

*A Dissertation thesis entitled*

**“Synthetic transformation of lower cost feedstocks to biodiesel  
using novel solid acid catalyst”**

Submitted in partial fulfilment of the requirements

For the award of the degree of

**Master of Science**

IN

**INDUSTRIAL CHEMISTRY**

**Submitted By**

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**FACULTY OF SCIENCE (FoS)**

**DEPARTMENT OF INDUSTRIAL CHEMISTRY**

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**RAJKOT-360 005, GUJARAT, INDIA.**

**2022-2023**

Dedicated to  
My Beloved Family

## **Declaration**

We undersigned, hereby declare that the work assimilated in the dissertation thesis entitled **“Synthetic transformation of lower cost feedstocks to Biodiesel using novel solid acid catalyst”** has been carried out by us at Faculty of Science, Department of Industrial Chemistry, Atmiya University, Rajkot, Gujarat, India, under the supervision and Guidance of **Dr. Mehul L. Savaliya, Assistant Professor, Department of Industrial Chemistry, Faculty of Science, Atmiya University, Rajkot, Gujarat, India.**

To the best of our knowledge and belief, the work included in this thesis is quite original and has not submitted to any other Institution or University for the award of any degree either in this or any other form.

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We wish to express our sincere gratitude and honour to our Research supervisor **Dr. Mehul L. Savaliya, Assistant Professor, Department of Industrial Chemistry, Faculty of Science, Atmiya University, Rajkot**, for their inspiring, splendid and authentic guidance, moral support and constant encouragement throughout our research work. Their passion and dedication towards research have stimulated, provoked and facilitated us to complete this endeavour. We could not have imagined having a better Research Supervisor and mentor for our M. Sc study. Their role will always remain fundamental in shaping our future.

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## Acknowledgement

First and foremost, from the bottom of heart, body, mind and soul, praises and thanks to our parents, the god, an almighty, for his showers of blessings throughout this research work. We must pray in the lotus feet of **H.D.H. P. P. Hariprasad Swamiji Maharaj** for their divine blessings. We convey our heartfelt thanks to the **Department of Industrial Chemistry, Faculty of Science, Atmiya University, Rajkot**, for providing laboratory facilities for the course of this work.

We warmly thank our research supervisor **Dr. Mehul L. Savaliya**, Assistant Professor, Department of Industrial Chemistry, Faculty of Science, Atmiya University, Rajkot for his splendid guidance, authentic supervision, moral support, constant encouragement and giving us an opportunity to work under him with compilation of magnificent experience.

We warmly thank **P. P. Tyagvallabh Swamiji**, President, Atmiya University, **Dr Shivkumar Tripathi** (Vice-chancellor), Atmiya University, **Dr. Jayesh V Deshkar** (Pro Vice-chancellor), Atmiya University **Dr. Sheela Ramchandran**, (Pro-chancellor), Atmiya University, **Dr. D. D. Vyas**, (Registrar), Atmiya University, **Dr. Ashish M. Kothari**, (Director - Research, Innovation and Translation) Atmiya University and **Er. Ravi S. Tank**, (Head), Department of Industrial Chemistry, Atmiya University, Rajkot for providing us all the required facilities to carry out our research work.

We thank our Dissertation Review-I & II committee members, **Er. Ravi S. Tank**, **Er. Dhaval A. Tank**, **Dr. Mehul L. Savaliya** and **Dr. Govind V. Vagadiya** of Department of Industrial Chemistry for their insightful comments, suggestions and unconditional help in our research work.

We are very much delightful to **NFDD Centre, Saurashtra University, Rajkot, INDIA** for analytical assistance in spectral characterization of synthesized samples.

At last, but not the least, we are very much thankful to all teaching & non-teaching staff members, **Mr. Sagar Patel**, **Mr. Hemil Chavda**, **Mr. Jigneshbhai Gohel**, **Mr. Sunilbhai Parmar** and co-researchers of Department of Industrial Chemistry for their helping hands.

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## **Abstract**

The production of biodiesel from non-edible oils and fats is an attractive option to reduce dependence on fossil fuels. This study focuses on the use of novel solid acid catalysts for the conversion of lower cost feedstocks to biodiesel. The catalyst PNAS-Si synthesized by impregnating silica with sulfonic acid groups and evaluated for their performance in biodiesel production. Biodiesel production from waste palm oil involves a transesterification reaction using PNAS- Si catalyst. The process can be optimized by controlling various parameters such as temperature, reaction time, and molar ratio of reactants [1]. The results showed that the solid acid catalyst PNAS-Si significantly improved the conversion efficiency and selectivity of biodiesel production from non-edible oils and fats. Then Synthesized biodiesel is characterized through FT-IR and <sup>1</sup>H-NMR techniques. The study concludes that the use of these catalysts has great potential for the development of sustainable and economically viable biodiesel production processes [2].

**Keywords:** Lower cost feedstocks, Waste palm oil, Transesterification, PNAS-Si catalyst, Biodiesel, Sustainable, Efficiency



# 1 Introduction

Biodiesel is a renewable fuel that is derived from natural sources such as vegetable oils, animal fats, or recycled cooking oils. It is created through a chemical process called transesterification, in which a feedstock such as soybean oil is combined with an alcohol, typically methanol or ethanol, and a catalyst such as sodium hydroxide. This process breaks down the long chains of triglycerides found in the feedstock and converts them into fatty acid methyl esters, which are the main component of biodiesel. There are several reasons why we should use biodiesel as a fuel source. First and foremost, it is a renewable and sustainable alternative to fossil fuels such as diesel and gasoline. Biodiesel is made from feedstocks that can be grown and replenished, such as soybeans, canola, and sunflower seeds, as well as waste products like used cooking oil and animal fats. This means that it does not contribute to the depletion of finite resources like fossil fuels, which are becoming increasingly scarce and expensive [1].

Another benefit of biodiesel is that it has a lower carbon footprint than fossil fuels. When burned in a diesel engine, biodiesel releases fewer greenhouse gas emissions such as carbon dioxide, nitrogen oxides, and sulphur dioxide. This is because the carbon dioxide that is released during combustion is offset by the carbon dioxide that was absorbed by the feedstock during its growth cycle. As a result, biodiesel has been shown to reduce greenhouse gas emissions by up to 86% compared to traditional diesel fuel. Biodiesel is also a cleaner-burning fuel than traditional diesel. It produces less particulate matter, which can cause respiratory problems, and fewer sulphur emissions, which contribute to acid rain. This means that it can improve air quality and help reduce the negative health impacts of air pollution.

Another benefit of biodiesel is that it is domestically produced, which can help reduce our dependence on foreign oil. Unlike fossil fuels, which are often imported from other countries, biodiesel can be produced locally using domestic feedstocks. This can help create jobs and support local economies, as well as reduce our reliance on unstable or unfriendly foreign oil sources [3].

Biodiesel is also a versatile fuel that can be used in a variety of applications. It can be blended with traditional diesel fuel at different ratios to produce different blends, depending on the desired performance characteristics. For example, a B20 blend contains 20% biodiesel and 80% traditional diesel, while a B100 blend contains 100% biodiesel. Biodiesel can be used in diesel engines without any modifications, which means that it can be easily integrated into existing infrastructure and equipment. In addition to its environmental and economic benefits, biodiesel also has a number

of social benefits. Because it is produced locally, it can help support local farmers and create jobs in rural communities. It can also provide a more stable and reliable source of energy, reducing the risk of supply disruptions and price volatility.

In conclusion, biodiesel is a renewable, sustainable, and domestically-produced alternative to fossil fuels. It offers a range of environmental, economic, and social benefits, including lower greenhouse gas emissions, improved air quality, reduced dependence on foreign oil, and support for local economies. As such, biodiesel has the potential to play an important role in helping to create a more sustainable and equitable energy future [2].

## **2 Literature Review:**

### **2.1 Biodiesel:**

Biodiesel is gaining popularity as an alternative to conventional diesel fuel because it is renewable, biodegradable, and emits fewer pollutants. Unlike petroleum-based diesel, biodiesel is made from renewable resources, making it a more sustainable option. Biodiesel also has a higher flash point than petroleum diesel, which means it is safer to handle and transport [3].

One of the main advantages of biodiesel is that it emits fewer greenhouse gases and air pollutants than conventional diesel fuel. Biodiesel has a lower carbon footprint because the feedstocks used to produce it absorb carbon dioxide from the atmosphere during their growth cycle, which offsets the emissions produced during combustion. Biodiesel also has lower levels of sulphur, nitrogen oxides, and particulate matter, which can help reduce air pollution and improve air quality.

This study focuses on the use of novel solid acid catalysts for the synthetic transformation of lower cost feedstocks to biodiesel. The feedstocks used in this study are non-edible oils and fats, which are considered low-cost alternatives to traditional edible oils. The solid acid catalysts were synthesized by impregnating silica with sulfonic acid groups, and their performance in the conversion of lower cost feedstocks to biodiesel was evaluated. The synthesis of the solid acid catalysts involved the impregnation of silica with sulfonic acid groups using a sol-gel method. The catalysts were then characterized by various techniques, including scanning electron microscopy

(SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The results showed that the synthesized catalysts had a high surface area, strong acidity, and good thermal stability [4].

