EFFICACY AND OPTIMIZATION OF SUSTAINABLE BIODIESEL PRODUCTION FROM A BLEND OF NEEM AND YELLOW OLEANDER OILS USING A BIFUNCTIONAL CATALYST DERIVED FROM CHICKEN BONES AND DROPPINGS

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EDO STATE, NIGERIA

FEBRUARY, 2025

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A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING,

UNIVERSITY OF BENIN, BENIN CITY, NIGERIA

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOT THE AWARD OF

BACHELOR OF ENGNEERING IN CHEMICAL

FEBRUARY, 2025

CERTIFICATION

This is to certify that this research project was carried out by **I, NESTOR EMILE OPEYEMI** with matriculation number **ENG1905020** in the Department of Chemical Engineering, University of Benin, Benin City, Edo State Nigeria.

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DEDICATION

This project work is dedicated to God, for guiding and enlightening my path and to myself, for my perseverance and ingenuity.

And to my family; Mom, Sis and my brothers.

ACKNOWLEDGEMENT

For guiding me through the course of this study and always coming through in numerous unexpected ways, I want to offer my sincere gratitude to God.

I am grateful to my project supervisor, Engr. Prof. N.A. Amenaghawon, for his guidance and vast knowledge in the support of this project. It was indeed a learning phase for me.

Special appreciation goes to my project team members, for their unwavering support and commitment into completion of this project.

Special appreciations to my parents, Mr. and Mrs. Nestor, for their continuous interest in my welfare.

To my course mates and friends as well, notably, Voltman, Destiny, The Michaels, Khadijah, and a whole other, I appreciate the numerous inputs received.

And to my family, Mom, Bro, Sis, you will always have my gratitude.

Thank you.

ABSTRACT

This research aimed to develop a sustainable and efficient method for making biodiesel from a mix of neem and yellow oleander oils, using a catalyst made from chicken bones. The oils' properties were examined, created and tested the catalyst, optimized the transesterification process, and checked that the biodiesel meets ASTM D6751 and EN14214 standards. The oil analysis looked at free fatty acids (FFA), viscosity, density, iodine value, and fatty acid profiles. Neem oil had an FFA of 5.2%, viscosity of 5.93 mm^2/s, and an iodine value of 76.4; yellow oleander oil had an FFA of 3.8%, viscosity of 4.02 mm^2/s, and iodine value of 73.86. The catalyst was prepared by calcining chicken bones at 800°C for 3 hours, resulting in calcium oxide with a surface area of 154 m^2/g. Tests with SEM, XRD, XRF, FTIR, and BET confirmed it was effective and stable.

By optimizing the transesterification process through Response Surface Methodology (RSM), a biodiesel yield of 88.46% was achieved. The optimal conditions identified were a methanol-to-oil ratio of 14:1, a reaction duration of 180 minutes, a catalyst loading of 6% by weight, all maintained at a steady temperature of 65°C. The statistical validation of the model was highly

reliable, with an R^2 of 0.9804, an adjusted R^2 of 0.9552, and a predicted R^2 of 0.7946. The comparison graph of actual versus predicted yields showed minimal discrepancies, and the 3D response surface plots illustrated how the various process factors interacted with each other.

Neem and yellow oleander oils are promising feedstocks for biodiesel. Using chicken bone catalysts offers an affordable and efficient alternative to traditional methods. The produced biodiesel meets ASTM D6751 and EN14214 standards, showing its potential as a renewable energy source. This research supports sustainable biodiesel, boosts food security, and promotes waste reuse, helping advance cleaner energy solutions.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF PLATES

LIST OF TABLES

.

NOMENCLATURE

AV = Acid Value (mg KOH/g)

SV = Saponification Value (mg KOH/g)

IV = Iodine Value (g I2/100g)

PV = Peroxide Value (meq/kg)

CN = Cetane Number

CP = Cloud Point (°C)

FP = Flash Point (°C)

KV = Kinematic Viscosity (mm^2/s)

D = Density (g/cm^3)

ASTM = American Society for Testing and Materials

FFA = Free Fatty Acid (%)

GC-MS = Gas Chromatography-Mass Spectrometry

SEM = Scanning Electron Microscopy

XRD = X-ray Diffraction

XRF = X-ray Fluorescence

BET = Brunauer-Emmett-Teller (Surface Area Analysis)

FTIR = Fourier Transform Infrared Spectroscopy

RSM = Response Surface Methodology

FAME = Fatty Acid Methyl Esters

KOH = Potassium Hydroxide

HCl = Hydrochloric Acid

NaOH = Sodium Hydroxide

ME: OL = Methanol Oil Ratio

R = Gas Constant

P = Pressure (atm)

T = Temperature (K)

V = Volume (L)

M = Molarity (mol/L)

CHAPTER ONE

INTRODUCTION

1.1. BACKGROUND OF STUDY

Earth's global energy resources contain the most significant potential for producing energy from all available sources. As the world's population grows, so does the demand for energy.

Global population growth, urbanization, and industrialization will all contribute to a continued significant increase in energy demand. Oil, coal, and renewable energy sources have all seen increases in global energy consumption as a result of this demand. It is still anticipated that oil, a fossil fuel, will rule the energy industry until 2050. But according to projections, the amount of energy coming from renewable sources will rise from 27 Exajoules (EJ) in 2018 to 114 EJ in 2040 and then to 161 EJ in 2050 (Awogbemi et al., 2021).

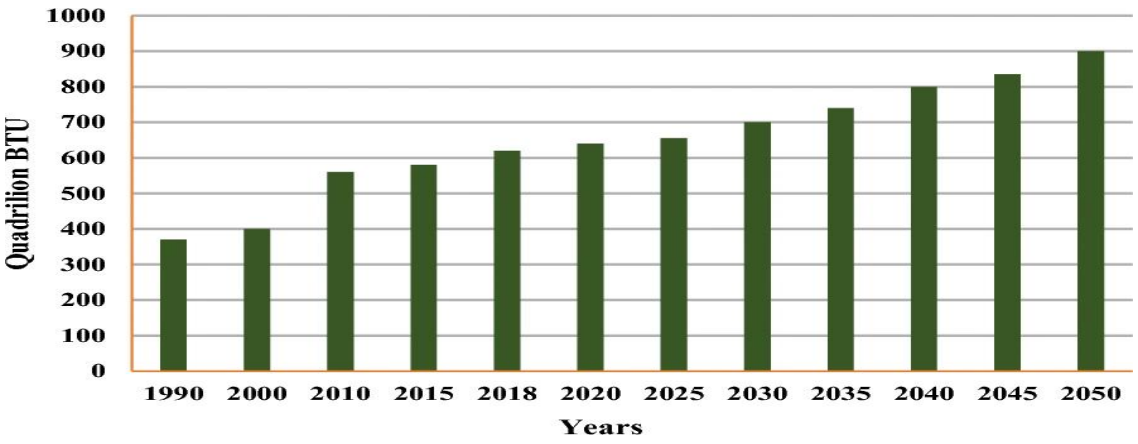


Figure 1. 1: Worldwide energy consumption from 1990 to 2050 (Ang et al., 2022)

80 % of the primary energy consumed in the modern world comes from fossil fuels. Of this total, the road transportation sector consumes 56 % of which 24 % is attributed to harmful carbon emissions (V. Gupta & Pal Singh, 2023).

Due to the depletion of fossil resources, rising petroleum prices, and hazardous greenhouse gas emissions, finding alternative energy sources to meet these demands has become essential (Babadi et al., 2022). Thus, using renewable fuels has become a must in order to provide energy that satisfies performance and environmental requirements. Over the past few decades, a significant amount of financial and human resources has been dedicated to the exploration, development, and utilization of renewable fuels such as biodiesel, bioethanol, biogas, and others. These fuels have gained recognition as viable alternatives to conventional non-renewable fuels. The numerous benefits of biodiesel have made it one of the most popular renewable fuels. The process of producing biodiesel must be accelerated in order to fulfill the growing demand for the fuel.

Additional reaction time, expense, energy consumption, temperature, and other harsh production conditions are associated with uncatalyzed biodiesel manufacturing. When producing biodiesel without the use of catalysts, conversion efficiency, reaction speed, and product yield are all low (Felix et al., 2017; Gutiérrez-López et al., 2022).

Biodiesel, or fatty acid methyl ester, is a biodegradable, renewable, nontoxic, viable, and environmentally friendly fuel for size replacement of systems that run based on fossil fuels (A. R. Gupta & Rathod, 2020; Mahmood Khan et al., 2020). It is a liquid fuel with almost similar physicochemical properties to traditional diesel fuels and offers several advantages: (1) high combustion efficiency due to its high cetane number (Vera-Rozo et al., 2022), (2) high flash

point—above 130 C, which makes it safe for storage and vehicle transportation; (3) excellent lubricity, low net emissions; (4) low viscosity; (5) a high octane number; and (6) is free of aromatics and sulfur, which prolongs the life span of diesel engines (Xie & Wan, 2018, 2019; Xie & Wang, 2020). Moreover, biodiesel reduces the exhaust emission of particulate matter, unburned hydrocarbons, and carbon monoxide into the atmosphere, (V. Gupta & Pal Singh, 2023). This results in lesser hydrocarbon emissions by 67%, particulate matter by 47%, and greenhouse gas emissions by 86% (Farouk et al., 2024). Other advantages of biodiesel utilization include engine performance and the ability to be directly homogenized with petrodiesel without altering the design of the engine or required parameters (Ma & Liu, 2019; Oyekunle et al., 2023). However, the challenge remains for researchers, manufacturers, and the scientific community: producing high-purity biodiesel. One of the many strategies to produce biodiesel is the transesterification process; it is the simplest and most economical one (Mendonça et al., 2019; Xie & Wan, 2019). Generally, biodiesel is produced by triglyceride transesterification, found in non-edible oils, edible oils, and animal fats with low-density alcohol like ethanol or methanol, in the presence of a suitable catalyst (Bekhradinassab et al., 2022; Oyekunle & Oyekunle, 2018).

The transesterification process is also called ''alcoholysis". In organic chemistry, transesterification is defined as the process in which the organic group of an ester is exchanged with the organic group of alcohol (V. Gupta & Pal Singh, 2023).

The transesterification reaction involves four unique factors; reaction time, temperature, methanol-to-oil ratio, and catalyst concentration. Triglycerides are converted to fatty acid alkyl

ester using a catalyst to increase the rate of synthesis. The alcohol to oil molar ratio also highly affects the yield of biodiesel. When there is not enough methanol, a reverse reaction occurs; hence, the output drops. On the other hand, when there is too much alcohol, a higher conversion rate results, which raises the yield (V. Gupta & Pal Singh, 2023).

Moreover, methanol, with its polar hydroxyl group, causes emulsification of both the biodiesel and glycerol produced during the reaction. This will favor the reverse reaction, or recombination of glycerol and esters, to lower the output of biodiesel. Therefore, it is essential to keep in mind that the transesterification process is reversible, and that large quantities of alcohol are required to keep the reaction moving. In general, it has been found that with an increase in reaction time, biodiesel yield increases. Nevertheless, too much reaction time also reduces biodiesel yield, causing it to decrease.

On the other hand, it is found that a rise in temperature speeds the reaction and increases yield. This may be because raising the temperature causes the viscosity of the oil to decrease, which improves the mixing of the oil with the alcohol, and speeds up the separation of glycerol from biodiesel. The type and quantity of the catalyst used in the reaction significantly affect the reaction time and temperature (Vishal et al., 2020).

According to (Alsaiari et al., 2023), the by-product glycerol is usable in the production of glycerol fuels and the cosmetics industry. It can also be used in water electrolysis technology instead of oxygen evolution reaction (Ghaith et al., 2020; Mawlid et al., 2022).

A catalyst is a substance that increases the rate of a chemical reaction without changing the reaction itself. Factors such as activation energy, temperature, reactant concentration, pressure, surface area, and the chemical nature of catalysts, along with the presence of promoters or inhibitors, can change the thermodynamic response speed and give guidance on the rate at which experiments proceed.

The presence of a catalyst has no effect on the reaction's equilibrium constant because it affects the reaction uniformly. During the initial phase of the reaction, the amount of stimulus should be used in a lower quantity to give the reaction enough time to finish, while increasing the amount can reduce the amount of biodiesel produced by diffusion reactions (V. Gupta & Pal Singh, 2023).

It becomes more difficult to produce biodiesel as the catalyst amount is increased since it causes emulsions to form and increases viscosity. When esterification is used to treat free fatty acids (FFA), water is produced as a byproduct. Water presence lowers catalytic reactivity, which lowers biodiesel output. The production of biodiesel is significantly influenced by the alcohol to oil molar ratio. Lower methanol volumes cause the opposite reaction, which lowers the amount of biodiesel produced; greater alcohol volumes cause a higher conversion reaction, which raises the amount of biodiesel produced.

1.2. PROBLEM STATEMENT

Global dependence on fossil energy sources has engendered critical environmental and economic problems, including greenhouse gases emissions, global warming, and unstable oil

prices. With the growing population and economic upsurge, which consequentially increases the energy demand, there is a need to find sustainable and renewable energy sources in Nigeria.

Biodiesel is one of the renewable and environmentally friendly options as an alternative fuel that has come up. It is processed by transesterification of vegetable oils, animal fats, or waste oils with catalysts. Homogeneous catalysts have conventionally been utilized in the production of biodiesel; however, there are several drawbacks associated with these catalysts, which include problems in separation, non-reusability, and soap and wastewater generation.

New developments in the heterogeneous catalysis area are again bringing reason to hope for a solution to these problems. Heterogeneous catalysts, being in a different phase than the reactants, make them easily separable and reusable—which reduces the cost of production and harm to the environment. Different heterogeneous catalysts, like solid acid, solid base, and bio-catalysts, have been tested or considered to show potential for being used in improving the yield and efficiency of biodiesel. Consequently, the use of a heterogeneous catalyst, which addresses all of these issues, becomes a compelling choice.

Materials constitute over 70% of the production expenses. Various strategies have been implemented to mitigate these costs, including the utilization of non-edible oils, cost-effective cooking oils, and animal fats (Mandari & Devarai, 2022). Nonetheless, the use of edible oils, such as sunflower oil, palm kernel oil, soybean oil, and corn oil, is being discouraged to prevent the food versus fuel dilemma (Amenaghawon et al., 2022). Recently, (Kusuma et al., 2024) reported an improved biodiesel yield through the combination of two non-edible oils. However,

achieving optimal overall biodiesel yield hinges on accurately identifying the ideal blending ratios for these oils.

1.3. AIM AND OBJECTIVES

1.3.1. Aim:

This research aims to explore the feasibility of utilizing a blend of non-edible oils, specifically neem and yellow oleander oils, as a sustainable feedstock for biodiesel production.

1.3.2. Objectives:

The study encompasses the following key components:

1. Individual characterization of each oil
2. Creation of an oil blend
3. Numerical optimization to refine the oil blend composition
4. Assessment of the oil blend to evaluate its properties

1.4. SCOPE OF STUDY

This research was conducted at the Bio-resources Valorization Laboratory at the University of Benin, located in Benin City. Neem and Yellow Oleander oils were sourced locally. An optimal design was employed to determine the proportions of the oil blend to be examined for the viability of sustainable biodiesel production.

It will also compare the catalytic activities, reusability, and efficiencies of the chicken bones-derived catalysts in an analysis of their transesterification process with conventional catalysts for commercial viability. Environmental and economic impacts arising from using agricultural

waste as catalysts will also be assessed in this bid, delineating possible cost savings and even reducing problems associated with waste disposal.

1.5. RELEVANCE OF STUDY

The study's significance stems from its ability to drastically lower the price of producing biodiesel by using chicken bones and droppings—a cheap and easily accessible waste product—as catalysts. Wider acceptance of biodiesel may result from this cost reduction, which can make it a more attractive substitute for fossil fuels.

By lessening the environmental effect of waste disposal and encouraging the recycling of organic materials, the use of agricultural wastes as catalysts supports sustainable waste management techniques. By creating effective and affordable catalysts, this research also advances renewable energy and increases the viability of biodiesel as a sustainable energy source. This can lessen dependency on fossil fuels and increase energy security.

Overall, this study provides a sustainable, cost-effective, and environmentally friendly solution to current challenges in the biodiesel industry.

CHAPTER TWO

2.0. LITERATURE REVIEW

2.1. BIODIESEL

Biodiesel, a liquid biofuel made from vegetable or animal fats and alcohol, can be used in diesel engines either by itself or in combination with diesel oil. Animal fats and vegetable oils, both edible and non-edible, are renewable biological sources that are used to make biodiesel, an alternative fuel. For use in diesel engines, biodiesel is defined as a blend of long-chain monoalkylic esters from fatty acids derived from renewable resources, per the American Society for Testing and Materials (ASTM) 6751 standard specification.

The primary method for biodiesel production, known as transesterification, generally entails the reaction between an alkyl alcohol and a long-chain ester in the presence of a catalyst, resulting in the formation of mono-alkyl esters (biodiesel) and glycerol (Verma & Sharma, 2016). Biodiesel is characterized as a renewable diesel fuel composed of mono-alkyl esters of long-chain fatty acids sourced from vegetable oils or animal fats. The process involves the reaction of lipids with alcohol, yielding fatty acid esters. Despite the significant differences in chemical composition between biodiesel and petroleum-derived diesel, their combustion characteristics, including energy content and cetane ratings, are remarkably similar. This similarity positions biodiesel as a viable alternative to conventional petroleum diesel. It can be utilized in its pure form (B100) or blended with petroleum diesel at various concentrations, making it compatible with most diesel engines equipped with injection pumps.

The production of biodiesel and its application within the transportation sector and other industrial processes is an area that warrants increased research attention. Recent studies have concentrated on biodiesel and the methodologies for its production. This fuel is recognized for its non-toxic, biodegradable, and renewable properties, produced through the alcoholysis of plant oils or animal fats, utilizing either homogeneous or heterogeneous catalysts (Maheshwari et al., 2022).

2.1.1. Historical Development of Biodiesel

Rudolf diesel invented the diesel engine in the 1890s (4). By the time he showed his engine at the world exhibition in Paris in 1900, his engine was running on 100% peanut oil (Owolabi et al., 2012). However, because cheap petroleum fuels were easily available, few people were interested in alternatives (V. Gupta & Pal Singh, 2023).

