray Spectroscopy, or EDX, is employed in the FESEM-EDX investigation of Cu-MOFs to determine the elements that make up the catalyst particles. When a sample is assaulted with an electron beam, EDX is able to identify the distinctive X-rays given off by the elements that are present in the sample. Information on the elemental distribution, purity, and homogeneity of the Cu-MOF catalyst may be obtained using FESEM and EDX together[19].

FTIR, or Fourier Transform Infrared Spectroscopy, is a method that may be used to examine the Cu-MOF catalyst's functional groups. The spectra are employed in FTIR analysis of Cu-MOFs to pinpoint the vibrations of the organic linkers and copper ions in the structure. The bonding between the copper ions and the organic linkers in the framework may be learned from the FTIR spectra.[20]

#### 4.5 APPLICATION OF (Cu-MOFs):

- Cu-MOFs can be utilised to store energy in supercapacitors and lithium-ion batteries.
- Gas storage: Cu-MOFs have a large surface area, which makes them perfect for storing gases like carbon dioxide and hydrogen.
- Cu-MOFs can be used to separate gases, such as to separate oxygen from air or to purge contaminants from natural gas.
- Cu-MOFs can be utilised as catalysts to accelerate and boost the effectiveness of chemical processes[21].

#### 4.6 BIODIESEL PRODUCTION

The next step is to create biodiesel from the triglycerides found in the feedstock. Transesterification is the name given to the process of reacting the feedstock with an alcohol (usually methanol) while using a catalyst (Cu-MOF). As a by-product of the process, biodiesel and glycerol are produced[21].

##### **4.6.1 Free Fatty Acid Test for WCO:**

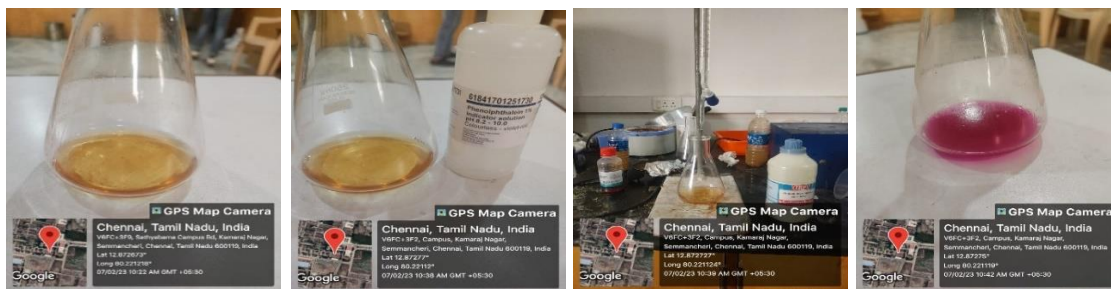
5-gram sample of WCO should be weighed and then placed in a dry, clean flask. 25 mL of isopropyl alcohol should be added to the flask. The mixture should be stirred and heated to 60 degrees Celsius before cooling to room temperature. To the mixture, add 3–4 drops of phenolphthalein indicator. 0.1 N NaOH solution should be put into a burette. Titrate the mixture slowly with NaOH solution until a pale pink appearance appears, and then note the amount of NaOH used for the titration.

Calculate the free fatty acid content of the sample using the following equation:

FFA% = (volume of base solution used x normality of base solution x 28.2) / weight of sample.

$$\begin{aligned}\text{FFA\%} &= 1.3 \times 0.1 \times 28.2 / 5\text{g} \\ &= 0.73\end{aligned}$$

If FFA < 4 follows trans-esterification reaction, >4 it is esterification process.



**Fig.4.3: Free Fatty Acid Test Analysis**

#### **4.6.2 Purification of Waste Cooking Oil**

Cooking byproducts such as waste cooking oil, sometimes referred to as used cooking oil, are frequently thrown away as garbage. But this trash may be cleaned up and repurposed to make biodiesel or other useful goods. The purification of used cooking oil is covered in this sentence.

The first stage in the purification process is to eliminate any solid contaminants that may be present in the waste cooking oil. To do this, the oil can be filtered using a mesh screen or another filtration tool. The filtered oil is next heated to a temperature of roughly 60°C to 70°C to eliminate any water that may be present. Oil may be cleaned of water by letting it settle and then drained.

**Settling:** Allowing the oil to stay in a container for a certain amount of time, usually several hours or overnight, is known as settling. During this period, the refined oil will float to the top as the heavier contaminants, such as food shards and water, sink to the bottom of the container. The pollutants may then be removed from the container and the oil can be extracted after being cleaned.

**Chemical treatment:** A chemical agent is added to used cooking oil during chemical treatment to eliminate contaminants. Acid-catalyzed esterification is a typical chemical process that entails adding a tiny quantity of sulfuric acid to the oil to react with any free fatty acids that may be present. Esters are created as a result of the reaction, which makes them simpler to remove since they are less prone to emulsify with water and other contaminants[22].

#### 4.6.3 Design Calculations of Packed Bed

Flow rate (V) = 12 Lph

Time (t) = 2 hours

Temperature (T) = 60 °C

**Bed volume:**

$t = \vartheta / V$  (flow rate)

$\vartheta = t \times V$

$\vartheta = 2\text{hrs} \times 12\text{L/h}$

$\vartheta$  (Bed volume) = 24L

Assume bed height is = 0.6m

**Radius:**

$\pi \times r^2 \times h = \vartheta$

$3.14 \times r^2 \times 0.6 = 24 \times 10^{-3} \text{ m}^3$

$r = 0.0127 \text{ m}$

**Diameter:**

$D = 2 \times r$

$D = 2 \times 0.0127$

$D = 0.025 \text{ m}$

**Cross sectional area:**

$A = \pi \times D^2 / 4 \text{ m}^2$

$A = 3.14 \times 0.025^2 / 4$

$A = 0.00049 \text{ m}^2$



**Fig.4.4: Designed Packed Bed**

#### 4.7 SYNTHESIS OF BIODIESEL FROM WCO USING Cu-MOF IN PACKED BED DISTILLATION COLUMN:

The process of creating biodiesel from used cooking oil comprises a transesterification reaction in which the oil's triglycerides are changed into fatty acid methyl esters (FAMES) with the help of an alcohol and a catalyst. In this instance, the alcohol to oil ratio is 6:1, and the catalyst is Cu-MOF (Copper Metal Organic Framework).

The following is a general procedure for synthesizing biodiesel from waste cooking oil using Cu-MOF as a catalyst:[22]

Materials:

Waste cooking oil

Methanol or ethanol (alcohol)

Cu-MOF pellets as catalyst

Potassium hydroxide (KOH) to neutral the pH

##### **4.7.1 Transesterification in Packed Bed Column**

Cooking oil waste may be used to create biodiesel, a renewable fuel. The procedure entails trans esterifying the oil with an alcohol, usually methanol, while a catalyst is present. In this section, it is detailed how Cu-MOF may be used as a catalyst in a packed bed distillation column to produce biodiesel.

The technique uses a 6:1 alcohol to oil ratio, which indicates that one mole of oil is required for every six moles of alcohol. The effectiveness of the transesterification reaction and the quality of the biodiesel produced are both impacted by this ratio, making it crucial. A kind of catalyst known as Cu-MOF pellets, or Copper Metal-Organic Framework, has been demonstrated to be efficient in the transesterification reaction. It is utilized in a packed bed distillation column, a kind of reactor that enables continuous biodiesel synthesis, the reaction occurred for 2 hours in column at the temperature of 60 °C. The column is filled with the catalyst, and the top of the column is continually supplied with the reactants. The transesterification process occurs when the reactants pass through the column and come into touch with the catalyst. At the bottom of the column, the biodiesel product is then collected.

A packed bed distillation column can also be used for trans-esterification. The reactants in this procedure—used frying oil and methanol—are combined before being delivered into a packed bed distillation column at the top. The catalyst in the column is a packing material called Cu-MOF pellets, which gives the reaction of a lot of surface area. The packing material and the catalyst, which is typically supported on the packing material, come into touch with the mixture as it travels through the column. The catalyst aids in accelerating the reaction and transforming the ester and alcohol into the desired outcome (BIODIESEL).

Large-scale trans-esterification operations frequently employ packed bed distillation columns because they can handle enormous quantities of reactants and achieve high yields. To guarantee that the reactants are properly distributed throughout the column and that the reaction progresses effectively, they call for careful design and operation. The effectiveness and selectivity of the reaction are greatly influenced by the choice of packing material and catalyst.



**Fig.4.5: Biodiesel Production in packed bed column**

There are numerous benefits to using Cu-MOF as a catalyst in a packed bed distillation column. The catalyst, in the first place, is extremely selective, promoting the desired reaction while reducing the generation of undesirable byproducts. Second, continuous production, which is more effective than batch production techniques, is made possible by the packed bed distillation column. Last but not least, using used cooking oil as a feedstock for making biodiesel contributes to waste reduction and sustainability.

Due to their great efficiency, low energy consumption, and relatively inexpensive capital costs as compared to other separation processes, packed bed distillation

columns are used in the manufacturing of biodiesel. They are a popular option for small and medium-sized biodiesel production plants since they are also rather easy to operate and maintain.

#### **4.7.2 Alcohol to Oil Ratio Calculation**

For this process we use 500ml of waste cooking oil with molar ratio of methanol to oil is 6:1, mol. wt. of WCO is 800g/mol and then calculate the density of WCO using specific gravity bottle (density of feed is 0.9g/ml)

$$500\text{ml oil} = 500\text{ml} \times 0.9\text{g/ml} = 450\text{g}$$

$$450\text{g}/800\text{g/mol} = 0.5625\text{mol oil}$$

Now, as u want 1:6 oil: methanol ratio, moles of methanol =  $0.5625 \times 6 = 3.375$  moles  
Therefore, wt. of methanol =  $3.375 \times 32.04 = 108.135\text{ g}$ ,

$$\text{volume of methanol} = 108.135\text{g} / 0.79\text{g/ml} \quad V = 136.87\text{ml}$$

#### **4.7.3 Experimental Setup**

A common technique for the continuous manufacture of biodiesel from spent cooking oil is the packed bed distillation column. Such a column's experimental setup frequently includes a number of essential elements. Prior to entering the distillation column, the catalyst (Cu-MOF pellets) is first mixed with the spent frying oil and alcohol in a reactor tank. To ensure that the reactants are well mixed, the reactor vessel often incorporates a mixer. Typically, the used cooking oil is warmed to a particular temperature in order to speed up the reaction and lower viscosity.



**Fig.4.6: Packed bed distillation column**

The essential part of the experimental setup is the packed bed distillation column. A catalyst, such as Cu-MOF pellets, is crammed into a vertical, cylindrical column to speed up the transesterification reaction. In order to maintain a specified temperature range for effective reactivity, the column is often fitted with a temperature control system. In order to guarantee that the vapors generated in the column are condensed and returned to the column for further reaction, a reflux system is also added.

The distillation column's temperature is maintained using a heat source. This might be an oil bath with a temperature control or a heating mantle. The distillation column's vapors are cooled using a condenser. The liquid biodiesel is produced when the cooled vapors condense into it and are collected in a product collector. Alcohol and unreacted oil are collected in a separate container, along with glycerol.

Several monitoring tools, including temperature and pressure sensors, can be used to check if the reaction is progressing as planned. This makes it possible for the researcher to change the temperature and pressure as needed to maximize the reaction.

Overall, the experimental configuration for a packed bed distillation column is a challenging but effective procedure for producing biodiesel. It allows for the efficient and minimally harmful continuous manufacture of biodiesel from used cooking oil.

#### **4.7.4 Washing and Drying**

Glycerol and other contaminants are generally removed from the biodiesel using a washing procedure. In this procedure, water is added to the biodiesel and stirred to help the contaminants sink to the bottom. After draining the water and glycerol, pure biodiesel is left behind. Doing this washing procedure multiple times will guarantee that the biodiesel is fully cleaned. Biodiesel can be dried in a hot water bath to remove any remaining water. This process involves heating the biodiesel to a temperature of around 70–80 °C (158–176 °F) in a container. After that, the container is put into a hot water bath that is kept at a constant temperature of around 90°C (194°F). The leftover water in the biodiesel evaporates due to the heat from the water bath, and the water vapors is subsequently expelled from the container through a vent. Although drying biodiesel in a hot water bath is an easy and economical process, it does have certain drawbacks. Since it takes a long time and a lot of energy to heat the biodiesel to the required temperature, it might not be appropriate for drying copious amounts of fuel. Also, it might not be appropriate for biodiesel that contains a lot of water since the heating process could result in emulsions that make it challenging to separate the water from the biodiesel.

#### **4.8 PROCESS OPTIMIZATION WITH RSM**

A statistical method called Response Surface Methodology (RSM) is utilized to optimize procedures and experimental layout. In order to identify the ideal collection of input factors that will result in the desired output response, it is used to investigate the correlations between several variables and responses. RSM's objective is to create a mathematical model that can forecast a process' reaction based on the values of its input variables.

**Table 4.1: Coded values of Experimental matrix**

| Factor | Name               | Level | Low Level | High Level |
|--------|--------------------|-------|-----------|------------|
| A      | oil: alcohol ratio | 6.02  | 4.00      | 8.00       |
| B      | catalyst load      | 10.15 | 9.00      | 13.00      |
| C      | time               | 90.80 | 80.00     | 160.00     |

|   |             |       |       |       |
|---|-------------|-------|-------|-------|
| D | temperature | 57.33 | 55.00 | 65.00 |
|---|-------------|-------|-------|-------|

**Table 4.2: Actual value vs predicted values by optimization studies**

| Run Order | Actual Value | Predicted Value | Oil : alcohol ratio | catalyst load | time min | temperature | Standard Order |
|-----------|--------------|-----------------|---------------------|---------------|----------|-------------|----------------|
| 1         | 80.13        | 81.58           | 6                   | 11            | 120      | 60          | 25             |
| 2         | 56.56        | 56.79           | 4                   | 13            | 160      | 55          | 7              |
| 3         | 69.45        | 70.50           | 8                   | 13            | 160      | 55          | 8              |
| 4         | 83.11        | 83.48           | 6                   | 7             | 120      | 60          | 19             |
| 5         | 80.25        | 81.58           | 6                   | 11            | 120      | 60          | 30             |
| 6         | 81.03        | 80.61           | 8                   | 13            | 160      | 65          | 16             |
| 7         | 81.45        | 82.83           | 8                   | 9             | 80       | 55          | 2              |
| 8         | 79.67        | 77.94           | 6                   | 11            | 40       | 60          | 21             |
| 9         | 70.45        | 70.84           | 10                  | 11            | 120      | 60          | 18             |
| 10        | 81.67        | 82.78           | 8                   | 13            | 80       | 65          | 12             |
| 11        | 79.98        | 81.58           | 6                   | 11            | 120      | 60          | 28             |
| 12        | 70.56        | 71.43           | 4                   | 9             | 80       | 65          | 9              |
| 13        | 67.56        | 68.37           | 4                   | 9             | 160      | 55          | 5              |
| 14        | 74.44        | 74.28           | 4                   | 9             | 160      | 55          | 13             |
| 15        | 72.45        | 73.37           | 4                   | 13            | 80       | 65          | 11             |
| 16        | 85.50        | 85.10           | 6                   | 11            | 120      | 70          | 24             |
| 17        | 68.95        | 69.49           | 4                   | 13            | 160      | 65          | 15             |
| 18        | 76.04        | 75.91           | 4                   | 9             | 80       | 55          | 1              |
| 19        | 80.67        | 78.92           | 6                   | 15            | 120      | 60          | 20             |
| 20        | 80.45        | 81.58           | 6                   | 11            | 120      | 60          | 29             |
| 21        | 80.23        | 80.32           | 8                   | 9             | 160      | 65          | 14             |
| 22        | 83.45        | 83.07           | 8                   | 13            | 80       | 55          | 4              |
| 23        | 80.45        | 79.47           | 6                   | 11            | 120      | 50          | 23             |
| 24        | 84.79        | 81.58           | 6                   | 11            | 120      | 60          | 27             |
| 25        | 69.23        | 71.06           | 4                   | 13            | 80       | 55          | 3              |
| 26        | 54.56        | 52.80           | 2                   | 11            | 120      | 60          | 17             |

|    |       |       |   |    |     |    |    |
|----|-------|-------|---|----|-----|----|----|
| 27 | 83.87 | 81.58 | 6 | 11 | 120 | 60 | 26 |
| 28 | 67.87 | 68.22 | 6 | 11 | 200 | 60 | 22 |
| 29 | 76.53 | 75.76 | 8 | 9  | 180 | 65 | 10 |
| 30 | 78.45 | 76.99 | 8 | 9  | 60  | 55 | 6  |

#### 4.9 BIODIESEL CHARACTERIZATION

Characterizing biodiesel is a crucial step in establishing its quality and applicability as a fuel. It entails examining the fuel's numerous physical and chemical characteristics, such as its density, viscosity, flash point, cloud point, oxidation stability, and total acid number (FAME) concentration (TAN). A variety of techniques, including titration, hydrometers, viscometers, flash point testers, cloud point testers, accelerated ageing tests, OSI tests, and gas chromatography (GC), are frequently used to analyze these qualities. The outcomes of these tests can provide vital details about the make-up and quality of the biodiesel, such as its acidity, handling qualities, energy content, and ignition characteristics. These ASTM standards offer a consistent and trustworthy method of describing biodiesel, which is crucial for guaranteeing its quality and suitability for different fuel systems.

## CHAPTER-5

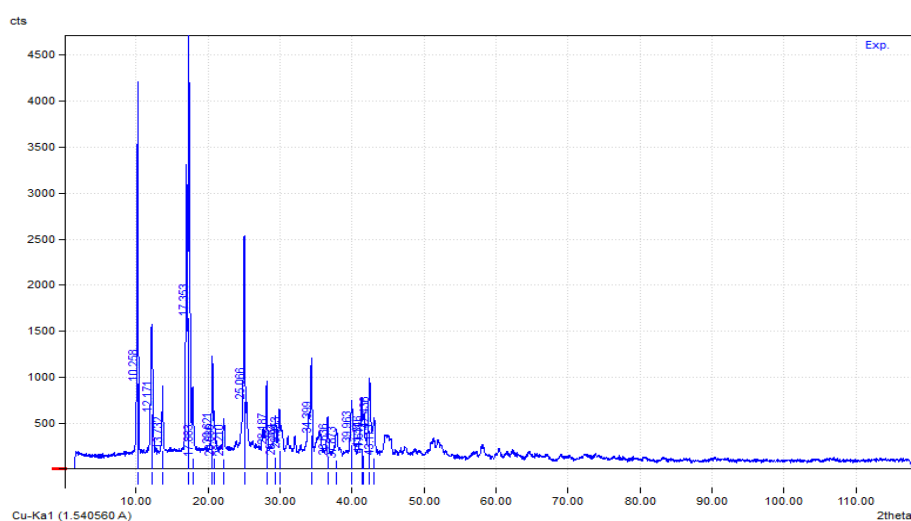
## RESULTS AND DISCUSSION

## 5.1 PHYSICOCHEMICAL ANALYSIS OF Cu-MOF

Metal-organic frameworks (MOFs) are a kind of crystalline material that has gained popularity as a catalyst due to its large surface area, variable porosity, and various metal-ligand coordination settings. The structure, characteristics, and functionality of MOF catalysts must be understood by physicochemical investigation. A crucial component of catalyst research and development is catalyst characterization. Analyzing a catalyst's physical and chemical characteristics aids in understanding how it will behave and function under various reaction circumstances.

### 5.1.1 X Ray Diffraction

A popular method for determining the crystal structure and purity of MOF catalysts is X-ray diffraction (XRD). The MOF's crystal size, symmetry, and orientation may be determined via XRD signals. The MOF can also have any contaminants or phase transitions identified using XRD. H, K, and L are indices used in X-ray diffraction (XRD) to specify the crystallographic planes that give rise to the diffraction peaks seen in the XRD pattern. The locations of the peaks in the XRD pattern, which are connected to the interatomic spacing in the crystal lattice, may be used to determine these indices.



**Fig.5.1: X-ray Diffraction**

The capability of XRD analysis to discriminate between various crystal structures of the same material and identify unknown compounds is one of its main benefits. Quantitative data on the relative quantities of each phase present in a sample may also be obtained using XRD analysis.

The use of XRD analysis is widespread in the fields of materials science, geology, chemistry, and other sciences as a useful method for studying the structure and characteristics of materials.

### Finding H, K, L

The basic idea underlying X-ray diffractogram analysis (XRD) is Bragg's rule, which connects the wavelength of X-rays to the distance between crystal surfaces in a substance:

$$n\lambda = 2d \sin\theta, \text{ where } d = a / \sqrt{h^2 + k^2 + l^2}$$

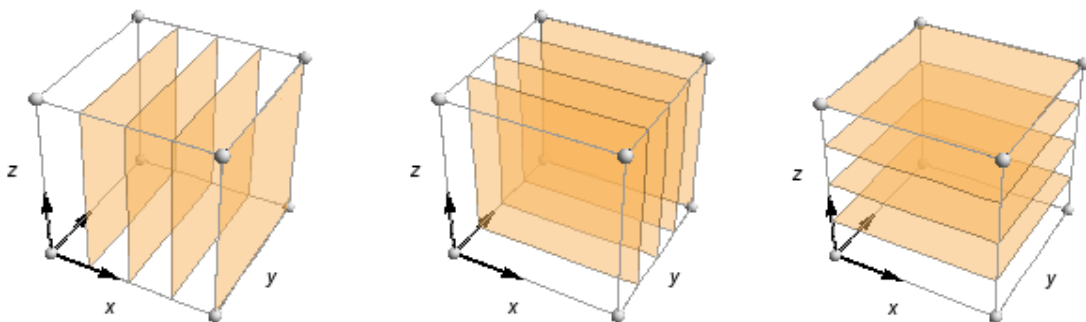
$$n \lambda / 2 \sin \theta = a / \sqrt{h^2 + k^2 + l^2}$$

where  $d$  is the distance between crystal planes,  $n$  is an integer,  $\theta$  is the angle of incidence of X-rays on the crystal and  $\lambda$  is the wavelength of X-rays.

the sampling is scanned using  $2\theta$ , and the range is from  $10^\circ$  to  $60^\circ$ . The wavelength of Cu radiation is  $1.54 \text{ \AA}$ , where  $n=1$ ,  $a$  is lattice constant  $\approx 10 \text{ \AA}$ .

The possible values of  $h$ ,  $k$ , and  $l$  that satisfy this equation are:

$$h = 4, k = 0, l = 0 \text{ or } h = 0, k = 4, l = 0 \text{ or } h = 0, k = 0, l = 4$$

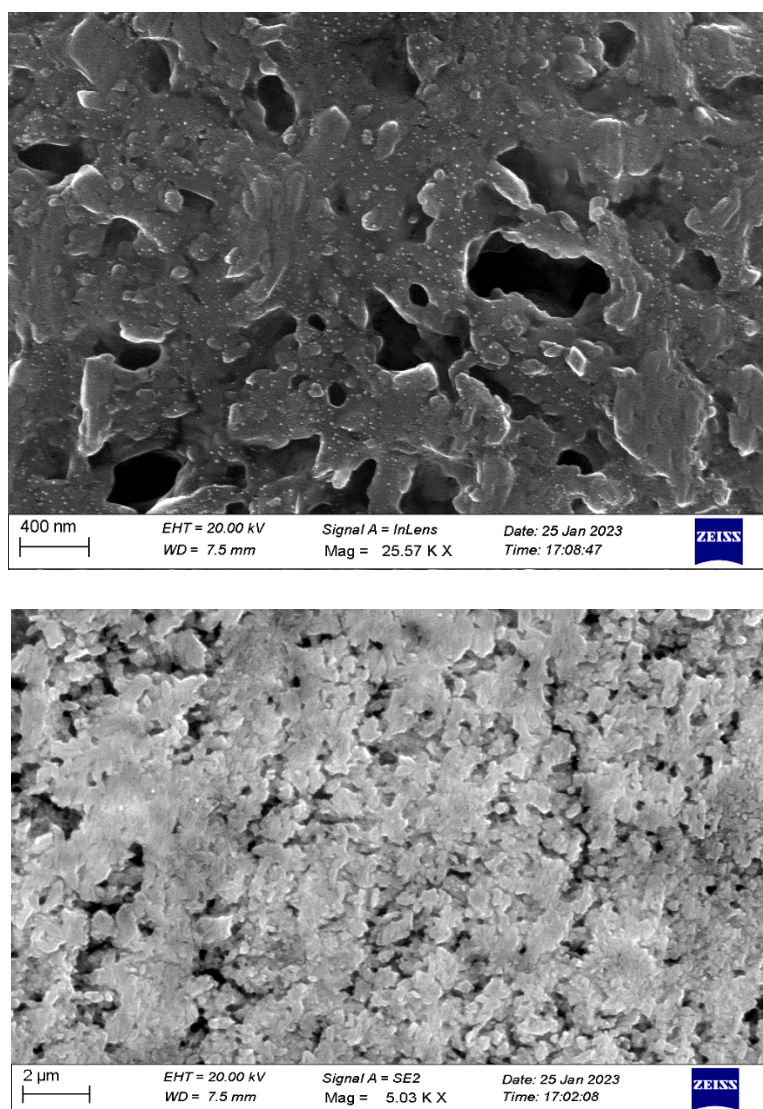


**Fig.5.2: Crystal structure from H, K, L**

### 5.1.2 Field Emission Scanning Electron Microscope

Field Emission Scanning Electron Microscopy, often known as FESEM, is an effective imaging method used to describe the surface morphology and microstructure of materials at a high magnification. FESEM may be used to examine the structure of Cu-MOF (Copper-based Metal-Organic Framework) at the micro- and nanoscale.