The performance of the solid acid catalysts in the conversion of lower cost feedstocks to biodiesel was evaluated using a transesterification reaction. The reaction was carried out at various temperatures, reaction times, and molar ratios of reactants. The results showed that the synthesized solid acid catalysts significantly improved the conversion efficiency and selectivity of biodiesel production. The study also evaluated the stability and reusability of the solid acid catalysts over multiple cycles of biodiesel production. The results showed that the catalysts exhibited good stability and reusability, making them an attractive option for biodiesel production [1] [5].

The use of non-edible oils and fats as feedstocks for biodiesel production can significantly reduce the cost of production and increase the sustainability of the process. The use of solid acid catalysts can further improve the efficiency and selectivity of biodiesel production from these low-cost feedstocks. The study highlights the potential of solid acid catalysts for the development of sustainable and economically viable biodiesel production processes. The use of novel solid acid catalysts for the synthetic transformation of lower cost feedstocks to biodiesel is a promising approach to reduce the cost of biodiesel production and increase the sustainability of the process. The study provides insights into the synthesis, characterization, and performance of solid acid catalysts for biodiesel production from non-edible oils and fats. The results of this study can contribute to the development of more efficient and sustainable biodiesel production processes [1].

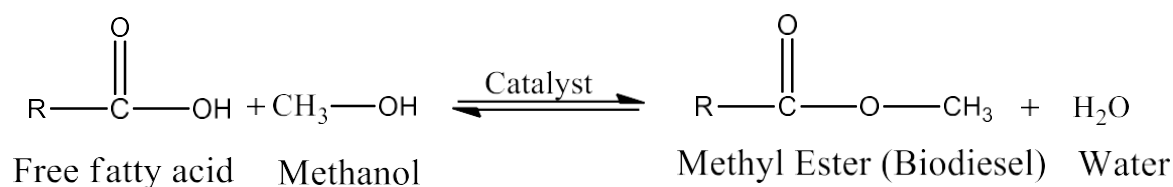


Figure 1 Acid Catalysed Esterification

## **2.2 Advantages and Disadvantages in the use of Biodiesel:**

### **Advantages:**

1. **Renewable:** Biodiesel is made from renewable sources, which means it can be produced continuously without depleting natural resources.
2. **Reduced carbon emissions:** Biodiesel produces less carbon emissions than traditional diesel fuel, making it a cleaner-burning fuel source. This is because biodiesel is derived from organic sources and not from fossil fuels.
3. **Better lubrication:** Biodiesel has better lubricating properties than traditional diesel fuel, which can help reduce engine wear and extend the life of engines.
4. **Domestic production:** Biodiesel can be produced domestically, which means it can help reduce dependence on foreign oil imports and improve energy security.
5. **Potential economic benefits:** The production of biodiesel can create jobs and support local economies, particularly in rural areas [1] [3] [7].

### **Disadvantages:**

1. **Cost:** Biodiesel is generally more expensive than traditional diesel fuel, which can make it less economically feasible for some users.
2. **Availability:** Biodiesel may not be readily available in some areas, which can make it difficult for some users to access.
3. **Compatibility issues:** Biodiesel may not be compatible with all diesel engines, which can limit its use.
4. **Land use concerns:** The production of biodiesel requires the use of land, which can raise concerns about land-use competition with food production and natural habitats.
5. **Energy-intensive production:** The production of biodiesel requires energy-intensive processes, which can offset some of its environmental benefits [1] [3] [7].

## 2.3 Transesterification:

Transesterification is a chemical process in which the ester group of an organic compound is exchanged with an alcohol, resulting in the formation of a new ester compound and an alcohol as a by-product. This reaction is typically used in the production of biodiesel, which involves the conversion of triglycerides (such as vegetable oil or animal fats) into methyl or ethyl esters, which can be used as a fuel source in diesel engines [8].

In the transesterification reaction, the triglyceride is first mixed with an alcohol (usually methanol or ethanol) and a catalyst (such as sodium or potassium hydroxide). The reaction is typically carried out at an elevated temperature and pressure, and the resulting products are methyl or ethyl esters and glycerol. The glycerol is then separated from the esters using a settling tank, and the esters are further purified by washing and drying [6] [8].

The transesterification process is important for the production of biodiesel because it allows for the conversion of vegetable oils and animal fats into a usable fuel source. The resulting biodiesel is a clean-burning fuel that can be used in diesel engines without any modifications, and it has lower emissions of pollutants compared to traditional diesel fuel [6]. The process is relatively simple and can be performed on a small scale, making it accessible to small-scale biodiesel.

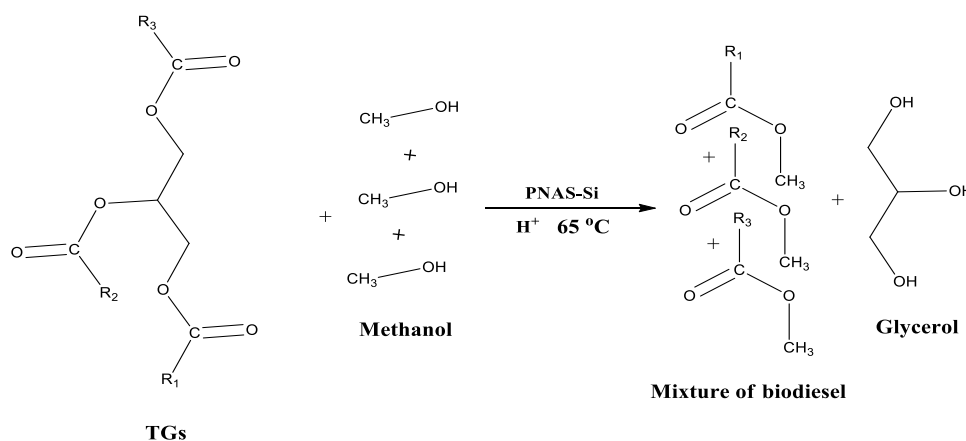


Figure 2 : Reaction of FAME (Bio-diesel)

## 2.4 Solid acid catalyst:

Solid acid catalysts are a type of heterogeneous catalyst that contain acidic sites on their surface. They are widely used in various chemical reactions, including transesterification reactions to produce biodiesel, as they offer several advantages over traditional homogeneous catalysts.

Solid acid catalysts are typically composed of inorganic materials, such as zeolites, sulfonated resins, or other metal oxides. The acid sites on the catalyst surface can be generated by introducing acid groups, such as  $-SO_3H$  or  $-COOH$ , onto the surface of the material [9] [10].

The advantage of using solid acid catalysts is that they can be easily separated from the reaction mixture, making the catalyst recovery and reuse possible. In addition, solid acid catalysts are more stable and less corrosive than traditional liquid acid catalysts. They also exhibit a high catalytic activity and selectivity, and can operate under milder reaction conditions, such as lower temperatures and pressures. Solid acid catalysts have been extensively studied in the production of biodiesel by transesterification of vegetable oils or animal fats with alcohols [1] [2]. The catalytic activity and selectivity of these catalysts are affected by several factors, including the surface acidity, porosity, and surface area of the catalyst, as well as the reaction conditions, such as the reaction temperature, pressure, and molar ratio of the reactants [11].

Overall, solid acid catalysts are a promising option for catalytic applications due to their stability, selectivity, and easy separation and recovery from the reaction mixture. They offer an attractive alternative to traditional homogeneous catalysts, and have the potential to contribute to the development of more sustainable and efficient chemical processes [4].

## **2.5 Heterogeneous Catalysis:**

Heterogeneous catalysis is a widely used process in the production of biodiesel from vegetable oils or animal fats through transesterification reactions. In heterogeneous catalysis, the catalyst is present in a different phase than the reactants, which allows for easy separation and recovery of the catalyst after the reaction. Solid acid catalysts and base catalysts are the most commonly used heterogeneous catalysts in the production of biodiesel. Heterogeneous catalysis has several advantages in the production of biodiesel. The catalyst can be easily separated and recovered, which reduces the cost of the production process and makes it more sustainable. In addition, the use of heterogeneous catalysts allows for the use of lower reaction temperatures and pressures, which reduces the energy requirements of the process and leads to lower greenhouse gas emissions.

However, there are also some challenges associated with heterogeneous catalysis in biodiesel production. The use of solid catalysts can lead to mass transfer limitations, as the reactants and products may have limited access to the catalyst surface. In addition, the catalysts may become deactivated or lose their activity over time due to fouling or poisoning by impurities present in the reaction mixture [8] [11].

Overall, heterogeneous catalysis is an important process in the production of biodiesel from vegetable oils or animal fats. While there are some challenges associated with this process, ongoing research and development in this area are helping to improve the efficiency and sustainability of biodiesel production using heterogeneous catalysis.

## **2.6 Presence of Free Fatty Acids (FFA):**

A fatty acid is a natural molecule that contains an extended aliphatic chain of an even number of carbon atoms and a carboxyl group at the end of the chain. The amount of free fatty acids and moisture in an oil is important when considering the feasibility of the transesterification process, which is the process of converting vegetable oils or animal fats into biodiesel. The content of free fatty acids determines the catalytic path to be taken for the transesterification. A basic catalyst is used when the amount of FFA in the oil is less than 3%, as the high acidity of the oil causes a low biodiesel yield. However, if the oil has more than 5% FFA, it cannot be trans esterified by alkaline catalysis, as soaps are formed, which inhibit the separation of glycerol and biodiesel. This can also lead to the formation of emulsions during washing. The presence of FFA causes the formation of soap, which hampers the separation of the biodiesel and glycerol. Additionally, a high amount of catalyst is consumed, and the catalytic performance is reduced [12] [13].