During World War II (1939-1945), when petroleum fuel supplies were interrupted, vegetable oil was used as fuel by several countries. However, when the war ended and petroleum supplies were again cheap and plentiful, vegetable oil fuel was forgotten.

The petroleum embargo of the 1970s caused many countries to look to vegetable oil as a possible fuel but the viscosity (thickness) of the vegetable oil caused damage to the engines. Scientists then conducted experiments to convert the vegetable oil into biodiesel. The word “biodiesel” was probably first used in about 1984 (Van Gerpen, 2005).

The first biodiesel manufacturing plant specifically designed to produce fuel was started in 1985 at an agricultural college in Austria. Biodiesel was first manufactured commercially in 1991 in Kansas City, Missouri (Van Gerpen, 2005).

The establishment and commercialization of biodiesel in many countries around the world has triggered the development of standards to ensure and promise high quality of product and user confidence. Two of the widely used biodiesel standards are ASTM D6751 (ASTM = American Society for Testing and Materials) and the European standard EN14214 (Solaimuthu et al., n.d.).

In order to mitigate the issue of high viscosity in vegetable oils, a variety of synthetic techniques have been proposed. Traditional methods such as pyrolysis, micro emulsion, direct blending, and transesterification have been utilized, alongside more innovative approaches including in-situ transesterification, reactive distillation, microwave technology, membrane technology, ultrasound-assisted transesterification, and non-catalytic supercritical fluid technology (Athar et al., 2020; Bhatia et al., 2021; Qadeer et al., 2021; Tan et al., 2019).

2.1.2. Biodiesel Development Status in Nigeria

The initiative for biofuels development in Nigeria originally came from the private sector, though it did not take too long to get the government to buy-in. Mitigation of climate change is often presented by governments as a key policy goal for biomass fuel developments, but in the case of Nigeria, the government is explicit about its reasons for promotion of biofuels. The reasons, among others, are energy security through the use of biofuels and to improve the balance of trade by import substitution and new export market development. Following population growth and economic development, the need for more modern fuels has increased significantly over the years.

In general, the demand for petroleum in the country indicates that there is a gradual increase from a year of 2000 to 2008. A Biofuels Development and Utilization Strategy have been formulated by the

Ministry of Mines and Energy in August 2007. The objective of the strategy is to facilitate sufficient production of biofuels from indigenous resources so as to substitute imported petroleum and export excess products. The biofuels strategy document identified some energy crops such as sugarcane, Jatropha, castor and palm trees as potential feedstock for biofuels production.

2.2. PROPERTIES AND COMPOSITION OF BIODIESEL

Biodiesel known as an environmentally friendly fuel that produces energy approximately equal to the diesel fuel. Hence it can be considered as the most efficient alternative to diesel fuel. Biodiesel is considered approximately free of sulfur fuel (sulfur-free <10 ppm) and a total reduction of pollutants such as carbon dioxide, unburned hydrocarbons and smoke is visible compared to diesel fuel. Biodiesel is an alternative fuel with a high flash point, with low emissions and high security that can be used in existing diesel engines and equipment used (Hasheminezhad et al., 2018). Biodiesel stands out among all of these biodegradable fuels as being the one that most closely resembles conventional diesel in terms of its physicochemical properties like low aromatic and sulphur content, high viscosity, low volatility, low calorific value, lubricity, high flash point and cetane content, and overall feedstock renewability, which can guarantee particulate matter by 47%, hydrocarbon emission by 67%, and approximately 70–90% reduction in GHG emission. These properties make them useful in several automobiles including ships, cars and airplanes (O Amune & K Otoikhian, 2022).

Biodiesel exhibits chemical and thermal properties which are significantly similar to diesel fuels. Biodiesel has a higher cetane number; and thus more suitable for combustion in a diesel engine. Biodiesel has a good lubricant and can compensate for the loss of lubricant due to the removal of sulphur from the blend with low sulphur diesel fuel. Instead of using biodiesel, blended biodiesel can

be used for the diesel engine; blended biodiesel is a blend of diesel and biodiesel. Biodiesel is completely miscible with diesel. Blending can be done at any rate to improve fuel properties. However, due to the variant chemical nature of biodiesel and diesel, changes in physicochemical properties can occur, affecting engine performance and emissions (Miyuranga et al., 2022).

(Peng et al., 2018) reported that Biodiesel had been considered the most favorable substitute for conventional petroleum-based diesel because it is biodegradable, energy efficient, non-toxic, and most importantly, environmentally benevolent. However, one of the major impediments to biodiesel marketability has been ascribed to its high cost, because of the cost of vegetable oil. Furthermore, the biodiesel price is nearly 1.5 times greater than the diesel gasoline petroleum price. Among many alternative renewable, biodiesel has attracted greater attention for some reasons.

Biodiesel can be produced from various feed stocks, oils and fats of varying origin and quality. It can be produced from various resources, including waste cooking oil and grease trap waste. The diesels produced from these different sources are of different qualities and therefore need to meet the standard condition for biodiesel which is specified by ASTM D6751. The parameters which define the quality of biodiesel include the following:

2.2.1. Density

Density is defined as the mass per unit volume of a substance, it is defined mathematically as:

$$\rho = \frac{m}{v}$$

The density of a material varies with temperature and pressure. Density is a very important fuel

property because it affects the mass of fuel injected into the combustion chamber, and thus air-fuel ratio which affects the engine performance. Biodiesel density mainly depends on its ester content and the remained quantity of alcohol, hence the density of biodiesel is affected mainly by the feedstock used for the biodiesel production.

Fuel density significantly impacts other critical characteristics of fuel, such as cetane number and calorific value (Krishnasamy & Bukkarapu, 2021). Consequently, density is an essential attribute of fuel that influences its application in diesel engines. The fuel density at a specified temperature can be measured using a conventional pycnometer (Baier & Seebacher, 2019; Gülüm & Bilgin, 2017). The EN-ISO 12185 and EN-ISO 3675 standards outline the appropriate testing procedures. Biodiesel density is assessed at 15 ◦C to evaluate fuel quality (Krishnasamy & Bukkarapu, 2021). In comparison to methyl ester fuels, pyrolysis-derived liquid fuels exhibit a greater density (approximately 980 kg/m3) (Alagu & Sundaram, 2018; Kalargaris et al., 2017). Diesel generally has a lower density than biodiesel, and the density of the blend improves as the proportion of biodiesel increases. Moreover, the level of unsaturation influences the density of fatty acid methyl esters (FAME) (Sharma et al., 2019). Apart from composition, temperature, and purity—particularly water content—also affect biodiesel density. As illustrated in Figure 2.1, biodiesel density decreases at elevated temperatures and increases under higher pressures (Krishnasamy & Bukkarapu, 2021). These variations impact the mass of fuel injected per cycle and the mixture distribution within the combustion chamber.

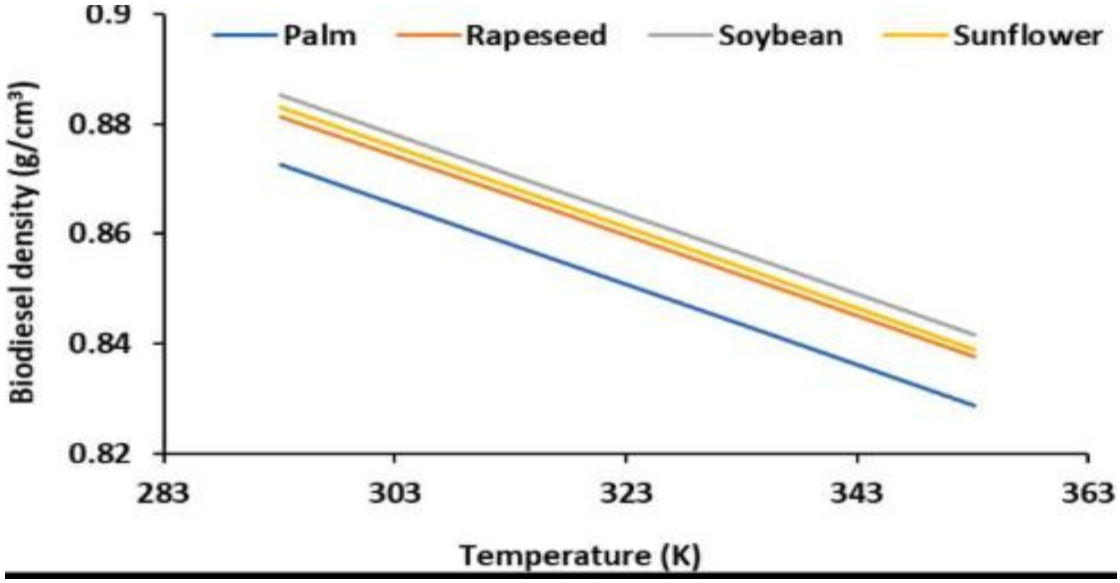


Figure 2. 1: Temperature's effects on biodiesel density made from various feedstocks source (Krishnasamy & Bukkarapu, 2021)

2.2.2. Specific Gravity

Specific gravity is the ratio of the density of a substance to the density of a reference substance. The reference substance for liquids is water while that for gases is air. Mathematically, for a liquid, the specific gravity (SG) is given as:

$$SG = \frac{\rho liquid}{\rho water}$$

2.2.3. Viscosity

The viscosity of a fluid is the measure of its resistance to gradual deformation by shear stress or tensile stress. It can also be referred to as a measure of the fluid's resistance to flow due to internal friction.

Kinematic viscosity is the measure of the inherent resistance of a fluid to flow when no external force is exerted, except gravity, it is the ratio of the dynamic viscosity to its density.

Viscosity is an important property of biodiesel because it affects the engine fuel injection system predominantly at low temperatures. A highly viscous fuel will result in poor fuel atomization, incomplete combustion and carbon deposition on the injectors. High viscosity also leads to loss of engine power, production of smoke and operational problems such as difficulty in engine starting, unreliable ignition, and deterioration in thermal efficiency, therefore the viscosity of the biodiesel must be low.

Due to their significantly higher viscosity compared to allowable levels for diesel fuel, vegetable oils cannot be safely utilized in compression ignition engines without prior heating (as viscosity decreases exponentially with increasing temperature), and only at minimal blending ratios. However, the transesterification process effectively reduces the viscosity of FAME to levels comparable to, although still exceeding, those of petro diesel (Giakoumis, 2013). In general, the time required for a fixed volume of fuel to flow under gravity can be used to assess the fuel's viscosity with a calibrated viscometer (Hoang et al., 2021). Kinematic viscosity of biodiesel is determined using standards EN ISO 3104 (3.5–5 mm^2/s) and ASTM D445 (1.90–6 mm^2/s) (Sakthivel et al., 2018). As illustrated in Figure 2.2, a moderate correlation was observed between viscosity and unsaturation level, or the presence of double bonds.

Biodiesel is slightly more viscous than petroleum diesel but the values are close. Viscosity is one of the main reasons vegetable oils are not used as fuels.

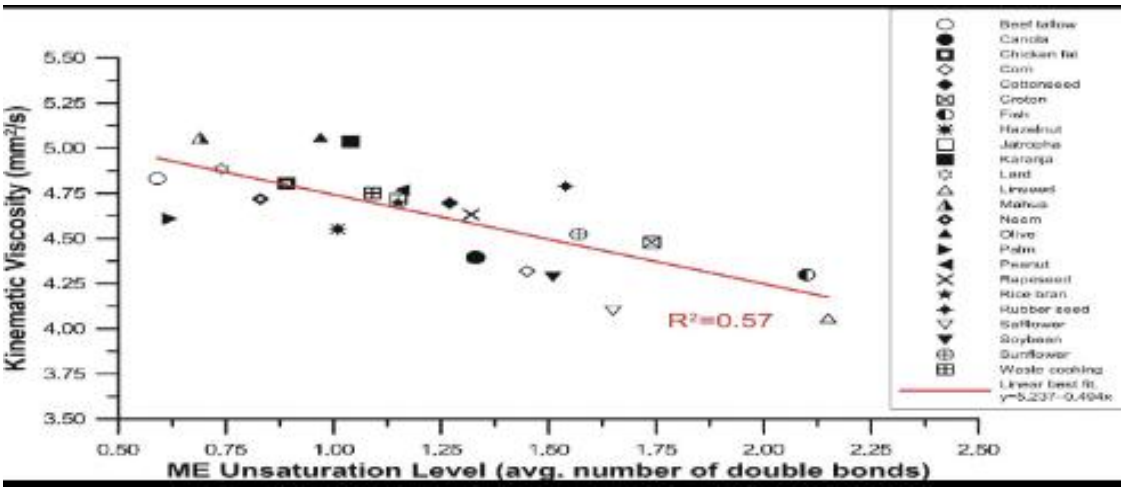


Figure 2. 2: Relationship between the average kinematic viscosity of biodiesel derived from 24 feedstocks and the degree of oil/fat unsaturation source (Giakoumis, 2013)

2.2.4. Flash Point

The flash point of a volatile material is the minimum temperature at which the material will ignite (flash) on application of an ignition source. Flash point minimum temperatures are required for proper safety and handling of fuels. The flash point of biodiesel is higher than that of petroleum diesel; this makes it safe for transport purpose because high values of flash point decreases the risk of fire.

2.2.5. Cloud Point (CP)

This is the temperature at which wax crystals first appear in diesel or bio wax. In biodiesel sample that is cooled under conditions described by ISO 3015. Solidified waxes and thickening of oils clogs air filters also injection ports in engines.

2.2.6. Cetane Number (CN)

This property significantly influences the ignition delay phase of fuel. The term "ignition delay" signifies the duration between the injection of fuel into the cylinder or combustion chamber and the initiation of ignition (Feng et al., 2021). A higher cetane number (CN) reflects the fuel's propensity to ignite spontaneously upon entering the combustion chamber (Naser et al., 2018). A lower CN value correlates with increased engine exhaust emissions, a greater accumulation of deposits due to incomplete combustion, and heightened knocking phenomena (Krishnamoorthi & Vinayagasundram, 2019). The levels of saturation and the length of fatty acids affect the CN of biodiesel. With a higher oxygen content and combustion efficiency, biodiesel typically exhibits a superior CN (Sharma et al., 2019). The cetane number of biodiesel is defined by EN ISO 5165, ASTM D613, and ISO 5156/P9. The European standard mandates a minimum cetane number of 51, representing a more rigorous requirement (Martínez-Martínez et al., 2016). The high CN threshold established by EN presents challenges for biodiesel sourced from sunflower, camelina, safflower, and soybean, as these are borderline feedstocks and may struggle to meet specific sample specifications. Generally, petroleum diesel has a lower CN compared to biodiesel. An increase in the proportion of biodiesel blends enhances the cetane number. Biodiesel derived from feedstocks with elevated saturated fatty acid concentrations, such as palm and tallow, boasts a higher CN than biodiesel from soy and rapeseed, which contain lower saturated fatty acids. The effect of branching appears minimal and its influence on the CN of biodiesel fuel is challenging to discern (Singh et al., 2019a).

2.2.7. Iodine Number

The iodine number (IN), also referred to as the iodine value (IV), is a critical parameter utilized to evaluate the degree of unsaturation in animal fats or vegetable oils. This metric denotes the mass of iodine (I_2) in grams required to completely saturate the molecules of 100 grams of a specific oil through a stoichiometric reaction (Anwar et al., 2019; Giakoumis et al., 2014). Biodiesel derived from soybean and sunflower oils exhibits an IN value exceeding 120, whereas biodiesel produced from rapeseed oil registers an IN value below 120. Due to its superior IN, biodiesel derived from Camelina does not meet EN14214 standards. Other biodiesel fuels have IN values significantly lower than 120. The degree of unsaturation in FAME molecules is closely related to the IN, which can be quantified by assessing the amount of I2 that reacts with the C-C double bonds in FAMEs. IN serves as an indicator to ensure adequate oxidative stability in biodiesel; however, while the number of double bonds in FAME molecules influences oxidative stability, the iodine value exclusively assesses overall unsaturation. Consequently, recommendations regarding the necessity for a standard iodine value differ across the board (Singh et al., 2019a). Although European regulations stipulate that compression ignition engines utilizing biodiesel maintain a maximum IN value of approximately 120, U.S. regulations do not impose such a requirement. This guideline is predicated on the understanding that elevated iodine numbers in fuel indicate a propensity for polymerization, leading to deposit formation (Giakoumis, 2013). Furthermore, notable discrepancies in reported oxidation stability values among studies have been linked to high IN values and issues with storage stability (Singh et al., 2021b).

2.2.8. Calorific Value

Calorific value of a fuel is the thermal energy released per unit quantity of fuel when the fuel is burned completely and the products of combustion are cooled back to the initial temperature of the combustible mixture. It measures the energy content in a fuel. The calorific value of vegetable oils and their methyl esters were measured in a bomb calorimeter according to ASTMD240 standard method.

2.2.9. Sulphur Content

When fuel contains sulfur, an undesirable component, the production of soot particles during combustion is elevated (Kozina et al., 2020). The sulfur content in the fuel directly influences the quantity of sulfur oxides generated within the cylinder during combustion.

The lifespan of catalysts is diminished by the use of high-sulfur fuels, which also contributes to increased engine wear. Sulfur emissions pose significant risks to human health. Acid rain, a key contributor to cancer, forms when sulfur reacts with rainwater, resulting in the production of sulfur oxides and sulfuric acid (Krishnasamy & Bukkarapu, 2021).