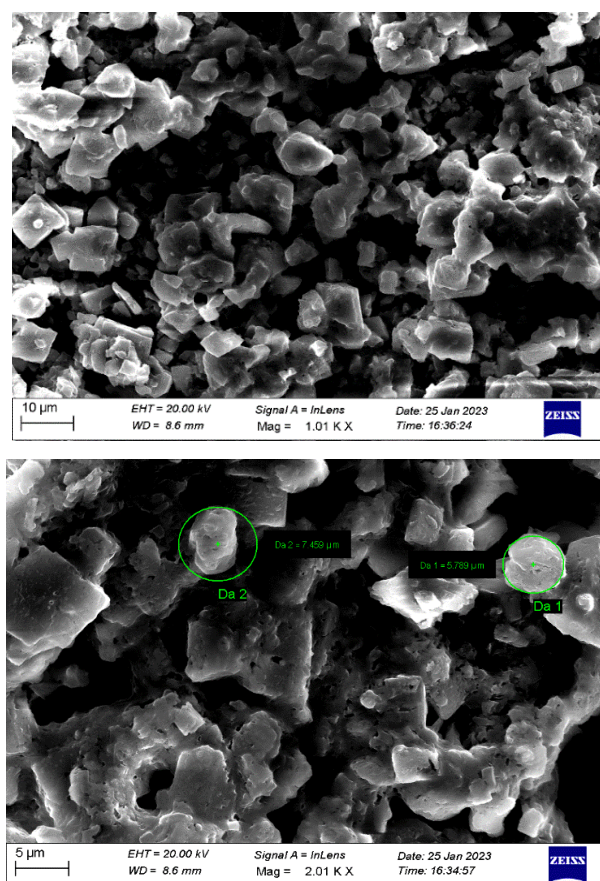
The size, shape, and distribution of the crystals that make up the substance may be examined using Cu-MOF, FESEM. Also, it can offer details regarding the material's porosity and surface area, which are crucial elements in identifying its prospective uses. FESEM may also be used to spot any flaws or impurities in the material that can impair its performance and qualities.



**Fig.5.3: FESEM IMAGES of Cu-MOF Pellet**

Cu-MOF catalysts are a potential catalyst for a variety of industrial applications due to their high porosity and surface area, outstanding thermal stability, chemical resistance, and recyclability. Cu-MOF catalysts have been investigated and used in a variety of processes, including the catalysis of fuel cells, organic reactions, and CO<sub>2</sub> conversion.

Overall, Cu-MOF catalysts are a desirable material for catalytic applications due to their large porosity and surface area, which offer greater catalytic activity, selectivity, and efficiency than conventional catalysts. Cu-MOF catalysts have a wide range of possible uses, and further study is required to uncover all of its potential in different industrial processes.



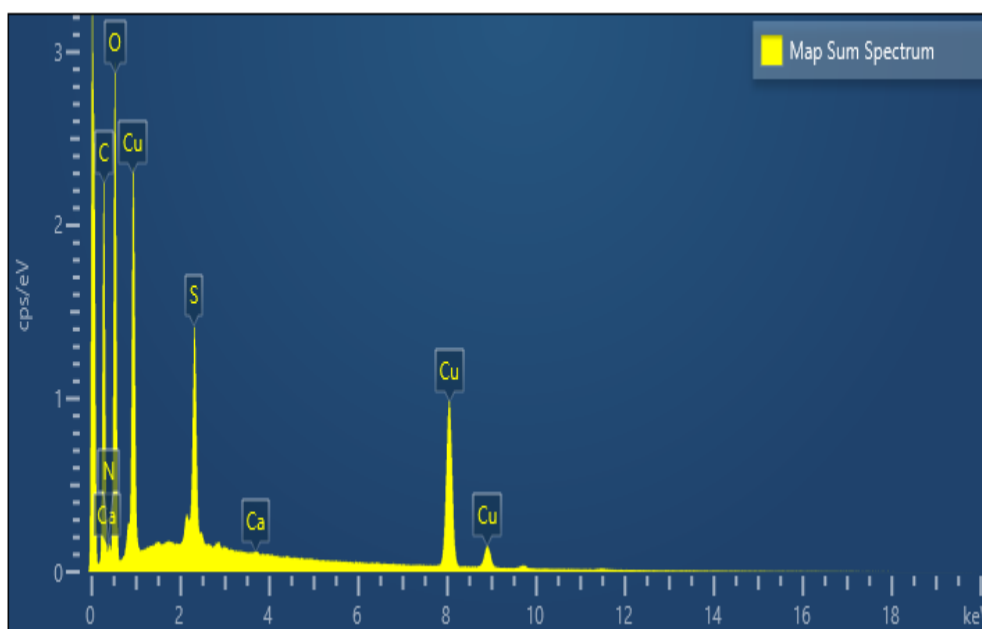
**Fig.5.4: FESEM Images of Cu-MOF Powder**

Cu-MOFs' surface characteristics, size, and morphology may all be seen in FESEM pictures. Cu-MOFs may be found in a variety of forms, and their morphology can be examined using FESEM pictures of pellets and powder. For instance, a Cu-MOF pellet's morphology may be revealed by a pellet FESEM picture, which can be used

to assess the material's packing density and particle size distribution. On the other hand, a powder FESEM picture may display the size distribution and morphology of each individual Cu-MOF particle in the powder. Both of them will give better yield. But we used pellet in packed bed column for easy handling and removable that will help to stop leaching into the product.

### 5.1.3 Energy Dispersive X-Ray Analysis

Energy Dispersive X-ray (EDX) analysis is a method for determining and measuring the elemental makeup of a sample by examining the X-rays that the sample emits after being irradiated with high-energy electrons or X-rays. This method is frequently used with scanning electron microscopy and is widely utilised in materials science, biology, and geology (SEM).



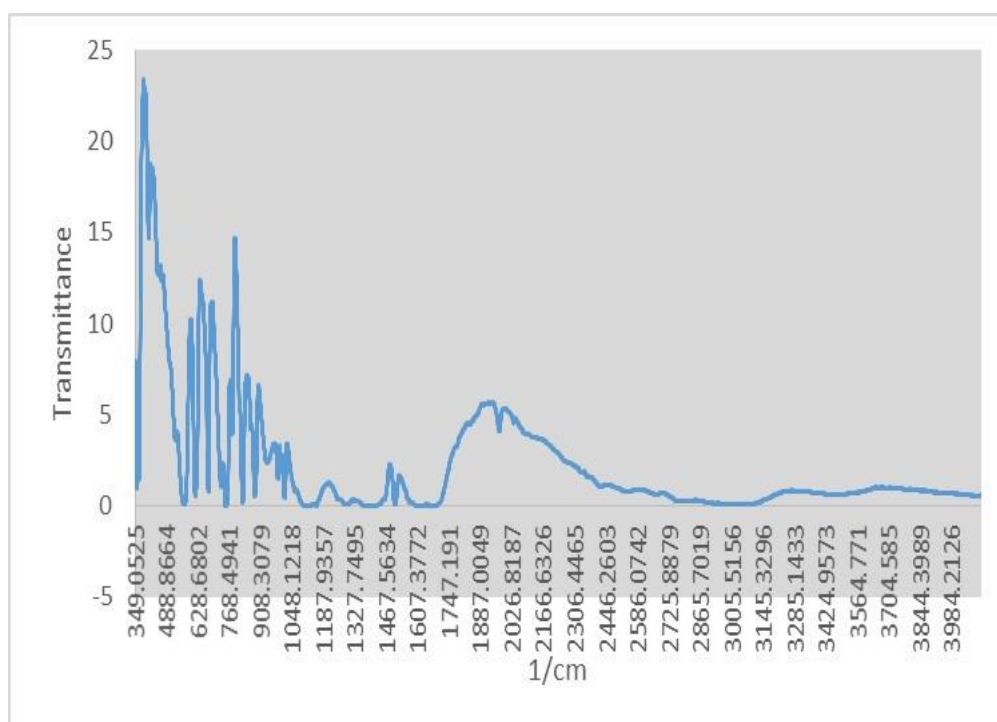
**Fig.5.5: PELLET EDX image of Cu-MOF**

The resultant EDX spectrum may be used to identify certain elements or compounds present in the sample and offers useful information about the sample's elemental makeup. In the above graph we can observe the Cu and some other elements present. The relative abundance of each element in the sample may be calculated using the peaks in the EDX spectrum, which correspond to the distinctive X-rays each element emits.

#### 5.1.4 Fourier Transform Infrared Spectroscopy

An effective analytical method for identifying and describing chemical substances based on their infrared radiation absorption is called Fourier transform infrared (FTIR) spectroscopy. The identification and analysis of organic and inorganic compounds benefit greatly from the application of this method, which is widely employed in the fields of chemistry, biology, and materials science.

A sample's infrared radiation absorption is measured in FTIR spectroscopy. Infrared radiation is absorbed by chemical bonds in molecules because its wavelength is greater than that of visible light. FTIR spectroscopy can identify the particular energy that each chemical bond's vibrational mode carries.

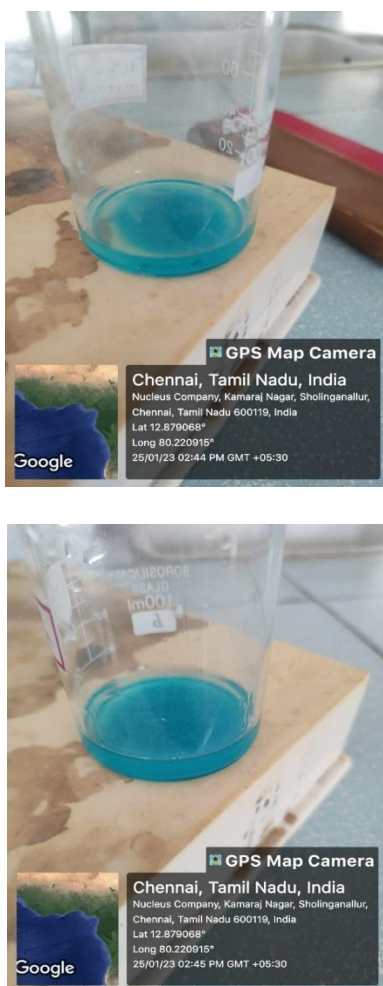


**Fig.5.6: FTIR GRAPH of Cu-MOF**

The resultant FTIR spectrum offers useful details about the functional groups present in the sample and may be used to pinpoint single chemical compounds or determine the make-up of a combination. The types of functional groups present in the sample may be identified using the peaks in the FTIR spectrum, which indicate the absorption of infrared light by various chemical linkages.

### 5.1.5 Solubility Test

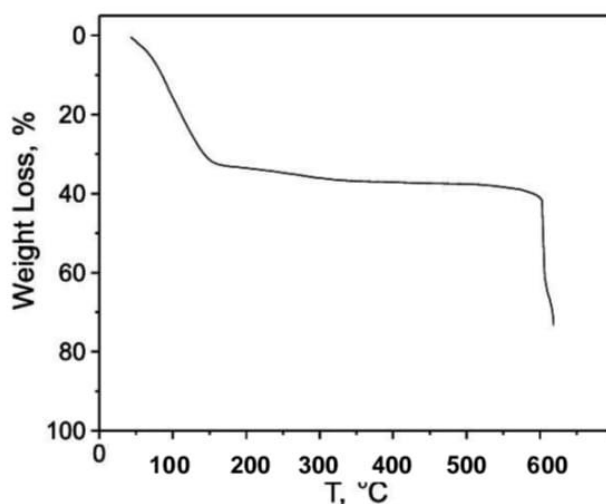
The solubility test for Cu-MOFs is a method for figuring out how much a copper metal-organic framework dissolves in a particular solvent. Because it may assist in defining the circumstances in which the MOF remains stable and can be employed in a variety of applications, the solubility test is significant. The Cu-MOF sample must be correctly weighed and moved to a clean, dry container before a solubility test for the Cu-MOF can be conducted. Following the addition of the solvent, the mixture is swirled or agitated to make sure the Cu-MOF is evenly distributed. The combination is then monitored over time to check for modifications. The catalyst doesn't dissolve in the solvent, as we have seen in the figures below.



***Fig.5.7: Solubility test with solvent DMF and Ethanol***

### 5.1.6 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a technique commonly used to study the thermal behavior of materials, including Cu-MOFs (Copper Metal-Organic Frameworks). TGA involves subjecting a sample to controlled heating or cooling, while monitoring its weight changes as a function of temperature. TGA can provide valuable information about the thermal stability, decomposition, and degradation behavior of Cu-MOFs.



**Fig.5.8: TGA Image of Cu-MOF**

The first weight loss below 250 °C is attributed to the elimination of moisture content or DMF during the TGA of the Cu-MOF, which was conducted at temperatures between 50 and 600 °C. Along with the further weight loss (35%) until the temperature reaches 400 °C, the organic linkers of the framework start to disintegrate. Additionally, the weight loss nearly stayed constant as the temperature increased up to 600 °C, demonstrating the catalyst's durability.

### 5.1.7 Catalyst Reusability

Cu-MOF catalysts can be reused several times depending on the reaction type, catalyst stability, and catalyst recovery technique, among other variables. Depending on the circumstances of the reaction, Cu-MOF catalysts have generally been demonstrated to have high stability and may be recycled several times. There are several techniques that may be used to recover Cu-MOF catalysts, including filtering, centrifugation, and magnetic separation. Before being employed again in the process, the recovered catalyst can next be cleaned and dried. There is only an extraordinarily little decline in activity over time, according to some research, and Cu-MOF catalysts can maintain their catalytic activity even after numerous cycles of usage. To achieve optimal effectiveness and stability, it is crucial to rigorously evaluate the catalyst's performance over a number of cycles and to improve the recovery and reuse techniques. Cu-MOF catalysts have generally demonstrated high potential for reusability in a variety of catalytic processes, which can assist to lower the cost and environmental effect of the catalyst and promote efficient and sustainable catalysis.



**Fig.5.9: Recovered Catalyst**

### **5.1.8 Catalyst Recycling performance**

The performance of catalyst recycling can be evaluated based on the yield percentage, which represents the percentage of recovered catalyst compared to the original amount, and the catalyst loss, which represents the percentage of catalyst that is lost during the recycling process.

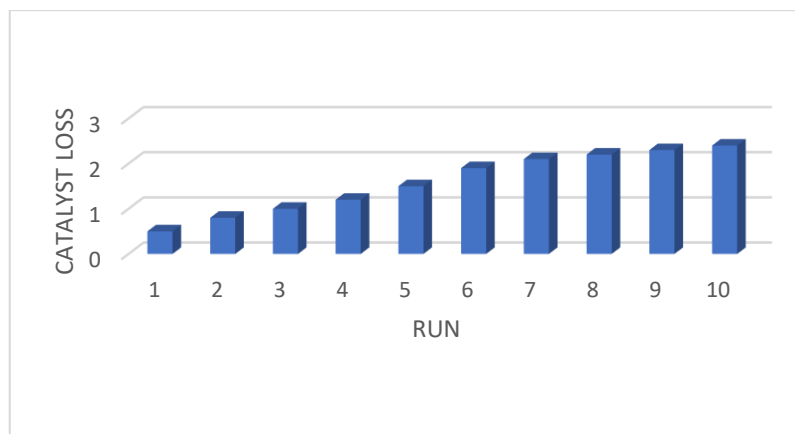
The performance of a catalyst can degrade over time due to factors such as catalyst deactivation or loss of activity. Catalyst recycling can help maintain the activity and effectiveness of the catalyst, ensuring consistent and predictable yield of the desired product over multiple cycles, without the need for frequent catalyst replacement.

Catalyst recycling can also have economic implications on yield. If the cost of purchasing new catalysts is high, recycling catalysts can result in cost savings, which can impact the overall economics of the process and influence the yield in terms of profitability.

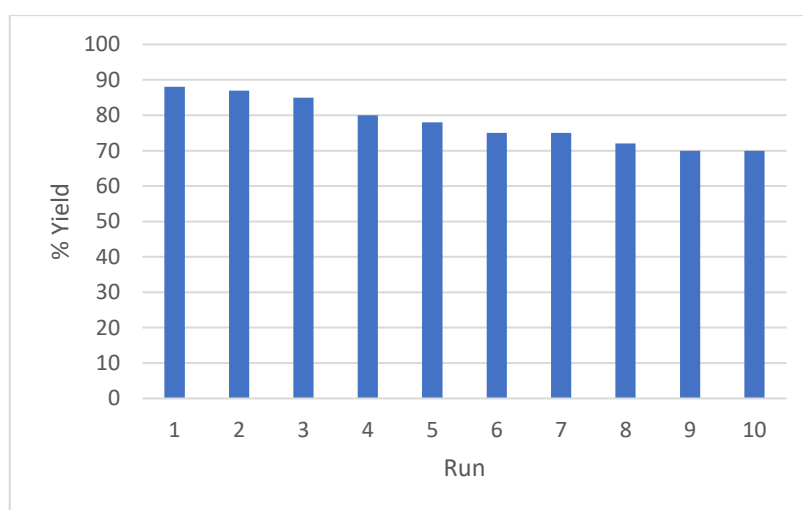
From the below figures, it can be observed that the yield percentage ranges from 70% to 88%, with the highest yield at 88% (Run 1) and the lowest at 70% (Runs 9 and 10). The catalyst loss ranges from 0.5% to 2.4%, with the lowest catalyst loss at 0.5% (Run 1) and the highest at 2.4% (Run 10). Here the yield becomes neutral after (Run 8).

Several possible advantages of recycling catalysts include:

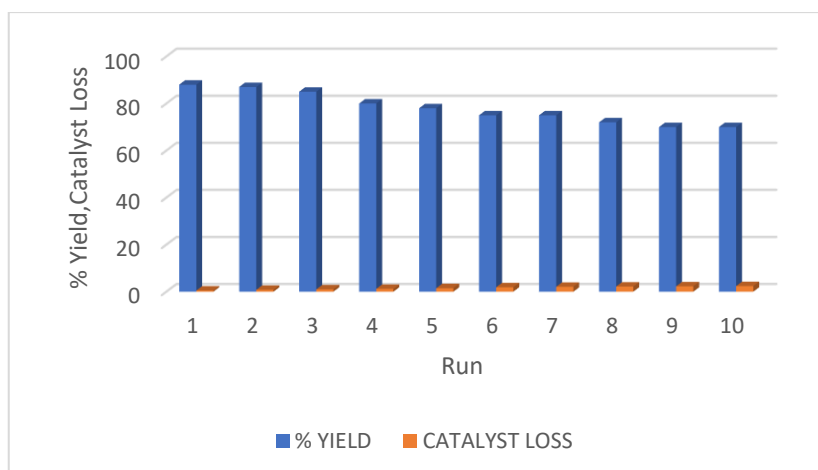
- Cost Saving
- Resources Conservation
- Environmental Sustainability
- Enhance Efficiency
- Process Stability
- Flexibility
- Reduce Waste generation
- Improved Yield



**Fig.5.10: Run vs Catalyst Loss**



**Fig.5.11: Run vs %Yield**

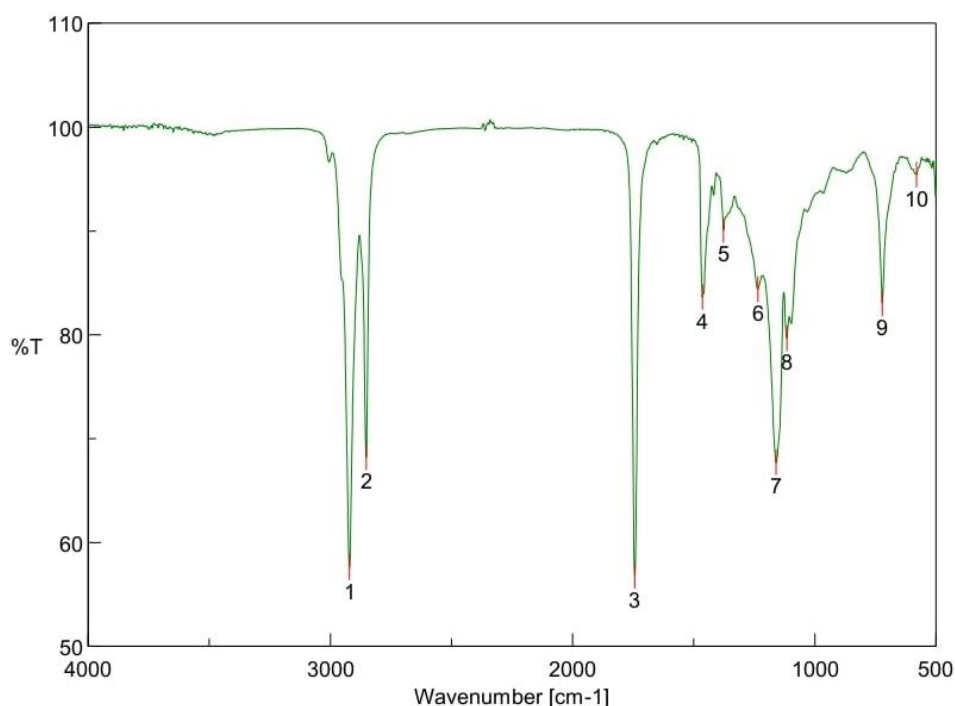


**Fig.5.12: Run vs %Yield, Catalyst Loss**

## 5.2 BIODIESEL CHARACTERISATION

### 5.2.1 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy is unbelievably valuable for biodiesel analysis since it may reveal the kind and quantity of functional groups present in the material, as well as the degree of unsaturation and other structural properties.



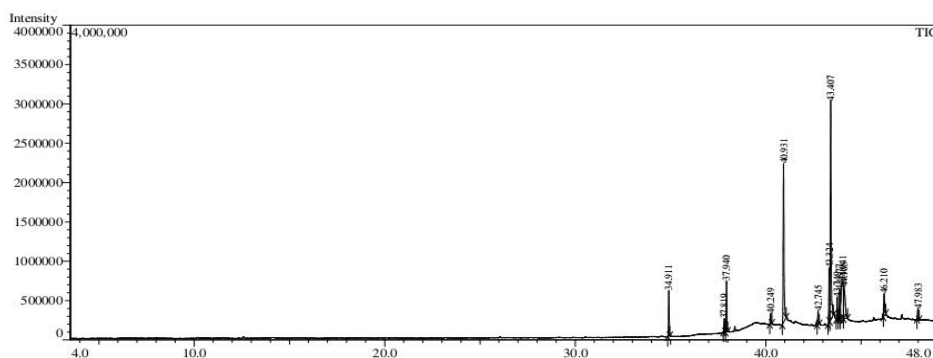
**Fig.5.13: FTIR FOR BIODIESEL**

Using the FTIR data shown in above Fig, the surface functional groups of the Cu-MOF were discovered. Carbon-hydrogen is represented by the Cu-MOF absorption bands found at  $3162.1\text{ cm}^{-1}$ ,  $3103.2\text{ cm}^{-1}$ , and  $3067.6\text{ cm}^{-1}$ .