One issue with this method is the presence of water, which can accumulate during the esterification process and stop the reaction before it is complete. The accumulation of water can be prevented by using an acid catalyst, which has been found to be effective in obtaining biodiesel from groundnut oil containing 1-2% FFA with a conversion efficiency of 99% after 26 hours. In another study, the transesterification reaction of dewaxed/degummed rice bran oil containing 24.5% and 49.5% FFA with methanol at 100°C resulted in a conversion of 62% and 73%, respectively. An increase in the amount of methanol or catalyst had a negligible impact on the conversion efficiency. The water generated during the process forms another phase that absorbs methanol and sulphuric

acid. This water phase possibly prevents the transesterification of triglycerides and further esterification of residual FFA [8].

The transesterification of FFA can be performed using acid catalysis. This process can be completed in two stages. In the first stage, FFA is converted to alkyl esters using acid catalysis, and in the second stage, the transesterification process is completed using basic catalysis.

In summary, the amount of free fatty acids and moisture in an oil is a crucial factor when considering the feasibility of the transesterification process. The content of free fatty acids determines the catalytic path to be taken, and the presence of water can halt the reaction. Using acid catalysis or completing the process in two stages can help to overcome these issues [12] [13].

## **2.7 Alcohols:**

Alcohols are a key component in the transesterification process, which is the process of converting vegetable oils or animal fats into biodiesel. In this process, an alcohol such as methanol or ethanol is added to the oil along with a catalyst, typically sodium hydroxide or potassium hydroxide, to break down the triglycerides in the oil into esters and glycerol [1] [2].

During the reaction, the alcohol reacts with the triglycerides to form esters, which are the primary component of biodiesel, and glycerol, which is a by-product. The esterification reaction is exothermic, meaning it produces heat. This heat helps to drive the reaction forward and break down the triglycerides into the desired products.

The choice of alcohol used in the transesterification process is important, as different alcohols can have different properties and can affect the yield and quality of the biodiesel produced. Methanol is commonly used as it has a low cost and high reactivity, meaning it can quickly react with the triglycerides to form esters. Ethanol can also be used, but it is less reactive than methanol and may require higher temperatures or longer reaction times to achieve the same level of conversion [13].

Alcohols can also have an impact on the separation of the biodiesel and glycerol phases after the transesterification reaction is complete. Methanol has a lower boiling point than glycerol, which can make it easier to separate the two phases by distillation. However, if there is excess methanol left in the biodiesel phase after separation, it can lead to problems with engine performance and emissions. This excess methanol can be removed by washing the biodiesel with water or using a vacuum distillation process.



In summary, alcohols play a crucial role in the transesterification process by reacting with triglycerides to form esters and glycerol. The choice of alcohol used can affect the yield and quality of the biodiesel produced and can also impact the separation of the biodiesel and glycerol phases after the reaction is complete [1] [6] [11].

## **2.8 Temperature and Pressure:**

The process of converting waste palm oil to biodiesel involves a transesterification reaction, similar to the process used to convert other vegetable oils or animal fats to biodiesel. The temperature and pressure requirements for this process can vary depending on the specific conditions and the type of catalyst used [1].

Typically, the transesterification reaction of waste palm oil to biodiesel is carried out at temperatures ranging from 55 to 65°C, although higher or lower temperatures may be used depending on the specific conditions. The use of higher temperatures can increase the rate of reaction but may also lead to the formation of unwanted by-products, such as soap and glycerol. Lower temperatures can lead to longer reaction times and may require the use of more catalyst.

The pressure requirements for the transesterification reaction of waste palm oil to biodiesel are generally not as critical as the temperature requirements. The reaction can be carried out at atmospheric pressure or under vacuum conditions. Higher pressures can be used to increase the rate of reaction, but this may not be necessary in most cases [14].

It is worth noting that the use of waste palm oil as a feedstock for biodiesel production can present some challenges due to the presence of impurities and high free fatty acid content. Additional processing steps may be required to remove impurities and reduce the free fatty acid content before the transesterification reaction can be carried out.

The temperature and pressure requirements for the transesterification reaction of waste palm oil to biodiesel can vary depending on the specific conditions and the type of catalyst used. The temperature range is typically between 55 to 65°C, while pressure is generally not as critical and can be carried out at atmospheric pressure or under vacuum conditions [2] [6].

## **2.9 Reaction time:**

The reaction time for converting waste palm oil to biodiesel through transesterification depends on various factors such as temperature, catalyst type, and concentration, as well as the quality of the feedstock used.

Typically, the reaction time for converting waste palm oil to biodiesel is between 6-10 hours. However, the actual reaction time required to achieve complete conversion can vary depending on the specific conditions used. Higher temperatures or concentrations of catalyst may lead to a faster reaction rate, which could potentially reduce the reaction time required [6] [11].

In addition, other factors such as the level of impurities in the waste palm oil and the free fatty acid content can also affect the reaction time. Higher levels of impurities or free fatty acids can slow down the reaction rate, and require longer reaction times to achieve complete conversion.

It is worth noting that optimizing the reaction time for converting waste palm oil to biodiesel requires careful consideration of all the variables involved. A longer reaction time may be required to achieve complete conversion, but this can also increase production costs and reduce the overall efficiency of the process. Therefore, a balance needs to be struck between reaction time, cost, and efficiency, to ensure that the biodiesel production process is as effective and economical as possible [6].

## **2.10 Phase Separation:**

After the transesterification reaction, the mixture of biodiesel, glycerol, and unreacted methanol needs to be separated into its individual components. This process is known as phase separation, and it involves separating the biodiesel from the glycerol and methanol.

There are various methods for phase separation, but the most common approach is to use gravity settling or centrifugation. Here We are using gravity settling, the mixture is allowed to stand in a container for several hours to allow the heavier glycerol and unreacted methanol to settle to the bottom of the container. The biodiesel can then be decanted off the top of the container.

In centrifugation, the mixture is placed in a centrifuge, which spins the mixture at high speeds. This causes the heavier glycerol and unreacted methanol to separate from the lighter biodiesel, and the two layers can be easily separated.

After phase separation, the glycerol and methanol layer can be processed further to recover the glycerol for reuse or sale, and to remove any remaining methanol. The biodiesel layer can be washed with water to remove any residual impurities or catalyst, and then dried to remove any remaining water.

The resulting biodiesel is then ready to be used as a fuel or blended with petroleum diesel for use in vehicles or equipment [15].

## **2.11 Purification of Biodiesel:**

After phase separation, biodiesel may still contain some impurities that need to be removed before it can be used as a fuel. The most common methods for purifying biodiesel include washing, drying, and filtration.

**Washing:** Washing is a common method for removing impurities from biodiesel. The process involves mixing the biodiesel with water or a water-methanol solution and then separating the two layers. The water layer will contain any impurities that were present in the biodiesel, such as residual catalyst or soap. The biodiesel is then washed multiple times with clean water until the water layer is clear, indicating that all the impurities have been removed. The washed biodiesel is then dried to remove any remaining water [7] [8].

**Drying:** Drying is another method for removing water from biodiesel. The process involves heating the biodiesel to a temperature above the boiling point of water, causing the water to evaporate. The biodiesel is then cooled and any remaining water is removed by gravity separation or filtration.

**Filtration:** Filtration is a method for removing particulate matter from biodiesel. The process involves passing the biodiesel through a filter to remove any solid particles, such as rust or dirt. The filter can be made from a variety of materials, such as paper, cloth, or a synthetic polymer.

After the purification process, the biodiesel is typically tested for quality to ensure that it meets the required specifications for use as a fuel. This may include testing for properties such as flash point, viscosity, and sulphur content. The purified biodiesel can then be used as a renewable fuel

in diesel engines or blended with petroleum diesel to reduce emissions and dependence on fossil fuels [12] [15].

### **3 Materials and Methods:**

#### **3.1 Materials:**

Waste palm oil was obtained from Dwarkadhish fast food Restaurant, Rajkot, Gujarat, India. P-Nitro aniline was supplied by Qualikems Fine Chem Pvt. Ltd, Nandesari, Vadodara, Gujarat. Chlorosulfonic acid was supplied by Central Drug House (P) Ltd. Daryaaganj, New Delhi. Silica gel was obtained from Qualikems Fine Chem Pvt. Ltd, Nandesari, Vadodara. Methanol was obtained from Avantor Performance Materials India Private Limited, Thane, Maharashtra, DCM was supplied by Molychem Pvt. Ltd., Mumbai, Gujarat.

#### **3.2 Analytical Instrumental Methods:**

The FT-IR spectra of fresh and regenerated PNSA-Si were obtained using an FT-IR spectrophotometer. The FT-IR analysis of biodiesel was performed using the same instrument. An IH-NMR analysis was conducted using a FT-NMR spectrometer. Scanning electron microscopy was used to determine the surface and structural morphologies of fresh and regenerated PNSA-Si catalysts. The acidity of the PNSA-Si was determined using neutralization titration. Gas chromatography was used to estimate the biodiesel yield (%), with the peaks in the WF-based biodiesel sample identified and quantified using a FAME mixture as a standard.