Conversely, biodiesel derived from vegetable oils contains minimal sulfur levels (Sharma et al., 2019)

Table 2. 1: Standard Specification for Diesel and Biodiesel

Fuel Property	**Diesel**	**Biodiesel**	**Unit**
Fuel Standard	ASTM D975	ASTM PS 121	
Fuel composition	C10-21HC*	C12-22	Not applicable
Lower heating value	36.6x103	32.6x103	Calories

Kinematic viscosity@40°C	1.3-4.1	1.9-6	mm^2/s
Specific gravity @15.5°C	0.85	0.88	No units
Density @ 15°C	848	878	g/cm3
Carbon	87	77	Wt. %
Hydrogen	13	12	Wt. %
Sulphur	0.05	0.0-0.0024	Wt. %
Boiling point (°C)	188-343	182-338	°C
Flash point	60-80	100-170	°C
Cloud point	-15 to5	-3 to 12	°C
Pour point	-35 to -15	-15 to 10	°C
Cetane number	40-55	48-65	Not applicable
Stoichiometric air/fuel	15	13.8	

2.3. PHYSICOCHEMICAL PROPERTIES AND SPECIFICATIONS OF BIODIESEL

The fuel specification defines and sets the quality standards for biodiesel. It is based on the standard ASTM D6751. The biodiesel standards in Brazil and the U.S. are applicable for both fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE), whereas the current European biodiesel standard is only applicable for fatty acid methyl esters (FAME). The ASTM and EU biodiesel property specifications with the recommended test methods are given in Table 2.2

Table 2. 2: ASTM Standards for Biodiesel

Property	**Test method**	**Limits**	**Units**
Ca and mg combined	EN14538	5 max.	Ppm
Flash point	D93	93.0 min	^{o}C
Alcohol control: one of the following must be met: methanol content flash point	EN14110 D93	0.2 max. 130 min.	Vol% ^{o}C
Water and sediment	D2709	0.050 max.	Vol%

Kinematic viscosity @40^{o}C	D445	1.9-6.0	mm^2/s
Sulfated ash	D874	0.020	% mass
Sulfur	D5453	0.0015max.(S15) 0.05 max.(S500)	% mass
Copper strip corrosion	D130	No.3 max	
Cetane number	D613	47 min.	
Cloud point	D2500	Report to customer	^{o}C
Carbon residue	D4530	0.050 max	% mass
Acid number	D664	0.50 max	mgKOH/g
Free glycerin	D6584	0.20 max.	%mass

Total glycerin	D6584	0.240 max	%mass
Na and K combined	EN14538	5max	Ppm
Oxidation stability	EN14112	3min	H

2.3.1. Advantages and Limitations of Biodiesel

2.3.1.1. Advantages of Biodiesel

Due to having better properties than that of petroleum diesel itself, it can be concluded that the search for biodiesel is indeed beneficial to mankind as it has many advantages as a substituent.

The advantages of biodiesel include:

I. Biodiesel is a renewable source of energy i.e. it has a continuous source of supply and it will decrease the country's dependence on imported petroleum.

II. Biodiesel is biodegradable and non-toxic. It degrades about four times faster than petroleum diesel. This is enhanced by its oxygen content, higher than the oxygen content of mineral diesel (Igbokwe & Nwafor, 2014).

III. Biodiesel has higher cetane number than petroleum diesel and therefore ignites faster. Cetane number is used as indicator to determine diesel fuel quality, especially the ignition quality. It is

to measure the readiness of the fuel to auto-ignite when injected into the engine (Igbokwe and Nwafor, 2014).

IV. Biodiesel does not contribute to global warming due to its closed carbon cycle. It reduces the emission of greenhouse gases such as carbon monoxide (CO) and carbon dioxide (CO2). A life cycle analysis of biodiesel showed that overall CO2 emissions were reduced by 78% compared with petroleum-based diesel fuel.

V. Biodiesel contains less Sulphur and aromatics than diesel, which means lower Sulphur and aromatic emissions.

VI. It provides a market for excess production of vegetable oils and animal fats.

VII. It has lubricating properties that lengthen the lifespan of engines (Solaimuthu et al., n.d.).

VIII. Higher combustion efficiency: Biodiesel is much less combustible, with a flash point greater than 423 K compared to 350 K for petroleum-based diesel fuel (Demirbas, 2006).

Generally, biodiesel is preferred over conventional diesel due to its advantages of biodegradability, zero sulfur content, higher flash point, and inherent lubricity. Moreover, it releases less particulate matter, carbon monoxide and hydrocarbons. Thus, greater use of biodiesel could result in a reduced output of pollutants and transferable carcinogenic matters.

2.3.1.2. Limitations of Biodiesel

Even if biodiesel has several advantages, its use also implies some disadvantages that should be mentioned:

I. Agricultural feedstock is needed to produce biodiesel and at some times its availability might be constrained due to its necessity to produce food. This may impose limits on the production of biodiesel.

II. The kinematic viscosity of biodiesel is higher than that of diesel fuel.

III. Oxidation of biodiesel happens more easily than oxidation of diesel, so, when it is stored for long periods some products that may be harmful to the vehicle components might be produced.

IV. A modified refueling infrastructure is needed to handle biodiesel, which adds to its total cost.

2.4. FEEDSTOCK FOR BIODIESEL PRODUCTION

There are different types of suitable raw materials for biodiesel production. This includes many types of vegetable oils and animal fats. Most of the raw materials used are first generation feedstock which are edible. “Price and availability are important factors that determine different types of feedstock used for biodiesel production from one region of the world to another.

Edible feedstock should not be used as it will not be cost effective and it is not feasible to be used in a larger scale. There will be fight over for sustainability and food for fuel production.

Table 2. 3: List of Biodiesel Feedstock

Vegetable oils	**Non-edible oils**	**Animal fats**	**Other sources**

Soybeans	Almond Babassu	Lard	Bacteria
Rapeseed	Brassica	Tallow	Algae Fungi
Canola	carinata	Poultry	Micro algae
Safflower	cardunculus	fat Fish oil	Tapenes
Barley	Jatropha curcas		Latexes
Coconut	Jatropha nana		Cooking oil
Copra	Jojoba oil		(Yellow grease)
Cotton	Laurel		Microalgae
seed	Palm		(Chlorellavulgaris)
Groundnut	Karang		
Oat	Tobacco		
Rice	seed Rubber		
Sorghum	seed Rice		
Wheat	bran Sesame		
Winter rapeseed oil	Salmon oil		

The oils most used for worldwide biodiesel production are rapeseed (mainly in the European Union countries), soybean (Argentina and the United States of America), palm (Asian and Central American countries) and sunflower, although other oils are also used, including peanut, linseed, safflower, used vegetable oils, and also animal fats. Methanol is the most frequently used alcohol although ethanol can also be used. Since cost is the main concern in biodiesel production and trading (mainly due to oil prices), the use of non-edible vegetable oils has been studied for several years with good results (Jabbaria & Pesyanb, 2017).

Besides its lower cost, another undeniable advantage of non-edible oils for biodiesel production lies in the fact that no foodstuffs are spent to produce fuel. These and other reasons have led to medium- and large-scale biodiesel production trials in several countries, using non-edible oils such as castor oil, tung, cotton, jojoba and jatropha. Animal fats are also an interesting option, especially in countries with plenty of livestock resources, although it is necessary to carry out preliminary treatment since they are solid; furthermore, highly acidic grease from cattle, pork, poultry, and fish can be used.

Microalgae appear to be a very important alternative for future biodiesel production due to their very high oil yield; however, it must be taken into account that only some species are useful for biofuel production. Although the properties of oils and fats used as raw materials may differ, the properties of biodiesel must be the same, complying with the requirements set by international standards.

2.5. TYPICAL OIL CROPS USEFUL FOR BIODIESEL PRODUCTION

Globally, the feedstock supplies used for biodiesel production are predominantly comprised of four oil crops. Rapeseed oil leads the market with a share exceeding 75%, closely followed by soybean, palm, and sunflower seed oils (Ullah et al., 2018). In addition to the dominant four—rapeseed, soybean, palm, and sunflower seed oils—other edible plant oils have also been successfully transesterified to produce biodiesel. Biodiesel production employs four generations of feedstock: first, second, third, and fourth generation (D. Singh et al., 2020).

2.5.1. First Generation Feedstock (Edible Oil)

The principal sources of first-generation feedstocks are biomass and edible crop oils (D. Singh et al., 2020). Common examples of these feedstocks include sunflower, soybean, palm, and rapeseed oils

(Jogarao & Swarna Kumari, 2019; Mohiddin et al., 2021; Senatore et al., 2019; A. R. Singh et al., 2022; D. Singh et al., 2020; Syafiuddin et al., 2020). Due to their abundant availability, first-generation feedstocks are the most widely utilized sources for biodiesel production (Mohiddin et al., 2021). However, the extensive use of these feedstocks adversely affects food pricing (Esfandabadi et al., 2022; Mat Aron et al., 2020). The competition for feedstocks driven by the food and fuel industries can lead to food insecurity. Typically, the market for edible oils is more profitable than that for fuel, making the production of biodiesel from first-generation feedstocks somewhat inefficient (Mohiddin et al., 2021). In addition to their food applications, vegetable oils have been extensively employed in various industrial sectors, including biodiesel, soaps, lighting, medicinal oils, cosmetics, emulsifiers, lubricants, and greases, among numerous other industrial applications (Alsultan et al., 2016).

2.5.1.1. Soybean Oil

It is a legume originating in East Asia. Depending on environmental conditions and genetic varieties, the plants show wide variations in height. Leading soybean producing countries are the United States, Brazil, Argentina, China, and India.

Soybean oil is a crucial edible oil due to its numerous health benefits. Global production of soybean oil is estimated at 222 million tons, with Brazil, the United States, and East Asia as the leading producers (Kumar et al., 2021)The majority of biodiesel produced in the United States is derived from soybean oil, requiring 1.3 liters of soybean oil to produce 1 liter of biodiesel. The soybean plant typically grows between 0.5 to 1.2 meters in height. When compared to other crops, soybean produces a lower oil yield per hectare (Istadi et al., 2015). Due to its ability to fix nitrogen, soybeans can thrive in both tropical and temperate climates. Additionally, soybeans contribute to the replenishment of nitrogen in

the soil. For soybeans, which maintain a favorable fossil energy balance, reduced fertilizer inputs are required.

Biodiesel production from soybean yields other valuable sub-products in addition to glycerin: soybean meal and pellets (used as food for livestock) and flour (which have a high content of lecithin, a protein). Grain yield varies between 2,000 and 4,000 kg/hectare. Since the seeds are very rich in protein, oil content is around 18%.

2.5.1.2. Oil Palm

Oil palm is a tropical plant that reaches a height of 20–25 m with a life cycle of about 25 years. Full production is reached 8 years after planting. Two kinds of oil are obtained from the fruit: palm oil proper, from the pulp, and palm kernel oil, from the nut of the fruit (after oil extraction, palm kernel cake is used as livestock food). Several high oil-yield varieties have been developed. Indonesia and Malaysia are the leading producers.

International demand for palm oil has increased steadily during the past years, the oil being used for cooking, and as a raw material for margarine production and as an additive for butter and bakery products. It is important to remark that pure palm oil is semisolid at room temperature (20–22oC), and in many applications is mixed with other vegetable oils, sometimes partially hydrogenated.

Palm oil is a significant edible oil, with over 75% utilized by the food industry while the remainder is allocated for industrial applications (Elgharbawy et al., 2021).

In the last decade, Indonesia and Malaysia have emerged as the two leading producers of palm oil (Ayompe et al., 2021). Brazil and Nigeria also possess considerable potential for palm oil production

(Kaniapan et al., 2021). The demand for palm biodiesel oil is experiencing rapid growth across Europe. Notably, two principal advantages of palm oil compared to other edible oils are its cost-effectiveness and remarkably high oil yield per acre. Specifically, 1 liter of biodiesel can be derived from 1.25 liters of palm oil, underscoring the efficiency associated with palm oil production (Rodionova et al., 2017). Palm oil is extracted from the seeds of palm trees, which contain approximately 21% oil content by weight (Elgharbawy et al., 2021). Prior to the transesterification process, it is essential to treat palm oil to eliminate water, solid particles, color, and odor. Post-treatment, the free fatty acid (FFA) content in the oil is reduced to below 0.1%.

2.5.2. Second-generation feedstock (Non-Edible Oil)

The term "non-edible oil" denotes oils that are unsuitable for human consumption due to inadequate hygienic standards. These oils are predominantly utilized in industrial applications, including biofuels, detergents, soaps, and paints. Because non-edible oils require multiple chemical processes to make them suitable for specific uses, they are typically more economical when used in industrial settings (Elgharbawy et al., 2021).

The widespread accessibility of non-edible oils has sparked significant global interest. Moreover, their utilization eliminates conflicts regarding the use of these resources for energy compared to nutrition. This particular generation of feedstock is also considered to be more environmentally sustainable and efficient. The by-products created during processing hold value, making the use of non-edible oils economically advantageous as well (Zhou et al., 2021). Non-edible oils, recognized as the second generation of feedstock for biodiesel, include sources such as *Cerbera odollam* (sea mango), *Jatropha curcas L., Hevea* brasiliensis (rubber seed), *Moringa oleifera, Pongamia pinnata* (Karanja), Neem

(*Azadirachta indica*), and Yellow oleander (*Thevetia peruviana Schum)* (Alalwan et al., 2019; Boopathi et al., 2020; Foroutan et al., 2021; Maheshwari et al., 2022; Shaah et al., 2021; D. Singh et al., 2020).

Most non-edible oils contain a relatively high percentage of free fatty acids (FFA) (Abdul Hakim Shaah et al., 2021b). When high FFA feedstock undergoes transesterification using an alkali-based catalyst, a considerable amount of soap is produced. The emulsifying properties of soaps complicate the separation of the ester phase and glycerol. Significant catalyst quantities are required since soaps formed from catalysts lose their effectiveness in facilitating biodiesel synthesis (Kasirajan, 2021). To manage this challenge, a two-step approach is generally employed. The initial step involves converting FFA into esters using acid catalysis, followed by a second phase of transesterification through base catalysis (Thoai et al., 2019).

2.5.2.1. Jatropha oil

Jatropha oil is extracted from the seeds of the Jatropha plant. Given that jatropha thrives in warm climates and can utilize sewage water, it represents a viable biodiesel resource in Egypt, with regions such as Africa and Asia leading its cultivation (Suthar et al., 2019). The oil content in jatropha seeds ranges from 30 to 35 wt%, making it a high-yield source for biodiesel production (Elgharbawy et al., 2021). Jatropha seeds contain approximately 20–60% oil. At 15 °C, Jatropha oil exhibits a heating value of 38.96 MJ/kg, a density of 916 kg/m3, and a viscosity of 37.28 mm2/s (Singh et al., 2019b). The applications for jatropha oil include various industries such as soap, cosmetics, and lubricants (Moniruzzaman et al., 2016).

2.5.2.2. Castor oil

Castor oil is a vegetable oil derived from castor beans. It is a clear, tasteless liquid with a subtle yellow hue and a boiling point of 313 °C, possessing a density of 961 kg/m3. Castor oil has a viscosity approximately seven times greater than that of other vegetable oils. Despite its low pour and cloud points, which make it suitable for colder climates, its viscosity does not meet the international standards for biodiesel fuel (Demirbas et al., 2016a).

2.5.3. Third generation feedstock

Third-generation biodiesel is derived from waste oils and microalgae (Kumar et al., 2021; Luque & Clark, 2011). The primary advantages of this category include reduced greenhouse gas emissions, accelerated growth and productivity, minimized land use conflicts, a higher oil yield, and less impact on the food supply**.**

To eliminate contaminants, the utilization of waste oils necessitates further processing (Singh, Sharma, Soni, Sharma, et al., 2020b).

Using used cooking oil presents numerous advantages, rendering it a viable alternative for biodiesel production. It is readily available from residential and commercial kitchens, tends to be more cost-effective than other oil varieties, and is amenable to recycling (Suthar et al., 2019). Additionally, it minimizes the land requirement for crops grown for biodiesel. Nevertheless, while used cooking oils play a vital role in biodiesel production, many countries discharge them improperly, resulting in environmental pollution (Esfandabadi et al., 2022; Ullah et al., 2018)). Used frying oil often contains high levels of free fatty acids (FFAs), which hinder the transesterification process and diminish biodiesel yield, thus necessitating management and reduction to acceptable levels**.**

2.5.4. Fourth Generation Feedstock

The emergence of fourth-generation feedstock has been made feasible through advancements in synthetic biology (Mohiddin et al., 2021). Photobiological solar fuels and electrofuels are included in this new generation of biodiesel (Syafiuddin et al., 2020). A potentially cost-effective and renewable source of biodiesel feedstock can be developed by integrating solar energy with specially engineered biological systems (Singh, Sharma, Soni, Sharma, et al., 2020a). It is essential to explore innovative approaches to creating synthetic organisms and engineered microbes that can convert solar energy directly and efficiently into fuel to support sustainable development. A growing trend in efficient fuel production and liquid fuel storage involves combining photovoltaic technologies or inorganic water-splitting catalysts with metabolically designed microbial fuel production (Singh, Sharma, Soni, Sharma, et al., 2020b). The production of fourth-generation biodiesel feedstock can incorporate a combination of three methodologies: (i) utilizing specially engineered Photosynthetic microorganisms, (ii) the production of microbial fuel and photovoltaics, and (iii) the synthesis of synthetic cells (Mat Aron et al., 2020).

2.6. NON-EDIBLE OIL AS A FEEDSTOCK FOR BIODIESEL

The utilization of non-edible oil as a feedstock for biodiesel encompasses numerous factors, including the facilitation of environmental advantages, the generation of employment opportunities, the prevention of fuel resource monocultures, and the promotion of energy sustainability and independence, particularly within rural communities. Various potential methods, such as the process of generating biodiesel from non-edible oil sources as feedstock in regions, including Fatty Acid Methyl Esters (FAME), are also significant. With over 61% of the global population residing in regions such as

Asia, there is an increasing demand for food and energy in these areas. By employing non-edible oils as a feedstock, biodiesel production can be achieved more sustainably while exerting minimal direct impact on the food supply (Issariyakul & Dalai, 2014). It is feasible to cultivate non-edible oil plants on degraded lands worldwide, thus mitigating the necessity for further deforestation and addressing food supply challenges (Trutnevyte et al., 2016). The two critical variables influencing the decision to utilize a feedstock for biodiesel production are the volume of oil that can be extracted and the agricultural yield from the cultivated area. Due to their low sulfur and aromatic content, biodegradability, renewable characteristics, ease of transfer in liquid form, and effective combustion, non-edible oils represent promising feedstocks for biodiesel (Abdul Hakim Shaah et al., 2021c; Munir et al., 2019).

2.6.1. Neem Oil

Commonly known as the "neem tree," Azadirachta indica is a rapidly growing species. In general, neem trees are resilient to high temperatures and can thrive in degraded and less fertile soils. Although native to the Indian subcontinent, this tree has proliferated across various continents and countries, including Africa, Central and South America, Bangladesh, Myanmar, Malaysia, Pakistan and Sri Lanka (Demirbas et al., 2016b). Neem trees begin to bear fruit in three to five years, but after fifteen years of planting, their optimum seed yield starts. The shape of the neem fruit can be oval or circular and It has an annual fruit production of up to 50 kg, and requires little water.