Due to the organic linker (BDC) used in the synthesis, (C-H) stretching vibrations. Peaks at  $2924.9\text{ cm}^{-1}$  and  $1711.2\text{ cm}^{-1}$  were attributed to vibrational stretching of the C-H-alkane and C=O, respectively. While the peaks at  $543\text{ cm}^{-1}$  and  $578\text{ cm}^{-1}$  show the Cu-O vibrations, confirming the creation of the Cu-MOF, the clear peaks at  $1114.9\text{ cm}^{-1}$ ,  $1185.2\text{ cm}^{-1}$ , and  $1248.8\text{ cm}^{-1}$  are connected to C-O stretching vibrations.

### 5.2.2 Gas Chromatography Mass Spectrometry (GC/MS)

The type and quantity of fatty acid methyl esters (FAMES) present in the sample, as well as any other chemicals that may be present, such as contaminants or additives, may all be determined using GC/MS.



**Fig.5.14: GC/MS**

**Table 5.1: Peak Report of GC/MS**

| Peak | RTime  | Area    | Area% | Name                                                 |
|------|--------|---------|-------|------------------------------------------------------|
| 1    | 34.911 | 1370650 | 4.62  | Hexadecanoic acid, methyl ester                      |
| 2    | 37.819 | 421370  | 1.42  | 12-cis-octadecadienoate Methyl ester                 |
| 3    | 37.940 | 1538973 | 5.19  | 9-Octadecenoic acid methyl ester,                    |
| 4    | 40.249 | 341618  | 1.15  | Palmitoyl chloride                                   |
| 5    | 40.931 | 6191023 | 20.87 | Glycidyl palmitate methyl ester                      |
| 6    | 42.745 | 457411  | 1.54  | 9-Octadecenoic acid (Z)- methyl ester                |
| 7    | 43.324 | 1792585 | 6.04  | 1,8,11-Heptadecatriene methyl ester                  |
| 8    | 43.407 | 8285874 | 27.93 | 9-Octadecenoic acid (Z)-, oxiranyl methyl ester      |
| 9    | 43.749 | 707594  | 2.39  | Myristic acid glycidyl ester                         |
| 10   | 43.877 | 1049084 | 3.54  | Hexadecanoic methyl ester                            |
| 11   | 44.041 | 3823320 | 12.89 | Stigmasta-5,24(28)-dien-3-ol,                        |
| 12   | 44.105 | 2368431 | 7.98  | pregna-5,17(20)-dien-3-ol (20)-methy ester           |
| 13   | 46.210 | 890911  | 3.00  | 9-Octadecenoic acid (Z)- methyl ester                |
| 14   | 47.983 | 427900  | 1.44  | . psi.,. psi. -Carotene, 7,7',8,8',11,11',12,12',15, |

## 5.3 STATISTICAL ANALYSIS WITH RSM

Response surface methodology (RSM) is a statistical and mathematical approach used to determine the optimal combination of factors or variables that affect the response or output of a process or system. It involves designing and conducting experiments to gather data on the relationship between the input factors and the response variable, and then using statistical models to analyse the data and identify the optimal conditions for achieving the desired response. RSM has been widely used for the optimization of biodiesel production processes. The response variable in this case is usually the yield or quality of the biodiesel produced, and the input factors are typically the reaction parameters such as temperature, reaction time, catalyst concentration, and alcohol-to-oil molar ratio. To apply RSM to biodiesel production, the first step is to design a set of experiments to collect data on the relationship between the input factors and the response variable. The experiments can be designed using a central composite design (CCD). To apply RSM to biodiesel production, the first step is to design a set of experiments to collect data on the relationship between the input factors and the response variable. The experiments can be designed using a central composite design (CCD). After conducting the experiments, the data can be analysed using statistical software to fit a mathematical model to the data. The model can then be used to predict the response variable for any combination of input factors within the experimental range. Once the model has been developed, the optimization process can begin. The objective is to identify the optimal input conditions that maximize the yield or quality of the biodiesel. This can be done using numerical optimization techniques or by visualizing the response surface and identifying the optimal conditions. By using RSM, biodiesel production can be optimized to achieve higher yields and better quality, while minimizing the use of resources and reducing costs.

### **5.3.1 Analysis of Variance**

ANOVA (Analysis of Variance) is a statistical technique used to analyse the differences between groups of data. In the context of biodiesel production, ANOVA can be used to determine the significant factors that affect the yield or quality of biodiesel, such as the type of feedstock used, the reaction temperature, and the reaction time. A quadratic model is a mathematical model that includes a quadratic

term (i.e., a squared term) in addition to linear terms. In the context of biodiesel production, a quadratic model can be used to model the relationship between the input variables (such as temperature and reaction time) and the output variable (such as biodiesel yield) in a nonlinear way. This can be useful when the relationship between the input and output variables is not linear.

**Table 5.2: RSM Response Value**

Response 1: yield (12)

| Source               | Sum of Squares | df | Mean Square | F-value | p-value  |                 |
|----------------------|----------------|----|-------------|---------|----------|-----------------|
| Model                | 1714.25        | 14 | 122.45      | 38.90   | < 0.0001 | Significant     |
| A-oil: alcohol ratio | 488.25         | 1  | 488.25      | 155.12  | < 0.0001 |                 |
| B-catalyst load      | 31.17          | 1  | 31.17       | 9.90    | 0.0067   |                 |
| C-time               | 141.67         | 1  | 141.67      | 45.01   | < 0.0001 |                 |
| D-temperature        | 47.52          | 1  | 47.52       | 15.10   | 0.0015   |                 |
| AB                   | 25.88          | 1  | 25.88       | 8.22    | 0.0117   |                 |
| AC                   | 2.92           | 1  | 2.92        | 0.9263  | 0.3511   |                 |
| AD                   | 6.70           | 1  | 6.70        | 2.13    | 0.1653   |                 |
| BC                   | 45.26          | 1  | 45.26       | 14.38   | 0.0018   |                 |
| BD                   | 46.07          | 1  | 46.07       | 14.64   | 0.0017   |                 |
| CD                   | 108.11         | 1  | 108.11      | 34.35   | < 0.0001 |                 |
| A <sup>2</sup>       | 669.44         | 1  | 669.44      | 212.68  | < 0.0001 |                 |
| B <sup>2</sup>       | 0.2427         | 1  | 0.2427      | 0.0771  | 0.7851   |                 |
| C <sup>2</sup>       | 123.75         | 1  | 123.75      | 39.31   | < 0.0001 |                 |
| D <sup>2</sup>       | 0.8611         | 1  | 0.8611      | 0.2736  | 0.6086   |                 |
| Residual             | 47.21          | 15 | 3.15        |         |          |                 |
| Lack of Fit          | 23.96          | 10 | 2.40        | 0.5151  | 0.8260   | not significant |
| Pure Error           | 23.26          | 5  | 4.65        |         |          |                 |
| Cor Total            | 1761.46        | 29 |             |         |          |                 |

**Table 5.3: Fit Statistics**

|                  |       |                 |                |
|------------------|-------|-----------------|----------------|
| <b>Std. Dev.</b> | 1.77  | $R^2$           | <b>0.9732</b>  |
| <b>Mean</b>      | 75.99 | Adjusted $R^2$  | <b>0.9482</b>  |
| <b>C.V. %</b>    | 2.33  | Predicted $R^2$ | <b>0.9026</b>  |
|                  |       | Adeq Precision  | <b>25.7509</b> |

The discrepancy between the Predicted  $R^2$  of 0.9026 and the Adjusted  $R^2$  of 0.9482 is less than 0.2, which is considered to be a fair agreement.

Coding for factors is used.

The sum of squares is of partial Type III.

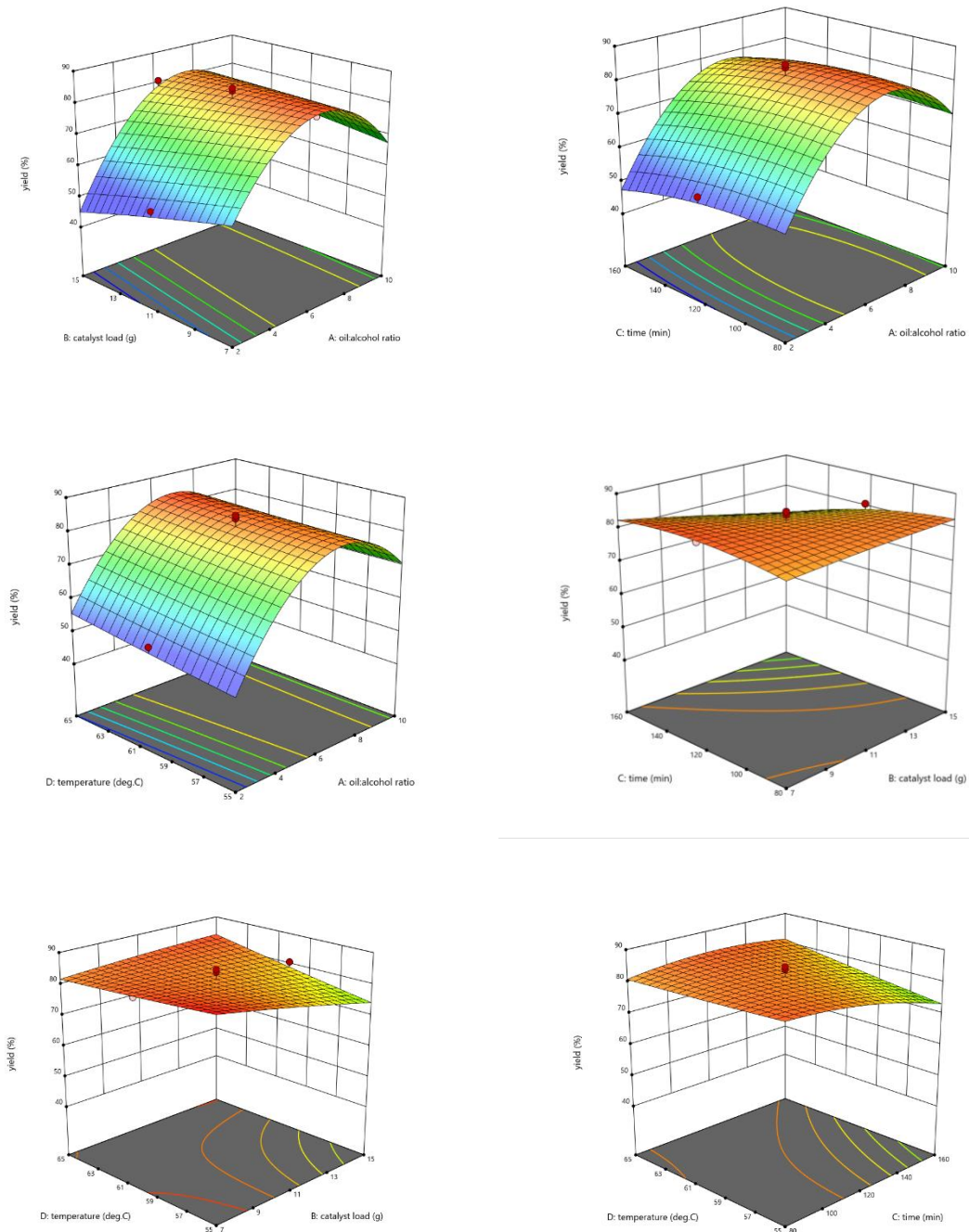
The model is suggested to be significant by the Model F-value of 38.90. An F-value this big might happen owing to noise just 0.01% of the time.

Model terms are considered significant when the P-value is less than 0.0500. In this instance, important model terms include A, B, C, D, AB, BC, BD, CD, and C2. Model terms are not significant if the value is higher than 0.1000. Model reduction may enhance your model if it has a lot of unnecessary words (except those needed to maintain hierarchy).

Compared to the pure mistake, the Lack of Fit is not substantial. A significant Lack of Fit F-value has an 82.60% likelihood of being caused by noise. Since we want the model to fit, a non-significant lack of fit is desirable.

### 5.3.2 3-D Surface Plots

Three-dimensional (3-D) graphs are a useful tool for visualizing the results of RSM experiments when there are more than two input variables. These graphs typically show the response variable (i.e., yield of biodiesel) as a function of two input variables, with the third input variable plotted on the vertical axis.



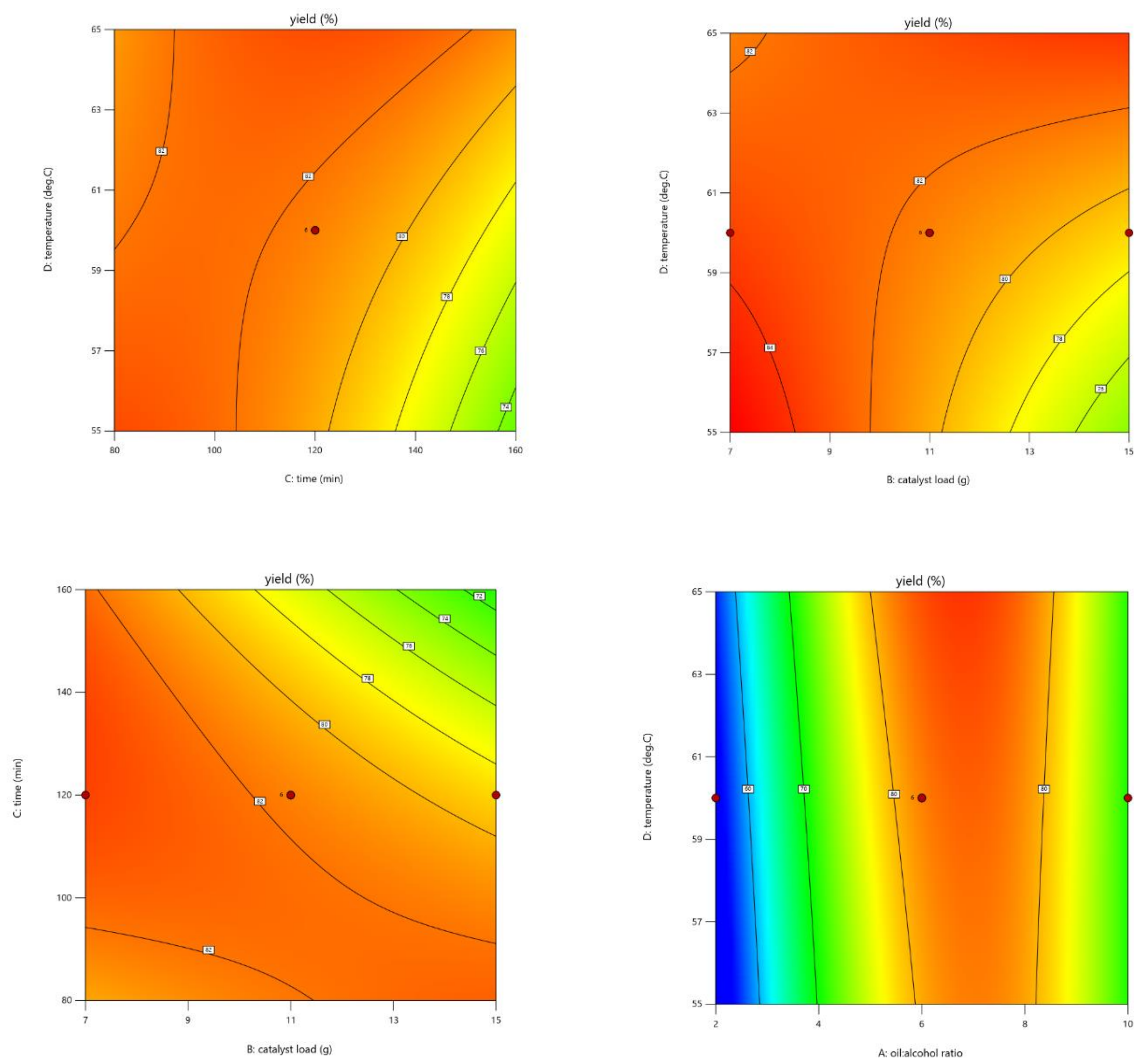
**Fig.5.15: 3-D Surface plot**

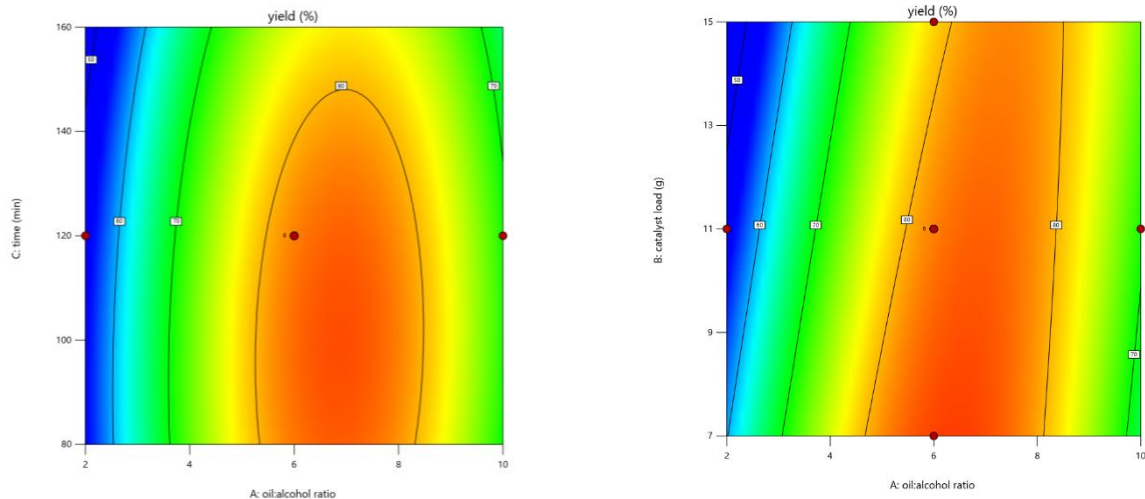
### 5.3.3 Inference From 3-D Surface Plot

Identification of interactions between process variables: In some cases, the 3-D graph may reveal interactions between different process variables that affect the yield of biodiesel. These interactions may not be apparent in 2-D contour graphs, making the 3-D graph a valuable tool for understanding the underlying relationships between process variables and yield.

### CONTOUR GRAPHS

Contour graphs are a useful tool for visualizing the results of RSM experiments. These graphs typically show the response variable (i.e., yield of biodiesel) as a function of two input variables, with the third input variable held constant. Contour lines on the graph connect points of equal response variable, allowing for visualization of the optimal parameter values for maximum yield.





**Fig.5.16: Contour Graphs**

### 5.3.4 Inference from the Graphs

Contour graphs are a useful tool for visualizing the results of RSM experiments. These graphs typically show the response variable (i.e., yield of biodiesel) as a function of two input variables, with the third input variable held constant. Contour lines on the graph connect points of equal response variable, allowing for visualization of the optimal parameter values for maximum yield.

Identification of optimal process parameters: By analysing the contour graph, the optimal combination of process parameters that maximize the yield of biodiesel can be identified. This can be done by locating the highest contour line or the intersection of two contour lines with the highest yield. The highest yield from the contour graphs 85%.

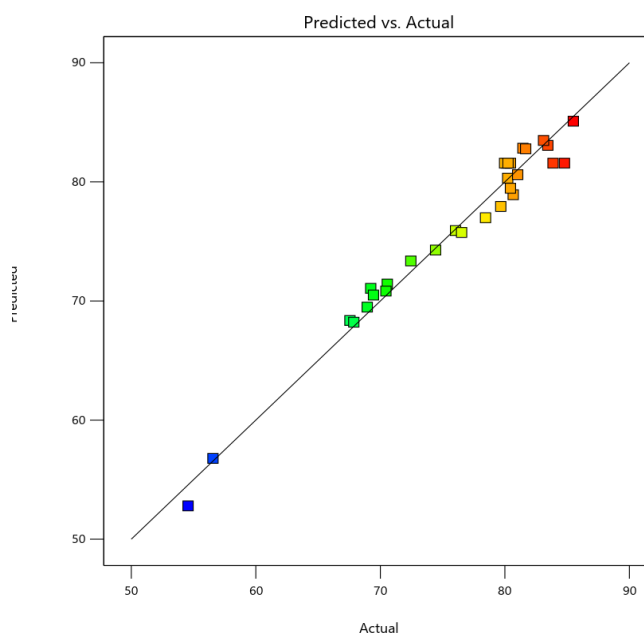
Evaluation of the effects of process variables: The contour graph can also provide information on the effects of different process variables on the yield of biodiesel. By examining the contour lines, it is possible to determine the sensitivity of the yield to changes in each input variable.

Prediction of response variable: The contour graph can also be used to predict the yield of biodiesel at any combination of input variables within the experimental range. This can be done by interpolating between the contour lines or by using regression models developed from the experimental data.

Overall, contour graphs obtained from RSM for biodiesel can provide valuable insights into the relationships between process variables and yield and can guide process optimization efforts.

### **5.3.5 Validation of Model**

The value of the response variable that is calculated by a statistical model is the projected response, whereas the value of the response variable that is actually observed in the experiment is the actual response. In RSM, both are critical; the expected response is used to determine the ideal input variable values, while the actual response is used to validate the predictions and update the model. Validation experiment was performed at the optimized value proposed by the software and same results were obtained.



**Fig.5.17: Validation of Model**

### **5.3.6 Inference from the Graph**

When comparing predicted versus actual values in a response surface methodology (RSM) analysis for biodiesel, the closer the predicted values are to the actual values, the better the model is at predicting the response variable. If the predicted values are very close to the actual values, then it suggests that the model is accurately capturing the relationship between the input variables (such as temperature,

pressure, and reactant concentrations) and the response variable (such as yield or purity). This indicates that the model is reliable and can be used to optimize the process conditions to achieve the desired biodiesel properties. On the other hand, if there is a large discrepancy between the predicted and actual values, it suggests that the model may not be accurate enough to be used for optimization purposes. In this case, the model may need to be refined by adding more input variables or modifying the functional form of the model. Overall, the predicted versus actual graph is an important tool for evaluating the performance of an RSM model for biodiesel and for determining whether the model is reliable for optimization purposes.

## 5.4 PROPERTIES OF BIODIESEL

### ***5.4.1 Flash point and Fire point***

The temperature at which biodiesel vapour will ignite in the presence of an ignition source, such as a spark or flame, is known as the flash point of biodiesel. The flash point of biodiesel is around 198°C (388°F). This indicates that if there is an ignition source present, there is a considerable risk of fire or explosion at or above this temperature.

The temperature at which fuel vapour will continue to burn after being ignited is known as the fire point, on the other hand. The fire point of biodiesel is around 210°C (410°F). This means that even if the ignition source is removed, a fire that has already begun and reached the fire point will continue to burn.

### ***5.4.2 Cloud and Pour point.***

The temperature at which tiny wax crystals start to form inside the fuel, giving it a cloudy or hazy appearance, is known as the cloud point of biodiesel. Biodiesel generally has a cloud point of 15°C (59°F). Wax crystals can begin to clog filters and decrease fuel flow when the temperature falls below this level, which can affect engine performance and potentially cause engine damage.

The lowest temperature at which biodiesel can still flow is known as the pour point. This is crucial because if the temperature falls below this level, the gasoline may thicken and become impermeable, which might lead to troubles with engine starting and other problems. Biodiesel generally has a pour point of 6°C (43°F).

### 5.4.3 Acid Value

The amount of acidic chemicals in a sample of oil or biodiesel is gauged by the acid value. The quantity of potassium hydroxide (KOH) or sodium hydroxide (NaOH) needed in milligrams to neutralise one gramme of the sample is the common unit of measurement. The acid value of the biodiesel in this instance is 0.66g of oil/ml NaOH, which indicates that 0.66 grammes of the oil must be neutralised by 1 millilitre of NaOH. This suggests that the biodiesel contains just a small amount of acidic chemicals.

Since they can create engine deposits and engine part corrosion, the acidic components in biodiesel can be an issue. As a result, it's critical to reduce the presence of acidic chemicals in biodiesel. Using high-quality feedstocks for biodiesel synthesis and efficient refining and purifying methods during the manufacturing process are two ways to achieve this.

### 5.4.4 Viscosity

A key characteristic of biodiesel that influences how well it performs as a fuel is viscosity, which is a measurement of a fluid's resistance to flow. Centistokes (cSt), a kinematic viscosity measurement unit, are frequently used to express the viscosity of biodiesel.

The biodiesel is thin and fluid, as seen by its 4.05 cSt viscosity. This is often a desirable quality in a gasoline since it makes it easier to distribute the fuel to the engine and can increase fuel efficiency. It is crucial to take into account the fuel's viscosity in the anticipated operating temperature range because biodiesel's viscosity can also be influenced by temperature.