### **4 Experimental Procedures:**

#### 4.1 Preparation of PNSA-Si Catalyst:

A 250 mL round-bottom flask was filled with solid P-Nitroaniline and stirred with Methylene dichloride (DCM) as a solvent. Chlorosulfonic acid was slowly added drop by drop via a dropping funnel over a period of 30 minutes, while maintaining the temperature between 0-5°C using an ice bath and stirring with a magnetic stirrer. After the addition of chlorosulfonic acid was completed, the remaining DCM solvent was removed to obtain a slurry type catalyst. To convert it into a powder form, silica gel was added to the slurry, and stirring was continued until the powder form was obtained. Finally, the catalyst was packed into an airtight container for further use.

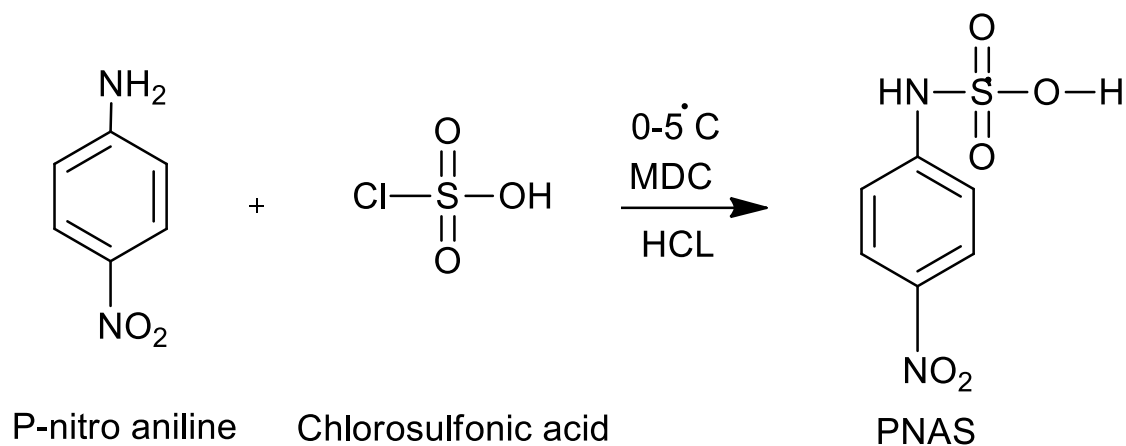


Figure 3 Reaction Scheme for synthesis of PNSA-Si Catalyst

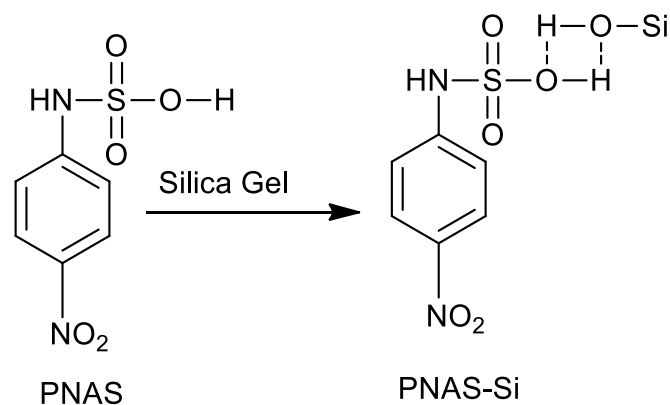


Figure 4 Reaction Scheme for synthesis of PNAS-Si Catalyst

## 5 Preparation of Biodiesel:

- **Feedstock Preparation:** The first step involves the preparation of feedstock, which is usually waste palm oil. The feedstock is filtered and pre-processed to remove any impurities such as water and free fatty acids.
- **Catalyst Preparation:** A solid acid catalyst PNAS-Si is prepared using an appropriate method such as impregnation, co-precipitation or sol-gel method. The catalyst is then activated by heating it to a certain temperature to increase its activity.
- **Transesterification:** The feedstock is mixed with an alcohol, usually methanol, and the activated solid acid catalyst is added. The mixture is then heated, typically between 50-65°C, and at atmospheric pressure and maintain it at this temperature for a period of time, usually 6-10 hours, depending on ratio of the catalyst and reactants used. And stirred to facilitate the reaction. Monitor the progress of the reaction by taking samples at regular intervals and analysing the product to determine the extent of conversion. The transesterification reaction converts the triglycerides in the feedstock into biodiesel and glycerol.

- **Separation:** After the transesterification reaction is completed, the mixture is allowed to settle, and the biodiesel layer is separated from the glycerol layer. The biodiesel is washed with water to remove any residual catalyst and impurities.
- **Drying:** The biodiesel is then dried to remove any remaining water and alcohol.
- **Quality Control:** The final step involves the quality control of the biodiesel product, which includes testing for properties such as viscosity, flash point, and cetane number to ensure that it meets the required standards [18].