Studies conducted in Nigeria demonstrate the use of non-edible oils to produce biodiesel from neem seed oils reported high oil yield Aransiola et al. (2012).

Table 2. 4: The physiochemical characteristics of Neem oil (Hundie et al., 2022)

Property	Value
Palmiticacid	12.01wt%
Stearicacid	12.59wt%
Oleicacid	34.09wt%
Linoleicacid	38.26wt%
Linolenicacid	0.3wt%
Density	0.875 g/cm^3
Viscosity	35.83mm^2/s
Saponificationvalue	206.7mgKOH/g
Acidvalue	1.81mgKOH
Iodinenumber	82-98g$I_2$100g^{-1}

2.6.2. Yellow Oleander Oil

Thevetia Peruviana, commonly referred to as the yellow oleander, is a highly toxic plant noted for its remarkable drought resistance (Yadav et al., 2019). This plant is native to Central and South America and thrives in tropical and subtropical regions around the globe. The yellow oleander tree typically reaches heights of 11 to 18 feet. Each hectare yields approximately 52 tonnes of yellow oleander seeds,

of which 60-65% by weight consists of oil. A recent investigation conducted in Nigeria by Dallatu et al. (2017) highlighted a substantial oil yield, demonstrating the viability of oleander oil in biodiesel production.

Table 2. 5: The physiochemical characteristics of Yellow oleander oil (Yadav et al., 2019)

Property	Value
Palmitic acid	23.24wt%
Stearic acid	7.46wt%
Oleic acid	44.23wt%
Linoleic acid	21.82wt%
Linolenic acid	2.66wt%
Density	0.835 g/cm^3
Viscosity	23.28mm^2/s
Saponification value	196.3mgKOH/g
Acid value	1.26mgKOH/g
Iodine number	76gI_2/100g

2.7. OIL BLENDS FOR BIODIESEL PRODUCTION

The choice of feedstock for biodiesel production is influenced by factors such as availability, high productivity, short seed maturation cycles, local growth potential, minimal input requirements, and the necessity to minimize competition for fertile agricultural land (Singh Pali et al., 2021). Addressing the availability of sufficient quantities of various oils, as well as enhancing the fuel quality of lower-grade or waste oils, can be achieved by blending these oils with high-quality edible or non-edible oils for biodiesel synthesis (Singh Pali et al., 2021).

Furthermore, it has been established that mixed oils can be utilized to produce biodiesel with fuel qualities that meet ASTM biodiesel standards, by reducing the viscosity of the blend through the combination of high-viscosity and low-viscosity oils (Calvi & Phung Van, 2011). Research conducted by Mujtaba et al. (2020) indicates that the integration of high-acid and low-acid oils can adjust the mixture's acid value into a range that both shortens the esterification process and reduces costs prior to transesterification.

According to existing literature, Qiu et al. (2011) successfully generated biodiesel through the transesterification of soybean oil mixed with rapeseed oil, achieving a yield of 94%. Additionally, a separate study by Dharma et al. (2016) produced biodiesel from a blend of jatropha curcas and ceiba pentandra, resulting in an optimal yield of 93.33%.

Advantages of Mixed Oil Biodiesel (Singh Pali et al., 2021):

1. Enhanced production rates

2. Incorporation of high-viscosity non-edible oils

3. Use of cost-effective oils

4. Reduced production expenses

5. Improved feedstock availability

6. Minimal or no need for additives to achieve biodiesel fuel quality

2.7.1. Waste cooking oil as raw materials for biodiesel

Waste cooking oil (WCO) consists of residual frying substances derived from both plant and animal fats, combined with cooking oil. Cooking oil itself is a glycerol ester that contains various essential fatty acids, which are soluble only in organic solvents. The disposal of cooking oil waste poses significant risks to environmental health and consumer safety, particularly when such waste is ingested. It is posited that the toxic compounds formed during the oxidation of cooking oil can lead to carcinogenic effects when fried foods are consumed. Although WCO is abundantly available, it is frequently discarded after use, especially post-frying. In Malaysia, it is estimated that approximately 540,000 tonnes of WCO from both vegetable and animal sources are discarded annually without proper treatment, with much of it being disposed of in drainage systems and soil. To address these environmental concerns, one viable solution is to repurpose WCO as a raw material for biodiesel production, which is both cost-effective and environmentally sustainable. The potential for increased WCO availability makes it an attractive feedstock for biodiesel.

The frying process induces various chemical reactions, including oxidation, hydrolysis, polymerization, and the transfer of materials between food and oil, which alter the characteristics of WCO compared to fresh oil. Nevertheless, WCO retains similar properties necessary for biodiesel production, such as density, kinematic viscosity, acid value, and iodine value, thereby meeting quality standards. Notably,

WCO has a higher concentration of free fatty acids (FFA) than standard vegetable oil, which is a critical factor in selecting an appropriate catalyst for the biodiesel manufacturing process. In scenarios where FFA concentrations are elevated, the feasibility of large-scale biodiesel production diminishes, leading to a preference for soap production instead.

Research indicates that the levels of kinematic viscosity, saponification, flash point, moisture content, and free fatty acids in Waste Cooking Oil (WCO) are considerably elevated. These chemical properties significantly affect the quality and quantity of biodiesel production. Additionally, high oil concentrations or viscosities can hinder effective fuel injection from the tank to the engine, potentially impairing atomization.

WCO is typically 2 to 3 times less expensive than fresh vegetable oil, leading to a notable decrease in overall processing costs. The retail price of biodiesel is heavily influenced by raw material costs, with as much as 75–90% of biodiesel production expenses allocated to sourcing these essential materials. Utilizing WCO provides a solution to challenges such as the food vs. fuel debate and various environmental concerns.

The benefits of employing waste cooking oils for biodiesel production include cost-effectiveness and the mitigation of environmental pollution. Proper disposal of waste oil often results in significant challenges, including water and soil contamination, health risks to humans, and disruptions to the amphibious ecosystem. A study by Anastasia Kharina et al. highlights the harmful effects associated with consuming used cooking oil, as numerous toxic compounds can infiltrate food, leading to serious health conditions such as Stroke, Alzheimer’s, Parkinson’s, and Huntington’s diseases.

Despite its adverse effects and environmental implications, WCO serves as an efficient and economical feedstock for biodiesel production, given its availability and accessibility. The use of animal lipids also presents notable considerations and may involve various technical challenges during processing. Moreover, consuming used cooking oil may elevate LDL ("bad" cholesterol) levels while decreasing HDL ("good" cholesterol) [9]. Collected WCO can also be utilized in the production of soaps and lubricants through the glycerine by-product of biodiesel manufacturing. Numerous studies have confirmed the successful conversion of cooking oil into biodiesel. Vegetable oils comprise saturated hydrocarbons (triglycerides), which are made up of glycerol and fatty acid esters. In certain regions, WCO from prominent restaurants is resold to street vendors for frying foods; this waste oil, referred to as second-use cooking oil, can also be effectively converted into biodiesel.

Waste vegetable oils help alleviate the need for biodiesel crops and reduce competition with food sources. The chemical and physical properties of WCO differ from those of fresh oil due to various chemical reactions—such as oxidation, acidity changes, hydrolysis, polymerization, and material transfer during the frying process. WCO presents a low-cost feedstock that requires minimal processing for biodiesel production. The characteristics of WCO are detailed in Table 2.5

Table 2. 6: Properties of WCO (Oyekunle et al., 2023)

Property	**Method**	**Standard Value**
Density at 16°C (g/mL)	ASTM D4052-91	0.9 – 0.92
Kinematic Viscosity at 40°C (mm^2s^{-1})	ASTM D445	1.9 – 6.5

Flash Point (T_F)	ASTM D93	180.5
Acid Number (mg KOH/g)	ASTM D664	≤ 0.50
Saponification Value (S_v)	ASTM D5555-95	< 312
Iodine Number (g I_2/100g of oil)	Hanus Method	<120
Cloud Point (°C)	ASTM D2500	-3 to 12
Pour Point (°C)	ASTM D2500	-15 to 10
Distillation Curve	ASTM D1160	
Cetane Index	Willard, 1997	>47

The American Society for Testing and Materials (ASTM) standards and the European Specification (EN Standard) for biodiesel and conventional diesel were utilized to compare various oil characteristics, fuel properties, and process parameter assessments of Waste Cooking Oil (WCO). These standards serve as an international benchmark across various industries, ensuring regulatory consistency for quality control, contamination detection, formulation, trace analysis, investigative analysis, and beyond.

The quality of the oil is quantified through its chemical properties, including Acid Value, Saponification Value, Iodine Value, and others. According to research, biodiesel exhibits a higher Cetane number than diesel fuel, lacks aromatics, contains negligible sulfur, and includes 10% to 11% oxygen by weight. Another critical aspect of WCO is its Free Fatty Acid (FFA) content, which can be vital for biodiesel production from any feedstock. Numerous studies illustrate its significance. The FFA value can be determined by halving the acid value of the WCO.

Edible oils utilized for cooking are often discarded. Fatty acid profiles in studies have shown the presence of Oleic, Linoleic, Lauric acids, among other essential fatty acids, in varying percentages. Common vegetable oils used for frying include olive oil, sunflower oil, and peanut oil. These oils are primarily composed of oleic and linoleic fatty acids, with smaller amounts of stearic and palmitic acids.

Research has established that the reaction achieves a high biodiesel yield of up to 97%. This was contingent upon the Waste Vegetable Oil (WVO) being initially filtered through cloth or any filtration system to eliminate food residues via a funnel. Subsequently, it was suitable for an acid-catalyzed Esterification process, with an FFA level of less than 1 mg KOH/g. Conversely, the yielded biodiesel was lower at 80–88% in another study due to an FFA content below 2 mg KOH/g. WCO stands out as a viable alternative feedstock for biodiesel production due to its efficiency and cost-effectiveness.

Consequently, converting WCO into biodiesel presents a strategic method for managing and reducing domestic waste while addressing global energy challenges. Beyond biodiesel, WCO can also produce soap and additives for lubricant oils. Additionally, utilizing WCO for biodiesel production curtails crop cultivation demands and aids in addressing food security concerns.

2.8. METHANOL

Methanol (CH3OH), or methyl alcohol, is the simplest form of alcohol, consisting solely of a methyl group (CH3) bonded to a hydroxyl group (OH). Historically, it was manufactured through the destructive distillation of wood, hence the term wood alcohol. Methanol is a light, volatile, colorless, flammable liquid with a boiling point of 65°C and emits a distinctive odor reminiscent of ethanol (the alcohol used for consumption).

Methanol and ethanol are widely used alcohols for the transesterification reaction. Methanol's cost advantage contributes to its prevalence in use. Conversely, ethanol is produced from renewable sources (bioethanol), but commercial-grade ethanol often contains water, which can negatively impact the reaction rate. The majority of commercial biodiesel production relies on methanol to produce Fatty Acid Methyl Esters (FAME) (Babadi et al., 2022)..

2.8.1. Properties of Methanol

5. Methanol is a flammable, colorless, volatile liquid
6. It is miscible in water, ethanol, ether, benzene and ketones
7. It burns with a non-luminous bluish flame
8. It is a highly polar substance
9. Methanol burns in air forming carbon dioxide and water

2.8.2. Manufacture of Methanol

There are several processes for manufacturing methanol but the most used process is the catalytic reaction of carbon monoxide and hydrogen. The most widely used catalyst is a mixture of copper and zinc oxides, supported on alumina.

$CO + 2H_2 \rightarrow CH_3OH$

2.8.3. Uses of Methanol

1. Methanol is a key component in the production of biodiesel.
2. It is used as a feedstock to produce chemicals such as acetic acid and formaldehyde, which in turn are used in products like adhesives, foams, plywood, solvents, paints and explosives.

3. Methanol can be used on its own as a vehicle fuel or blended directly into gasoline to produce a high-octane efficient fuel with lower emissions than conventional gasoline.
4. It is also used to produce methyl tertiary butyl ether (MTBE), a gasoline component that improves air quality, and dimethyl ether (DME), a clean-burning fuel with similar properties to propane.
5. Methanol is used as a feedstock for the plastics industry
6. It is also used as a solvent and as antifreeze in pipelines and windshield washer fluid.

2.9. PROCESS OF SYNTHESIZING BIODIESEL

Used vegetable oil is categorized as a 'renewable fuel' since it contributes no additional carbon dioxide emissions to the environment, distinguishing it from fossil fuels. The conversion efficiency from pure triglycerides to fatty acid methyl esters is notably high. The reaction time required is relatively short, making vegetable oil sourced from plants the optimal starting material for biodiesel production. Trans-Esterification is the predominant method utilized for biodiesel synthesis, employing a catalyzed chemical reaction between vegetable oil and alcohol to produce fatty acid alkyl esters and glycerol (V. Gupta & Pal Singh, 2023).

Research on biodiesel production (Mandari & Devarai, 2022) has revealed various processes applicable for biodiesel synthesis, including direct use and blending, micro emulsion techniques, thermal cracking, and the most practical approach: trans-esterification. This method stands as the most widely adopted process in biodiesel manufacturing. Biodiesel and glycerol are generated by combining alcohol with vegetable oil in the presence of a catalyst. The resulting biodiesel exhibits lower viscosity, which

mitigates potential damage to engine components due to incomplete combustion and poor fuel atomization (Maheshwari et al., 2022).

2.9.1. Direct Use and Blending/Dilution

The direct use of vegetable oils, or their blend with petro-diesel, has generally been deemed inadequate and impractical for diesel engines due to inherent shortcomings. Consequently, biodiesel fuel necessitates a chemical transformation before it can be utilized. Historical research has addressed this issue extensively over the past decades, and experimentation has persisted for nearly a century. Additionally, certain diesel engines, especially turbocharged models such as trucks, can operate on pure vegetable oils without significant energy consumption disparity compared to diesel fuel.

Dilution of vegetable oils can be achieved using diesel fuels, solvents, or ethanol. This dilution process decreases both the viscosity and density of vegetable oils. Incorporating 4% ethanol into diesel fuel enhances brake thermal efficiency, brake torque, and brake power, while simultaneously reducing brake-specific fuel consumption. Given that ethanol's boiling point is lower than that of diesel, it aids in the enhancement of the combustion process through an unburned blend spray.

2.9.2. Micro-Emulsion Process

The development of micro-emulsions represents a promising approach to addressing the issue of viscosity in vegetable oils. Micro-emulsions are characterized as clear, thermodynamically stable colloidal dispersions, with droplet diameters ranging from 100 to 1000 Å. These micro-emulsions can be formulated using vegetable oils in combination with esters and dispersants (co-solvents), or utilizing vegetable oils, alcohols, surfactants, and cetane improvers, with or without the inclusion of diesel fuels.

It has been observed that all micro-emulsions containing butanol, hexanol, and octanol have satisfied the maximum viscosity requirement for diesel fuel. Notably, 2-octanol has been identified as an effective amphiphile for the micellar solubilization of methanol within triolein and soybean oil.

According to Zahan K. A, the study delineated the micro-emulsion biodiesel production process, whereby vegetable or animal oils are dissolved in a solvent and surfactant until the desired viscosity is attained. A simplified process can be considered an advantage of this method. Nevertheless, drawbacks such as elevated viscosity, poor stability, propensity for adherence, incomplete combustion, and carbon deposition should be noted.

2.9.3. Thermal Cracking (Pyrolysis)

Pyrolysis is defined as a chemical transformation induced by applying thermal energy in an inert atmosphere, free from air or nitrogen. This process involves the decomposition of vegetable or animal oils at elevated temperatures, irrespective of the presence of a catalyst. The resulting gas and liquid products are analyzed based on their boiling points. The liquid fractions obtained through the thermal degradation of vegetable oils closely resemble diesel fuels. The pyrolyzate exhibits lower viscosity, flash point, and pour point compared to conventional diesel fuel, while maintaining equivalent calorific values. However, the cetane number of the pyrolyzate is relatively lower. Additionally, pyrolyzed vegetable oils contain acceptable levels of sulfur, water, and sediments, yielding satisfactory copper corrosion values; however, they may produce excessive ash, carbon residue, and unfavorable pour points (12). This method is effective as it does not require washing or filtering, but it necessitates expensive equipment and high temperatures for the separation process.

2.9.4. Ultrasonication

Ultrasonication is a widely recognized intensification technique for the catalyzed transesterification of biodiesel. This method enhances mass transfer by increasing the interfacial surface area between immiscible reactants while simultaneously decreasing both the reaction time and production costs. Compared to conventional reactors, it requires significantly less energy. Ultrasonic cavitation, characterized by the periodic formation, growth, and collapse of small bubbles in the ultrasound-irradiated liquid, occurs when ultrasound waves propagate through the liquid, as illustrated in Fig. 1(a). This process creates high local temperature and pressure regions, referred to as “hotspots,” accompanied by high-speed micro-jets, micro-streaming, and shockwaves. These phenomena facilitate improved mass and heat transfer within the reaction mixture. The physical characteristics of ultrasonication efficiently promote solution mixing, disrupt immiscible liquid layers, and enhance mass transfer at liquid-solid interfaces. Additionally, the radial motion of cavitation bubbles generates microturbulence, which aids in emulsifying immiscible liquid reactants; both emulsion stability and viscosity are observed to increase with the duration of sonication. During the brief phases of cavitation bubble collapse, free radicals are generated as a secondary chemical effect. Low-frequency ultrasound (LFU), operating between 28 and 40 kHz, represents an effective and time-efficient method of agitation that is also cost-efficient due to its minimal catalyst requirement and its consumption of only one-third to one-half of the energy typically used in mechanical stirring. Ultrasonication can be performed in either continuous or pulse mode. Research conducted by Chand et al. compared these two methods, assessing their efficiency and yields relative to conventional approaches. Their findings indicate that pulse mode ultrasonic treatment achieved a biodiesel yield of 96 wt% in under 90 seconds, compared

to the conventional method's 30-45 minutes, which yielded 83-86%. In continuous sonication mode, a maximum biodiesel output of 86 wt% was achieved in just 15 seconds.94 Fallah Kelarijani et al. investigated nanomagnetic catalysts (Li/Fe3O4 or Li/ZnO–Fe3O4) and attained a remarkable yield of 99.8% using ultrasonic waves at a frequency of 37 kHz. They found that mechanical stirring required an optimal yield with only 0.8% catalyst loading at an ambient temperature of 35 °C for 35 minutes when utilizing ultrasonication. Additionally, Bhangu et al. highlighted the successful integration of ultrasonication with enzymatic transesterification, demonstrating that ultrasonic irradiation can significantly reduce the reaction time from 22–24 hours to just 1.5 hours.