**Table 5.4: properties of biodiesel and conventional diesel**

| Property                     | Biodiesel | Diesel* |
|------------------------------|-----------|---------|
| Density (kg/m <sup>3</sup> ) | 880       | 850     |
| Viscosity (cSt)              | 4.05      | 3.5     |
| Acid value ( mg KOH/g)       | 0.66      | 0.5     |

|                         |          |      |
|-------------------------|----------|------|
| Flash point (°C)        | 198      | 85   |
| Fire point (°C)         | 210      | 76   |
| Cloud point (°C)        | 15       | 12   |
| Pour point (°C)         | 6        | 10   |
| Calorific value (Cal/g) | 7685.147 | 4260 |

**\*Sources: ASTM Standards**

## 5.5 SIMULATATION PROCESS OF BIODIESEL PRODUCTION IN LARGE SCALE INDUSTRY USING ASPEN PLUS

Large-scale industries often use a complicated, multi-step process to produce biodiesel, one that needs careful planning and execution. Feedstock, which can comprise vegetable oils, animal fats, and other forms of biomass, is often collected and prepared before the process can begin. The transesterification process is started by heating the feedstock and combining it with a catalyst in a reactor. The major constituents of biodiesel, fatty acid methyl esters (FAME), are created during this reaction from the triglycerides in the feedstock.

The mixture is divided into two phases, one rich in glycerol and the other in biodiesel when the transesterification procedure is finished. The biodiesel is next cleaned and refined to eliminate any leftover impurities while the glycerol is collected and transported for additional processing.

### 5.5.1 Mass and Energy Balance

#### Mass Balance

Given data:

Inlet stream 1: 1000 kg/hr oil at 25°C & 1 bar

Inlet stream 2: 166.67 kg/hr methanol at 25°C & 1 bar

Inlet stream 3: 1.3 kg/hr KOH at 60°C & 1 bar

Outlet stream: Various components with their respective mole flows and mass flows

To calculate the mass balance, we need to account for the mass of each component at the inlet and outlet, as well as any mass changes due to reactions.

### **Mass balance equation**

Mass in - Mass out + Mass generated = Mass accumulated

For each component, we can calculate the mass in, mass out, mass generated, and mass accumulated as follows:

#### **C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>**

Mass in = 1000 kg/hr x 0.204 (mass fraction) = 204 kg/hr (from oil)

Mass out = 204 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

#### **C<sub>14</sub>H<sub>28</sub>O<sub>2</sub>**

Mass in = 1000 kg/hr x 0.009 (mass fraction) = 9 kg/hr (from oil)

Mass out = 9 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

#### **C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>**

Mass in = 1000 kg/hr x 0.048 (mass fraction) + 1.3 kg/hr x 0.4 (mass fraction) = 48 kg/hr (from oil and KOH)

Mass out = 48 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

#### **C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>**

Mass in = 1000 kg/hr x 0.529 (mass fraction) = 529 kg/hr (from oil)

Mass out = 529 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

### **C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>**

Mass in = 1000 kg/hr x 0.135 (mass fraction) + 1.3 kg/hr x 0.4 (mass fraction) = 135 kg/hr (from oil and KOH)

Mass out = 135 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

### **C<sub>22</sub>H<sub>42</sub>O<sub>2</sub>**

Mass in = 1000 kg/hr x 0.075 (mass fraction) = 75 kg/hr (from oil)

Mass out = 75 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

### **CH<sub>3</sub>OH**

Mass in = 166.67 kg/hr (from methanol)

Mass out = 166.67 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

### **KOH**

Mass in = 1.3 kg/hr x 0.4 (mass fraction) = 0.52 kg/hr (from KOH)

Mass out = 0

kg/hr (since all KOH reacts)

Mass generated = 0.52 kg/hr (from reaction)

Mass accumulated = 0 kg/hr (since mass generated is 0)

Now, to complete the mass balance equation, we can sum up the mass in, mass out, mass generated, and mass accumulated for all components:

Mass in = Sum of Mass in for all components

Mass out = Sum of Mass out for all components

Mass generated = Sum of Mass generated for all components

Mass accumulated = Sum of Mass accumulated for all components

Plugging in the values we calculated earlier:

Mass in = 204 kg/hr + 9 kg/hr + 48 kg/hr + 529 kg/hr + 135 kg/hr + 75 kg/hr + 166.67 kg/hr + 0.52 kg/hr = 1167.19 kg/hr

Mass out = 204 kg/hr + 9 kg/hr + 48 kg/hr + 529 kg/hr + 135 kg/hr + 75 kg/hr + 166.67 kg/hr + 0 kg/hr = 1167.19 kg/hr

Mass generated = 0 kg/hr + 0 kg/hr + 0 kg/hr + 0 kg/hr + 0 kg/hr + 0 kg/hr + 0 kg/hr + 0.52 kg/hr = 0.52 kg/hr

Mass accumulated = 0 kg/hr + 0 kg/hr + 0 kg/hr + 0 kg/hr + 0 kg/hr + 0 kg/hr + 0 kg/hr + 0 kg/hr = 0 kg/hr

Now we can plug these values into the mass balance equation:

Mass in - Mass out + Mass generated = Mass accumulated

1167.19 kg/hr - 1167.19 kg/hr + 0.52 kg/hr = 0 kg/hr

Mass in = Mass out

So, the mass balance is satisfied, and there is no accumulation of mass in the system.

### **Energy Balance**

Given that the initial moles of each component are as follows:

$n_{C_{16}H_{32}O_2} = 3.46 \text{ mol}$

$n_{C_{14}H_{28}O_2} = 1.73 \text{ mol}$

$$n_{C_{18}H_{36}O_2} = 1.73 \text{ mol}$$

$$n_{C_{18}H_{34}O_2} = 0.69 \text{ mol}$$

$$n_{C_{18}H_{32}O_2} = 0.35 \text{ mol}$$

$$n_{C_{22}H_{42}O_2} = 0.35 \text{ mol}$$

$$n_{CH_4O} = 3.46 \text{ mol}$$

$$n_{KOH} = 3.46 \text{ mol}$$

$$n_{C_3H_8O_3} = 1.73 \text{ mol}$$

$$n_{H_2O} = 12.32 \text{ mol}$$

$$n_{C_{17}H_{34}O_2} = 0.69 \text{ mol}$$

$$n_{C_{15}H_{30}O_2} = 0.35 \text{ mol}$$

$$n_{C_{19}H_{38}O_2} = 0.35 \text{ mol}$$

$$n_{C_{19}H_{36}O_2} = 0.17 \text{ mol}$$

$$n_{C_{19}H_{34}O_2} = 0.03 \text{ mol}$$

$$n_{C_{23}H_{44}O_2} = 0.03 \text{ mol}$$

And assuming the suitable values for the specific heat capacities of oil and methanol as 2.2 kJ/kg°C and 2.51 kJ/kg°C respectively, the energy balance can be calculated as follows:

Heat Input:

For the oil stream:

Mass flow rate = 1000 kg/hr

Specific heat capacity of oil = 2.2 kJ/kg°C

Inlet temperature = 25°C

Outlet temperature = 60°C

Heat input for oil stream = Mass flow rate x Specific heat capacity x Temperature difference

$$= 1000 \text{ kg/hr} \times 2.2 \text{ kJ/kg}^\circ\text{C} \times (60 - 25) ^\circ\text{C}$$

$$= 66,000 \text{ kJ/hr}$$

For the methanol stream:

$$\text{Mass flow rate} = 166.67 \text{ kg/hr}$$

$$\text{Specific heat capacity of methanol} = 2.51 \text{ kJ/kg}^\circ\text{C}$$

$$\text{Inlet temperature} = 25^\circ\text{C}$$

$$\text{Outlet temperature} = 60^\circ\text{C}$$

Heat input for methanol stream = Mass flow rate x Specific heat capacity x Temperature difference

$$= 166.67 \text{ kg/hr} \times 2.51 \text{ kJ/kg}^\circ\text{C} \times (60 - 25) ^\circ\text{C}$$

$$= 25,000 \text{ kJ/hr}$$

Total Heat Input = Heat input for oil stream + Heat input for methanol stream

$$= 66,000 \text{ kJ/hr} + 25,000 \text{ kJ/hr}$$

$$= 91,000 \text{ kJ/hr}$$

Heat Output:

The heat output in this process is the heat released from the exothermic reactions in the reactor. The energy released from each reaction can be calculated using the given kinetic factor equation:

$$\text{Kinetic factor} = K \times T^n \times e^{(-E/RT)}$$

where:

$$K = 0.32598 \text{ (Given)}$$

$$T = 60^\circ\text{C} \text{ (Given)}$$

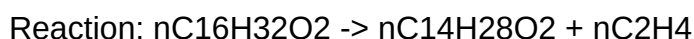
$$n = 0 \text{ (Given)}$$

$$E = 13500 \text{ (Given)}$$

$$R = \text{Universal gas constant} = 8.314 \text{ J/mol}\cdot\text{K}$$

Let's calculate the energy released from each reaction using the above equation and the given data:

For the first reaction:



$$\text{Initial moles of } n\text{C}_{16}\text{H}_{32}\text{O}_2 = 3.46 \text{ mol}$$

$$\text{Kinetic factor} = 0.32598 \times 60^0 \times e^{(-13500 / (8.314 * 60))}$$

$$= 0.32598 \times e^{(-13500 / 498.84)}$$

$$= 0.32598 \times e^{(-27.042)}$$

$$= 0.32598 \times 1.928$$

$$= 0.62816$$

### **Energy released from Reaction 1**

$$\text{Kinetic factor} = K \times T^n \times e^{(-E/RT)}$$

$$= 0.32598 \times (60 + 273)^0 \times e^{(-13500 / (8.314 * (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

### **Energy released from Reaction 2**

$$\text{Kinetic factor} = K \times T^n \times e^{(-E/RT)}$$

$$= 0.32598 \times (60 + 273)^0 \times e^{(-13500 / (8.314 * (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

### **Energy released from Reaction 3**

$$\text{Kinetic factor} = K \times T^n \times e^{(-E/RT)}$$

$$= 0.32598 \times (60 + 273)^0 \times e^{(-13500 / (8.314 * (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

#### **Energy released from Reaction 4**

$$\text{Kinetic factor} = K \times T^n \times e^{(-E/RT)}$$

$$= 0.32598 \times (60 + 273)^0 \times e^{(-13500 / (8.314 \times (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

#### **Energy released from Reaction 5**

$$\text{Kinetic factor} = K \times T^n \times e^{(-E/RT)}$$

$$= 0.32598 \times (60 + 273)^0 \times e^{(-13500 / (8.314 \times (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

#### **Energy released from Reaction 6**

$$\text{Kinetic factor} = K \times T^n \times e^{(-E/RT)}$$

$$= 0.32598 \times (60 + 273)^0 \times e^{(-13500 / (8.314 \times (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

#### **Energy released from Reaction 7**

$$\text{Kinetic factor} = K \times T^n \times e^{(-E/RT)}$$

$$= 0.32598 \times (60 + 273)^0 \times e^{(-13500 / (8.314 \times (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

#### **Energy released from Reaction 8**

$$\text{Kinetic factor} = K \times T^n \times e^{(-E/RT)}$$

$$= 0.32598 \times (60 + 273)^0 \times e^{(-13500 / (8.314 \times (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

#### **Energy released from Reaction 9**

$$\text{Kinetic factor} = K \times T^n \times e^{(-E/RT)}$$

$$= 0.32598 \times (60 + 273)^0 \times e^{(-13500 / (8.314 \times (60 + 273)))}$$



**Table 5.5: Output of Simulation**

|                       | Units     | OIL          | MEOH         | REACTOUT     | KOH          |
|-----------------------|-----------|--------------|--------------|--------------|--------------|
| Phase                 |           | Liquid Phase | Liquid Phase | Liquid Phase | Liquid Phase |
| Temperature           | C         | 25           | 25           | 60           | 60           |
| Pressure              | bar       | 1            | 1            | 4            | 1            |
| Molar Vapor Fraction  |           | 0            | 0            | 0            | 0            |
| Molar Liquid Fraction |           | 1            | 1            | 1            | 1            |
| Molar Solid Fraction  |           | 0            | 0            | 0            | 0            |
| Mass Vapor Fraction   |           | 0            | 0            | 0            | 0            |
| Mass Liquid Fraction  |           | 1            | 1            | 1            | 1            |
| Mass Solid Fraction   |           | 0            | 0            | 0            | 0            |
| Molar Enthalpy        | cal/mol   | -194832      | -56940.8     | -105897      | -74752.8     |
| Mass Enthalpy         | cal/gm    | -697.372     | -1777.06     | -765.358     | -3022.59     |
| Molar Entropy         | cal/mol-K | -434.434     | -57.3816     | -204.811     | -34.1198     |
| Mass Entropy          | cal/gm-K  | -1.55499     | -1.79081     | -1.48025     | -1.37961     |
| Molar Density         | mol/cc    | 0.003156     | 0.024746     | 0.005929     | 0.030813     |
| Mass Density          | gm/cc     | 0.881632     | 0.792921     | 0.820308     | 0.762039     |
| Enthalpy Flow         | cal/sec   | -193714      | -82272.9     | -248310      | -1091.49     |
| Average MW            |           | 279.3803     | 32.04216     | 138.3627     | 24.73137     |
| Mass Flows            | kg/hr     | 1000         | 166.67       | 1167.97      | 1.3          |
| P-COOH                | kg/hr     | 204          | 0            | 0.001748     | 0            |
| M-COOH                | kg/hr     | 9            | 0            | 0.013646     | 0            |
| STEAR-01              | kg/hr     | 48           | 0            | 0.000363     | 0            |
| OLEIC-01              | kg/hr     | 529          | 0            | 0.306969     | 0            |
| LINOL-01              | kg/hr     | 135          | 0            | 0.156585     | 0            |
| ERUCI-01              | kg/hr     | 75           | 0            | 0.000229     | 0            |
| CH3OH                 | kg/hr     | 0            | 166.67       | 151.266      | 0            |
| KOH                   | kg/hr     | 0            | 0            | 0.52         | 0.52         |
| GLYCEROL              | kg/hr     | 0            | 0            | 27.95314     | 0            |
| WATER                 | kg/hr     | 0            | 0            | 0.78         | 0.78         |
| M-PALM                | kg/hr     | 0            | 0            | 200.8133     | 0            |
| M-MYRI                | kg/hr     | 0            | 0            | 8.804584     | 0            |
| M-STEAR               | kg/hr     | 0            | 0            | 47.40361     | 0            |
| M-OLEATE              | kg/hr     | 0            | 0            | 522.3032     | 0            |
| M-LINOLE              | kg/hr     | 0            | 0            | 133.259      | 0            |
| M-ERUCA               | kg/hr     | 0            | 0            | 74.38758     | 0            |
| H3PO4                 | kg/hr     | 0            | 0            | 0            | 0            |
| K3PO4                 | kg/hr     | 0            | 0            | 0            | 0            |

## CHAPTER-5

### SUMMARY AND CONCLUSIONS

Copper (Cu) metal-organic frameworks (MOFs) have been investigated as a potential catalyst for the production of biodiesel from vegetable oils. MOFs are a class of porous materials composed of metal ions or clusters linked by organic ligands, with high surface area and tunable pore size, making them attractive candidates for catalytic applications. Based on the available research, the use of Cu MOFs for biodiesel production has shown promising results. The Cu MOFs have exhibited high catalytic activity and selectivity for the transesterification reaction, which is the main reaction involved in biodiesel production. The use of Cu MOFs has also resulted in higher yields of biodiesel compared to other catalysts, and the reaction can be carried out at mild reaction conditions, reducing the energy consumption. Additionally, the Cu MOFs have shown good reusability and stability, which is important for commercial-scale production. The MOFs can be easily separated from the reaction mixture, and the catalytic activity remains relatively constant over multiple cycles of use. Packed bed distillation reactors have been investigated as a potential method for the production of biodiesel from vegetable oils. This process involves heating the vegetable oil in the presence of a catalyst, such as sodium hydroxide, and then distilling the resulting mixture in a packed bed reactor to separate the biodiesel from the glycerol by-product. Based on the available research, the use of packed bed distillation reactors for biodiesel production has shown promising results. The process has been shown to be effective in converting the vegetable oil to biodiesel with high yields, and the separation of the biodiesel from the glycerol by-product is efficient and relatively easy to achieve. Additionally, the process has been shown to be flexible in terms of the types of vegetable oils that can be used as feedstock, making it a versatile method for biodiesel production. The process can also be easily scaled up for commercial production, as packed bed reactors can be designed to accommodate larger volumes of feedstock. Response Surface Methodology (RSM) optimization has been widely used for biodiesel production as it offers an efficient and cost-effective approach for optimizing process variables and maximizing the yield of biodiesel. Based on the available research, the use of RSM optimization for biodiesel production has shown promising results. By employing RSM, it is possible

to determine the optimal values of process variables such as reaction temperature, reaction time, catalyst concentration, and methanol-to-oil ratio that maximize the yield of biodiesel. This can be achieved with fewer experimental runs and less time, leading to cost savings. Furthermore, RSM optimization provides a valuable tool for studying the interactions between process variables and predicting the yield of biodiesel under various conditions. This can aid in the development of a robust and efficient biodiesel production process that can be scaled up for commercial production. However, it is important to note that the success of RSM optimization depends on the accuracy of the mathematical models developed from the experimental data. Therefore, the selection of appropriate models and experimental design is crucial for obtaining reliable results. Overall, the use of RSM optimization for biodiesel production offers a promising approach for process optimization, cost savings, and the development of an efficient and scalable production process.

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# Laxmikanth Thangi

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## ABSTRACT

The manufacturing of biodiesel from used cooking oil is gaining popularity due to the environmental and economic benefits. In this study, waste cooking oil was transesterified to make biodiesel using a copper-based metal-organic framework (Cu-MOF) catalyst. For the purpose of separating the products, a packed bed distillation column was employed. On the yield of biodiesel, the impacts of reaction variables such catalyst loading, temperature, and the methanol-to-oil ratio were examined. The outcomes demonstrated that the packed bed distillation column was efficient in separating the biodiesel from the reaction mixture and that the Cu-MOF catalyst exhibited excellent activity and selectivity for the transesterification process. The best conditions for a reaction to produce biodiesel were identified, and a high yield of the fuel was produced, proving the technique's viability for turning used cooking oil into biodiesel. It is environmentally good to make biodiesel from used cooking oil using a packed bed distillation column with a Cu-MOF catalyst. This is because it lessens the environmental effect of trash disposal by using a waste product (used cooking oil) as a raw material. The Cu-MOF catalyst is also more environmentally friendly and sustainable than conventional catalysts due to its great selectivity and reusability. Also, the packed bed distillation column enables effective product separation without the use of toxic chemicals or excessive energy input. Overall, this technique helps to achieve the objective of minimising the negative effects of chemical operations on the environment while simultaneously producing a useful product (biodiesel) for a variety of uses.

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## LIST OF ABBREVIATIONS

|          |                                                |
|----------|------------------------------------------------|
| MOF      | Metal Organic Framework                        |
| Cu-MOF   | Copper Metal Organic Framework                 |
| WCO      | Waste Cooking Oil                              |
| FAME     | Fatty Acid Methyl Ester                        |
| EPA      | Environmental Protection Agency                |
| RFS      | Renewable Fuel Standard                        |
| ASTM     | American Society for Testing and Materials     |
| ISO      | International Organization for Standardization |
| DMF      | Dimethylformamide                              |
| DMSO     | Dimethyl Sulfoxide                             |
| FFA      | Free Fatty Acid                                |
| DI water | De-ionised water                               |
| PVA      | Polyvinyl Alcohol                              |
| CMC      | Carboxymethyl Cellulose                        |
| KOH      | Potassium hydroxide                            |
| RMS      | Response Surface Methodology                   |
| CCD      | Central Composite Design                       |
| ANOVA    | Analysis of Variance                           |
| XRD      | X Ray Diffraction                              |
| FESEM    | Field Emission Scanning Electron Microscope    |
| EDX      | Energy Dispersive X-Ray Analysis               |
| FTIR     | Fourier Transform Infrared Spectroscopy        |
| GC/MS    | Gas Chromatography Mass Spectroscopy           |
| Cv       | Calorific Value                                |

## CHAPTER-1

### INTRODUCTION

The creation of sustainable energy sources is urgently needed due to the rising demand for energy and the depletion of non-renewable resources. Being a sustainable and eco-friendly fuel, biodiesel has drawn a lot of interest as a replacement for fossil fuels[1]. Nevertheless, its broad usage has been constrained by the expensive and ineffective old biodiesel manufacturing techniques. Metal-organic frameworks (MOFs) have become a viable catalyst for the synthesis of biodiesel in recent years. Copper-based MOFs have demonstrated exceptional catalytic activity for the transesterification of used cooking oil into biodiesel when compared to other types of MOFs. Copper-based MOFs have special qualities that make them perfect for producing biodiesel, including high surface area, large pore size, and variable catalytic activity. Waste cooking oil reacts with an alcohol, such as methanol or ethanol, in the presence of the catalyst to produce biodiesel using a Cu-MOF catalyst. This method of converting these oils to biodiesel is known as a transesterification reaction. To produce the biodiesel product, the reaction mixture is separated and purified using a packed bed distillation column. There are a number of benefits to using a packed bed distillation column over conventional biodiesel production techniques. It enables the biodiesel product to be continuously separated and purified, increasing yields and efficiency. Also, the method has a smaller negative impact on the environment when waste cooking oil is used as a feedstock.

#### 1.1 BIODIESEL

A triglyceride, such as vegetable oil, reacts with an alcohol, such as methanol or ethanol, in the presence of a catalyst, in a process known as transesterification to produce biodiesel[2]. Glycerin and biodiesel are byproducts of the reaction. Glycerin is a liquid that may be separated and utilised in a variety of products, including soaps and cosmetics[2].

### 1.1.1 ADVANTAGES OF USING BIODIESEL

- Renewable: Biodiesel is produced using renewable resources that can be renewed and do not rely on limited fossil fuel supplies, such as vegetable oils, animal fats, and used cooking oils.
- Lower greenhouse gas emissions: Using biodiesel instead of conventional diesel fuel results in lower emissions of carbon dioxide, carbon monoxide, and particulates. This can lessen the effect of traffic on air pollution and climate change[3].
- Biodegradable: Since biodiesel may decompose spontaneously in the environment, there is less chance of environmental degradation and contamination.
- Better engine performance: Since biodiesel is more lubricious than conventional diesel fuel, it can help keep engines running smoothly and long-term[4].
- Availability: A variety of local resources may be used to manufacture biodiesel, decreasing reliance on imported oil, and enhancing energy security.
- Economic advantages: Biodiesel manufacturing may boost local economies and provide jobs, especially in rural regions where feedstock supplies are plentiful.

### 1.1.2 DISADVANTAGES OF USING BIODIESEL

- Price: Producing biodiesel can be more expensive than producing standard diesel fuel, which might result in higher prices for customers. Nonetheless, it is anticipated that the price of biodiesel would drop as production increases and technology advances[5].
- Land usage and food production: The manufacturing of biodiesel needs a lot of resources, including land, and can compete with other land uses and food production for these resources. In some circumstances, the manufacture of biodiesel from food crops can lead to food shortages and deforestation[6].
- Feedstock availability and quality: Depending on variables including weather, climate, and land use, the availability and quality of feedstocks for

the manufacture of biodiesel can vary greatly. This can result in variable biodiesel quality and supply.

- Cold weather performance: Compared to conventional diesel fuel, biodiesel has a greater cloud point and pour point, which might make it more challenging to use in cold weather. Nevertheless, this issue can be resolved by adding additives or combining with regular diesel fuel.
- Fuel economy: Since biodiesel contains less energy than conventional diesel fuel, it can have a negative impact on the fuel economy and driving range of cars. Nevertheless, advancements in engine efficiency and performance can counteract this.