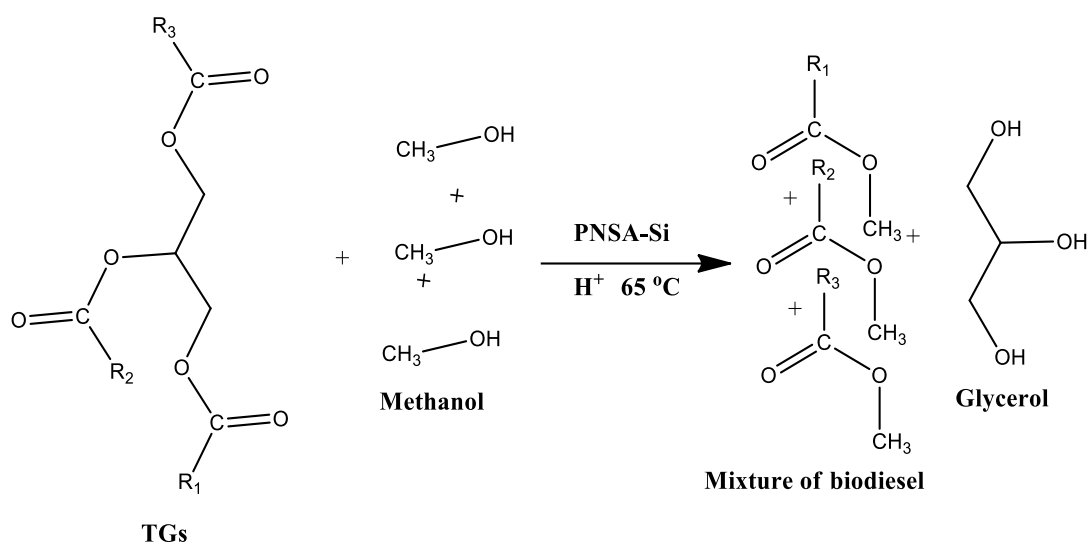


Figure 5: Reaction scheme via trans-esterification

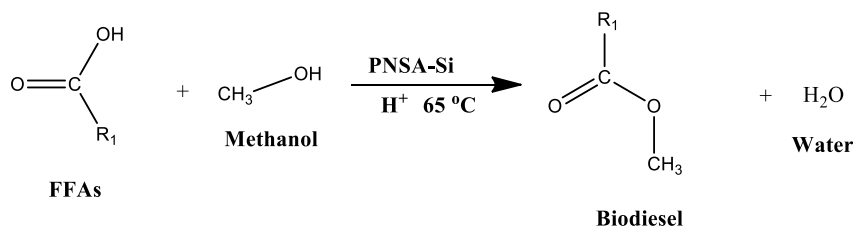


Figure 6: Reaction scheme via esterification

## 6 Transesterification Reaction:

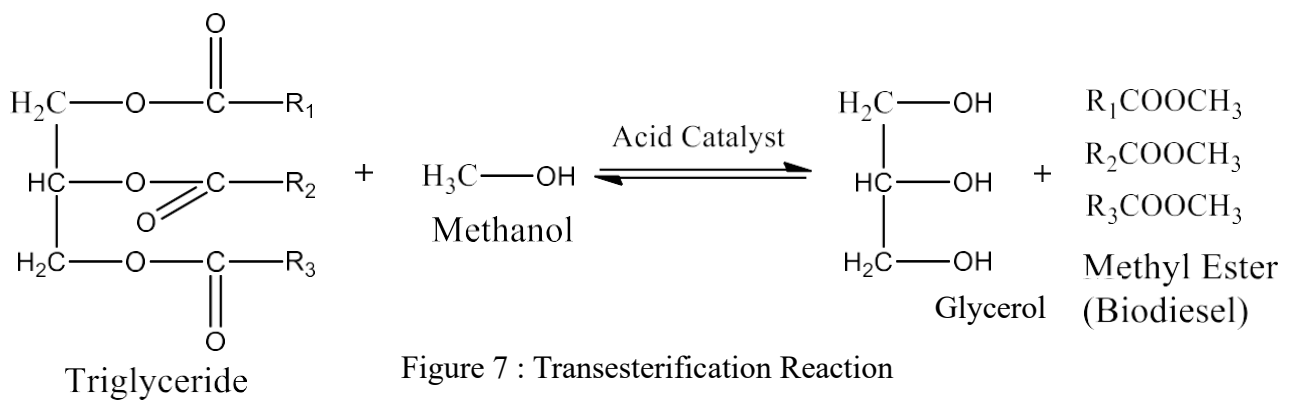
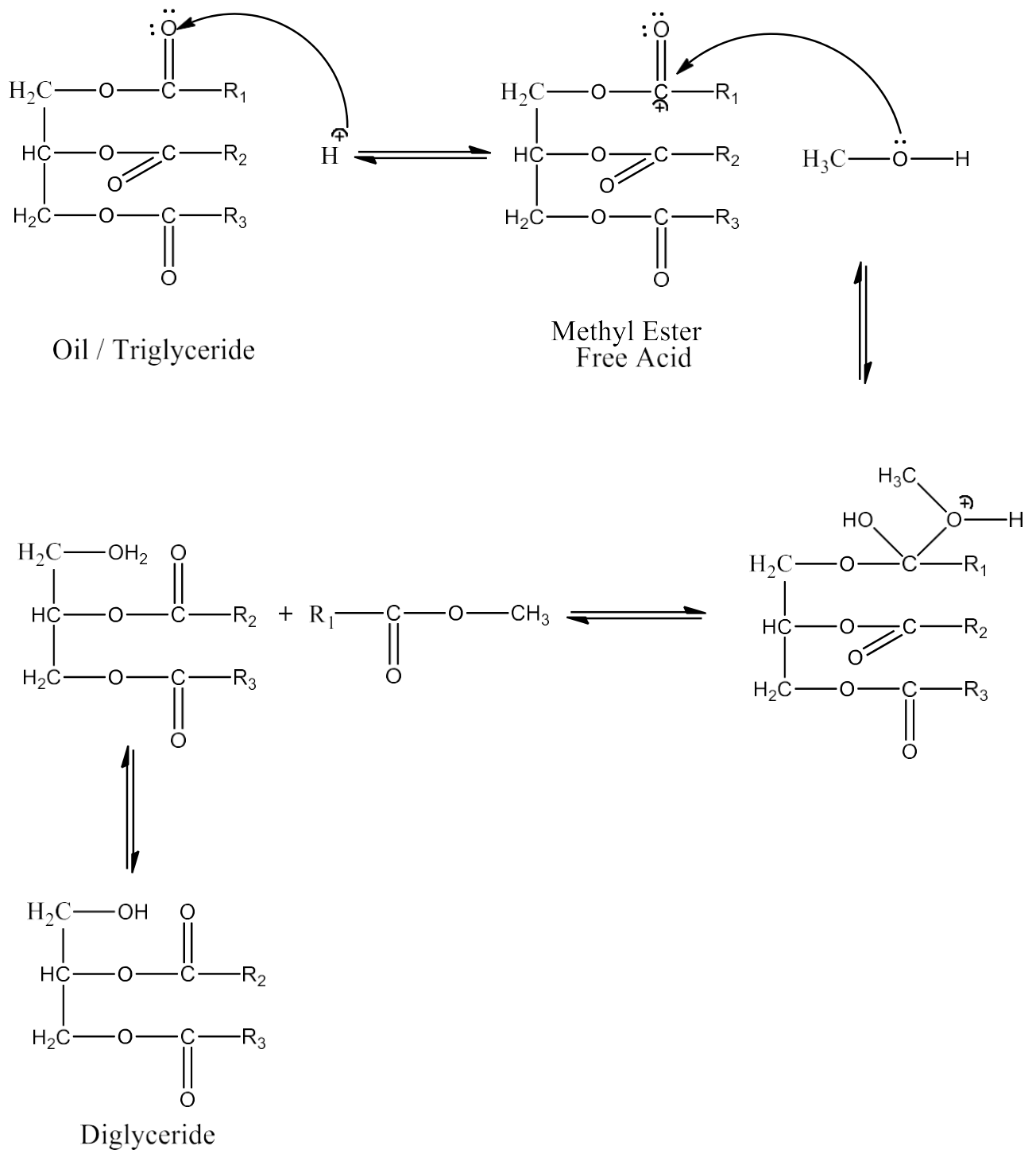


Figure 7 : Transesterification Reaction

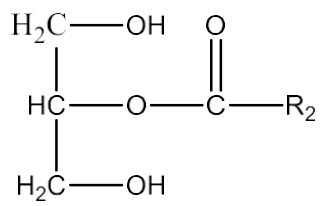
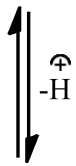
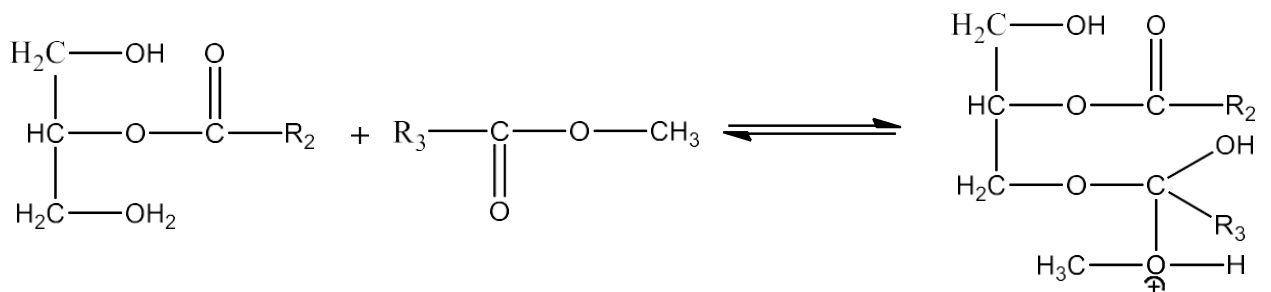
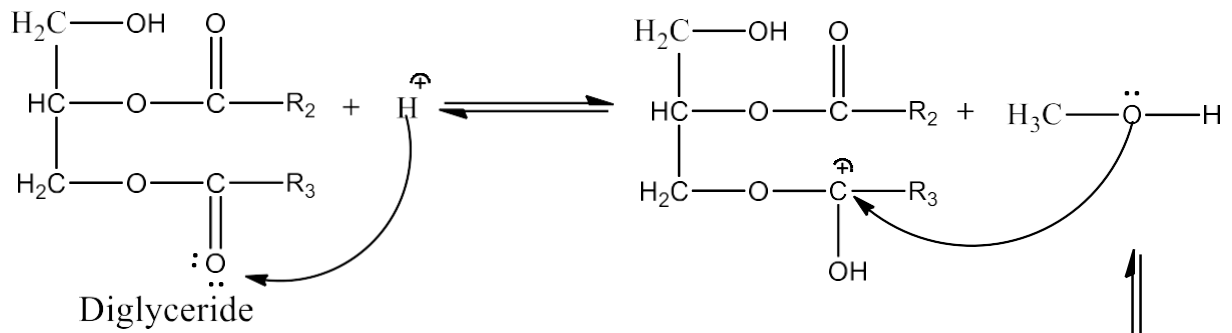
### 6.1 Mechanism:



STEP-1:

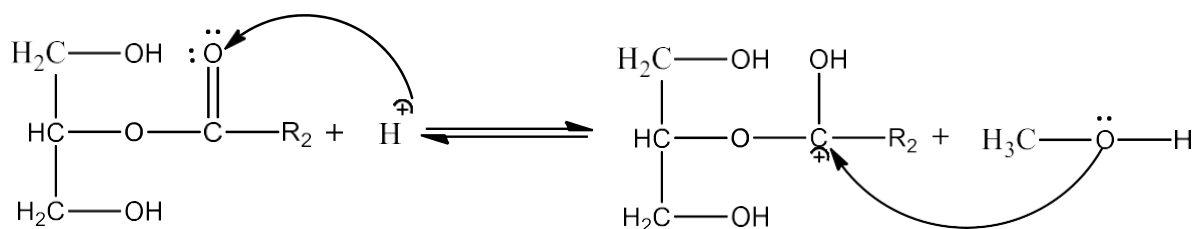


STEP-2:

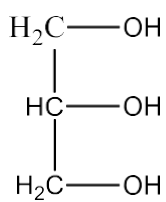
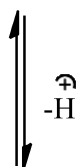
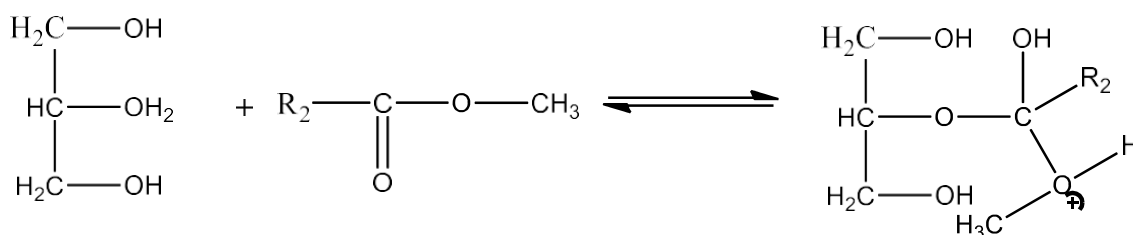


Monoglyceride

STEP-3:



Monoglyceride



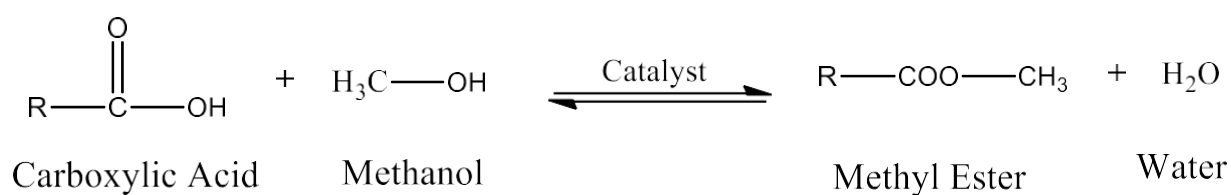
Glycerol

Figure 8 Transesterification Mechanism

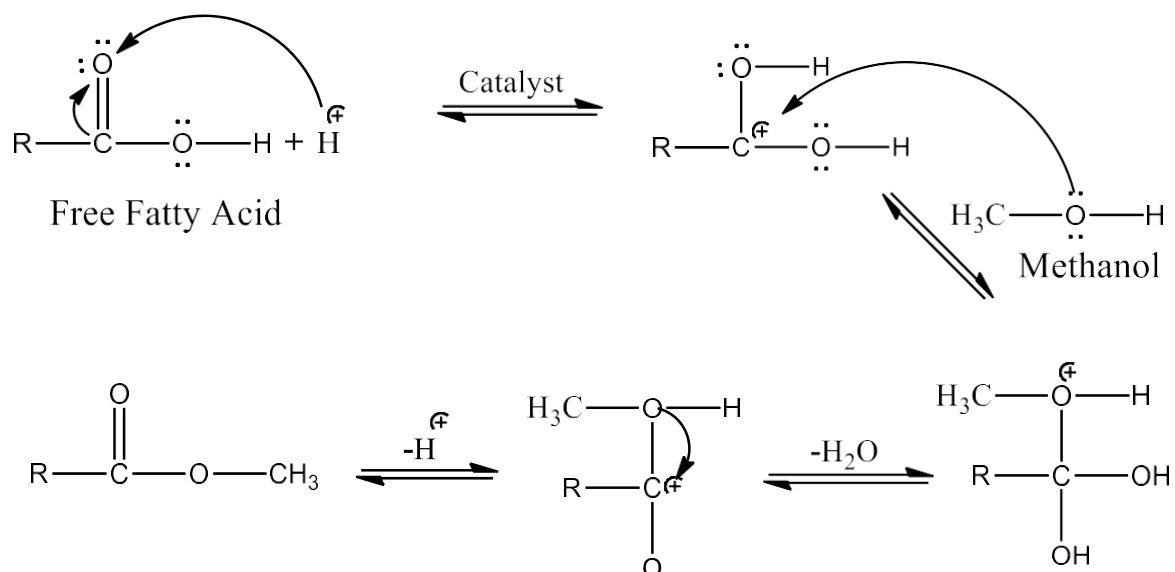
## 7 Esterification:

Esterification is reaction wherein reactant (alcohol and acid) form an ester as a reaction product. Ester is common in organic materials.

### 7.1 Esterification Reaction:



### 7.2 Mechanism:



## 8 Result Discussion:

Table 1 Result of % (Yield of Biodiesel with varying reaction parameters)

Sr. No.	O:M Molar ratio	PNSA-Si %(w/w)	Reaction Temp. (°C)	Reaction Time (t)	Yield
1.	1:9	5	65	6	60.12%
2.	1:9	5	65	7	62.54%
3.	1:9	5	65	8	66.52%
4.	1:9	5	65	9	67.23%
5.	1:9	5	65	10	70.03%
6.	1:10	5	65	6	72.56%
7.	1:10	5	65	7	75.25%
8.	1:10	5	65	8	73.25%
9.	1:10	5	65	9	73.89%
10.	1:10	5	65	10	76.96%
11.	1:11	5	65	6	75.88%
12.	1:11	5	65	7	77.36%
13.	1:11	5	65	8	78.52%
14.	1:11	5	65	9	79.45%
<b>15.</b>	<b>1:11</b>	<b>5</b>	<b>65</b>	<b>10</b>	<b>82.63%</b>
16.	1:12	5	65	6	67.25%
17.	1:12	5	65	7	65.52%
18.	1:12	5	65	8	66.78%
19.	1:12	5	65	9	67.48%
20.	1:12	5	65	10	68.25%
21.	1:11	1	65	10	52.96%
22.	1:11	2	65	10	53.58%
23.	1:11	3	65	10	58.45%
24.	1:11	4	65	10	59.64%

25.	1:11	6	65	10	62.52%
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The experimental results demonstrate that the biodiesel yield varies depending on the oil molar ratio, catalyst concentration, reaction temperature, and reaction time used. A biodiesel yield of 70.03% was obtained with a 1:9 oil molar ratio, 5% (w/w) catalyst, 65°C reaction temperature, and 10-hour reaction time. Similarly, a yield of 79.45% was obtained with a 1:11 oil molar ratio, 5% (w/w) catalyst, 65°C reaction temperature, and 9-hour reaction time. **A biodiesel yield of 82.63% was obtained with a 1:11 oil molar ratio, 5% (w/w) catalyst, 65°C reaction temperature, and 10-hour reaction time.** However, when the catalyst concentration was decreased to 1%, a biodiesel yield of only 52.07% was obtained with the same reaction conditions. With the same oil molar ratio, reaction temperature, and time, biodiesel yields increased as the catalyst concentration was increased from 2% to 6%, with yields of 53.58%, 58.45%, 69.64%, and 62.52%, respectively.

## 9 Spectral Characterization:

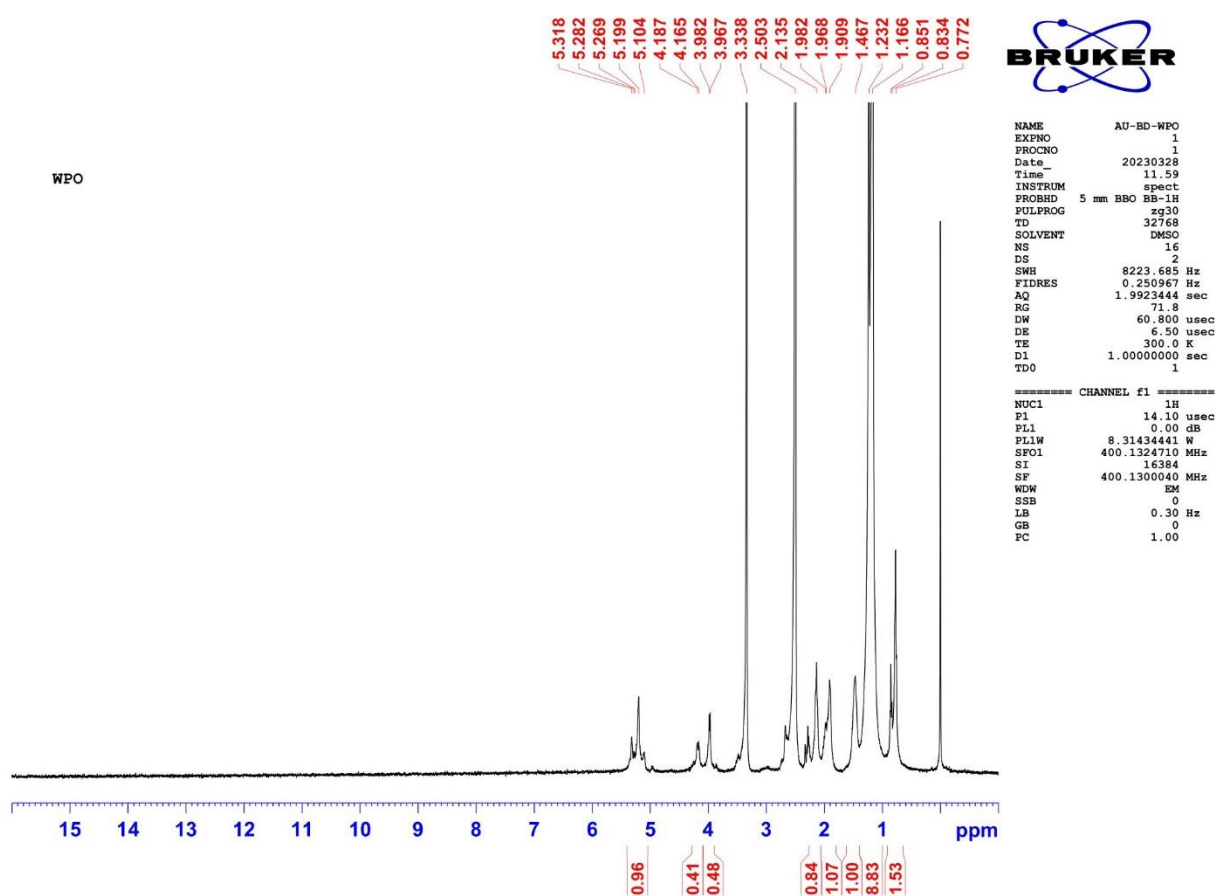


Figure 9 <sup>1</sup>H NMR of Waste Palm Oil

Figure 6 shows the <sup>1</sup>H NMR spectrum of waste palm oil obtained using a 400 MHz NMR spectrometer. The spectrum exhibits several distinct peaks corresponding to different proton environments in the oil. The peak at 1.16 and 1.23  $\delta$ ppm is attributed to the protons in the alkane group of the triglycerides which containing an 8H. The peak at 2.503 ppm corresponds to the protons in the -CH=CH- group, indicating the presence of unsaturated fatty acids in the oil. The peak at 3.518 ppm corresponds to the protons in the -OCH<sub>2</sub>- group of the triglyceride backbone, indicating the presence of glycerol esters in the oil. while the peak at 3.33- 3.90  $\delta$ ppm corresponds to the protons in the -OCH<sub>3</sub> group. The peak at 5.1-5.3  $\delta$ ppm is associated with the alkene group.