2.9.5. Microwave-assisted transesterification

Microwave-assisted transesterification is another prevalent method for process intensification.353 In comparison to the ultrasonic technique, microwave irradiation necessitates even shorter reaction times and reduced solvent volumes, demonstrating greater energy efficiency. Microwaves, as a form of electromagnetic radiation, possess the capacity to heat existing polar molecules within the reactants. This heating results from the alignment of these molecules with the electromagnetic field of the microwaves, generating heat through friction as depicted in Fig. 1(b). Microwave dielectric heating, which is a bulk effect stemming from dielectric loss, becomes practical when multiple species in the reaction mixture maintain a persistent dipole, such as methanol in the transesterification process. Microwave heating provides energy transfer to reactants from the inside out, contrasting with traditional heating methods that typically transfer heat through conduction or convection. This results in powerful microwave hotspots that significantly accelerate the reaction rate and effectively lower the activation energy required for biodiesel transesterification. Key advantages of microwave processing

include rapid heating and cooling, enhanced time and energy efficiency, precision in control, selective heating capabilities, uniform heating, and reduced processing durations, all of which purportedly improve the overall quality and characteristics of the final product. Rahul Soosai et al. reported employing microwave irradiation to produce biodiesel from inedible Ceiba pentandra seed oil, where the free fatty acid (FFA) content of the oil was initially as high as 6.87%. The oil underwent microwave-assisted esterification, successfully reducing the FFA to 0.83%. This esterified oil was later transesterified using CaO as the catalyst, yielding 97.4% in merely 114 seconds at 270 W. This reaction time effectively illustrates the significant reduction achieved through microwave irradiation. Waste cooking oil (WCO) has also served as a feedstock in microwave-assisted studies, as documented by Sharma et al. who utilized waste cotton seed oil with KOH and CaO catalysts. The use of homogeneous catalysts allowed the reaction to be completed in just 9.6 minutes, resulting in a yield of 96.55 ± 0.23% at a catalyst loading of 0.65 wt.%.

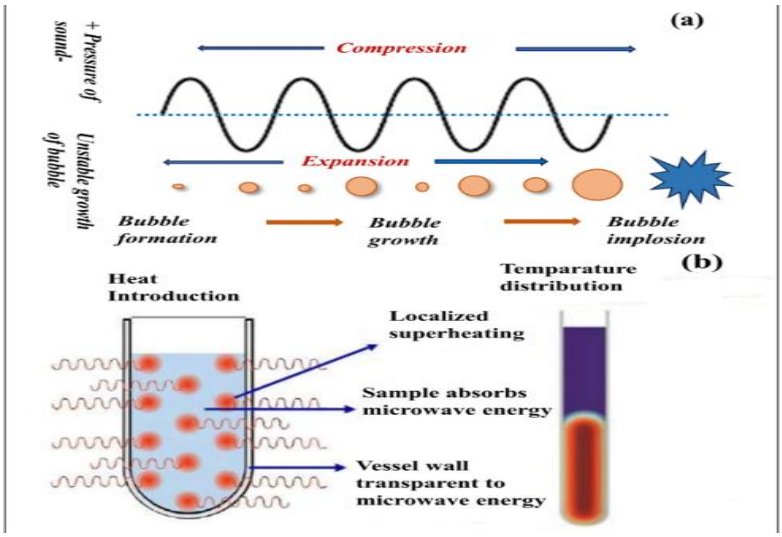


Figure 2. 3: Schematic workings of Microwave-assisted transesterification

2.9.6. Supercritical method

Transesterification refers to the chemical reaction between triglycerides and methanol under supercritical conditions. As previously outlined, this process typically involves the use of alcohols, predominantly methanol, ethanol, or a combination of the two. The term 'supercritical technology' denotes the application of high pressure and temperature settings beyond the critical point of the involved alcohol, such as 8.01 MPa and 512.6 K for methanol. When exceeding the critical temperature and pressure, significant alterations in methanol's mass density occur, affecting its solubility and mass-transfer capabilities. In supercritical methanol, triglycerides and methanol merge into a single phase owing to the heightened density and reduced dielectric constant of methanol. This increased density engenders a decrease in methanol's polarity due to hydrogen bonding. Consequently, it is advantageous to dissolve non-polar triglycerides in methanol under supercritical conditions to achieve a homogeneous phase. Additionally, supercritical conditions facilitate scaling and continuous operation. Under high pressure and temperature, methanol reacts with the carbonyl groups in triglycerides, releasing free monomers and forming an intermediate through methoxide transfer. This intermediate rearranges to yield more stable diglycerides and biodiesel. Subsequently, diglycerides interact with another methanol molecule to produce monoglycerides and biodiesel. The ultimate reaction between monoglycerides and methanol results in the production of biodiesel and glycerol. Ghoreishi & Moein explored the utilization of waste vegetable oils as feedstock for the supercritical method in a batch reactor, identifying the need for a high methanol-to-oil molar ratio of 33.8:1, a temperature of 271.1 °C, a pressure of 23.1 MPa, and a reaction duration of 20.4 minutes for a yield of 95.27%. Some limitations of supercritical biodiesel production include the necessity for elevated oil-to-alcohol molar ratios, high

pressure, and high temperature. The incorporation of co-solvents and catalysts has been proposed to address these challenges, with various reactants such as DMC, methanol, and methyl acetate being investigated.

2.9.7. Transesterification

Transesterification is the process whereby a triglyceride (derived from oils or fats) reacts with an alcohol (such as ethanol or methanol) to yield fatty acid methyl esters (FAME). This reaction may occur in the presence of a catalyst, enhancing the efficiency and yield of the process. Among the various methodologies available, transesterification stands out as a comprehensive, efficient, and highly promising technique for reducing the viscosity, density, and other properties of pure vegetable oils.

This method is frequently applied to lower the high viscosity of triglycerides. A catalyst is typically employed to accelerate the reaction rate and improve yield. Transesterification is a reversible reaction achieved by the amalgamation of the reactants. In this process, one mole of triglyceride reacts with three moles of alcohol to produce three moles of mono-alkyl esters and one mole of glycerol. However, the presence of a catalyst, such as KOH when reacting triglycerides with methanol (illustrated in Figure 1), expedites the process. The sequence involves a series of three consecutive reversible reactions, wherein triglycerides are transformed into diglycerides, which in turn become monoglycerides, and finally, monoglycerides are converted into glycerol.

The transesterification of triglycerides and methanol, aided by a catalyst, results in the formation of methyl esters and glycerol. Following this, the glycerol layer segregates and settles at the bottom of the separation funnel. Transesterification is classified as a reversible reaction and proceeds via the

interaction of triglycerides and methanol as reactants. Due to the presence of excess alcohol, the forward reaction is first-order, while the reverse reaction is second-order

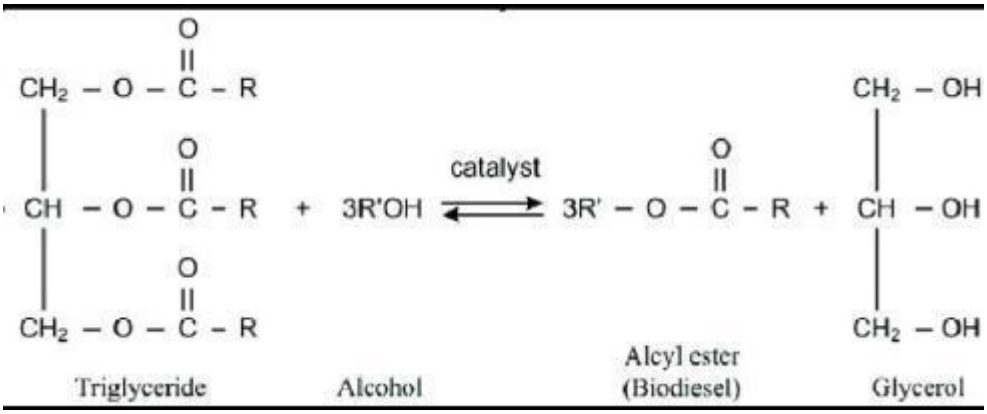


Figure 2. 4: A schematic representation of the transesterification reaction (Oyekunle et al., 2023)

2.10. TRANSESTERIFICATION

Biodiesel is most derived from a chemical reaction called transesterification. It is the chemical conversion of oil to its corresponding fatty ester in the presence of a catalyst. The reaction converts esters from long chain fatty acids into mono alkyl esters. Chemically, biodiesel is a fatty acid methyl ester.

Transesterification is the reaction of a lipid with an alcohol to form esters and a byproduct, glycerol (Mawlid et al., 2022). It is, in principle, the process of exchanging the organic group, R'' of an ester with the organic group R' of an alcohol. These reactions are often catalyzed by the addition of an acid or base catalyst.

Figure 2. 5: Alcohol + ester ——→ different alcohol + different ester

Methanol and ethanol are used most frequently but methanol is preferred because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol).

2.10.1. Transesterification Reaction Mechanism

The overall reaction between a triglyceride and an alcohol is given by;

Triglyceride + 3 ROH ↔ Glycerol + 3 alkyl ester

(i)

Reactions: (i) is supposed to take place in three consecutive and reversible steps where triglycerides are converted to diglycerides and then diglycerides are converted to monoglycerides followed by the conversion of monoglycerides to glycerol. In each step, an ester is produced and thus three ester molecules are produced from one molecule of triglycerides (Sharma and Singh, 2008);

Triglyceride + ROH ↔ Diglyceride + alkyl ester *(ii)*

Diglyceride + ROH ↔ Monoglyceride + alkyl ester

(iii)

Monoglyceride + ROH ↔ Glycerol + alkyl ester *(iv)*

In the above equations, ROH represents an alcohol. From stoichiometry, 3 moles of alcohols are required for each mole of triglyceride to produce 3 moles of alkyl ester (biodiesel). However, due to the reversible nature of the reaction an excess of alcohol is always employed for reactions to proceed in the forward direction. An alcohol to oil ratio of 6:1 is normally used in industrial processes to obtain high alkyl ester yields. According to a study carried out by Meher et al., (2006), molar ratios less than 6:1 caused incomplete reactions while molar ratios of 15:1 and above made the separation of glycerin difficult and decreased the apparent yield of esters because a part of the glycerol remained in the biodiesel phase. Akhihiero et al. (2013) reported the use of molar ratio 8:1 in the transesterification of jatropha seed oil.

In the transesterification mechanism, the carbonyl carbon of the starting ester ($RCOOR^1$) *undergoes nucleophilic attack by the incoming alkoxide (R2O-) to give a tetrahedral intermediate, which either reverts to the starting material, or proceeds to the transesterified product (*$RCOOR^2$*).*

The various species exist in equilibrium, and the product distribution depends on the relative energies of the reactant and product.

2.10.2. Factors Affecting Transesterification Reaction

Once the reaction is known, the conditions in which it happens should be determined. The parameters that will affect the reaction to a higher extent are:

1. Reaction Temperature
2. Reaction time
3. Molar Ratio (Alcohol to Oil ratio)
4. Catalyst Concentration
5. Mixing Intensity
6. Type of catalyst
7. Properties and Composition of the Feedstock

2.10.2.1. Reaction Temperature

Temperature values for the transesterification reaction vary depending on the literature source. It is well known that higher temperatures speed up the reaction and shorten the reaction time. Apart from that, higher temperatures usually mean obtaining higher ester yields (Rashid and Anwar, 2008).

However; It should also be noted that if the reaction temperature is higher than the boiling point of the alcohol, it will evaporate, resulting in a lower yield (Sharma et al, 2008). It is also an accepted fact that

usually the optimum temperatures for the transesterification range between 50 and 60ºC, depending on the kind of oil to be processed (Leung et al., 2010).

2.10.2.2. Reaction Time

The reaction time clearly influences the outcome of the reaction, since the conversion rate increases with the reaction time (Maa and Hannab, 1999). If the reaction time is not long enough the ester yield will be low, therefore, part of the oil will be unreacted.

2.10.2.3. Methanol/Oil Molar Ratio

This is one of the most important factors that can affect the ester yield. It is related to the type of catalyst used, depending on that, the optimum value for the process can be obtained. Higher molar ratios give a higher ester yield in a shorter time. Usually, when using acid catalysts higher molar ratios are needed, probably because the use of acid catalysts is related to oils with high FFA content (Gutiérrez-López et al., 2022).

2.10.2.4. Catalyst Concentration

This parameter is highly affected by the kind of catalyst used, different catalysts will require different concentrations. Even if they belong to the same group (as in the case of potassium hydroxide and sodium hydroxide), different concentrations will be necessary to attain the same yields. Therefore, the optimum value for every catalyst will have to be determined by titration. If the amount of catalyst is higher than the optimum, there will be a decrease in the yield of methyl esters due to the formation of soap in presence of high amount of catalysts, which apart from lowering the yield increases the viscosity of the reactants (Teo et al., 2014).

2.10.2.5. Mixing

It has been observed that during the transesterification reaction, the reactants initially form a two phase liquid system. To achieve perfect contact between the reagent and oil during transesterification, they are mixed together. The mixing effect has been found to play a significant role in the slow rate of reaction. Mixing is mandatory for the reaction to take place. Without mixing, the reaction only occurs in the interface between the methanol and the oil and it is very slow to be viable. Therefore, a mixing device is needed in the reactor used for the process (Agarwal et al., 2022).

2.10.2.6. Type of Catalyst

The type of catalyst used for a transesterification reaction affects the reaction. There are different classes of catalyst and they include homogeneous and heterogeneous catalysts, acid and base catalysts, organic and inorganic catalysts.

2.10.3. Properties, Composition and FFA Content of the Feedstock

The physical properties and chemical composition of the feedstock used in the transesterification reaction determines the type of fatty acid methyl ester produced and therefore affects the property of the biodiesel produced. The free fatty acid (FFA) content of the feedstock also affects the yield of biodiesel. Reactants with low FFA content gives higher biodiesel yield than those with high FFA content.

2.11. BIODIESEL PRODUCTION PROCESS

The production process of biodiesel is represented in Figure 2. Biodiesel, which is made from biological resources, is a sustainable fuel that has recently gotten much attention. The chemical makeup of biodiesel is a fatty acid methyl ester.

First of all, the selected WCO was filtered to remove food residues and other suspended matters to

complete the filtration process. Then it was heated at a high temperature to remove the soluble impurities and moistures. According to the study of M. Farooq et al., the washed WCO was treated with silica gel to remove the water content. Then the critical physicochemical properties of the WCO were determined using standard methods, as shown in Table 2. Even the paper said that they used CO for the pre-treatment step after filtered to remove impurities from local restaurants. The same research (V. Gupta & Pal Singh, 2023), said that the oil is filtered to remove any chunks of food particles passing the oil through a cotton cloth.

The acid number/acid value of the WCO should be measured to get the FFA value. The literature says, it is said that the acid number/acid value means the mass of KOH in milligrams that are required to neutralize one gram of chemical substances (Mahmood Khan et al., 2020). As follows, the acid number was measured by direct titration. A known amount of sample was dissolved in an organic solvent (like Isopropyl alcohol). Then, it was titrated with potassium hydroxide solution with a known concentration, and phenolphthalein is used as an indicator. The above procedure was used to determine the acid number of cooking oil for two samples with known quantities that included waste cooking oil and a blank sample (sample 3) that only included isopropyl alcohol and phenolphthalein indicator. The acid number is a measurement of the quantity of acid in a solution. It is expressed in milligrams of potassium hydroxide required to neutralize the acidic constituents in 1g of the sample. The biodiesel was synthesized from WCO using a two-step catalyst process, namely the Esterification process with ferric sulphate and transesterification step with KOH. Also, the addition of catalysts can increase the yield of biodiesel production. The purpose of pre-treatment and Esterification methods are to identify and reduction of the FFA value in WCO. In that case, it can reduce the FFA value using several methods,

namely steam distillation, extraction by alcohol, and Esterification by acid catalysts (D. Singh et al., 2020). However, the standard pre-treatment method is the Esterification of FFA with methanol in the presence of an acidic catalyst (usually sulphuric acid) (A. R. Gupta & Rathod, 2020). Those catalysts can be homogenous or heterogeneous acid catalysts (Mawlid et al., 2022).

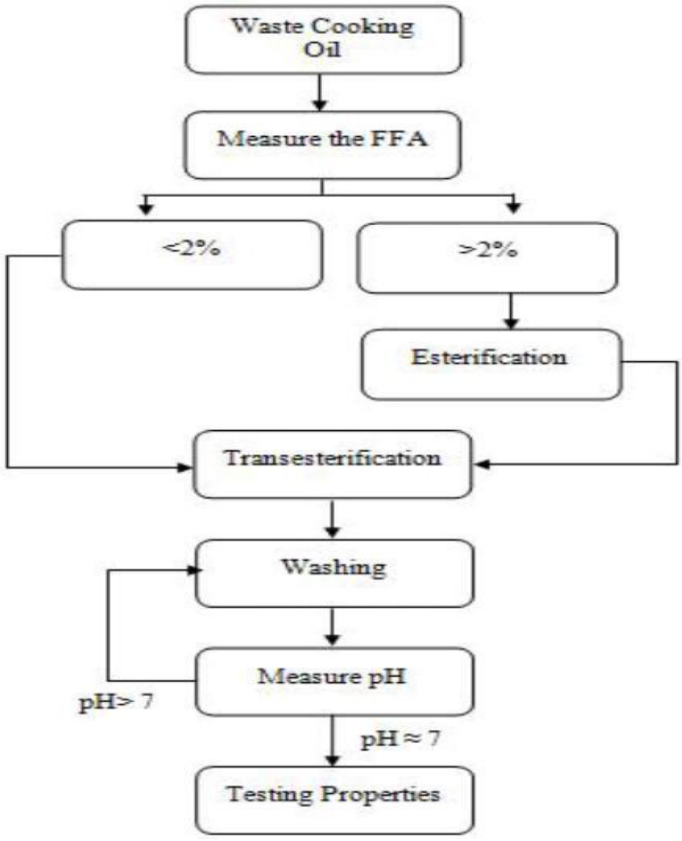


Figure 2. 6: A schematic process of biodiesel production (Owolabi et al., 2012)

Free fatty acids will be converted to biodiesel by direct acid Esterification, and the water needs to be removed (Verma & Sharma, 2016). Also, the FFA causes corrosion and low oxidation stability in WCO (Maheshwari et al., 2022). One of the studies (Tan et al., 2015), showed that Esterification could convert the FFA to biodiesel and reduce the FFA, as shown in Figure 2. In this reaction, FFA reacts with alcohol in the presence of a catalyst to give fatty acids. The most commonly used alcohol in these processes is methanol because of its low cost (Peng et al., 2018).