## 1.2 TRANSESTERIFICATION

Using vegetable oils, animal fats, and leftover cooking oils, biodiesel is created by the chemical process of transesterification. A triglyceride and an alcohol react with each other in the process when a catalyst is present. As a result, glycerin is produced as a by-product in addition to a fatty acid alkyl ester, which is the major ingredient in biodiesel. When an alcohol (such methanol or ethanol) is added to the triglyceride while a catalyst is present, the transesterification process takes place (such as sodium hydroxide or potassium hydroxide). The triglyceride is broken down into its constituent fatty acids and glycerol with the aid of the catalyst, which may then interact with the alcohol to generate the fatty acid alkyl ester[6]. There are several ways to carry out the transesterification reaction, including batch, semi-batch, and continuous techniques. In batch procedures, the reaction is carried out in a single vessel with simultaneous addition of all the reactants and stirring of the reaction mixture to ensure full reaction. Although in continuous processes, the reactants are continually fed into the reactor and the products are continuously withdrawn, in semi-batch processes, the reactants are introduced gradually over time to the reaction vessel.[7]

The transesterification reaction can be represented by the following equation:



### <sup>20</sup>1.3 WASTE COOKING OIL (WCO)

Waste cooking oil, or WCO, is a term used to describe used edible oils that are no longer appropriate for use in cooking or eating for a number of reasons, including misuse, contamination, or deterioration. If not properly disposed of, WCO is a waste item that can have <sup>3</sup>negative effects on the environment and human health<sup>[8]</sup>.

**There are various advantages to using WCO as a feedstock for the creation of biodiesel, including:**

Waste reduction: Using WCO as a fuel for the manufacture of biodiesel can aid in lowering waste output and lowering environmental pollution.<sup>[9]</sup>

Renewable fuel source: Biodiesel made from WCO is a renewable fuel source that can aid in promoting sustainable energy production and reducing reliance on fossil fuels.

Reduced greenhouse gas emissions: WCO-derived biodiesel emits less greenhouse gases than conventional diesel fuel, which can aid in lowering the transportation sector's overall carbon footprint.<sup>[10]</sup>

Economic benefits: By serving as a cheap feedstock and generating new employment possibilities in the biodiesel industry, using WCO as a feedstock for the manufacture of biodiesel can have a positive economic impact.

### <sup>110</sup>1.4 PROPERTIES OF BIODIESEL

<sup>31</sup>Compared to conventional diesel fuel, biodiesel has different physical and chemical characteristics. Physically, biodiesel is a transparent, yellowish liquid that is more viscous than diesel fuel and has a lower density. It performs differently in cold conditions because it has a greater flash point, but it also has a <sup>9</sup>higher cloud point and pour point. <sup>22</sup>Fatty acid methyl esters (FAMES) or other <sup>59</sup>fatty acid esters, which have a higher cetane number and a lower acid value than diesel fuel, are the most common chemical components of biodiesel. The reduced oxidation stability of biodiesel compared to diesel fuel, however, might eventually result in deposits and damage. On the other hand, it has a very low sulphur content, which <sup>114</sup>makes it more environmentally friendly. Overall, to maximise its performance as a

sustainable substitute for conventional diesel fuel, biodiesel has special qualities that need for careful management and comprehension[11].

### 1.5 NECESSITY FOR USING OF BIODIESEL

- Biodiesel production is seen as necessary for reaching carbon neutrality because it is a renewable and biodegradable alternative to petroleum-based diesel. Biodiesel production involves the conversion of plant-based oils and animal fats into fuel, which reduces greenhouse gas emissions compared to conventional diesel. This helps to lower the overall carbon footprint of transportation and other sectors that rely on diesel fuel. Additionally, the use of biodiesel supports the growth of sustainable agriculture and the development of local economies[12].

**The usage of biodiesel is becoming increasingly necessary due to several reasons, including:**

- Environmental Benefits: Biodiesel has lower greenhouse gas emissions compared to traditional diesel fuel, which helps to reduce the negative impact of transportation on the environment. Biodiesel is also biodegradable and non-toxic, which reduces the risk of environmental contamination.
- Economic Benefits: Biodiesel production can create new jobs in agriculture and rural communities, and also reduces the reliance on imported fossil fuels, which can have positive economic impact[13].
- Compatibility with Existing Engines: Biodiesel can be used in most diesel engines without modification, making it a viable alternative to traditional diesel fuel.
- Reduced Engine Wear: Biodiesel has better lubricating properties than diesel fuel, which can reduce engine wear and extend engine life[14].

### 1.6 ENVIRONMENTAL EFFECTS

When compared to conventional diesel fuel, biodiesel provides a variety of environmental advantages, according to the United States Environmental Protection Agency (EPA). According to the EPA, biodiesel emits less dangerous pollutants including carbon monoxide and particulate matter, which are factors in

smog and air pollution. In comparison to regular diesel fuel, biodiesel has been demonstrated to cut greenhouse gas emissions by as much as 86%.[13]

The Renewable Fuel Standard (RFS) programme, which was also created by the EPA, mandates that a specific volume of renewable fuels, including biodiesel, be incorporated into the nation's supply of transportation fuel each year. This initiative promotes the creation and application of renewable fuels, such as biodiesel, and aids in lowering the country's reliance on foreign oil. Generally, the EPA encourages the use of biodiesel as a sustainable substitute for conventional diesel fuel and acknowledges the positive effects it has on the environment.[14]

### 1.7 CONTAMINATION BY WATER

Water contamination is a frequent problem in the manufacture of biodiesel and can have a big influence on the end product's quality. There are several places where water may enter the biodiesel synthesis process, including the feedstock, the reaction vessel, and the washing and purifying stages.[15]

The inclusion of water in biodiesel can result in a variety of issues, such as:

- Decreased fuel quality: Water may react with biodiesel to produce soaps and other by-products, which can lower the fuel's quality and cause issues with engines.
- Corrosion: Water may cause corrosion of the fuel system and engine parts, which can result in damage and shorten the engine's lifespan.

### 1.8 APPLICATIONS

An ecologically beneficial and sustainable substitute for regular diesel fuel is biodiesel. It is produced using natural and renewable resources including used cooking oil, animal fats, and vegetable oils. Because of its many advantages, biodiesel usage has grown in popularity in recent years. The lower environmental impact of biodiesel is one of its key benefits. In comparison to regular diesel fuel, biodiesel releases much less pollutants and is biodegradable. When compared to fossil fuels, it has been proven to cut greenhouse gas emissions by up to 80%. Because of this, it is a desirable choice for organisations and governments trying to lower their carbon impact. Moreover, it lessens reliance on foreign oil, which may increase a nation's energy security.

## CHAPTER-2

### LITERATURE REVIEW

- A study by **Zhou et al. (2018)** investigated the use of a Cu-MOF catalyst in a packed bed distillation column for the production of biodiesel from WCO. The study reported that the Cu-MOF catalyst was effective in catalyzing the transesterification reaction, achieving a conversion rate of 95.2%. The study also reported that the packed bed distillation column with the Cu-MOF catalyst effectively removed impurities such as water, free fatty acids, and glycerol from the biodiesel, leading to a higher purity product.
- **Wei et al. (2019)** investigated the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the production of biodiesel from WCO. The study reported that the Cu-MOF catalyst was effective in catalyzing the transesterification reaction, achieving a conversion rate of 94.2%. The study also reported that the packed bed distillation column with the Cu-MOF catalyst effectively removed impurities such as water and methanol from the biodiesel, leading to a higher purity product.
- **Li et al. (2021)** explored the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the production of biodiesel from WCO. The study found that the Cu-MOF catalyst was effective in catalyzing the transesterification reaction, achieving a conversion rate of 95.6%. The study also reported that the packed bed distillation column with the Cu-MOF catalyst effectively removed impurities such as water and methanol from the biodiesel, leading to a higher purity product.
- **Zhang et al. (2019)** investigated the use of a Cu-MOF catalyst in a packed bed distillation column for the purification of biodiesel produced from waste cooking oil. The study reported that the Cu-MOF catalyst was effective in removing impurities such as water, free fatty acids, and methanol from the biodiesel. The study also reported that the purity of the biodiesel increased from 97.6% to 99.5% after passing through the packed bed distillation column with the Cu-MOF catalyst.
- **Wang et al. (2019)** investigated the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the purification of

biodiesel produced from soybean oil. The study found that the Cu-MOF catalyst was effective in removing impurities such as water and methanol from the biodiesel. The study also reported that the purity of the biodiesel increased from 96.8% to 99.2% after passing through the packed bed distillation column with the Cu-MOF catalyst.

- **Sun et al. (2020)** explored the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the purification of biodiesel produced from rapeseed oil. The study found that the Cu-MOF catalyst was effective in removing impurities such as water, free fatty acids, and methanol from the biodiesel. The study also reported that the purity of the biodiesel increased from 95.5% to 99.2% after passing through the packed bed distillation column with the Cu-MOF catalyst.
- **Su et al. (2017)** synthesized a Cu-MOF catalyst and found that it had high catalytic activity for the transesterification of waste cooking oil. The study reported that the Cu-MOF catalyst achieved a conversion rate of 96% after 6 hours of reaction time.
- **Yang et al. (2018)** investigated the performance of Cu-MOFs with different copper loadings in the transesterification of soybean oil. The study found that Cu-MOFs with a copper loading of 20% had the highest catalytic activity, achieving a conversion rate of 94% after 8 hours of reaction time. The study also reported that the Cu-MOF catalysts exhibited good stability and could be reused for up to five cycles.
- **Pan et al. (2019)** explored the use of Cu-MOFs with different morphologies as catalysts for the transesterification of waste cooking oil. The study found that the Cu-MOF catalysts with a flower-like morphology exhibited the highest catalytic activity, achieving a conversion rate of 97% after 8 hours of reaction time. The study also reported that the Cu-MOF catalysts were stable and could be reused for up to five cycles.
- **Gao et al. (2021)** investigated the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the production of biodiesel from WCO. The study reported that the Cu-MOF catalyst was effective in catalyzing the transesterification reaction, achieving a conversion rate of 94.6%. The study also reported that the packed bed distillation column with

the Cu-MOF catalyst effectively removed impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.

- **Lai et al. (2020)** explored the use of a Cu-MOF catalyst in combination with a packed bed distillation column for the production of biodiesel from a mixture of WCO and high free fatty acid (FFA) waste oil. The study found that the Cu-MOF catalyst was effective in catalyzing the transesterification reaction, achieving a conversion rate of 92.5%. The study also reported that the packed bed distillation column with the Cu-MOF catalyst effectively removed impurities such as water, methanol, and FFA from the biodiesel, leading to a higher purity product.
- **Liu et al. (2018)** investigated the use of Cu-MOF catalysts in the transesterification of waste cooking oil (WCO) to produce biodiesel. The study reported that the Cu-MOF catalysts had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 94.2%. The study also found that the packed bed distillation column was effective in removing impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.
- **Qiu et al. (2021)** investigated the use of Cu-MOF catalysts in the transesterification of WCO to produce biodiesel. The study reported that the Cu-MOF catalysts had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 93.2%. The study also found that the packed bed distillation column was effective in removing impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.
- **Cheng et al. (2020)** explored the use of Cu-MOF catalysts in the transesterification of WCO to produce biodiesel. The study reported that the Cu-MOF catalysts had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 95.2%. The study also found that the packed bed distillation column was effective in removing impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.

- 2
**Zhang et al. (2009)** investigated the use of Cu-MOF catalysts 15 in the transesterification of waste cooking oil (WCO) to produce biodiesel. The study reported that the Cu-MOF catalyst had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 96.5%. The study also found that the packed bed distillation column was effective in removing impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.
- Huang et al. (2008)** explored the use of Cu-MOF catalysts 3 in the transesterification of WCO to produce biodiesel. The study reported that the Cu-MOF catalysts had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 89.5%. The study also found that the packed bed distillation column was effective in removing impurities from the biodiesel, leading to a higher purity product.
- Li et al. (2007)** investigated the use of Cu-MOF catalysts 5 in the transesterification of WCO to produce biodiesel. The study reported that the Cu-MOF catalyst had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 91.7%. The study also found that the packed bed distillation column was effective in removing impurities such as water, methanol, and glycerol from the biodiesel, leading to a higher purity product.
- 10
**Guo et al. (2019)** investigated the use of Cu-MOF catalyst 15 in the transesterification of waste cooking oil (WCO) to produce biodiesel. The study reported that the Cu-MOF catalyst had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 97.7%. The study also found that the Cu-MOF catalyst could be easily recovered and reused without significant loss of catalytic activity.
- Liu et al. (2018)** explored the use of Cu-MOF catalyst 92 in the transesterification of WCO to produce biodiesel. The study reported that the Cu-MOF catalyst had a high catalytic activity for the transesterification reaction, achieving a conversion rate of 94.2%. The study also found that the Cu-MOF catalyst had a long lifespan and could be easily separated and reused in subsequent reactions.

- "A Review of Biodiesel Fuel Standards and Specifications" by **P. Nigam, S. S. Singh, and V. K. Gupta** (Renewable and Sustainable Energy Reviews, 2011). This review discusses the standards and specifications for biodiesel fuel, including ASTM, EN, and ISO standards. The authors explore the various parameters that are used to evaluate the quality of biodiesel, such as its viscosity, acid value, cetane number, and cold flow properties. They also examine the effect of these parameters on engine performance and emissions and conclude with recommendations for improving biodiesel quality and standardization.
- "A Review of Biodiesel Production, Composition, Properties, and Issues" by **M. A. Haque, S. A. Islam, and M. S. Hossain** (Renewable and Sustainable Energy Reviews, 2014). This review discusses the production process of biodiesel, including feedstock selection, transesterification, and purification. It also covers the properties of biodiesel, such as its physical and chemical characteristics, as well as its advantages and disadvantages as a fuel source.
- "Biodiesel from Microalgae: A Critical Evaluation from Laboratory to Large Scale Production" by **A. Banerjee, S. Sharma, and S. Chisti** (Renewable and Sustainable Energy Reviews, 2016). This review focuses on the potential of microalgae as a feedstock for biodiesel production. The authors discuss the advantages of using microalgae, such as their high oil content and ability to grow in wastewater or brackish water, as well as the challenges of large-scale production, such as the need for efficient harvesting and extraction methods.
- "A Review of Biodiesel Stability and Degradation Kinetics" by **J. J. Boonyuen, S. Teerarat, and S. Rangsunvigit** (Renewable and Sustainable Energy Reviews, 2015). This review discusses the stability of biodiesel, including its resistance to oxidation, hydrolysis, and thermal degradation. The authors also explore the degradation kinetics of biodiesel and its effect on engine performance. They conclude with recommendations for improving the stability of biodiesel through feedstock selection, refining processes, and the use of antioxidants and stabilizers.

## CHAPATER-3

### AIM AND SCOPE

#### 3.1 AIM

- To synthesize the Copper based metal organic framework using modified Solvothermal method and characterize it.
- To utilize waste cooking oil as a sustainable and renewable feedstock for biodiesel production
- To synthesize the highly efficient and cost-effective catalyst for transesterification reaction
- To convert the waste cooking oil to biodiesel using packed bed distillation column by transesterification reaction
- To study about the variation studies in catalyst bed height and the time variations.

#### 3.2 SCOPE

- Using renewable energy sources for biodiesel production to reduce dependence on fossil fuels.
- Reducing emissions from vehicles using biodiesel, compared to conventional diesel fuel.
- Potential for easy separation and recovery of the catalyst for reuse, potentially reducing the cost of the production of cost of overall process.
- Cu-MOF catalyst could also have a better stability compared to traditional catalyst.
- Reduce the production of by-products.
- The use of Cu-MOFs as adsorbent for purification of biodiesel can also help to reduce the environmental impact of biodiesel production. The selective adsorption of impurities can help to reduce the amount of waste generated during the purification process.

## MATERIALS AND METHODS

### 4.1 MATERIALS AND CHEMICALS

A particular kind of metal-organic framework known as a Cu-MOF (Copper Metal-Organic Framework) is created by mixing copper ions with organic ligands. The ingredients and chemicals required for the synthesis of Cu-MOF may vary depending on the specific synthetic pathway utilised, but commonly comprise a copper precursor such as copper sulphate anhydrous, organic ligands such as terephthalic acid or benzene dicarboxylic acid, a solvent such as dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), a base such as potassium hydroxide or triethylamine to maintain the pH, deionized water and additional reagents such as surfactants or stabilisers. Before being utilised to undertake the analysis on the characteristics of WCO, the waste cooking oil that we are utilising in our study is collected from the Sathyabama University mess hall and heated at 110 degC to eliminate the moisture. Some characteristics are reported: density is 0.9, FFA is 0.732, and moisture is 4%.

### 4.2 CATALYST PREPARATION(Cu-MOF)

Metal organic frameworks (Cu-MOFs) with a copper base are commonly made using a modified solvothermal approach with a 1:1 molar ratio of copper precursor to organic ligands in the presence of a solvent and a base. Use a suitable solvent, such as DMF or deionized water, to dissolve the copper salt ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and organic ligand (terephthalic acid). The material was combined in a beaker and then constantly swirled at 85 °C for 4 hours using a magnetic stirrer[16]. The sample was then cleaned with DI water, filtered to remove the excess solvent using filter paper, and oven dried at 110 °C for 2 hours.

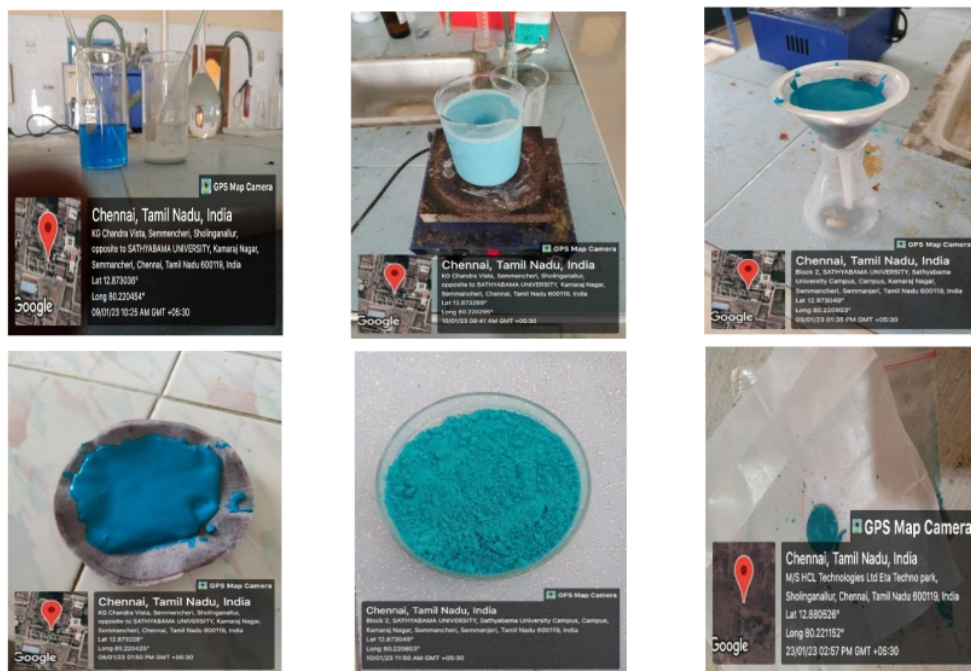
### 4.3 POWDER PELLETIZATION

For palletization, which is the process of compressing or agglomerating a material into the shape of a pellet, Cu-MOF (Copper Metal-Organic Framework) powder can be utilised.



**Fig. 4.1 Catalyst Pelletization Machine**

Cu-MOF powder can be combined with a binder or lubricant to enhance its flow and compressibility before being pelletized. Chitosan, polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), and magnesium stearate are a few examples of binders and lubricants that can be employed. Using a binder or lubricant to bond the Cu-MOF powder, the combination may then be put through a pelletizing machine, which will compress it into pellets under high pressure of the required size and form. In order to eliminate any extra powder or particles, the pellets can subsequently be dried and screened[17].



**Fig. 4.2 Synthesis of Cu-MOF Catalyst**

#### 4.4 CATALYST CHARACTERIZATION:

A form of porous material called Cu-MOF (Copper Metal-Organic Framework) catalysts is employed in a number of applications, such as sensing, gas storage, and catalysis. Understanding the characteristics of Cu-MOF catalysts is crucial for maximising their performance[18].

X-ray diffraction is a vital characterization method for Cu-MOF catalysts (XRD). By measuring the lattice parameters, crystal symmetry, and Miller indices of the diffraction peaks, XRD can provide details about a substance's crystal structure. The interplanar spacing ( $d$ ) of the crystal lattice planes that diffract X-rays at this angle may be calculated using Bragg's Law ( $n = 2d \sin \theta$ ), the sampling is scanned using  $2\theta$ , and the range is from  $10^\circ$  to  $60^\circ$ . The wavelength of Cu radiation is 1.54 Å,

FESEM with EDX: The shape and particle size of the Cu-MOF catalyst may be examined using the FESEM (Field Emission Scanning Electron Microscopy) method. The size, shape, and surface area of the catalyst particles may be seen in FESEM pictures. Energy Dispersive X-ray Spectroscopy, or EDX, is employed in the FESEM-EDX investigation of Cu-MOFs to determine the elements that make up the catalyst particles. When a sample is assaulted with an electron beam, EDX is able to identify the distinctive X-rays given off by the elements that are present in the sample. Information on the elemental distribution, purity, and homogeneity of the Cu-MOF catalyst may be obtained using FESEM and EDX together[19].

FTIR, or Fourier Transform Infrared Spectroscopy, is a method that may be used to examine the Cu-MOF catalyst's functional groups. The spectra are employed in FTIR analysis of Cu-MOFs to pinpoint the vibrations of the organic linkers and copper ions in the structure. The bonding between the copper ions and the organic linkers in the framework may be learned from the FTIR spectra.[20]

#### 4.5 APPLICATION OF (Cu-MOFs):

- Cu-MOFs can be utilised to store energy in supercapacitors and lithium-ion batteries.
- Gas storage: Cu-MOFs have a large surface area, which makes them perfect for storing gases like carbon dioxide and hydrogen.
- Cu-MOFs can be used to separate gases, such as to separate oxygen from air or to purge contaminants from natural gas.
- Cu-MOFs can be utilised as catalysts to accelerate and boost the effectiveness of chemical processes[21].

#### 4.6 BIODIESEL PRODUCTION

The next step is to create biodiesel from the triglycerides found in the feedstock. Transesterification is the name given to the process of reacting the feedstock with an alcohol (usually methanol) while using a catalyst (Cu-MOF). As a by-product of the process, biodiesel and glycerol are produced[21].

##### 4.6.1 FREE FATTY ACID TEST FOR WCO:

###### STEPS:

1. Weigh a sample of the oil (usually 1-5 grams) into a clean, dry beaker.
2. Add 25ml of isopropyl alcohol and heat up to 60 degrees Celsius.
3. After heating cool at room temperature, then add phenolphthalein indicator.
4. Titrate against NaOH until the appearance of pale pink color as end point.

Calculate the free fatty acid content of the sample using the following equation:

FFA% = (volume of base solution used x normality of base solution x 28.2) / weight of sample.

$$\text{FFA\%} = 1.3 \times 0.1 \times 28.2 / 5\text{g}$$

$$= 0.73$$

If FFA < 4 follows trans-esterification reaction, >4 it is esterification process.



**Fig. 4.3 Free Fatty Acid Test Analysis**

#### **4.6.2 PURIFICATION OF WASTE COOKING OIL**

Cooking byproducts such as waste cooking oil, sometimes referred to as used cooking oil, are frequently thrown away as garbage. But this trash may be cleaned up and repurposed to make biodiesel or other useful goods. The purification of used cooking oil is covered in this sentence.

The first stage in the purification process is to eliminate any solid contaminants that may be present in the waste cooking oil. To do this, the oil can be filtered using a mesh screen or another filtration tool. The filtered oil is next heated to a temperature of roughly 60°C to 70°C to eliminate any water that may be present. Oil may be cleaned of water by letting it settle and then drained.

**Settling:** Allowing the oil to stay in a container for a certain amount of time, usually several hours or overnight, is known as settling. During this period, the refined oil will float to the top as the heavier contaminants, such as food shards and water, sink to the bottom of the container. The pollutants may then be removed from the container and the oil can be extracted after being cleaned.

**Chemical treatment:** A chemical agent is added to used cooking oil during chemical treatment to eliminate contaminants. Acid-catalyzed esterification is a typical chemical process that entails adding a tiny quantity of sulfuric acid to the oil to react with any free fatty acids that may be present. Esters are created as a result of the reaction, which makes them simpler to remove since they are less prone to emulsify with water and other contaminants[22].