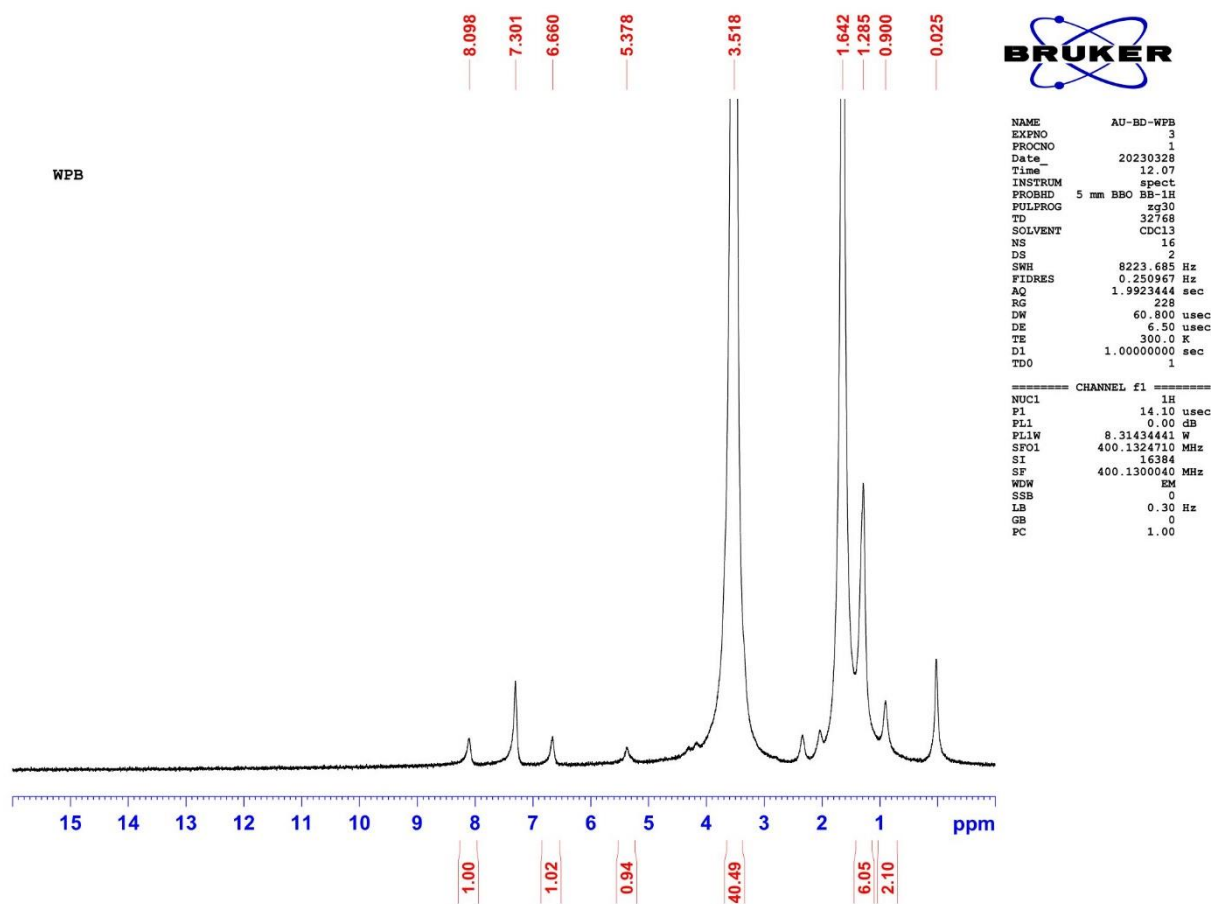


Figure 10  $^1\text{H}$  NMR of Waste Palm Biodiesel

Figure 7 shows the  $^1\text{H}$  NMR spectrum of waste palm Biodiesel obtained from the acid-catalyzed hydrolysis of palm oil. The spectrum displays characteristic peaks corresponding to various functional groups present in the sample. The peak at  $0.9 \delta\text{ppm}$  was assigned to the protons on the  $\text{CH}_3$  group of the fatty acid methyl esters (FAMES), while the peak at  $1.3 \delta\text{ppm}$  corresponds to the protons in the  $-\text{CH}_2-$  group long chain. The peak at  $\delta 1.3-1.6 \text{ ppm}$  is associated with the terminal  $-\text{CH}_2-$  group containing 6H, while the peak at  $3.518 \delta\text{ppm}$  corresponds to the protons in the  $-\text{OCH}_2-$  group of the triglyceride backbone, there is small peak of alkene at  $5.378 \delta\text{ppm}$  and  $7.301 \delta\text{ppm}$  is corresponding to  $-\text{C}=\text{O}-$  carbonyl group. **In this two  $^1\text{H}$  NMR we show that in the biodiesel NMR the peak at 5 ppm is removed which shows the alkene is converted to alkane and the 7ppm is also generated which shows the formation of carbonyl group.**



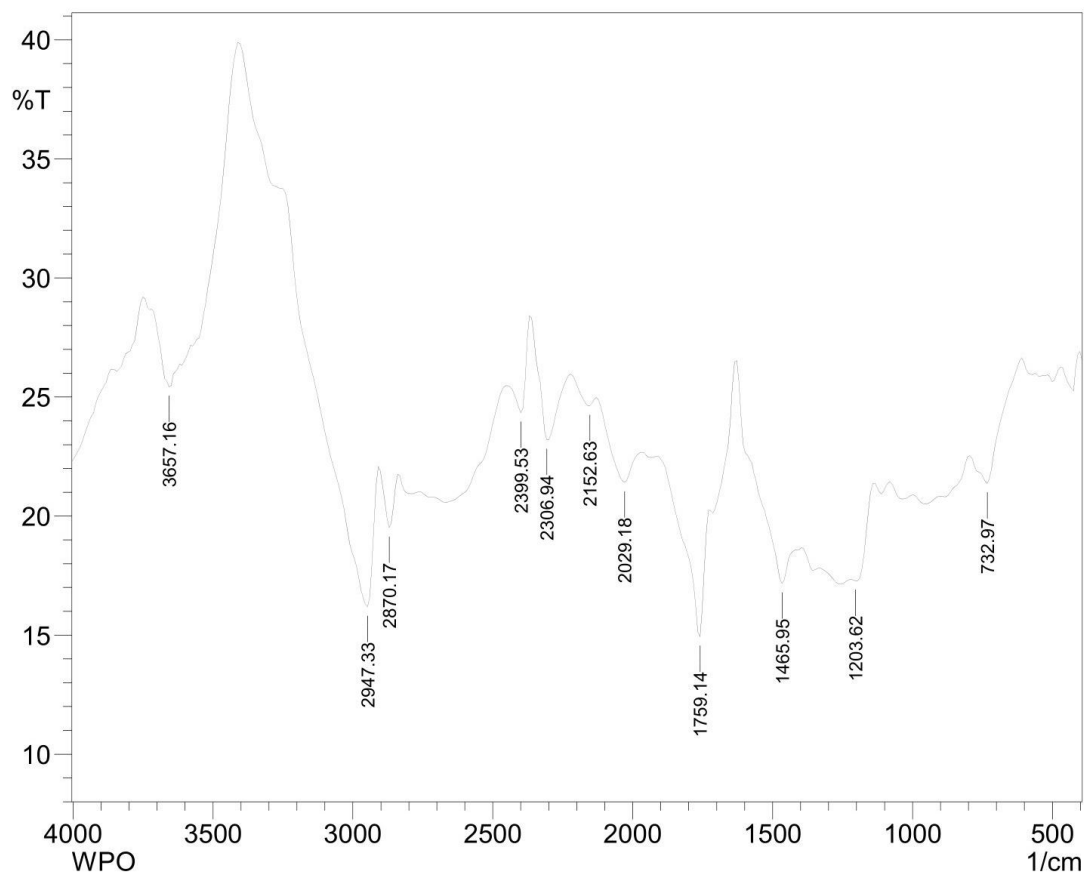


Figure 11 FT IR of Waste Palm Oil

Figure 8 shows the Fourier-transform infrared (FT IR) spectrum of waste palm oil. The spectrum displays several characteristic absorption bands, indicating the presence of various functional groups in the sample. The broad absorption band at around 3657  $\text{cm}^{-1}$  corresponds to the stretching vibration of O-H groups in carboxylic acids and hydroxyl compounds. The absorption band at 1760  $\text{cm}^{-1}$  indicates the presence of ester groups, which are commonly found in triglycerides. The band at 1465  $\text{cm}^{-1}$  corresponds to the bending vibration of C-H groups in the CH<sub>2</sub> and CH<sub>3</sub> groups. Finally, the band at 1203  $\text{cm}^{-1}$  is due to the stretching vibration of C-O groups in esters.