The Esterification step aims to minimize the acid value of Waste Cooking Oil. Usually, the Esterification process is an acid catalyzed homogenous process in which acids as sulphuric acid and hydrochloric acid. The research study of (Owolabi et al., 2012), said that if the acid value of the oil is very high, one-step Esterification may not reduce the FFA because of the high content of water produced during the process. So thus, the mixture of sulphuric acid and alcohol can be added to the oil three times as three-step Esterification. Furthermore, this reaction is slower than the base catalyzed trans-Esterification reaction, as

described earlier.

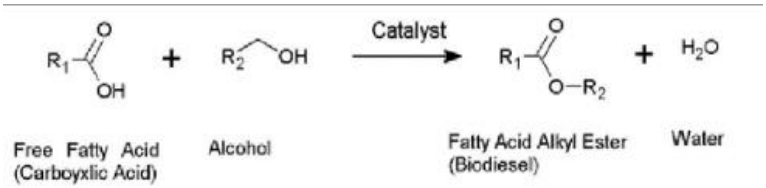


Figure 2. 7: A schematic representation of the Esterification reaction (V. Gupta & Pal Singh, 2023)

As described in the Esterification procedure, we aimed to reduce the FFA value of WCO to a value of less than or equal to 2% (Nasreen, Nafees, Qureshi, et al., 2018).

First, 1 wt. % Conc. Sulphuric acid (0.05g con. H2SO4/ 1g of FFA in oil) was mixed with a large amount (2 g CH3OH/1g FFA) of methanol. Then the mixture was added to oil with high FFA and stirred while maintaining the temperature at a constant temperature in the range of 50 – 55°C for 2 hours. Finally, the mixture was kept for 24 hours to settle down to two layers of ester and aqueous. Then the ester layer (bottom layer) was separated to measure FFA value, and for further alkaline Esterification, the aqueous layer (top layer) was discarded after the settle down. If not the FFA value of the ester layer is less than 2%, the above process must be repeated until it gives FFA content less than 2%. According to the previous study (Awogbemi et al., 2021), they have used 1 wt. % of sulphuric acid to Esterification and 1.5 wt. % of sodium methoxide to the trans-Esterification steps. Since the focus for this research is the development of an agricultural-based catalyst for biodiesel production by transesterification, more attention shall be focused on the transesterification method using chicken bones as a precursor for the catalyst.

2.12. AGRICULTURAL WASTES

Wastes are substances that are generated with no intention for further use and therefore has been discarded, rejected, disposed of, or abandoned. Agricultural wastes are remnants or non-useful products arising from agricultural activities or processes. They can also be the residues or leftovers from domestic consumption of agricultural products or the remainders of the industrial processing of agricultural products. If the cost of collection, transportation, and processing of the material is more than its economic values, such a material can be termed a waste. Wastes are generated during various agricultural operations and at every stage of the activities in the agricultural value chain beginning from land preparation, weeding, harvesting, to consumption or utilization of agricultural products at

domestic and industrial levels. The wastes can be in a solid or liquid state, and can be generated from crops, food, fruits, woods, vegetables, meat, poultry or dairy products.

Wastes from the agricultural industry constitute a substantial portion of global wastes and it is becoming a menace not only to environmentalists, town planners, but have also negatively impacted sanitation and air quality, caused environmental pollution thereby constituting health hazards to humans and animals alike. Inappropriate disposal and management of untreated agricultural waste exacerbate climate change by escalating the emission of greenhouse gases, releasing unpleasant odors, disrupting scenic landscapes. Global generation of agricultural wastes is almost five times of municipal solid waste and second only to industrial waste, particularly in countries with large farming and agricultural activities. In order to effectively manage wastes, systems of waste reduction, reusability, and recycling are being encouraged.

2.12.1. Classification of agricultural wastes

Agricultural wastes can be biodegradable, non-biodegradable, hazardous, or non-hazardous. Not many researchers have attempted to classify agricultural wastes. Obi et al. classified agricultural wastes based on the agricultural activities that generated the waste namely waste from cultivation activities (unused pesticides, herbicides, and fertilizers and their containers), livestock production (wastewaters, animal wastes, non-reusable animal food ruminants), and aquaculture (wastes from fish feeds and other water animals). Lakshmi et al. also categorized agricultural wastes into animal waste, food processing waste, crop waste, and hazardous agricultural waste. Examples of animal waste include manure, animal carcasses, while corn stalks, sugarcane bagasse, fruits, vegetables are crop waste. However, these efforts at classifying agricultural wastes appear inadequate as they do not seem to

cover all known examples of agricultural wastes. Any framework for agricultural wastes classification must be comprehensive, all-encompassing, and across-the-board. Building on the agricultural wastes classification by European Waste Catalogue, a more comprehensive framework for agricultural wastes classification are as follows:

2.12.2. Woody and crop residue

These are wastes generated from bush clearing, tree felling, and during post-harvesting of crops or after the crop have been processed.
They are the materials left on the farm after timber or crop has been harvested. They are mostly biodegradable and non-hazardous. Notable examples include leaves, sawdust, wood pellets, corn hob, corn cob, wheat bran, soybean hulls, molasses, rice husks, seed pods, roots citrus residues, sugarcane bagasse, palm leaves, banana trunks, etc.

2.12.3. Food and fruit residues

Food and fruit residues are the uneaten or discarded food and fruits. Examples are food wastes, eggshells, banana peels, orange peels, orange seeds, lemon peels, plantain peels, cassava peels, yam peels, groundnut shells, coconut shells, etc. This category of agricultural wastes is biodegradable and non-toxic.

2.12.4. Animal and wastewater wastes

Wastes are generated from animal husbandry, poultry, slaughterhouses, piggery, wastes from cattle, goats, cows, etc. They are generated in solid, semisolid manure or liquid (slurry) form. They usually have unpleasant odors, and are socio-culturally offensive. They include waste feed, cow blood waste,

cow dung, pig manure, animal fats, residual milk, chicken fats, feathers, animal bones, chicken bones, poultry droppings, chicken feeds, bedding material, dairy wastewater, wastewater from cleaning of animal houses, etc. Some of this category of agricultural wastes are non-biodegradable and pose a serious threat to humans and the environment.

2.12.5. Fishing and aquaculture wastes

These are wastes generated from agricultural activities at the aquatic habitat mainly from feed, chemicals, and pathogens. They can be in solid state wastes which originates from the uneaten feed and fecal droppings or dissolved wastes derived from food metabolism or decayed, discarded feed. They include dead fishes, fish fins, uneaten feed, fecal droppings of fish, exoskeleton of shrimp, etc. Though some of this category of agricultural wastes is biodegradable, they, however, generate offensive odors, socially unpleasant, litter the environment, and pollute terrestrial and aquatic habitats if not appropriately disposed of.

2.12.6. Wastes from agricultural activities

These are the categories of wastes generated from agricultural activities like farming, horticulture, hunting, etc. Notable examples include used wooden pallets and crates, foils, plant trimming, shrubs, grasses, animal skin, tree trunks and branches, wastewater, discarded guns, unsold flowers, dead animals, recovered decayed animal, cans, trays, etc. (Awogbemi et al., 2021). Some of them are biodegradable and produce nasty odors and an environmental nuisance when decaying. Those that are non-biodegradable are discarded indiscriminately and increase farm wastes.

2.12.7. Food preparation and processing wastes

These include waste foods, wastewater, eggshells, rice husks, wheat powder, coffee husks, waste barley, brewery wastewater, sugar refinery wastewater, banana peels, oil palm empty fruit bunch, olive mill wastewater, sugarcane bagasse, dairy wastewater, and other wastes generated at every stage of food preparation and processing, etc. (Parida et al., 2022). Some of these wastes are biodegradable though with social, environmental, and health consequences, if not well handled. For example, wastes from the kitchen, such as food leftovers, wastewater, etc. attract rodents, flies, mosquitoes, cockroaches, and other pests which are carriers of disease-causing agents.

2.12.8. Development of agricultural wastes into heterogeneous catalysts

Over the past few decades, commercial heterogeneous catalysts have been severally used and reported in the literature for the conversion of various feedstocks into biodiesel. Some of the metal oxides and mixed metal oxides obtained from commercial sources include calcium oxide (CaO) (Ma & Liu, 2019), calcium methoxide, calcium diglyceroxide, magnesium oxide, magnesium zirconate ($Mg_2Zr_5O_{12}$), aluminium oxide supported molybdenum oxide, aluminium oxide supported calcium oxide [60], magnesium pyrophosphate, sulphated zirconia, sodium molybdate, etc. Though some of these catalysts are reported to have high conversion efficiency, they are unsustainable as catalysts for biodiesel production owing to their complex and labour-intensive methods of preparation. Since they are commercial catalysts and produced from non-renewable sources, their application poses disposal problems and raises environmental concerns.

Catalysts derived from agricultural wastes are low-cost, non-toxic, non-corrosive, generates no wastewater, and are readily available. They have a high conversion rate, biodegradable, and a viable means of disposing of agricultural wastes by biodiesel producers [66–68]. In recent years, various agricultural wastes have been developed, converted, and utilized as low-cost and eco-friendly catalysts for the synthesis of biodiesel, using various low-grade feedstocks. Some of the agricultural wastes derived heterogeneous catalyst with high catalytic activities include eggshells, shrimp shell, animal bones, oyster shell, chicken bones, coal fly ash, banana peel, banana trunk ash, *musa balbisiana* peel ash, cocoa pod husk ash, coconut husk ash, pineapple (*Anan´as comosus*) leaves ash, waste fish (*Labeo rohita*) scale, waste fish bone, etc.

2.12.9. Preparation methods for catalysts derived from agricultural wastes

Over the years, various techniques have been used by various researchers to convert agricultural wastes to catalysts. These procedures are carefully selected to enhance their catalytic potentials. Awogbemi et al. employed washing, drying, grinding, sieving, and calcination to convert waste chicken eggshells into catalysts as depicted by the flowchart in Fig.4. Farooq et al. converted chicken bones into the catalyst by first washing the bones in hot water, drying them in the sun, drying them in the oven maintained at 110 ◦C for 6 h before pulverizing. The resulting powder was subjected to calcination at different temperatures for 4 h. Fig.5. Basumatary et al. adopted two routes in converting agricultural wastes to a heterogeneous catalyst, as shown by the flowchart in Fig. 2.

Similar procedures were followed by other authors for wastes from various shells and coconut wastes as shown Fig. 2(a) and (b). The preparation approaches for the conversion and

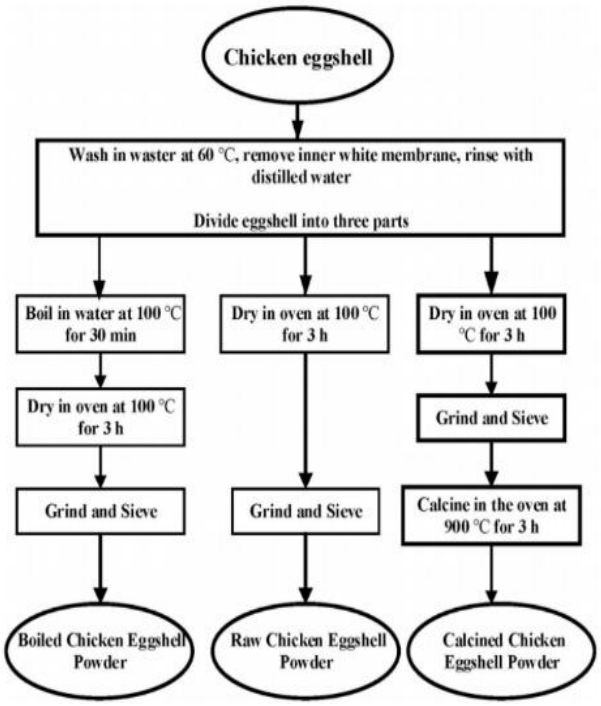


Figure 2. 8: Flowchart for modification of waste chicken eggshells into catalyst (Awogbemi et al., 2021)

development of agricultural wastes to solid catalysts involve the collection of the various waste materials from the farms, markets, factories, sorting of the wastes, and their transportation to the laboratories for further processing. The waste material is then subjected to cleaning to remove any unwanted object that has adhered to its body and drying, either in the sun or in an oven. Oven drying is faster and the drying rate can be controlled, but the cost of energy for drying is high. Sun-drying is cheaper but time consuming and the waste material is susceptible to contamination. After drying, the waste materials are ground using mortar and pestle. Further grinding into smaller particle sizes is done by an electrically powered grinder. The particle sizes are confirmed using a suitable sieve of appropriate

meshes. The waste material, now in powdered form, is subjected to high-temperature calcination over some time. The calcination temperature and time of calcination affect the performance of the catalyst and are carefully selected (Owolabi et al., 2012). Apart from calcination, there are other modification processes to enhance the performance and catalytic properties of the materials.

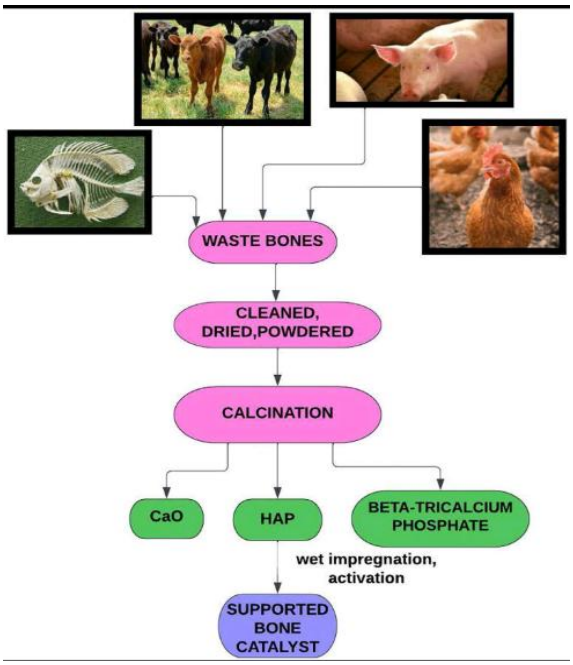


Figure 2. 9: A flow chart showing the general method of CaO preparation from various waste bones. Reproduced with permission of Elsevier from reference (Parida et al., 2022)

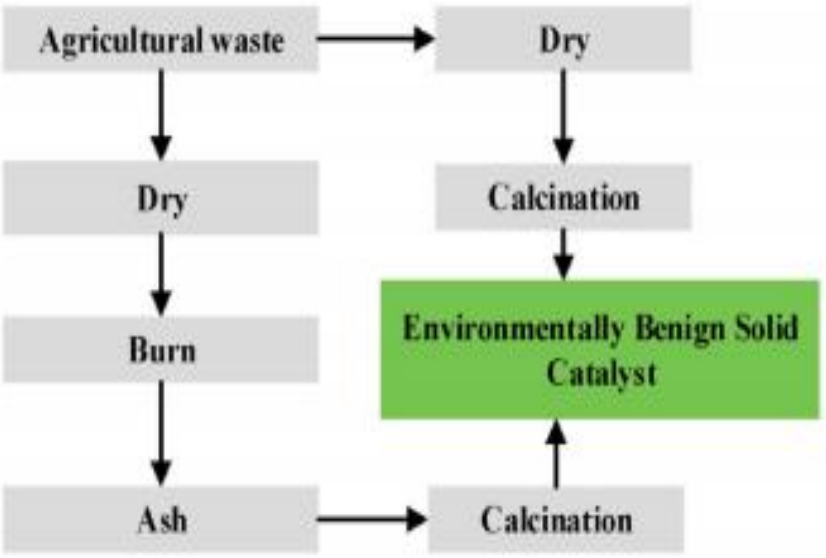


Figure 2. 10: Flowchart for the conversion of agricultural wastes into solid catalyst

Generally, agricultural wastes can be converted to solid catalysts by adopting the preparation methods as shown in Fig. 8. The catalysts can be used after grinding and sieving without any form of modification. The various modification processes are to improve the performance of the catalyst and allow further reusability. Major modification techniques include physical mixing, calcination, carbonization, wet impregnation, hydration, co-precipitation, calcination-hydration, etc.