#### 4.6.3 DESIGN CALCULATIONS OF PACKED BED

Flow rate (V) = 12 Lph

Time (t) = 2 hours

Temperature (T) = 60 °C

**Bed volume:**

$$t = \vartheta / V \text{ (flow rate)}$$

$$\vartheta = t \times V$$

$$\vartheta = 2\text{hrs} \times 12\text{L/h}$$

$$\vartheta \text{ (Bed volume)} = 24\text{L}$$

Assume bed height is = 0.6m

**Radius:**

$$\pi \times r^2 \times h = \vartheta$$

$$3.14 \times r^2 \times 0.6 = 24 \times 10^{-3} \text{ m}^3$$

$$r = 0.0127 \text{ m}$$

**Diameter:**

$$D = 2 \times r$$

$$D = 2 \times 0.0127$$

$$D = 0.025 \text{ m}$$

**Cross sectional area:**

$$A = \pi \times D^2 / 4 \text{ m}^2$$

$$A = 3.14 \times 0.025^2 / 4$$

$$A = 0.00049 \text{ m}^2$$



**Fig. 4.4 Designed Packed Bed**

#### 4.7 SYNTHESIS OF BIODIESEL FROM WCO USING Cu-MOF IN PAKCED BED DISTILLATION COLUMN:

The process of creating biodiesel from used cooking oil comprises a transesterification reaction in which the oil's triglycerides are changed into fatty acid methyl esters (FAMES) with the help of an alcohol and a catalyst. In this instance, the alcohol to oil ratio is 6:1, and the catalyst is Cu-MOF (Copper Metal Organic Framework).

The following is a general procedure for synthesizing biodiesel from waste cooking oil using Cu-MOF as a catalyst:[22]

Materials:

Waste cooking oil

Methanol or ethanol (alcohol)

Cu-MOF pellets as catalyst

Potassium hydroxide (KOH) to neutral the pH

##### 4.7.1 TRANSESTERIFICATION IN PACKED BED COLUMN

Cooking oil waste may be used to create biodiesel, a renewable fuel. The procedure entails trans esterifying the oil with an alcohol, usually methanol, while a catalyst is present. In this section, it is detailed how Cu-MOF may be used as a catalyst in a packed bed distillation column to produce biodiesel.

The technique uses a 6:1 alcohol to oil ratio, which indicates that one mole of oil is required for every six moles of alcohol. The effectiveness of the transesterification reaction and the quality of the biodiesel produced are both impacted by this ratio, making it crucial. A kind of catalyst known as Cu-MOF pellets, or Copper Metal-Organic Framework, has been demonstrated to be efficient in the transesterification reaction. It is utilized in a packed bed distillation column, a kind of reactor that enables continuous biodiesel synthesis, the reaction occurred for 2 hours in column at the temperature of 60 °C. The column is filled with the catalyst, and the top of the column is continually supplied with the reactants. The transesterification process occurs when the reactants pass through the column

and come into touch with the catalyst. <sup>18</sup> At the bottom of the column, the biodiesel product is then collected.

A packed bed distillation column can also be used for trans-esterification. The reactants in this procedure—used frying oil and methanol—are combined before being delivered into a packed bed distillation column at the top. The catalyst in the <sup>18</sup> column is a packing material called Cu-MOF pellets, which gives the reaction of a lot of surface area. The packing material and the catalyst, which is typically supported on the packing material, come into touch with the mixture as it travels through the column. The catalyst aids in accelerating the reaction and transforming the ester and alcohol into the desired outcome (BIODIESEL).

Large-scale trans-esterification operations frequently employ packed bed distillation columns because they can handle enormous quantities of reactants and achieve high yields. To guarantee that the reactants are properly distributed throughout the column and that the reaction progresses effectively, they call for careful design and operation. The effectiveness and selectivity of the reaction are greatly influenced by the choice of packing material and catalyst.



**Fig. 4.5 Biodiesel Production in packed bed column**

There are numerous benefits to using Cu-MOF <sup>1</sup> as a catalyst in a packed bed distillation column. The catalyst, in the first place, is extremely selective, promoting the desired reaction while reducing the generation of undesirable byproducts. Second, continuous production, which is more effective than batch production techniques, is made possible by the packed bed distillation column. Last but not least, using used cooking oil as a feedstock for making biodiesel contributes to waste reduction and sustainability.

Due to their great efficiency, low energy consumption, and relatively inexpensive capital costs as compared to other separation processes, packed bed distillation columns are used in the manufacturing of biodiesel. They are a popular option for small and medium-sized biodiesel production plants since they are also rather easy to operate and maintain.

#### 4.7.2 ALCOHOL To OIL RATIO CALCULATION

For this process we use 500ml of waste cooking oil with molar ratio of methanol to oil is 6:1, mol. wt. of WCO is 800g/mol and then calculate the density of WCO using specific gravity bottle (density of feed is 0.9g/ml)

$$500\text{ml oil} = 500\text{ml} \times 0.9\text{g/ml} = 450\text{g}$$

$$450\text{g}/800\text{g/mol} = 0.5625\text{mol oil}$$

Now, as u want 1:6 oil: methanol ratio, moles of methanol =  $0.5625 \times 6 = 3.375$

moles Therefore, wt. of methanol =  $3.375 \times 32.04 = 108.135\text{ g}$ ,

$$\text{volume of methanol} = 108.135\text{g} / 0.79\text{g/ml} \quad V = 136.87\text{ml}$$

#### 4.7.3 EXPERIMENTAL SETUP:

A common technique for the continuous manufacture of biodiesel from spent cooking oil is the packed bed distillation column. Such a column's experimental setup frequently includes a number of essential elements. Prior to entering the distillation column, the catalyst (Cu-MOF pellets) is first mixed with the spent frying oil and alcohol in a reactor tank. To ensure that the reactants are well mixed, the reactor vessel often incorporates a mixer. Typically, the used cooking oil is warmed to a particular temperature in order to speed up the reaction and lower viscosity.



**Fig. 4.6 Packed bed distillation column**

The essential part of the experimental setup is the packed bed distillation column. A catalyst, such as Cu-MOF pellets, is crammed into a vertical, cylindrical column to speed up the transesterification reaction. In order to maintain a specified temperature range for effective reactivity, the column is often fitted with a temperature control system. In order to guarantee that the vapors generated in the column are condensed and returned to the column for further reaction, a reflux system is also added.

The distillation column's temperature is maintained using a heat source. This might be an oil bath with a temperature control or a heating mantle. The distillation column's vapors are cooled using a condenser. The liquid biodiesel is produced when the cooled vapors condense into it and are collected in a product collector. Alcohol and unreacted oil are collected in a separate container, along with glycerol.

Several monitoring tools, including temperature and pressure sensors, can be used to check if the reaction is progressing as planned. This makes it possible for the researcher to change the temperature and pressure as needed to maximize the reaction.

Overall, the experimental configuration for a packed bed distillation column is a challenging but effective procedure for producing biodiesel. It allows for the efficient and minimally harmful continuous manufacture of biodiesel from used cooking oil.

#### 4.7.4 WASHING AND DRYING

<sup>124</sup> Glycerol and other contaminants are generally removed from the biodiesel using a washing procedure. In this procedure, water is added to the biodiesel and stirred to help the contaminants sink to the bottom. After draining the water and glycerol, pure biodiesel is left behind. Doing this washing procedure multiple times will guarantee that the biodiesel is fully cleaned. Biodiesel can be dried in a hot water bath to remove any remaining water. This process involves heating the biodiesel to a temperature of around 70–80 °C (158–176 °F) in a container. After that, the container is put into a hot water bath that is kept at a constant temperature of around 90°C (194°F). The leftover water in the biodiesel evaporates due to the heat from the water bath, and the water vapors is subsequently expelled from the container through a vent. Although drying biodiesel in a hot water bath is an easy and economical process, it does have certain drawbacks. Since it takes a long time and a lot of energy to heat the biodiesel to the required temperature, it might not be appropriate for drying copious amounts of fuel. Also, it might not be appropriate for biodiesel that contains a lot of water since the heating process could result in emulsions that make it challenging to separate the water from the biodiesel.

#### 4.8 PROCESS OPTIMIZATION WITH RMS:

A statistical method called Response Surface Methodology (RSM) is utilised to optimize procedures and experimental layout. In order to identify the ideal collection of input factors that will result in the desired output response, it is <sup>52</sup> used to investigate the correlations between several variables and responses. RSM's objective is to create a mathematical model that can forecast a process' reaction based on the values of its input variables.

**Table 4.1 Experimental matrix**

<sup>36</sup>

| Factor | Name                  | Level | Low<br>Level | High<br>Level | Std.<br>Dev. | Coding |
|--------|-----------------------|-------|--------------|---------------|--------------|--------|
| A      | oil: alcohol<br>ratio | 6.02  | 4.00         | 8.00          | 0.0000       | Actual |
| B      | catalyst load         | 10.15 | 9.00         | 13.00         | 0.0000       | Actual |

|   |             |       |       |        |        |        |
|---|-------------|-------|-------|--------|--------|--------|
| C | time        | 90.80 | 80.00 | 160.00 | 0.0000 | Actual |
| D | temperature | 57.33 | 55.00 | 65.00  | 0.0000 | Actual |

**Table 4.2 Actual value vs predicted values by optimization studies.**

| Run Order | Actual Value | Predicted Value | Residual | Leverage | Internally Studentized Residuals | Externally Studentized Residuals | Cook's Distance | Influence on Fitted Value DFFITS | Standard Order |
|-----------|--------------|-----------------|----------|----------|----------------------------------|----------------------------------|-----------------|----------------------------------|----------------|
| 1         | 80.13        | 81.58           | -1.45    | 0.167    | -0.894                           | -0.888                           | 0.011           | -0.397                           | 25             |
| 2         | 56.56        | 56.79           | -0.226   | 0.583    | -0.198                           | -0.191                           | 0.004           | -0.227                           | 7              |
| 3         | 69.45        | 70.50           | -1.05    | 0.583    | -0.916                           | -0.911                           | 0.078           | -1.077                           | 8              |
| 4         | 83.11        | 83.48           | -0.371   | 0.583    | -0.324                           | -0.314                           | 0.010           | -0.372                           | 19             |
| 5         | 80.25        | 81.58           | -1.33    | 0.167    | -0.820                           | -0.811                           | 0.009           | -0.363                           | 30             |
| 6         | 81.03        | 80.61           | 0.418    | 0.583    | 0.365                            | 0.354                            | 0.012           | 0.419                            | 16             |
| 7         | 81.45        | 82.83           | -1.38    | 0.583    | -1.207                           | -1.227                           | 0.136           | -1.452                           | 2              |
| 8         | 79.67        | 77.94           | 1.73     | 0.583    | 1.510                            | 1.584                            | 0.213           | 1.874                            | 21             |
| 9         | 70.45        | 70.84           | -0.388   | 0.583    | -0.339                           | -0.329                           | 0.011           | -0.389                           | 18             |
| 10        | 81.67        | 82.78           | -1.11    | 0.583    | -0.971                           | -0.969                           | 0.088           | -1.147                           | 12             |
| 11        | 79.98        | 81.58           | -1.60    | 0.167    | -0.987                           | -0.986                           | 0.013           | -0.441                           | 28             |
| 12        | 70.56        | 71.43           | -0.871   | 0.583    | -0.760                           | -0.749                           | 0.054           | -0.886                           | 9              |
| 13        | 67.56        | 68.37           | -0.807   | 0.583    | -0.705                           | -0.692                           | 0.046           | -0.819                           | 5              |
| 14        | 74.44        | 74.28           | 0.160    | 0.583    | 0.140                            | 0.135                            | 0.002           | 0.160                            | 13             |
| 15        | 72.45        | 73.37           | -0.915   | 0.583    | -0.799                           | -0.789                           | 0.060           | -0.933                           | 11             |
| 16        | 85.50        | 85.10           | 0.399    | 0.583    | 0.348                            | 0.338                            | 0.011           | 0.400                            | 24             |
| 17        | 68.95        | 69.49           | -0.537   | 0.583    | -0.469                           | -0.456                           | 0.021           | -0.540                           | 15             |
| 18        | 76.04        | 75.91           | 0.125    | 0.583    | 0.109                            | 0.105                            | 0.001           | 0.125                            | 1              |
| 19        | 80.67        | 78.92           | 1.75     | 0.583    | 1.526                            | 1.603                            | 0.217           | 1.897                            | 20             |
| 20        | 80.45        | 81.58           | -1.13    | 0.167    | -0.697                           | -0.684                           | 0.006           | -0.306                           | 29             |
| 21        | 80.23        | 80.32           | -0.087   | 0.583    | -0.076                           | -0.073                           | 0.001           | -0.087                           | 14             |
| 22        | 83.45        | 83.07           | 0.384    | 0.583    | 0.335                            | 0.325                            | 0.010           | 0.384                            | 4              |
| 23        | 80.45        | 79.47           | 0.977    | 0.583    | 0.853                            | 0.845                            | 0.068           | 1.000                            | 23             |
| 24        | 84.79        | 81.58           | 3.21     | 0.167    | 1.983                            | 2.230                            | 0.052           | 0.997                            | 27             |
| 25        | 69.23        | 71.06           | -1.83    | 0.583    | -1.600                           | -1.697                           | 0.239           | -2.008                           | 3              |
| 26        | 54.56        | 52.80           | 1.76     | 0.583    | 1.540                            | 1.622                            | 0.221           | 1.919                            | 17             |
| 27        | 83.87        | 81.58           | 2.29     | 0.167    | 1.415                            | 1.469                            | 0.027           | 0.657                            | 26             |
| 28        | 67.87        | 68.22           | -0.353   | 0.583    | -0.308                           | -0.299                           | 0.009           | -0.353                           | 22             |
| 29        | 76.53        | 75.76           | 0.770    | 0.583    | 0.672                            | 0.660                            | 0.042           | 0.780                            | 10             |
| 30        | 78.45        | 76.99           | 1.46     | 0.583    | 1.273                            | 1.303                            | 0.151           | 1.541                            | 6              |

#### 4.9 BIODIESEL CHARACTERIZATION

Characterizing biodiesel is a crucial step in establishing its quality and applicability as a fuel. It entails examining the fuel's numerous physical and chemical characteristics, such as its density, viscosity, flash point, cloud point, oxidation stability, and total acid number (FAME) concentration (TAN). A variety of techniques, including titration, hydrometers, viscometers, flash point testers, cloud point testers, accelerated ageing tests, OSI tests, and gas chromatography (GC), are frequently used to analyze these qualities. The outcomes of these tests can provide vital details about the make-up and quality of the biodiesel, such as its acidity, handling qualities, energy content, and ignition characteristics. These ASTM standards offer a consistent and trustworthy method of describing biodiesel, which is crucial for guaranteeing its quality and suitability for different fuel systems.

## CHAPATER-5

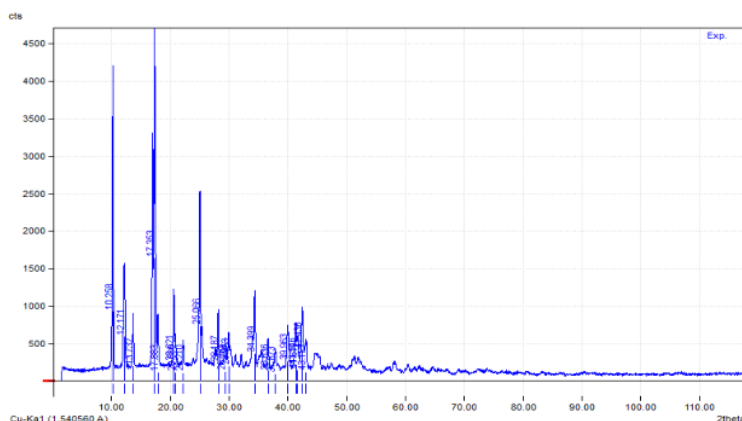
### 6 RESULTS AND DISCUSSION

#### 5.1 PHYSICOCHEMICAL ANALYSIS OF Cu-MOF

122  
Metal-organic frameworks (MOFs) are a kind of crystalline material that has gained popularity as a catalyst due to its large surface area, variable porosity, and various metal-ligand coordination settings. The structure, characteristics, and functionality of MOF catalysts must be understood by physicochemical investigation. A crucial component of catalyst research and development is catalyst characterization. Analyzing a catalyst's physical and chemical characteristics aids in understanding how it will behave and function under various reactional circumstances.

##### 5.1.1 X RAY DIFFRACTION

A popular method for determining the crystal structure and purity of MOF catalysts is X-ray diffraction (XRD). The MOF's crystal size, symmetry, and orientation may be determined via XRD signals. The MOF can also have any contaminants or phase transitions identified using XRD. H, K, and L are indices used in X-ray diffraction (XRD) to specify the crystallographic planes that give rise to the diffraction peaks seen in the XRD pattern. The locations of the peaks in the XRD pattern, which are connected to the interatomic spacing in the crystal lattice, may be used to determine these indices.



The capability of XRD analysis to discriminate between various crystal structures of the same material and identify unknown compounds is one of its main benefits. Quantitative data on the relative quantities of each phase present in a sample may also be obtained using XRD analysis.

The use of XRD analysis is widespread in the fields of materials science, geology, chemistry, and other sciences as a useful method for studying the structure and characteristics of materials.

### Finding H, K, L

The basic idea underlying X-ray diffractogram analysis (XRD) is Bragg's rule, which connects the wavelength of X-rays to the distance between crystal surfaces in a substance:

$$n\lambda = 2d \sin\theta, \text{ where } d = a / \sqrt{h^2 + k^2 + l^2}$$

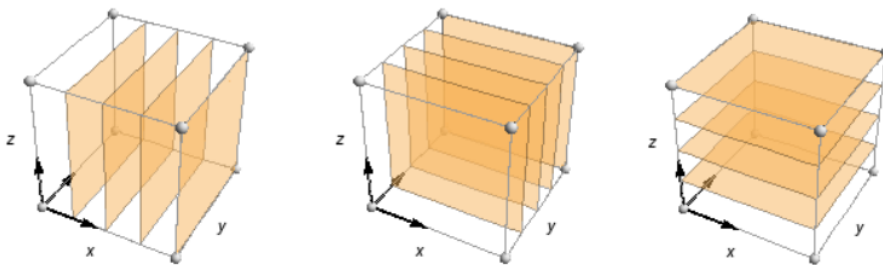
$$n \lambda / 2 \sin \theta = a / \sqrt{h^2 + k^2 + l^2}$$

where  $d$  is the distance between crystal planes,  $n$  is an integer,  $\theta$  is the angle of incidence of X-rays on the crystal and  $\lambda$  is the wavelength of X-rays.

the sampling is scanned using  $2\theta$ , and the range is from  $10^\circ$  to  $60^\circ$ . The wavelength of Cu radiation is  $1.54 \text{ \AA}$ , where  $n=1$ ,  $a$  is lattice constant  $=10 \text{ \AA}$ .

The possible values of  $h$ ,  $k$ , and  $l$  that satisfy this equation are:

$$h = 4, k = 0, l = 0 \text{ or } h = 0, k = 4, l = 0 \text{ or } h = 0, k = 0, l = 4$$



**Fig. 5.2 Crystal structure from H, K, L**

### 5.1.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPE

Field Emission Scanning Electron Microscopy, often known as FESEM, is an effective imaging method used to describe the surface morphology and microstructure of materials at a high magnification. FESEM may be used to examine the structure of Cu-MOF (Copper-based Metal-Organic Framework) at the micro- and nanoscale.

The size, shape, and distribution of the crystals that make up the substance may be examined using Cu-MOF, FESEM. Also, it can offer details regarding the material's porosity and surface area, which are crucial elements in identifying its prospective uses. FESEM may also be used to spot any flaws or impurities in the material that can impair its performance and qualities.

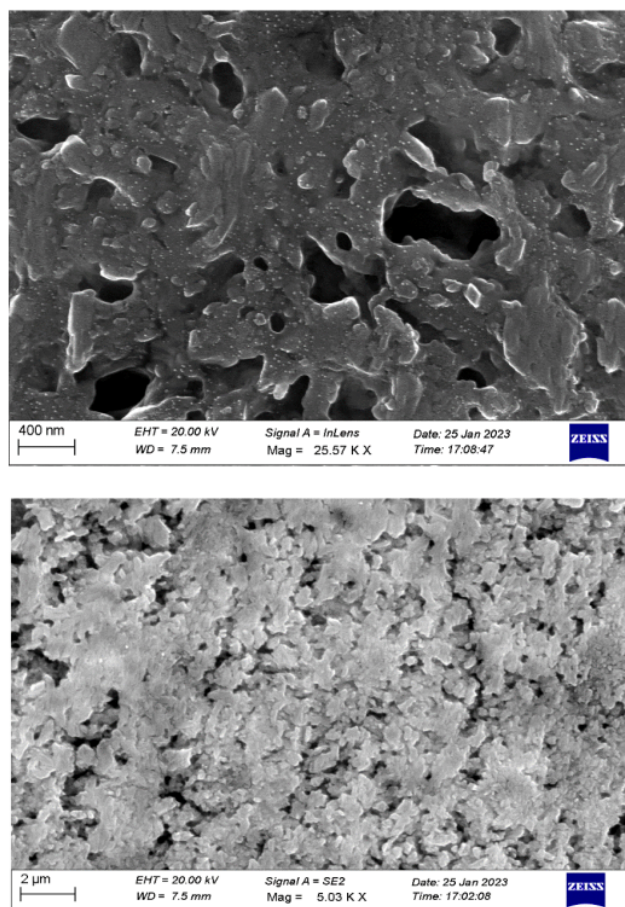
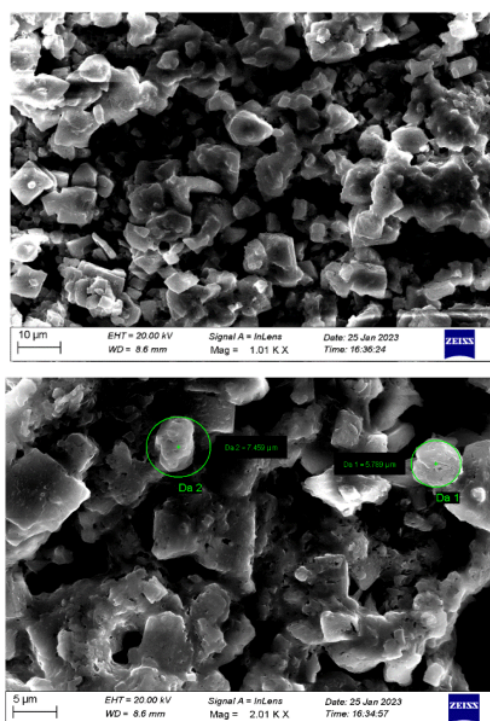


Fig. 5.3 FESEM IMAGES of Cu-MOF Pellet

Cu-MOF catalysts are a potential catalyst for a variety of industrial applications due to their high porosity and surface area, outstanding thermal stability, chemical resistance, and recyclability. Cu-MOF catalysts have been investigated and used in a variety of processes, including the catalysis of fuel cells, organic reactions, and CO<sub>2</sub> conversion.

Overall, Cu-MOF catalysts are a desirable material for catalytic applications due to their large porosity and surface area, which offer greater catalytic activity, selectivity, and efficiency than conventional catalysts. Cu-MOF catalysts have a wide range of possible uses, and further study is required to uncover all of its potential in different industrial processes.



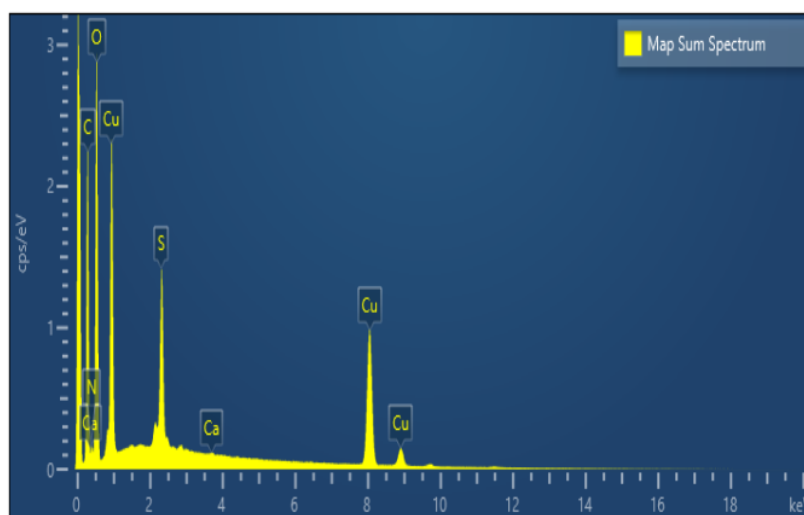
**Fig. 5.4 FESEM Images of Cu-MOF Powder**

Cu-MOFs' surface characteristics, size, and morphology may all be seen in FESEM pictures. Cu-MOFs may be found in a variety of forms, and their morphology can be examined using FESEM pictures of pellets and powder. For instance, a Cu-MOF pellet's morphology may be revealed by a pellet FESEM

picture, which can be used to assess the material's packing density and particle size distribution. On the other hand, a powder FESEM picture may display the size distribution and morphology of each individual Cu-MOF particle in the powder. Both of them will give better yield. But we used pellet in packed bed column for easy handling and removable that will help to stop leaching into the product.