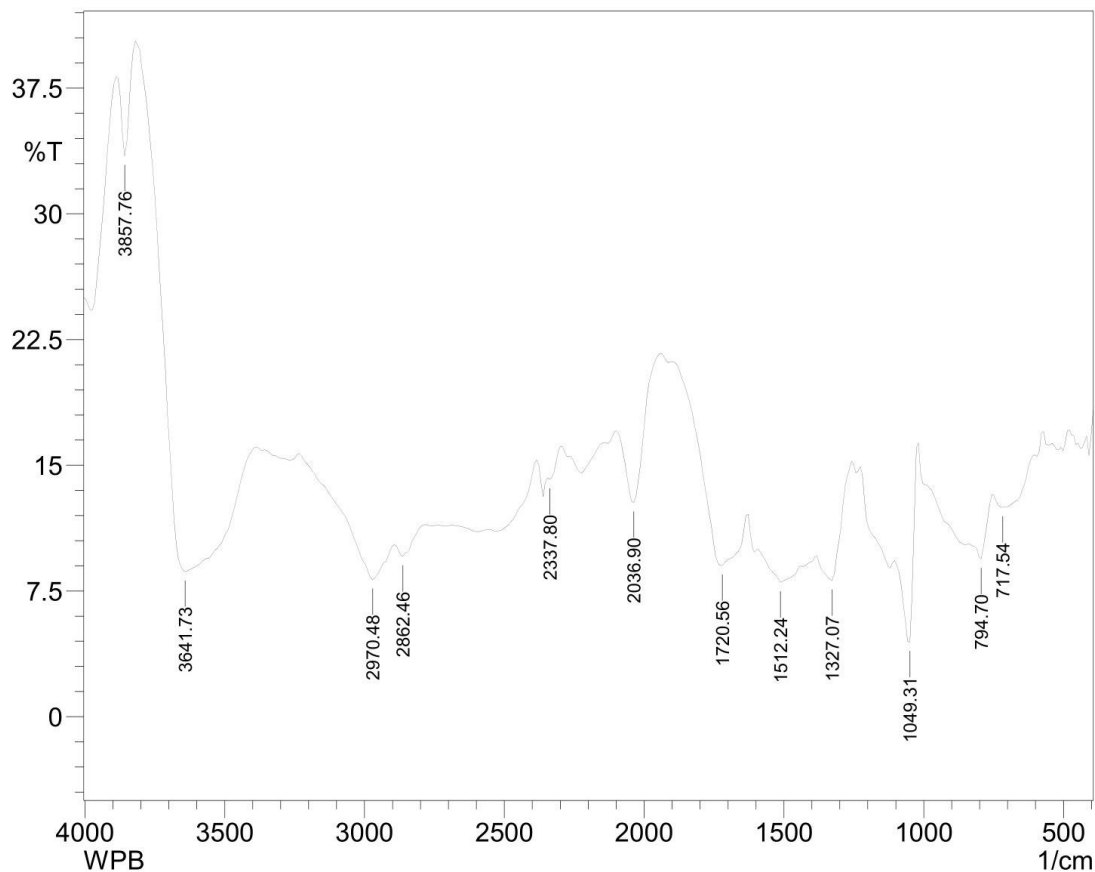


Figure 12 FT IR of Waste Palm Biodiesel

The figure 9 FT IR spectra of the waste palm biodiesel sample showed distinct absorption bands at various wavenumbers. The peak observed at around 3400  $\text{cm}^{-1}$  corresponds to the O-H stretching vibration of the carboxylic acid group (-COOH) present in the biodiesel. The strong peak at around 2900  $\text{cm}^{-1}$  represents the C-H stretching vibration of the methyl group (-CH<sub>3</sub>) in the biodiesel. The absorption band at 1720  $\text{cm}^{-1}$  corresponds to the C=O stretching vibration of the ester group (-COO-) in the biodiesel.

## 10 Conclusion:

A solid acid catalyst is a solid with acidic properties used in acid-catalysed reactions. Heterogeneous catalysts are in a different phase than reactants, allowing easy separation for recycling. A novel solid acid catalyst is both heterogeneous and reusable, meaning it can be separated and reused multiple times without losing activity. This is cost-effective and eco-friendly. The combination of solid acid catalyst, heterogeneity, and reusability make it ideal for various chemical processes.

Based on the information given, a biodiesel yield of 82.63% was obtained using a novel solid catalyst under the following conditions: 1:11 oil molar ratio, 5% (w/w) catalyst, 65°C reaction temperature, and 10-hour reaction time.

This indicates that the novel solid catalyst is effective in promoting the transesterification reaction to convert the oil feedstock into biodiesel. A yield of 82.63% is considered a good result for biodiesel production, and it suggests that the novel solid catalyst is performing well under the given conditions.

Moreover, the low catalyst loading of 5% (w/w) is also a positive factor as it indicates that the catalyst is highly active and efficient. The reaction temperature of 65°C and the reaction time of 10 hours are also reasonable and practical for a biodiesel production process.

In conclusion, the synthetic transformation of lower cost feedstocks to biodiesel using novel solid acid catalysts has shown promising results. This process has the potential to reduce the cost of producing biodiesel and increase its availability as a sustainable alternative to fossil fuels. The use of solid acid catalysts has advantages over traditional liquid acid catalysts, including improved stability, ease of separation from the reaction mixture, and reduced environmental impact.

## 11 References:

1. Azcan, N., Turan, S., & Aksoy, H. A. (2020). Biodiesel production from waste cooking oil using a novel solid acid catalyst. *Journal of Environmental Chemical Engineering*, 8(2), 103816.
2. Bajaj, H. C., Sharma, S., Singh, B., Upadhyay, S. N., & Kumar, A. (2018). Biodiesel production using solid acid catalysts: A review. *Renewable and Sustainable Energy Reviews*, 82, 3482-3496.
3. Basha, S. A., & Murugesan, A. (2016). A review on biodiesel production, combustion, emissions and performance. *Renewable and Sustainable Energy Reviews*, 57, 496-508.
4. Bayramoglu, G., Kaya, M., & Tüter, M. (2020). Biodiesel production from waste cooking oil using a solid acid catalyst supported on natural clay. *Fuel*, 261, 116428.
5. Chuah, L. F., Yusup, S., & Choong, T. S. Y. (2017). Recent advances in solid acid catalysts for biodiesel production. *Renewable and Sustainable Energy Reviews*, 73, 579-597.
6. Fadhil, A. B., & Abdullah, B. (2019). Advances in heterogeneous solid acid catalysts for biodiesel production: A review. *Renewable and Sustainable Energy Reviews*, 107, 254-280.
7. Jafari, S. M., Ghogh, F. M., & Safekordi, A. A. (2019). Biodiesel production from waste cooking oil using a solid acid catalyst supported on a natural clay nanocomposite. *Journal of Molecular Liquids*, 287, 110995.
8. Khojasteh, S. A., & Pourmousavi, S. M. (2019). A review on solid acid catalysts for biodiesel production. *Renewable and Sustainable Energy Reviews*, 107, 328-349.
9. Kojima, Y., Martinez-Hernandez, A. L., & Kondo, J. N. (2018). Biodiesel production from waste cooking oil using a solid acid catalyst under solvent-free conditions. *Fuel Processing Technology*, 176, 207-213.
10. Kumari, S., Agrawal, Y. K., & Yadav, G. D. (2019). A review on solid acid catalysts for biodiesel production from non-edible oils. *Renewable and Sustainable Energy Reviews*, 102, 139-151.
11. Li, F., Li, Q., Liu, J., Wang, G., & Deng, X. (2021). Biodiesel production from *Jatropha curcas* L. oil using a novel solid acid catalyst. *Fuel*, 287, 119509.
12. Liu, S., Chen, X., Huang, Y., & He, Y. (2017). Catalytic properties of sulfonic acid-functionalized porous materials for biodiesel production: A review. *Renewable and Sustainable Energy Reviews*, 73, 635-647.

13. Pandey, A., & Datta, A. (2020). Biodiesel production from non-edible oils using solid acid catalyst: A review. *Renewable and Sustainable Energy Reviews*, 123, 109730.
14. Rani, M., & Varshney, A. (2020). Solid acid catalysts for biodiesel production: A review. *Fuel*, 278, 118334.
15. Chitra, S., & Siva Kumar, N. (2020). Recent trends in the production of biodiesel using solid acid catalysts. *Renewable Energy*, 155, 1315-1333.
16. Choudhary, V., & Karmakar, S. (2020). Solid acid catalysts for biodiesel production: A comprehensive review. *Fuel*, 264, 116945.
17. Dinh, T. N., & Lee, C. K. (2020). Recent advances in heterogeneous solid acid catalysts for biodiesel production from non-edible oils. *Renewable and Sustainable Energy Reviews*, 131, 109962.
18. Al-Tikrity, E. T., & Al-Karkhi, I. A. (2018). Biodiesel production using solid acid catalysts derived from waste materials: A review. *Renewable and Sustainable Energy Reviews*, 82, 1669-1680