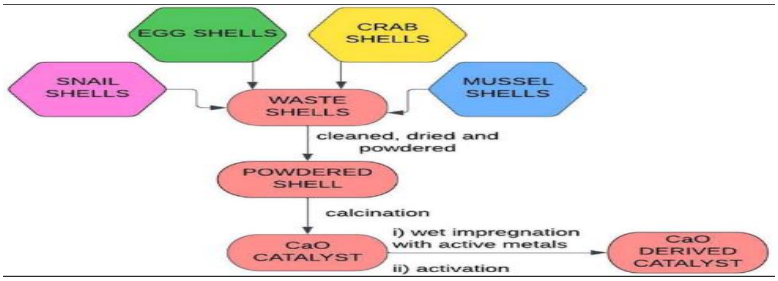


Figure 2. 11: A flow chart showing the general method of CaO preparation from various waste shells. Reproduced with permission of Elsevier from reference (Parida et al., 2022)

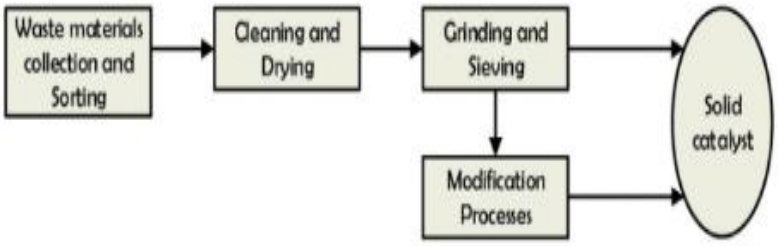


Figure 2. 12: Preparation methods for converting agricultural wastes to the solid catalyst

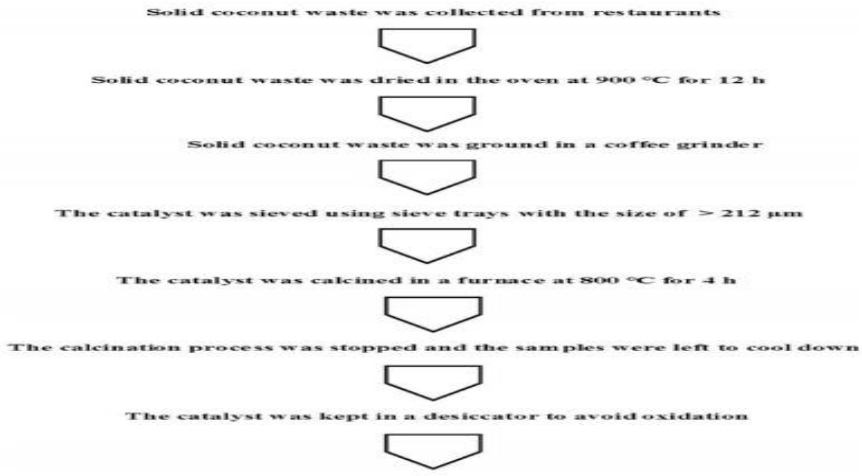


Figure 2. 13: Flowchart for the conversion of coconut waste into solid catalyst

2.13. CATALYSTS IN TRANSESTERIFICATION PROCESS

Catalysts play a significant role in the transesterification reaction. Catalyst types and concentrations are very important for achieving an optimal process (Issariyakul et al., 2014). Catalysts are usually used in the production of biodiesel to improve the reaction rate and yield (Tariq et al., 2012).

Catalytic activity is a function of its specific surface area, base strength and base site concentration. In general, a good catalyst must have several qualities (i.e. not be deactivated by water, be stable, be activated at low temperature and have high selectivity) (Rafaat et al., 2010). The selection of a catalyst depends on the amount of FFA in the feedstock while using WVO (Issariyakul et al., 2014). To achieve biodiesel that is economically feasible, the development of active and cheap catalysts for effective transesterification of different kinds of feedstock is absolutely necessary (Atadashi et al., 2012). There are three different types of catalysts that can be employed in the transesterification process of biodiesel: acid catalysts, base catalysts and biocatalyst (Pathak, 2015).

The usual industrial process employed for the commercial biodiesel production from plant-derived fats and oils is the catalyst-based Trans-E process. The process of transesterification involves oil/FFA reaction with alcohol and alkaline chemicals (NaOH or KOH). However, the synthesis of biodiesel using H-CAT (CaO) as an alternative to homogeneous catalysts can result in cost-effective biodiesel production due to recycle and reuse of catalyst. This research describes the synthesis and application of H-CAT for FAME synthesis. These catalysts were prepared using organic waste. Also, this research discusses the efficiency of H-CAT used to produce biodiesel. A process flow diagram of biodiesel generation from FFA/oil using H-CAT is shown in Fig.

2.13.1. Feedstock (oil/FFA) and catalyst

In recent years, alternatives to fossil fuels have been explored. Due to greenhouse gas emissions and global warming, pollutants from the burning of fossil fuels are associated with disease and climate change (Muthu et al., 2010). Alternative fuels for fossil fuels must be easily affordable, technically feasible, emit less GHG, and also meet pollution standards. Among various alternative fuels, biodiesel is

considered a non-toxic fuel. The use of biodiesel in engines without modification of the design is one of the critical advantages of using biodiesel (Luque & Clark, 2011)Various feedstock materials for biodiesel production via transesterification process: (i) Edible oil/FFA: canola, rapeseed, sorghum, rice, wheat, coconut, cottonseed, barley, copra, sunflower, safflower, oat, groundnut, waste cooking oil; (ii) Non-Edible oil/FFA: Jatropha, rice bran, salmon, tobacco seed, neem seed, Camelina, palm, pongam (karanj), rubber plant, tobacco seed, sesame, jojoba, and piqui; (iii) Animal FFA: Fish, chicken, tallow and lard; (iv) Other oil/FFA: Latexes, yellow grease, microalgae, tarpenes, fungi and bacteria (Abomohra et al., 2020; Athar and Zaidi, 2020; Chen et al., 2020b; Singh et al., 2021). The rate of Trans-E process and biodiesel yield can be enhanced using different types of catalyst. These catalysts are divided into three types, such as homogenous, heterogeneous, and enzymatic. Further, these catalysts are subdivided into different classes based on their nature and materials. The catalyst used in the conversion of oil to biodiesel is classified into homogenous, heterogeneous, and biocatalyst, as shown in Fig (Nasreen, Nafees, Zeeshan, et al., 2018). The homogeneous and H-CAT is divided into two types; (a) acid, and (b) base. The materials used during the preparation of catalyst define them as an acid/base catalyst. Compared to the homogeneous acid catalyst, base-catalyst has been reported to possess critical impact on increasing biodiesel yield from oil/fat within short duration during the Trans-E process (Nasreen et al., 2018). Therefore, homogeneous base catalysts are being used in industrial-scale biodiesel production from vegetable fats/oils containing low FFA and water. Although this approach is promising, some of the challenges that are being faced by the industry are (a) recovery of the product formed during the process, (b) recovery of the catalyst, and (c) reuse of the catalyst. The process of Trans-E is carried out usually at higher temperatures (>60 ◦C) when homogenous base/acid catalyst is used.

However, enzyme-catalyzed Trans-E takes place at moderate temperatures. Since higher temperatures have a considerable influence on enzyme activities during the process of Trans-E. Also, enzyme catalysts cannot be utilized for large scale production of biodiesel due to the longer reaction times, deactivation of enzymes, and high cost of enzymes (Kombe et al., 2012; Thanh et al., 2012). Currently, H-CAT derived from organic waste materials is considered promising to replace homogeneous catalysts. Compared with other catalysts, heterogeneous base catalysts are most effective due to the high conversion rate of glycerides to biodiesel. In a summarized version, the heterogeneous base catalyst is preferred for the Trans-E process because of shorter reaction time, lower temperature, and economically viable. Besides, the regeneration, reuse, and construction of these catalysts can lead to more extended activity as well as increased selectivity depending on the life of the catalyst (Sivasamy et al., 2009; Talha and Sulaiman, 2016). The use of H-CAT can reduce the current high costs spent for biodiesel production. Therefore, H-CAT with high catalytic activity, stability and eco-friendliness are being studied for biodiesel production. Some of the recent studies that have been carried out to convert oils to biodiesel via Trans-E process use calcined catalysts.

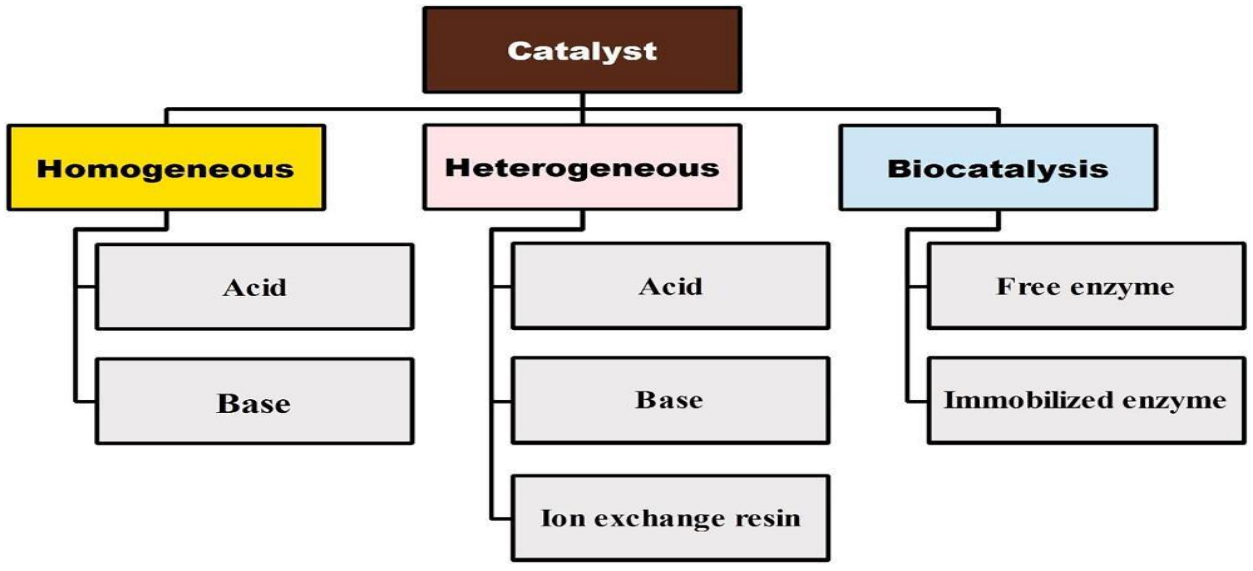


Figure 2. 14: Different types of catalyst for the conversion of oil to biodiesel (Nasreen et al., 2018)

2.13.2. Homogeneous acid and base catalysts

Homogeneous catalysts are conventionally used in commercial biodiesel production processes. The homogeneously-catalyzed process often offers a reaction yield higher than 97% in short period of time (10min-2h) with a reaction temperature between 25°C and 70°C (Issariyakul et al., 2014). Homogeneous catalysts are catalysts that exist in the same phase as the reactants and are limited to quality of the feedstock being anhydrous and acid value lower than 1mg of KOH/g of oil in the transesterification process (Chouhan et al., 2011). These catalysts can either be acidic (H_2SO4, HCl, H_3PO4, etc.) or alkaline (NaOH, KOH, CH3ONa, CH3OK). They are associated with a number of disadvantages including the formation of soap during biodiesel processes with FFA higher than 0.5%, corrosion of the equipment, high energy consumption resulting in an increase in capital equipment cost, difficult separation of glycerol from methyl ester which leads to formation of emulsion, and increases in viscosity (Atadashi et al., 2012). Others disadvantages include consumption of catalyst with water content higher than 0.3% resulting in low reaction yield, difficult recovery of glycerol due to the solubility of catalyst, the need for excessive methanol, long reaction time, high temperature requirement, high catalyst loading and catalyst toxicity (Christopher et al., 2014). Metal alkoxides (CH_3ONa and CH_3OK) are more active even at lower molar concentration but they are more expensive than alkaline metal hydroxide (NaOH and KOH); thus their low price makes them preferable as catalysts as they can render a high conversion of oil simply by increasing the catalyst concentration (Atadashi et al., 2012). The most commonly used homogeneous catalysts are basic catalysts, as they are 4000 times

faster than homogeneous acid catalysts (Deshmane and Adewuyi, 2013). These catalysts require high quality feedstock and give high conversions of TG at short reaction times. However, these have been shown to be sensitive to water and FFA content in feedstock, leading to soap formation, reduction of catalysts, and performance and separation problems (Christopher et al., 2014). During homogeneously-catalyzed transesterification the glycerol produced is of low quality and requires distillation for purification (Chouhan et al., 2011). Homogeneous acid catalysts such as H_2SO4 can be used to transesterify oil with high FFA and water content; however, the process is slower than reactions mediated by homogeneous basic catalysts. This is less attractive for industrial purposes but can be used in the esterification step, which converts FFA to TG. Marchetti (2012) and Zhang et al. (2003) showed biodiesel production from waste oil characterized by an acid concentration of 1.5-3.5mol%, with excess methanol in the presence of H2SO4, at a high molar ratio of 50:1, and a temperature of 80°C.

A 97% conversion was reached at a reaction time of 10h. The ability of a homogeneous acid catalyst to act as an esterification reagent and play a solvent role in the process can mediate esterification and transesterification processes to occur in a single stage. Studies have shown that two-stage transesterification is more advantageous: no acid waste treatment, low equipment cost, and easy recovery of catalyst as compared to the limitation of a single step process (Talebian-kiakalaieh et al., 2013).

2.13.3. Heterogeneous base catalysts (metal oxide)

Presently, there are several heterogeneous-base catalysts available for biodiesel production. These include CaO, CaZrO3, Al2O3 - SnO, Li/MgO, Al2O3/KI, KOH/Al2O3, KOH/Nay and alumina/silicate supported K2CO3 (Shu et al., 2010). Base-catalyzed transesterification is associated with faster rates and greater yield as compared to the acid-catalyzed processes (Christopher et al., 2014). These catalysts are classified into six categories according to Hattori's classification for solid base catalyst:

1. Single metal oxide

2. Mixed metal oxide

3. Supported alkali

4. Alkaline earth metals

5. Hydrotalcites

6. Organic base solids

The most commonly used are single metal oxides (Lee et al., 2009).

Reaction rates in single metal oxides depend directly on the basicity of the oxide, especially of the strong base site. There are a variety of single metal oxides — including magnesium oxide (MgO), calcium oxide (CaO) and strontium oxide (SrO) — that have been employed as catalysts for the transesterification of biodiesel (Supper et al., 1999; Sharma et al., 2011).

Liu et al. (2008) used SrO metal oxide as a catalyst for transesterification of soybean oil after calcination of SrCO3 at 1200°C for 5h. A 95% yield was obtained at 65°C, 3wt% catalyst and 12:1 molar ratio methanolto-alcohol. From the economic and ecological point of view, CaO is the most popular and

promising metal oxide applied for biodiesel synthesis due to its low cost, excellent catalytic properties, high basic strength (H = 26.5), minor toxicity, and low environmental impact due to its low solubility in methanol and high availability (Deshmane & Adewuyi, 2013; Liu et al., 2008; Navajas et al., 2012; Rezaei et al., 2013; Suppes et al., 2001; Tan et al., 2015). The use of CaO as a heterogeneous catalyst has been around for many years as it can be produced from numerous sources: chicken eggshell, mollusk shell, bones, golden apple snail shell, mussel shell, oyster shell, meretrix venus shell and mud crab shell (Boey et al., 2011; Jazie et al., 2013).

2.14. WASTE AS A SOURCE OF SOLID BASE CATALYSTS

Agricultural and industrial plants such as paper and pulp mills, sugar mills, fertilizer industries, metal industries, and thermal power plants generate surplus amount of waste. Waste materials such as rice husk, eggshells, animal bones, slag, dolomite rocks, ash, lime mud, red mud, mollusk shells, snail shells, oyster shells, shrimp, fish scales have been used for production of environment friendly and sustainable heterogeneous catalysts. Various types of wastes have the potential to be used as heterogeneous catalysts as they contain calcium in large amount which have high catalytic activity. Also several researchers found that calcium oxide solid base catalysts are most active and efficient catalysts. It has high surface area, nontoxic nature, high basicity, low cost, and effective fatty acid methyl ester yields (Marwaha et al., 2018).

The raw carbide slag from chemical industries is grounded and sieved to obtain 100 mesh particle size (Li et al. 2015). The obtained powder is dried at around 105 C and further calcinated using muffle furnace at temperature greater than 700 ^{o}C for 4 hrs. to prepare CaO. Similar procedure is carried out for deriving CaO from different waste materials including eggshells, bones, etc. (Bennett et al. 2016;

Tan et al. 2015). It is mostly found that the CaO derived from waste shell materials is much suitable for catalysis applications due to their high calcium carbonate content which imparts properties similar to those imparted by typical limestone (Mairizal et al., 2020). For economical production of biodiesel, researchers focus on development of natural heterogeneous catalysts made up of agricultural waste derived from several plants. Also, these catalysts are biodegradable in nature and hence have no disposal problems. Mainly agricultural byproducts or waste contains several organic compounds of carbon, oxygen, and nitrogen with metals such as sodium, potassium, magnesium, calcium, and other trace elements.

2.14.1. Chicken Bones as Heterogeneous Catalysts

The transformation of chicken bones into heterogeneous catalysts is a sustainable innovation in green chemistry, addressing both waste management and the need for environmentally benign catalysts in chemical reactions. Chicken bones, rich in calcium phosphate, particularly in the form of hydroxyapatite ($Ca_5(PO_4)_3OH$), can be thermally treated to produce porous, stable, and efficient catalytic materials. This process has gained prominence due to the abundance of bone waste, particularly from the poultry industry, and the increasing demand for low-cost, renewable materials for catalysis (Sharma et al., 2020).

2.14.2. Structure of Chicken Bones and Their Catalytic Potential

Chicken bones primarily consist of organic matter (mainly collagen) and inorganic minerals like hydroxyapatite, with the latter being of particular interest for catalysis. Hydroxyapatite has a large surface area, good thermal stability, and can be modified chemically to improve its catalytic activity (Taufiq-Yap et al., 2014). Upon calcination, organic components are removed, leaving behind the

mineral matrix, which can serve as a solid base catalyst due to its inherent basicity and structural properties (Igbokwe et al., 2021).

2.14.3. Preparation of Chicken Bone Catalysts

The preparation process for turning chicken bones into catalysts involves several key steps:

1. **Collection and Pre-treatment**: Chicken bones are collected as waste material, thoroughly cleaned to remove any residual organic matter such as fats and proteins, and dried.

2. **Calcination**: The dried bones undergo calcination, typically at temperatures ranging from 500°C to 900°C. This high-temperature process decomposes the organic components, leaving behind a calcined structure rich in calcium phosphate. During this process, the calcium phosphate adopts a porous structure, enhancing its surface area, which is crucial for catalytic activity (Sharma et al., 2020).

3. **Surface Modification**: To further improve the catalytic properties, calcined chicken bones are often impregnated with metal oxides such as zinc oxide (ZnO) or copper oxide (CuO). These metals serve as active sites for various chemical reactions, such as oxidation and reduction processes. Impregnation is achieved by soaking the bones in metal salt solutions, followed by drying and further calcination (Zhang et al., 2015).

4**. Characterization**: After preparation, the catalyst undergoes various characterization techniques to assess its structure, surface area, and active sites. Scanning electron microscopy (SEM) provides insights into the surface morphology, while X-ray diffraction (XRD) is used to identify the crystalline phases. Brunauer-Emmett-Teller (BET) analysis determines the surface area and porosity, both of which are critical for catalytic performance (Sharma et al., 2020).