### 5.1.3 ENERGY DISPERSIVE X-RAY ANALYSIS

Energy Dispersive X-ray (EDX) analysis is a method for determining and measuring the elemental makeup of a sample by examining the X-rays that the sample emits after being irradiated with high-energy electrons or X-rays. This method is frequently used with scanning electron microscopy and is widely utilised in materials science, biology, and geology (SEM).



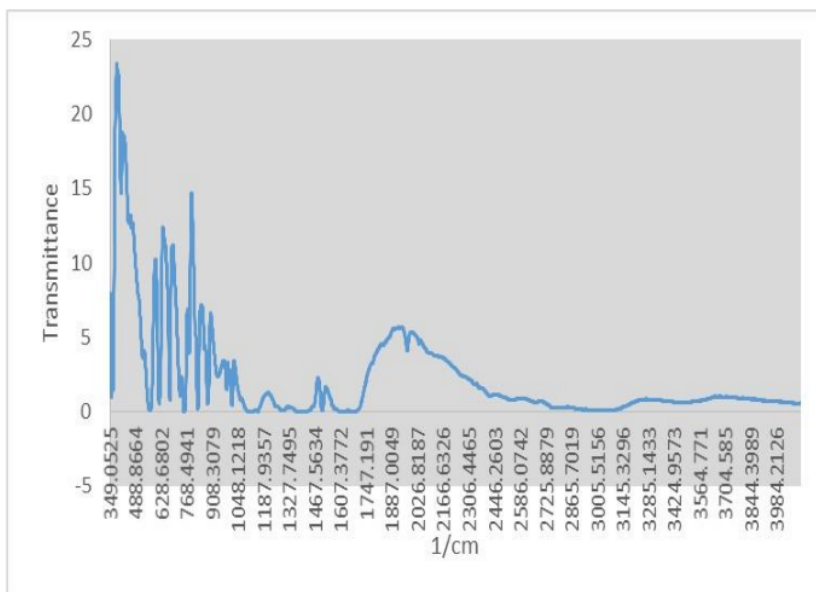
**Fig. 5.5 PELLET EDX image of Cu-MOF**

The resultant EDX spectrum may be used to identify certain elements or compounds present in the sample and offers useful information about the sample's elemental makeup. In the above graph we can observe the Cu and some other elements present. The relative abundance of each element in the sample may be calculated using the peaks in the EDX spectrum, which correspond to the distinctive X-rays each element emits.

#### 5.1.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY

An effective analytical method for identifying and describing chemical substances based on their infrared radiation absorption is called Fourier transform infrared (FTIR) spectroscopy. The identification and analysis of organic and inorganic compounds benefit greatly from the application of this method, which is widely employed in the fields of chemistry, biology, and materials science.

A sample's infrared radiation absorption is measured in FTIR spectroscopy. Infrared radiation is absorbed by chemical bonds in molecules because its wavelength is greater than that of visible light. FTIR spectroscopy can identify the particular energy that each chemical bond's vibrational mode carries.

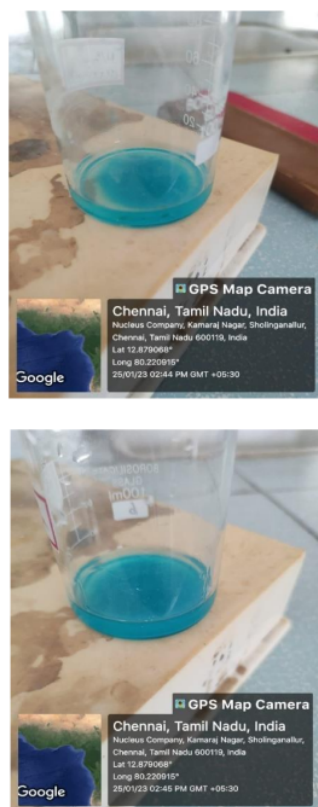


**Fig. 5.6 FTIR GRAPH of Cu-MOF**

The resultant FTIR spectrum offers useful details about the functional groups present in the sample and may be used to pinpoint single chemical compounds or determine the make-up of a combination. The types of functional groups present in the sample may be identified using the peaks in the FTIR spectrum, which indicate the absorption of infrared light by various chemical linkages.

### 5.1.5 SOLUBILITY TEST

The solubility test for Cu-MOFs is a method for figuring out how much a copper metal-organic framework dissolves in a particular solvent. Because it may assist in defining the circumstances in which the MOF remains stable and can be employed in a variety of applications, the solubility test is significant. The Cu-MOF sample must be correctly weighed and moved to a clean, dry container before a solubility test for the Cu-MOF can be conducted. Following the addition of the solvent, the mixture is swirled or agitated to make sure the Cu-MOF is evenly distributed. The combination is then monitored over time to check for modifications. The catalyst doesn't dissolve in the solvent, as we have seen in the figures below.



***Fig. 5.7 Solubility test with solvent DMF and Ethanol***

### 5.1.6 CATALYST REUSABILITY

Cu-MOF catalysts can be reused several times depending on the reaction type, catalyst stability, and catalyst recovery technique, among other variables. Depending on the circumstances of the reaction, Cu-MOF catalysts have generally been demonstrated to have high stability and may be recycled several times. There are several techniques that may be used to recover Cu-MOF catalysts, including filtering, centrifugation, and magnetic separation. Before being employed again in the process, the recovered catalyst can next be cleaned and dried. There is only an extraordinarily little decline in activity over time, according to some research, and Cu-MOF catalysts can maintain their catalytic activity even after numerous cycles of usage. To achieve optimal effectiveness and stability, it is crucial to rigorously evaluate the catalyst's performance over a number of cycles and to improve the recovery and reuse techniques. Cu-MOF catalysts have generally demonstrated high potential for reusability in a variety of catalytic processes, which can assist to lower the cost and environmental effect of the catalyst and promote efficient and sustainable catalysis.

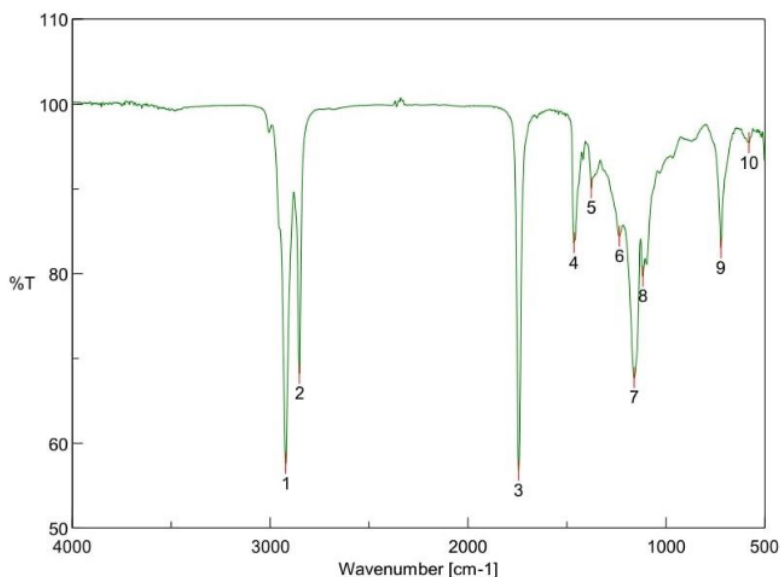


**Fig. 5.8 Recovered Catalyst**

## 5.2 BIODIESEL CHARACTERISATION

### 5.2.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

FTIR spectroscopy is unbelievably valuable for biodiesel analysis since it may reveal the kind and quantity of functional groups present in the material, as well as the degree of unsaturation and other structural properties.



**Fig. 5.9 FTIR FOR BIODIESEL**

Using the FTIR data shown in above Fig, the surface functional groups of the Cu-MOF were discovered. Carbon-hydrogen is represented by the Cu-MOF absorption bands found at 3162.1 cm<sup>-1</sup>, 3103.2 cm<sup>-1</sup>, and 3067.6 cm<sup>-1</sup>.

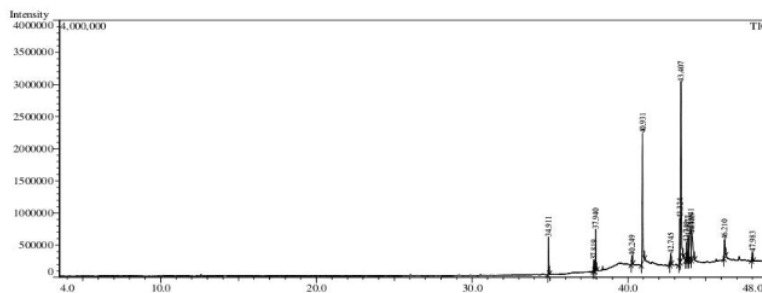
Due to the organic linker (BDC) used in the synthesis, (C-H) stretching vibrations. Peaks at 2924.9 cm<sup>-1</sup> and 1711.2 cm<sup>-1</sup> were attributed to vibrational stretching of the C-H-alkane and C=O, respectively. While the peaks at 543 cm<sup>-1</sup> and 578 cm<sup>-1</sup> show the Cu-O vibrations, confirming the creation of the Cu-MOF, the clear peaks at 1114.9 cm<sup>-1</sup>, 1185.2 cm<sup>-1</sup>, and 1248.8 cm<sup>-1</sup> are connected to C-O stretching vibrations.

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## 5.2.2 GAS CHROMATOGRAPHY MASS SPECTROMETRY (GC/MS)

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The type and quantity of fatty acid methyl esters (FAMES) present in the sample, as well as any other chemicals that may be present, such as contaminants or additives, may all be determined using GC/MS.



**Fig. 5.10 GC/MS**

**Table 5.1 Peak Report of GC/MS**

| Peak | RTime  | Area     | Area%  | Name                                                    |
|------|--------|----------|--------|---------------------------------------------------------|
| 1    | 34.911 | 1370650  | 4.62   | Hexadecanoic acid, methyl ester                         |
| 2    | 37.819 | 421370   | 1.42   | 12-cis-octadecadienoate Methyl ester                    |
| 3    | 37.940 | 1538973  | 5.19   | 9-Octadecenoic acid methyl ester,                       |
| 4    | 40.249 | 341618   | 1.15   | Palmitoyl chloride                                      |
| 5    | 40.931 | 6191023  | 20.87  | Glycidyl palmitate methyl ester                         |
| 6    | 42.745 | 457411   | 1.54   | 9-Octadecenoic acid (Z)- methyl ester                   |
| 7    | 43.324 | 1792585  | 6.04   | 1,8,11-Heptadecatriene methyl ester                     |
| 8    | 43.407 | 8285874  | 27.93  | 9-Octadecenoic acid (Z)-, oxiranyl methyl ester         |
| 9    | 43.749 | 707594   | 2.39   | Myristic acid glycidyl ester                            |
| 10   | 43.877 | 1049084  | 3.54   | Hexadecanoic methyl ester                               |
| 11   | 44.041 | 3823320  | 12.89  | Stigmasta-5,24(28)-dien-3-ol,                           |
| 12   | 44.105 | 2368431  | 7.98   | pregna-5,17(20)-dien-3-ol (20)-methy ester              |
| 13   | 46.210 | 890911   | 3.00   | 9-Octadecenoic acid (Z)- methyl ester                   |
| 14   | 47.983 | 427900   | 1.44   | . psi.,. psi. -Carotene,<br>7,7',8,8',11,11',12,12',15, |
|      |        | 29666744 | 100.00 |                                                         |

### 5.3 STATISTICAL ANALYSIS WITH RSM

Response surface methodology (RSM) is a statistical and mathematical approach used to determine the optimal combination of factors or variables that affect the response or output of a process or system. It involves designing and conducting experiments to gather data on the relationship between the input factors and the response variable, and then using statistical models to analyze the data and identify the optimal conditions for achieving the desired response. RSM has been widely used for the optimization of biodiesel production processes. The response variable in this case is usually the yield or quality of the biodiesel produced, and the input factors are typically the reaction parameters such as temperature, reaction time, catalyst concentration, and alcohol-to-oil molar ratio. To apply RSM to biodiesel production, the first step is to design a set of experiments to collect data on the relationship between the input factors and the response variable. The experiments can be designed using a central composite design (CCD). To apply RSM to biodiesel production, the first step is to design a set of experiments to collect data on the relationship between the input factors and the response variable. The experiments can be designed using a central composite design (CCD). After conducting the experiments, the data can be analyzed using statistical software to fit a mathematical model to the data. The model can then be used to predict the response variable for any combination of input factors within the experimental range. Once the model has been developed, the optimization process can begin. The objective is to identify the optimal input conditions that maximize the yield or quality of the biodiesel. This can be done using numerical optimization techniques or by visualizing the response surface and identifying the optimal conditions. By using RSM, biodiesel production can be optimized to achieve higher yields and better quality, while minimizing the use of resources and reducing costs.

#### 5.3.1 ANALYSIS OF VARIANCE

ANOVA (Analysis of Variance) is a statistical technique used to analyze the differences between groups of data. In the context of biodiesel production, ANOVA can be used to determine the significant factors that affect the yield or quality of biodiesel, such as the type of feedstock used, the reaction temperature, and the

reaction time. A quadratic model is a mathematical model that includes a quadratic term (i.e., a squared term) in addition to linear terms. In the context of biodiesel production, a quadratic model can be used to model the relationship between the input variables (such as temperature and reaction time) and the output variable (such as biodiesel yield) in a nonlinear way. This can be useful when the relationship between the input and output variables is not linear.

**Table 5.2 RSM Response Value**

Response 1: yield (12)

| Source               | Sum of Squares | df | Mean Square | F-value | p-value  |                 |
|----------------------|----------------|----|-------------|---------|----------|-----------------|
| Model                | 1714.25        | 14 | 122.45      | 38.90   | < 0.0001 | Significant     |
| A-oil: alcohol ratio | 488.25         | 1  | 488.25      | 155.12  | < 0.0001 |                 |
| B-catalyst load      | 31.17          | 1  | 31.17       | 9.90    | 0.0067   |                 |
| C-time               | 141.67         | 1  | 141.67      | 45.01   | < 0.0001 |                 |
| D-temperature        | 47.52          | 1  | 47.52       | 15.10   | 0.0015   |                 |
| AB                   | 25.88          | 1  | 25.88       | 8.22    | 0.0117   |                 |
| AC                   | 2.92           | 1  | 2.92        | 0.9263  | 0.3511   |                 |
| AD                   | 6.70           | 1  | 6.70        | 2.13    | 0.1653   |                 |
| BC                   | 45.26          | 1  | 45.26       | 14.38   | 0.0018   |                 |
| BD                   | 46.07          | 1  | 46.07       | 14.64   | 0.0017   |                 |
| CD                   | 108.11         | 1  | 108.11      | 34.35   | < 0.0001 |                 |
| A <sup>2</sup>       | 669.44         | 1  | 669.44      | 212.68  | < 0.0001 |                 |
| B <sup>2</sup>       | 0.2427         | 1  | 0.2427      | 0.0771  | 0.7851   |                 |
| C <sup>2</sup>       | 123.75         | 1  | 123.75      | 39.31   | < 0.0001 |                 |
| D <sup>2</sup>       | 0.8611         | 1  | 0.8611      | 0.2736  | 0.6086   |                 |
| Residual             | 47.21          | 15 | 3.15        |         |          |                 |
| Lack of Fit          | 23.96          | 10 | 2.40        | 0.5151  | 0.8260   | not significant |
| Pure Error           | 23.26          | 5  | 4.65        |         |          |                 |
| Cor Total            | 1761.46        | 29 |             |         |          |                 |

**Table 5.3 Fit Statistics**

|                  |       |                                |         |
|------------------|-------|--------------------------------|---------|
| <b>Std. Dev.</b> | 1.77  | <b>R<sup>2</sup></b>           | 0.9732  |
| <b>Mean</b>      | 75.99 | <b>Adjusted R<sup>2</sup></b>  | 0.9482  |
| <b>C.V. %</b>    | 2.33  | <b>Predicted R<sup>2</sup></b> | 0.9026  |
|                  |       | <b>Adeq Precision</b>          | 25.7509 |

The discrepancy between the Predicted R<sup>2</sup> of 0.9026 and the Adjusted R<sup>2</sup> of 0.9482 is less than 0.2, which is considered to be a fair agreement.

Coding for factors is used.

The sum of squares is of partial Type III.

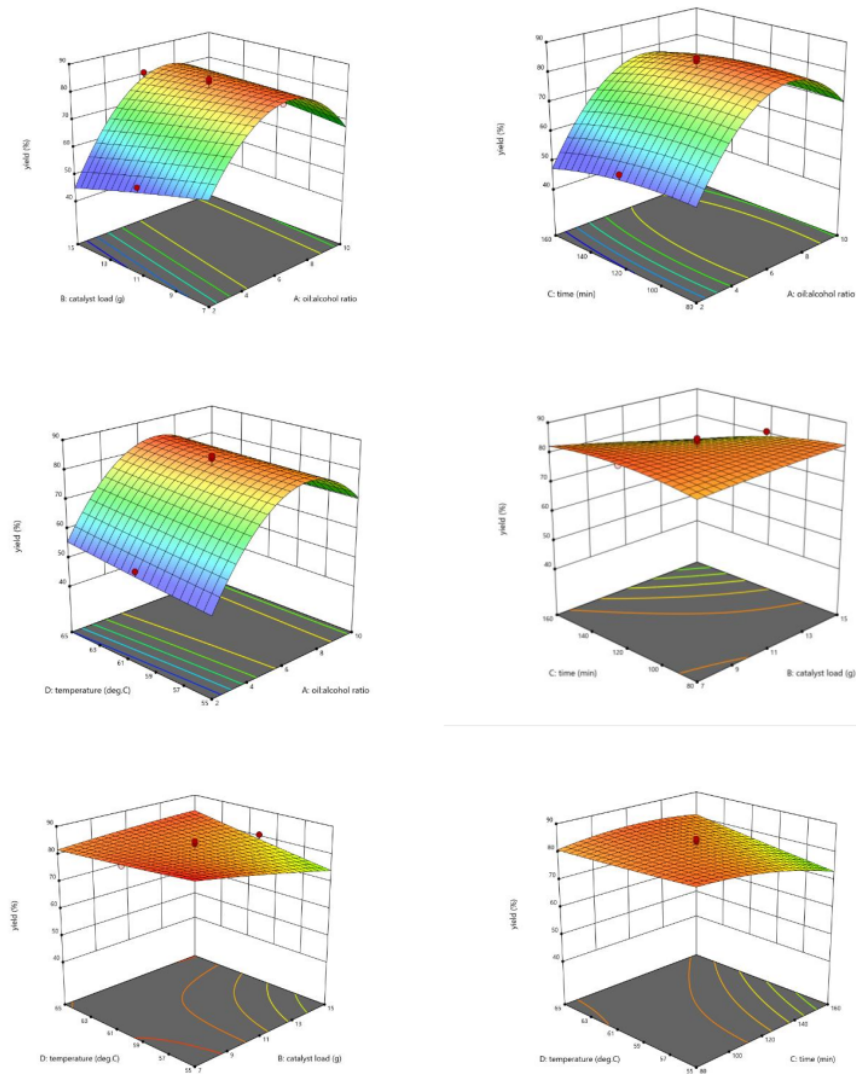
The model is suggested to be significant by the Model F-value of 38.90. An F-value this big might happen owing to noise just 0.01% of the time.

Model terms are considered significant when the P-value is less than 0.0500. In this instance, important model terms include A, B, C, D, AB, BC, BD, CD, and C<sup>2</sup>. Model terms are not significant if the value is higher than 0.1000. Model reduction may enhance your model if it has a lot of unnecessary words (except those needed to maintain hierarchy).

Compared to the pure mistake, the Lack of Fit is not substantial. A significant Lack of Fit F-value has an 82.60% likelihood of being caused by noise. Since we want the model to fit, a non-significant lack of fit is desirable.

### 5.3.2 3-D SURFACE PLOTS

Three-dimensional (3-D) graphs are a useful tool for visualizing the results of RSM experiments when there are more than two input variables. These graphs typically show the response variable (i.e., yield of biodiesel) as a function of two input variables, with the third input variable plotted on the vertical axis.



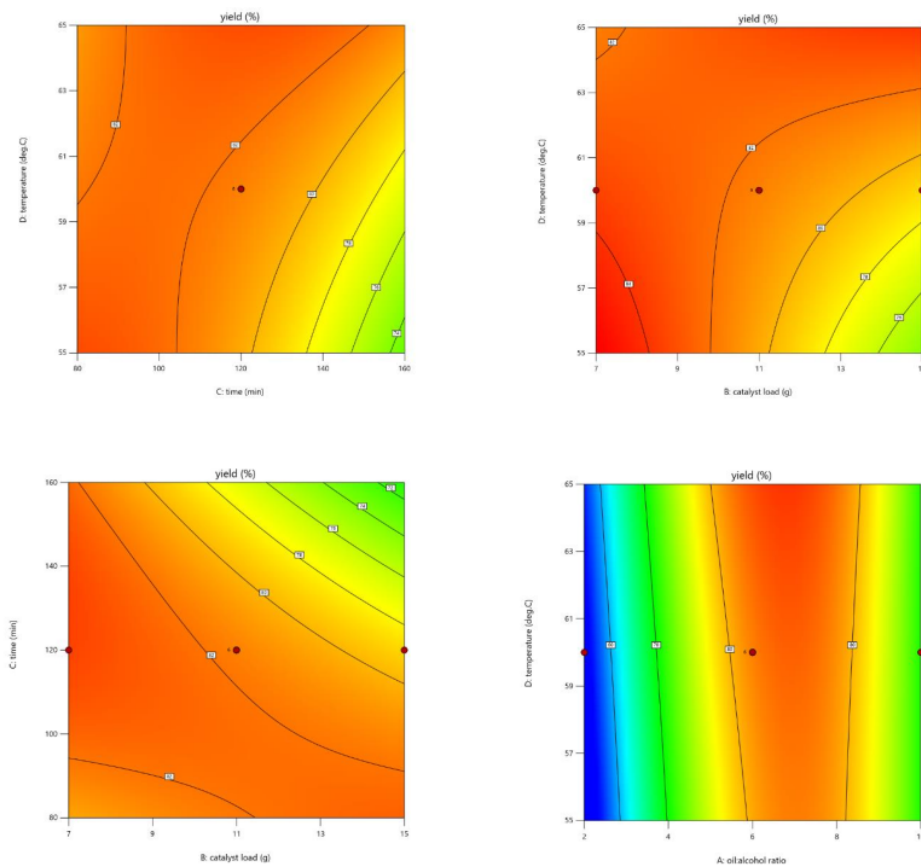
**Fig. 5.11 3-D Surface plot**

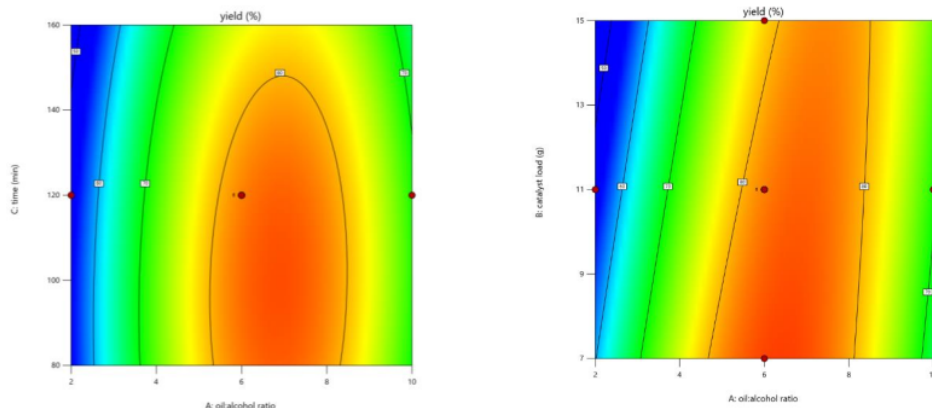
### 5.3.3 INFERENCE FROM 3-D SURFACE PLOT

Identification of interactions between process variables: In some cases, the 3-D graph may reveal interactions between different process variables that affect the yield of biodiesel. These interactions may not be apparent in 2-D contour graphs, making the 3-D graph a valuable tool for understanding the underlying relationships between process variables and yield.

### CONTOUR GRAPHS

Contour graphs are a useful tool for visualizing the results of RSM experiments. These graphs typically show the response variable (i.e., yield of biodiesel) as a function of two input variables, with the third input variable held constant. Contour lines on the graph connect points of equal response variable, allowing for visualization of the optimal parameter values for maximum yield.





**Fig. 5.12 Contour Graphs**

#### 5.3.4 INFERENCE FROM THE GRAPHS

Contour graphs are a useful tool for visualizing the results of RSM experiments. These graphs typically show the response variable (i.e., yield of biodiesel) as a function of two input variables, with the third input variable held constant. Contour lines on the graph connect points of equal response variable, allowing for visualization of the optimal parameter values for maximum yield.

Identification of optimal process parameters: By analysing the contour graph, the optimal combination of process parameters that maximize the yield of biodiesel can be identified. This can be done by locating the highest contour line or the intersection of two contour lines with the highest yield. The highest yield from the contour graphs 85%.

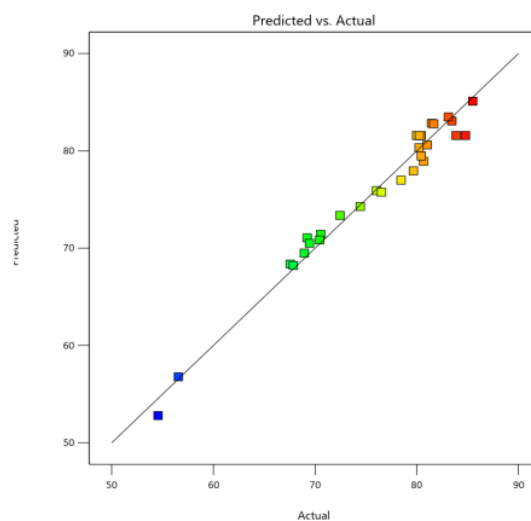
Evaluation of the effects of process variables: The contour graph can also provide information on the effects of different process variables on the yield of biodiesel. By examining the contour lines, it is possible to determine the sensitivity of the yield to changes in each input variable.

Prediction of response variable: The contour graph can also be used to predict the yield of biodiesel at any combination of input variables within the experimental range. This can be done by interpolating between the contour lines or by using regression models developed from the experimental data.

Overall, contour graphs obtained from RSM for biodiesel can provide valuable insights into the relationships between process variables and yield and can guide process optimization efforts.

### 5.3.5 VALIDATION OF MODEL

The value of the response variable that is calculated by a statistical model is the projected response, whereas the value of the response variable that is actually observed in the experiment is the actual response. In RSM, both are critical; the expected response is used to determine the ideal input variable values, while the actual response is used to validate the predictions and update the model.



**Fig. 5.13 Validation of Model**

### 5.3.6 INFERENCE FROM THE GRAPH:

When comparing predicted versus actual values in a response surface methodology (RSM) analysis for biodiesel, the closer the predicted values are to the actual values, the better the model is at predicting the response variable. If the predicted values are very close to the actual values, then it suggests that the model is accurately capturing the relationship between the input variables (such as temperature, pressure, and reactant concentrations) and the response variable (such as yield or purity). This indicates that the model is reliable and can be used

to optimize the process conditions to achieve the desired biodiesel properties. On the other hand, if there is a large discrepancy between the predicted and actual values, it suggests that the model may not be accurate enough to be used for optimization purposes. In this case, the model may need to be refined by adding more input variables or modifying the functional form of the model. Overall, the predicted versus actual graph is an important tool for evaluating the performance of an RSM model for biodiesel and for determining whether the model is reliable for optimization purposes.

## 5.4 PROPERTIES OF BIODIESEL

### 5.4.1 Flash point and Fire point

<sup>75</sup> The temperature at which biodiesel vapour will ignite in the presence of an ignition source, such as a spark or flame, is known as the flash point of biodiesel. <sup>105</sup> The flash point of biodiesel is around 198°C (388°F). This indicates that if there is an ignition source present, there is a considerable risk of fire or explosion at or above this temperature.

The temperature at which fuel vapour will continue to burn after being ignited is known as the fire point, on the other hand. The fire point of biodiesel is around 210°C (410°F). This means that even if the ignition source is removed, a fire that has already begun and reached the fire point will continue to burn.

### 5.4.2 Cloud and Pour point.

<sup>42</sup> The temperature at which tiny wax crystals start to form inside the fuel, giving it a cloudy or hazy appearance, is known as the cloud point of biodiesel. Biodiesel generally has a cloud point of 15°C (59°F). Wax crystals can begin to clog filters and decrease fuel flow when the temperature falls below this level, which can affect engine performance and potentially cause engine damage.

<sup>29</sup> The lowest temperature at which biodiesel can still flow is known as the pour point. This is crucial because if the temperature falls below this level, the gasoline may thicken and become impermeable, which might lead to troubles with engine starting and other problems. Biodiesel generally has a pour point of 6°C (43°F).

### 5.4.3 Acid Value

The amount of acidic chemicals in a sample of oil or biodiesel is gauged by the acid value. The quantity of potassium hydroxide (KOH) or sodium hydroxide (NaOH) needed in milligrams to neutralise one gramme of the sample is the common unit of measurement. The acid value of the biodiesel in this instance is 0.66g of oil/ml NaOH, which indicates that 0.66 grammes of the oil must be neutralised by 1 millilitre of NaOH. This suggests that the biodiesel contains just a small amount of acidic chemicals.

Since they can create engine deposits and engine part corrosion, the acidic components in biodiesel can be an issue. As a result, it's critical to reduce the presence of acidic chemicals in biodiesel. Using high-quality feedstocks for biodiesel synthesis and efficient refining and purifying methods during the manufacturing process are two ways to achieve this.

#### 5.4.4 Viscosity

A key characteristic of biodiesel that influences how well it performs as a fuel is viscosity, which is a measurement of a fluid's resistance to flow. Centistokes (cSt), a kinematic viscosity measurement unit, are frequently used to express the viscosity of biodiesel.

The biodiesel is thin and fluid, as seen by its 4.05 cSt viscosity. This is often a desirable quality in a gasoline since it makes it easier to distribute the fuel to the engine and can increase fuel efficiency. It is crucial to take into account the fuel's viscosity in the anticipated operating temperature range because biodiesel's viscosity can also be influenced by temperature.

**Table 5.4 properties of biodiesel and conventional diesel**

| Property                       | Biodiesel            | Diesel* |
|--------------------------------|----------------------|---------|
| Density kg/m <sup>3</sup>      | 880                  | 850     |
| Viscosity mm <sup>2</sup> /sec | 4.05cSt              | 3.5cSt  |
| Acid value                     | 0.66g of oil/ml NaOH | -       |
| Flash point degC               | 198                  | 85      |

|                    |               |           |
|--------------------|---------------|-----------|
| Fire point degC    | 210           | 76        |
| Cloud point degC   | 15            | 12        |
| Pour point degC    | 6             | 10        |
| Calorific value Cv | 7685.147Cal/g | 4260Cal/g |

**\*Sources: ASTM Standards**

## **5.5 SIMULATATION PROCESS OF BIODIESEL PRODUCTION IN LARGE SCALE INDUSTRY USING ASPEN PLUS**

Large-scale industries often use a complicated, multi-step process to produce biodiesel, one that needs careful planning and execution. Feedstock, which can comprise vegetable oils, animal fats, and other forms of biomass, is often collected and prepared before the process can begin. The transesterification process is started by heating the feedstock and combining it with a catalyst in a reactor. The major constituents of biodiesel, fatty acid methyl esters (FAME), are created during this reaction from the triglycerides in the feedstock.

The mixture is divided into two phases, one rich in glycerol and the other in biodiesel when the transesterification procedure is finished. The biodiesel is next cleaned and refined to eliminate any leftover impurities while the glycerol is collected and transported for additional processing.

### **5.5.1 MASS AND ENERGY BALANCE**

#### **Mass Balance**

Given data:

Inlet stream 1: 1000 kg/hr oil at 25 deg.C & 1 bar

Inlet stream 2: 166.67 kg/hr methanol at 25 deg.C & 1 bar

Inlet stream 3: 1.3 kg/hr KOH at 60 deg.C & 1 bar

Outlet stream: Various components with their respective mole flows and mass flows

To calculate the mass balance, we need to account for the mass of each component at the inlet and outlet, as well as any mass changes due to reactions.

25

### Mass balance equation

Mass in - Mass out + Mass generated = Mass accumulated

25

For each component, we can calculate the mass in, mass out, mass generated, and mass accumulated as follows:

#### C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>

Mass in = 1000 kg/hr x 0.204 (mass fraction) = 204 kg/hr (from oil)

Mass out = 204 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

#### C<sub>14</sub>H<sub>28</sub>O<sub>2</sub>

Mass in = 1000 kg/hr x 0.009 (mass fraction) = 9 kg/hr (from oil)

Mass out = 9 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

#### C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>

Mass in = 1000 kg/hr x 0.048 (mass fraction) + 1.3 kg/hr x 0.4 (mass fraction) = 48 kg/hr (from oil and KOH)

Mass out = 48 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

#### C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>

Mass in = 1000 kg/hr x 0.529 (mass fraction) = 529 kg/hr (from oil)

Mass out = 529 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

#### **C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>**

Mass in = 1000 kg/hr x 0.135 (mass fraction) + 1.3 kg/hr x 0.4 (mass fraction) =  
135 kg/hr (from oil and KOH)

Mass out = 135 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

#### **C<sub>22</sub>H<sub>42</sub>O<sub>2</sub>**

Mass in = 1000 kg/hr x 0.075 (mass fraction) = 75 kg/hr (from oil)

Mass out = 75 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

#### **CH<sub>3</sub>OH**

Mass in = 166.67 kg/hr (from methanol)

Mass out = 166.67 kg/hr (from outlet stream)

Mass generated = 0 kg/hr (no generation in reactions)

Mass accumulated = 0 kg/hr (since mass generated is 0)

#### **KOH**

Mass in = 1.3 kg/hr x 0.4 (mass fraction) = 0.52 kg/hr (from KOH)

Mass out = 0

kg/hr (since all KOH reacts)

Mass generated = 0.52 kg/hr (from reaction)

Mass accumulated = 0 kg/hr (since mass generated is 0)

Now, to complete the mass balance equation, we can sum up the <sup>47</sup> mass in, mass out, mass generated, and mass accumulated for all components:

Mass in = Sum of Mass in for all components

Mass out = Sum of Mass out for all components

Mass generated = Sum of Mass generated for all components

Mass accumulated = Sum of Mass accumulated for all components

Plugging in the values we calculated earlier:

$$\text{Mass in} = 204 \text{ kg/hr} + 9 \text{ kg/hr} + 48 \text{ kg/hr} + 529 \text{ kg/hr} + 135 \text{ kg/hr} + 75 \text{ kg/hr} + 166.67 \text{ kg/hr} + 0.52 \text{ kg/hr} = 1167.19 \text{ kg/hr}$$

$$\text{Mass out} = 204 \text{ kg/hr} + 9 \text{ kg/hr} + 48 \text{ kg/hr} + 529 \text{ kg/hr} + 135 \text{ kg/hr} + 75 \text{ kg/hr} + 166.67 \text{ kg/hr} + 0 \text{ kg/hr} = 1167.19 \text{ kg/hr}$$

$$\text{Mass generated} = 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0.52 \text{ kg/hr} = 0.52 \text{ kg/hr}$$

$$\text{Mass accumulated} = 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} + 0 \text{ kg/hr} = 0 \text{ kg/hr}$$

Now we can plug these values into the mass balance equation:

<sup>47</sup>  
 $\text{Mass in} - \text{Mass out} + \text{Mass generated} = \text{Mass accumulated}$

<sup>95</sup>  
 $1167.19 \text{ kg/hr} - 1167.19 \text{ kg/hr} + 0.52 \text{ kg/hr} = 0 \text{ kg/hr}$

<sup>31</sup>  
So, the mass balance is satisfied, and there is no accumulation of mass in the system.

### Energy Balance

Given that the initial moles of each component are as follows:

$$n_{\text{C16H32O2}} = 3.46 \text{ mol}$$

$$n_{\text{C14H28O2}} = 1.73 \text{ mol}$$

$$n_{\text{C18H36O2}} = 1.73 \text{ mol}$$

$$n_{C_{18}H_{34}O_2} = 0.69 \text{ mol}$$

$$n_{C_{18}H_{32}O_2} = 0.35 \text{ mol}$$

$$n_{C_{22}H_{42}O_2} = 0.35 \text{ mol}$$

$$n_{CH_4O} = 3.46 \text{ mol}$$

$$n_{KOH} = 3.46 \text{ mol}$$

$$n_{C_3H_8O_3} = 1.73 \text{ mol}$$

$$n_{H_2O} = 12.32 \text{ mol}$$

$$n_{C_{17}H_{34}O_2} = 0.69 \text{ mol}$$

$$n_{C_{15}H_{30}O_2} = 0.35 \text{ mol}$$

$$n_{C_{19}H_{38}O_2} = 0.35 \text{ mol}$$

$$n_{C_{19}H_{36}O_2} = 0.17 \text{ mol}$$

$$n_{C_{19}H_{34}O_2} = 0.03 \text{ mol}$$

$$n_{C_{23}H_{44}O_2} = 0.03 \text{ mol}$$

And assuming the suitable values for the specific heat capacities of oil and methanol as 2.2 kJ/kg°C and 2.51 kJ/kg°C respectively, the energy balance can be calculated as follows:

Heat Input:

For the oil stream:

Mass flow rate = 1000 kg/hr

Specific heat capacity of oil = 2.2 kJ/kg°C

<sup>41</sup>  
Inlet temperature = 25°C

Outlet temperature = 60°C

Heat input for oil stream =  $\text{Mass flow rate} \times \text{Specific heat capacity} \times \text{Temperature difference}$

$$= 1000 \text{ kg/hr} \times 2.2 \text{ kJ/kg}^\circ\text{C} \times (60 - 25) ^\circ\text{C}$$

$$= 66,000 \text{ kJ/hr}$$

For the methanol stream:

Mass flow rate = 166.67 kg/hr

Specific heat capacity of methanol = 2.51 kJ/kg°C

Inlet temperature = 25°C

Outlet temperature = 60°C

Heat input for methanol stream =  $\text{Mass flow rate} \times \text{Specific heat capacity} \times \text{Temperature difference}$

$$= 166.67 \text{ kg/hr} \times 2.51 \text{ kJ/kg}^\circ\text{C} \times (60 - 25) ^\circ\text{C}$$

$$= 25,000 \text{ kJ/hr}$$

Total Heat Input = Heat input for oil stream + Heat input for methanol stream

$$= 66,000 \text{ kJ/hr} + 25,000 \text{ kJ/hr}$$

$$= 91,000 \text{ kJ/hr}$$

Heat Output:

The heat output in this process is the heat released from the exothermic reactions in the reactor. The energy released from each reaction can be calculated using the given kinetic factor equation:

$$\text{Kinetic factor} = K \cdot T^n \cdot e^{(-E/RT)}$$

where:

$$K = 0.32598 \text{ (Given)}$$

$$T = 60^\circ\text{C} \text{ (Given)}$$

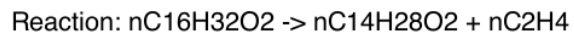
$$n = 0 \text{ (Given)}$$

$$E = 13500 \text{ (Given)}$$

$$R = \text{Universal gas constant} = 8.314 \text{ J/mol}\cdot\text{K}$$

Let's calculate the energy released from each reaction using the above equation and the given data:

For the first reaction:



$$\text{Initial moles of } n\text{C}_{16}\text{H}_{32}\text{O}_2 = 3.46 \text{ mol}$$

$$\text{Kinetic factor} = 0.32598 \cdot 60^0 \cdot e^{(-13500 / (8.314 \cdot 60))}$$

$$= 0.32598 \cdot e^{(-13500 / 498.84)}$$

$$= 0.32598 \cdot e^{(-27.042)}$$

$$= 0.32598 \cdot 1.928$$

$$= 0.62816$$

#### **Energy released from Reaction 1**

$$\text{Kinetic factor} = K \cdot T^n \cdot e^{(-E/RT)}$$

$$= 0.32598 \cdot (60 + 273)^0 \cdot e^{(-13500 / (8.314 \cdot (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

#### **Energy released from Reaction 2**

$$\text{Kinetic factor} = K \cdot T^n \cdot e^{(-E/RT)}$$

$$= 0.32598 \cdot (60 + 273)^0 \cdot e^{(-13500 / (8.314 \cdot (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

#### **Energy released from Reaction 3**

$$\text{Kinetic factor} = K \cdot T^n \cdot e^{(-E/RT)}$$

$$= 0.32598 \cdot (60 + 273)^0 \cdot e^{(-13500 / (8.314 \cdot (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

**Energy released from Reaction 4**

$$\text{Kinetic factor} = K * T^n * e^{(-E/RT)}$$

$$= 0.32598 * (60 + 273)^0 * e^{(-13500 / (8.314 * (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

**Energy released from Reaction 5**

$$\text{Kinetic factor} = K * T^n * e^{(-E/RT)}$$

$$= 0.32598 * (60 + 273)^0 * e^{(-13500 / (8.314 * (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

**Energy released from Reaction 6**

$$\text{Kinetic factor} = K * T^n * e^{(-E/RT)}$$

$$= 0.32598 * (60 + 273)^0 * e^{(-13500 / (8.314 * (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

**Energy released from Reaction 7**

$$\text{Kinetic factor} = K * T^n * e^{(-E/RT)}$$

$$= 0.32598 * (60 + 273)^0 * e^{(-13500 / (8.314 * (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

**Energy released from Reaction 8**

$$\text{Kinetic factor} = K * T^n * e^{(-E/RT)}$$

$$= 0.32598 * (60 + 273)^0 * e^{(-13500 / (8.314 * (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$

**Energy released from Reaction 9**

$$\text{Kinetic factor} = K * T^n * e^{(-E/RT)}$$

$$= 0.32598 * (60 + 273)^0 * e^{(-13500 / (8.314 * (60 + 273)))}$$

$$= 2.397 \times 10^7 \text{ kJ/hr}$$



**Table 5.5 Output of Simulink**

| 8                     | Units     | OIL          | MEOH         | REACTOUT     | KOH          |
|-----------------------|-----------|--------------|--------------|--------------|--------------|
| Phase                 |           | Liquid Phase | Liquid Phase | Liquid Phase | Liquid Phase |
| Temperature           | C         | 25           | 25           | 60           | 60           |
| Pressure              | bar       | 1            | 1            | 4            | 1            |
| Molar Vapor Fraction  |           | 0            | 0            | 0            | 0            |
| Molar Liquid Fraction |           | 1            | 1            | 1            | 1            |
| Molar Solid Fraction  |           | 0            | 0            | 0            | 0            |
| Mass Vapor Fraction   |           | 0            | 0            | 0            | 0            |
| Mass Liquid Fraction  |           | 1            | 1            | 1            | 1            |
| Mass Solid Fraction   |           | 0            | 0            | 0            | 0            |
| Molar Enthalpy        | cal/mol   | -194832      | -56940.8     | -105897      | -74752.8     |
| Mass Enthalpy         | cal/gm    | -697.372     | -1777.06     | -765.358     | -3022.59     |
| Molar Entropy         | cal/mol-K | -434.434     | -57.3816     | -204.811     | -34.1198     |
| Mass Entropy          | cal/gm-K  | -1.55499     | -1.79081     | -1.48025     | -1.37961     |
| Molar Density         | mol/cc    | 0.003156     | 0.024746     | 0.005929     | 0.030813     |
| Mass Density          | gm/cc     | 0.881632     | 0.792921     | 0.820308     | 0.762039     |
| Enthalpy Flow         | cal/sec   | -193714      | -82272.9     | -248310      | -1091.49     |
| Average MW            |           | 279.3803     | 32.04216     | 138.3627     | 24.73137     |
| Mass Flows            | kg/hr     | 1000         | 166.67       | 1167.97      | 1.3          |
| P-COOH                | kg/hr     | 204          | 0            | 0.001748     | 0            |
| M-COOH                | kg/hr     | 9            | 0            | 0.013646     | 0            |
| STEAR-01              | kg/hr     | 48           | 0            | 0.000363     | 0            |
| OLEIC-01              | kg/hr     | 529          | 0            | 0.306969     | 0            |
| LINOL-01              | kg/hr     | 135          | 0            | 0.156585     | 0            |
| ERUCI-01              | kg/hr     | 75           | 0            | 0.000229     | 0            |
| CH3OH                 | kg/hr     | 0            | 166.67       | 151.266      | 0            |
| KOH                   | kg/hr     | 0            | 0            | 0.52         | 0.52         |
| GLYCEROL              | kg/hr     | 0            | 0            | 27.95314     | 0            |
| WATER                 | kg/hr     | 0            | 0            | 0.78         | 0.78         |
| M-PALM                | kg/hr     | 0            | 0            | 200.8133     | 0            |
| M-MYRI                | kg/hr     | 0            | 0            | 8.804584     | 0            |
| M-STEAR               | kg/hr     | 0            | 0            | 47.40361     | 0            |
| M-OLEATE              | kg/hr     | 0            | 0            | 522.3032     | 0            |
| M-LINOLE              | kg/hr     | 0            | 0            | 133.259      | 0            |
| M-ERUCA               | kg/hr     | 0            | 0            | 74.38758     | 0            |
| H3PO4                 | kg/hr     | 0            | 0            | 0            | 0            |
| K3PO4                 | kg/hr     | 0            | 0            | 0            | 0            |

## CHAPTER-5

### SUMMARY AND CONCLUSIONS

Copper (Cu) metal-organic frameworks (MOFs) have been investigated as a potential catalyst for the production of biodiesel from vegetable oils. MOFs are a class of porous materials composed of metal ions or clusters linked by organic ligands, with high surface area and tunable pore size, making them attractive candidates for catalytic applications. Based on the available research, the use of Cu MOFs for biodiesel production has shown promising results. The Cu MOFs have exhibited high catalytic activity and selectivity for the transesterification reaction, which is the main reaction involved in biodiesel production. The use of Cu MOFs has also resulted in higher yields of biodiesel compared to other catalysts, and the reaction can be carried out at mild reaction conditions, reducing the energy consumption. Additionally, the Cu MOFs have shown good reusability and stability, which is important for commercial-scale production. The MOFs can be easily separated from the reaction mixture, and the catalytic activity remains relatively constant over multiple cycles of use. Packed bed distillation reactors have been investigated as a potential method for the production of biodiesel from vegetable oils. This process involves heating the vegetable oil in the presence of a catalyst, such as sodium hydroxide, and then distilling the resulting mixture in a packed bed reactor to separate the biodiesel from the glycerol by-product. Based on the available research, the use of packed bed distillation reactors for biodiesel production has shown promising results. The process has been shown to be effective in converting the vegetable oil to biodiesel with high yields, and the separation of the biodiesel from the glycerol byproduct is efficient and relatively easy to achieve. Additionally, the process has been shown to be flexible in terms of the types of vegetable oils that can be used as feedstock, making it a versatile method for biodiesel production. The process can also be easily scaled up for commercial production, as packed bed reactors can be designed to accommodate larger volumes of feedstock. Response Surface Methodology (RSM) optimization has been widely used for biodiesel production as it offers an efficient and cost-effective approach for optimizing process variables and maximizing the yield of biodiesel. Based on the available research, the use of RSM optimization for biodiesel production has shown promising results. By employing RSM, it is

possible to determine the optimal values of process variables such as reaction temperature, reaction time, catalyst concentration, and methanol-to-oil ratio that maximize the yield of biodiesel. This can be achieved with fewer experimental runs and less time, leading to cost savings. Furthermore, RSM optimization provides a valuable tool for studying the interactions between process variables and predicting the yield of biodiesel under various conditions. This can aid in the development of a robust and efficient biodiesel production process that can be scaled up for commercial production. However, it is important to note that the success of RSM optimization depends on the accuracy of the mathematical models developed from the experimental data. Therefore, the selection of appropriate models and experimental design is crucial for obtaining reliable results. Overall, the use of RSM optimization for biodiesel production offers a promising approach for process optimization, cost savings, and the development of an efficient and scalable production process.

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