2.14.4. Applications of Chicken Bone-Derived Catalysts

1. **Biodiesel Production**

One of the most well-researched applications of chicken bone-derived catalysts is in the production of biodiesel. Biodiesel is produced through the transesterification of triglycerides found in oils or fats with methanol or ethanol, where a catalyst is required to accelerate the reaction. Chicken bone catalysts have proven to be highly effective in this process due to their basic nature, which facilitates the conversion of triglycerides to methyl esters (biodiesel) (Taufiq-Yap et al., 2014).

For example, Igbokwe et al. (2021) used chicken bone ash as a heterogeneous catalyst for biodiesel production from waste oils. The study demonstrated that the calcined bones had a sufficiently high catalytic activity and could be reused multiple times without significant loss of activity. Furthermore, the catalytic efficiency was comparable to more expensive catalysts like sodium hydroxide (NaOH) but with the added benefit of being renewable and environmentally benign.

2. **Organic Synthesis**

In addition to biodiesel production, chicken bone catalysts have been employed in various organic synthesis reactions. One notable example is the **Knoevenagel condensation** reaction, which involves the condensation of aldehydes and active methylene compounds. The calcium phosphate in chicken bones provides a basic surface that promotes the deprotonating of methylene groups, thus facilitating the reaction (Zhang et al., 2015).

Similarly, calcined bones have been successfully used as catalysts for esterification reactions, which are essential in the production of various chemical intermediates. The porous nature and basic sites on the surface of calcined chicken bones accelerate these reactions, offering an efficient and reusable catalyst option (Sharma et al., 2020).

2.14.5. Advantages of Chicken Bone-Derived Catalysts

1. **Environmental Benefits**

One of the most significant advantages of using chicken bones as catalysts is the environmental impact. The poultry industry generates large quantities of bone waste, which can lead to environmental issues if not disposed of properly. Converting this waste into valuable catalysts not only reduces the environmental footprint but also contributes to the circular economy by transforming waste into a useful resource (Taufiq-Yap et al., 2014).

2. **Cost-Effectiveness**

Compared to conventional catalysts, which often rely on expensive and non-renewable materials, chicken bone-derived catalysts offer a cost-effective alternative. The raw materials are abundant and inexpensive, and the calcination process is relatively straightforward. Furthermore, the catalysts can be reused multiple times in reactions without significant loss of activity, further reducing operational costs (Igbokwe et al., 2021).

3. **Green Chemistry**

The use of chicken bones aligns with the principles of green chemistry, particularly in terms of using renewable resources and minimizing waste. By using a naturally occurring material, the process avoids

the need for synthetic chemicals that may have toxic or harmful environmental effects. Moreover, the reusability of the catalysts contributes to more sustainable chemical processes (Zhang et al., 2015).

2.15. CHALLENGES AND FUTURE PROSPECTS

While chicken bone-derived catalysts offer many advantages, some challenges remain. One challenge is the optimization of calcination conditions to maximize catalytic efficiency. Higher calcination temperatures can lead to sintering, reducing the surface area and catalytic activity. Thus, finding the optimal balance between temperature and catalyst performance is crucial (Sharma et al., 2020).

In addition, while chicken bone catalysts have shown promise in laboratory settings, further research is needed to scale up the process for industrial applications. Future research could focus on improving the mechanical strength and stability of the catalysts to ensure they can withstand the harsh conditions of industrial processes.

Chicken bones, typically considered waste, have proven to be a valuable resource in the field of catalysis. By undergoing thermal treatment and surface modification, they can be transformed into efficient and sustainable heterogeneous catalysts. These catalysts have shown potential in applications ranging from biodiesel production to organic synthesis, offering a green, cost-effective alternative to conventional catalysts. With continued research and development, chicken bone-derived catalysts could play a significant role in advancing sustainable chemistry.

2.15.1. Separation and Purification of Biodiesel

The biodiesel production process yields with it certain impurities and residues which are left in the biodiesel produced. These impurities and residues could be detrimental to the combustion system

and, therefore, have to be removed. The table below shows some of the effects of impurities and residues in biodiesel.

Table 2. 7: Effects of Impurities in biodiesel on Diesel Engine Performance

Impurity	Effects
FFAs	Corrosion, low oxidation stability. Hydrolysis
Water	Hydrolysis (free fatty acid and alcohols formation), corrosion, bacteriological growth (filter blockage).
Methanol	Low values of density and viscosity, low flash point (transport, storage and use problems).
Glycerides	High viscosity, deposits in the injectors (carbon residue), crystallization.
Metals(soap, catalyst)	Deposit in the injectors, filter blockage (sulphated ashes), engine weakening,
Glycerol	Settling problems, increased aldehyde and acrolein emissions

2.15.2. Phase Separation

This involves the separation of the glycerin layer from the ester layer. This process occurs naturally especially when methanol or absolute ethanol is used as a reacting partner in alkaline-catalyzed transesterification process since the glycerol has a higher density than the ester formed and therefore settles to the bottom. It can be quite a slow process (around 3 hours for complete

separation) and, therefore, to facilitate the separation, centrifugation has been suggested though it is not economical. Other means of facilitating the phase separation includes the addition of water. The addition of hexane and extra glycerol to the reaction mixture has also been proved to be helpful.

2.15.3. Purification of Biodiesel

Once phase separation has been achieved, the purification of the ester phase is necessary to ensure that the biodiesel meet specifications. After the phase separation of glycerol, the biodiesel still has an excessive amount of soaps, aggressive pH, catalyst, FFAs, water, methanol, glycerides and other impurities. These substances, if not reduced to their minimum, will have effects on the biodiesel. There are various means of removing the impurities mentioned that are left in the ester phase after transesterification.

Raw biodiesel must be refined and one of the most common approaches is water washing, in which clean water is passed through the biodiesel. Water is an excellent medium for neutralizing residual catalyst, as well as removing residual methanol and glycerol (13). In the water washing process, a certain amount of water mostly is added to the biodiesel and this is allowed to settle. As the water passes through the ester phase, it attaches to the impurities such as MG, DG, TG, catalyst etc. Once settled, the contaminated water is drained off together with the impurities.

This process continues until clear water is obtained. Once all the water is removed, the remaining biodiesel is dried and ready for final quality check. Traces of glycerol are removed by water or acid washing solutions (Karaosmanoglu et al., 1996).

Free fatty acids (FFA) are removed by distilling the ester phase making use of the fact that the boiling

points of methyl esters are generally 30^{o}C to 50^{o}C lower than the FFAs. Methanol is removed by heating the ester phase to a temperature of 70^{o}C.

Partial glycerides (MG, DG) can be removed from the ester phase by converting them into triglyceride which can then be separated from the methyl ester product. This is done by adding an extra alkaline catalyst to the ester phase and the reaction is heated to about 100^{o}C (Klok et al., 1990). In the process, the glycerol's and the partial glycerides react with the methyl esters and thus are converted to triglycerides which were then reintroduced into the transesterification reactor together with new oils.

Catalysts are generally removed by using an adsorbent such as bleaching earth (Wimmer, 1991), and also by the use of silica gel or magnesium silicate (Cooke, 2004). The method employed to purify biodiesel depends on the manufacturers and also the scale of the biodiesel produced.

2.16. OPTIMIZATION OF BIODIESEL PRODUCTION

Biodiesel production yield optimisation can be assessed using statistical analysis design expert software (e.g. Mini Tab, Design-Expert Stat-Ease 6.0.8, Design Expert 9). There are different approaches — response surface method (RSM), factorial design, fractional factorial, crossed and mixture design — used to discuss and explain the production yield generated from the experiment (Bezerra & Antoniosi Filho, 2014; Tan et al., 2015)Two are explained below:

- *Fractional factorial:* This is used to estimate main effect, interaction and screening of many factors to find significant few. This factorial can be irregular, general, D-optimal, placket Burman or Taguchi OA (Omar & Amin, 2011).
- *Response surface methodology:* This is used to investigate the influence of the reaction parameters of the process, to predict the optimum process condition, as well as to minimise the number of experiments. These properties may be determined by using different approaches: central composition design (CCD), Box-behnken, 3-level factorial, hybrid, 1-factor, pentagonal, hexagonal, D-Optimal, distance-based, modified distance, user-defined and historical data (Bezerra *et al*., 2008; Wan *et al*., 2011).

In this present study, Response Surface Methodology (RSM) was applied for data analysis with BBD technique tool to achieve optimum purity and yield of biodiesel production. This also was used to determine which variables have an impact on the response interest.

2.16.1. Response Surface Method (RSM)

The Response Surface Method (RSM) is a straightforward statistical approach primarily based on linear functions and is the most frequently employed technique for biodiesel optimization analyses (Bezerra et al., 2008). The purpose of RSM is to clarify the interaction effects among process variables derived from experimental data, facilitating the development of a three-dimensional response surface and contour plot driven by a regression model. This experimental design methodology not only provides an efficient means of evaluating uncertainty but also allows for inference with a minimal number of simulations. RSM encompasses two principal classes: Central Composite Design (CCD) and Box-Behnken Design, which each exhibit distinct structures. Prior to implementing RSM, it

is crucial to select an appropriate experimental design to determine the experiments to be conducted within the research area (Bezerra et al., 2008).

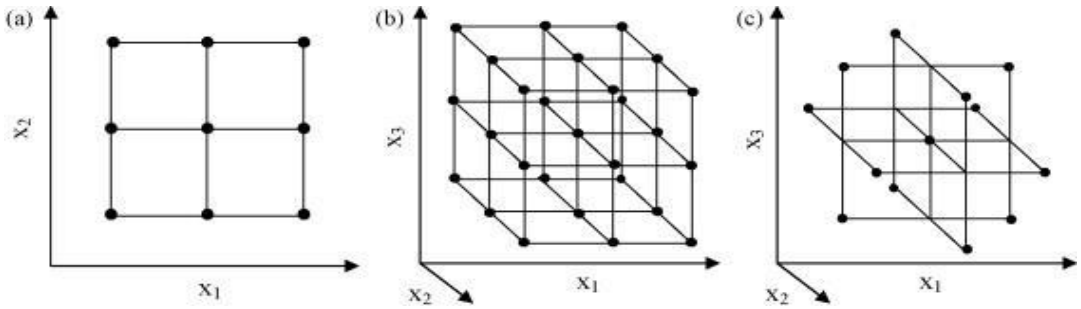
2.16.1.1. Box-Behnken Design

In Box-Behnken Design, each numerical factor is varied across three levels, requiring fewer experimental runs compared to three-level factorial designs. The factors are assigned one of three spaced values coded as -1, 0, or 1, and the design must conform to a quadratic model (Figure 2). The conceptual model can be visualized as a ball situated within a box defined by a wireframe constructed from the edges of the box. This method minimizes the necessity for numerous central points, as the exterior points are in closer proximity to the center (Rezaei et al., 2013).

Compared to Central Composite Design, the Box-Behnken Design has restricted capacity for orthogonal blocking and is particularly well-suited for studies involving a large number of variables

Nakatami et al. (2009) employed combusted oyster shell as a catalyst for the transesterification of soybean oil. The reaction conditions were optimized using factorial design. Findings indicated that the reaction duration (5 hours) and catalyst concentration (2.5 wt%) were the most critical factors influencing biodiesel purity, achieving a conversion rate of 98%. In a study conducted by Rezaei et al. (2013), the Box-Behnken design was utilized to assess the effects of calcination, temperature, catalyst concentration, and the methanol-to-oil molar ratio on the purity and yield of biodiesel. This approach proved effective, achieving 100% purity and a 94.5% yield at a 24:1 methanol/oil ratio with 2 wt.% catalyst concentration. The investigation also revealed that the molar ratio and catalyst loading were the most significant factors in biodiesel production. Additionally, Su et al. (2013)

employed the Box-Behnken design to explore reaction variables impacting the conversion of free fatty acids (FFA) during the esterification process involving enzyme-hydrolyzed FFA and methanol.



The study examined the effects of reaction time, temperature, methanol to FFA ratio, and hydrolyzed concentration, confirming that all factors were statistically significant with a confidence interval of 99.9%.

Figure 2. 15: Profile of Box-behnken design at three levels (adapted from Bezerra et al., 2008)

2.16.1.2. Central Composite Design (CCD)

Central Composite Design (CCD) is a widely recognized tool in Response Surface Methodology (RSM) used to analyze parameters affecting transesterification reactions and to predict outcomes. CCD is particularly suitable for sequential experiments and effectively fits a quadratic surface, which is typically advantageous for process optimization (Jazie et al., 2013). In the CCD framework, all corner points are represented on the surface using spherical coordinates, as illustrated in Figure 2.7. Each factor is varied across five levels: two axial points (plus and minus alpha), two factorial points (plus and minus one), and a central point. Compared to the Box-Behnken design, the CCD framework provides a more nuanced experimental design (Rezaei et al., 2013).

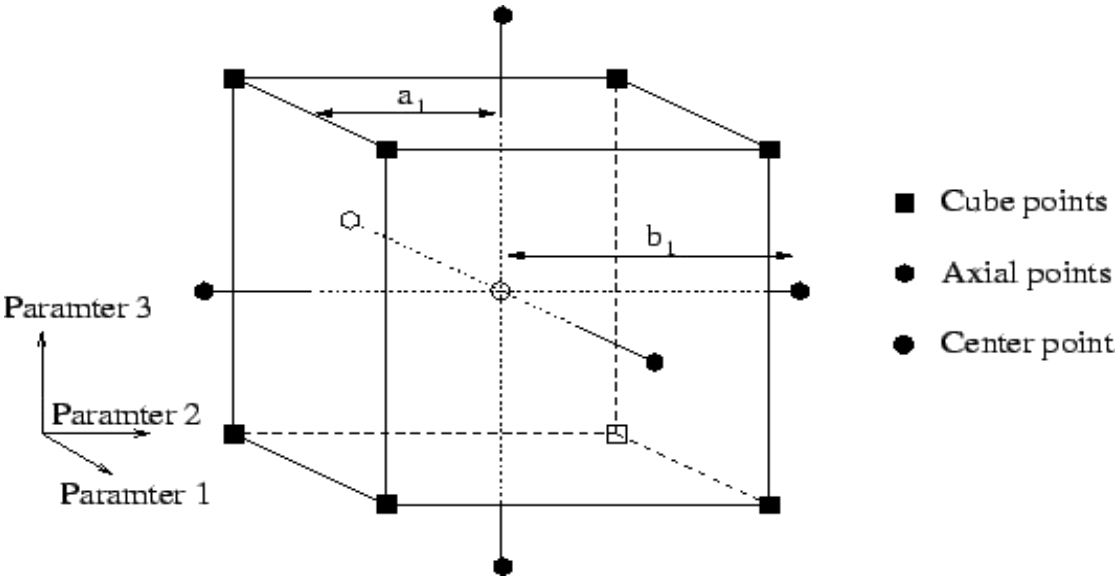


Figure 2. 16: Central composite design profile with three inputs

Omar et al. (2011) conducted a comprehensive study on the interactions of process variables utilizing the Central Composite Design (CCD) methodology to optimize conditions for Fatty Acid Methyl Ester (FAME) production. Through the application of Response Surface Methodology (RSM), the performance of the CaO catalyst was thoroughly analyzed, yielding a reliable prediction at a confidence level of 95% with full 24-factorial designs. In a similar vein, Jazei et al. (2013) implemented RSM in conjunction with the CCD tool, resulting in a quadratic polynomial equation. Omar and Amin (2011) also utilized RSM to examine the interplay between the methanol-to-oil ratio, reaction temperature, reaction time, catalyst loading, and Free Fatty Acid (FFA) conversion, employing a full 24-factorial design in the biodiesel production process from waste cooking palm oil using Sr/ZrO2 as a catalyst. Furthermore, Boey et al. (2011) explored the use of mud crab shells as a catalyst in biodiesel production, performing a statistical analysis

through CCD. The findings indicated that the primary factors influencing biodiesel yield were catalyst concentration, reaction temperature, and the methanol-to-oil molar ratio, achieving an impressive 93% yield. Based on these previous studies, this current research focuses on optimizing temperature, oil-to-methanol ratio, and catalyst loading.

2.17. KINETICS OF BIODIESEL PRODUCTION

The production of biodiesel presents significant complexities that challenge the formulation of a suitable kinetic model. Limited research has been conducted on the kinetics of biodiesel production, whether through experimental or computational methods (Herbinet et al., 2008; Boey et al., 2011; Quing et al., 2011). The intricate nature of biodiesel and the size of its constituent molecules have historically rendered direct combustion modeling unfeasible (Lai et al., 2011; Mohamed-Ismael et al., 2013). The overall reaction kinetics are contingent upon the individual rate constants for the conversion of triglycerides to diglycerides, monoglycerides, and the final ester product (Yusuf et al., 2011).

Numerous studies have addressed the kinetics of transesterification using a base catalyst (Casas et al., 2011; Quing et al., 2011; Yusuf et al., 2011). Kinetic models should be derived from three consecutive reversible reaction steps, each possessing distinct rate constants (Mohamed-Ismael et al., 2013). An increase in reaction temperature correlates with an increase in the rate constant, thereby accelerating the reaction rate (Issariyakul et al., 2014).

Consequently, it is necessary to maintain the reaction temperature below the boiling point of the alcohol: 65°C for methanol and 78°C for ethanol. If the reaction operates above the boiling point of the corresponding alcohol, pressure must be applied to keep the alcohol in a liquid state (Issariyakul et al., 2014). The most extensively studied methyl ester kinetically was methyl

butanoate, characterized by a four-carbon atom chain attached to the methyl ester group. Conclusions from these studies indicate that the fuel produced demonstrates kinetic features of methyl ester, while no kinetic features were observed with diesel fuel composed of longer chains with 16-18 carbon atoms (Herbinet et al., 2008; Mohamed-Ismael et al., 2013). Developing an accurate and detailed kinetics model for biodiesel remains challenging due to its composition as a mixture of various long hydrocarbon molecules (Mohamed-Ismail, 2013). Most models in biodiesel research have been developed following the framework provided by Curran et al. (1998), with variations based on the catalyst composition employed in the transesterification process (Herbinet et al., 2008).

Therefore, there is a pressing need for additional studies to more comprehensively evaluate the advantages and disadvantages associated with the kinetics of biodiesel fuel.

One way to alleviate this situation is by constructing a model approximate to the one in the form of the surrogate fuel model (Mohamed-Ismael *et al*., 2013). In response to this challenge, the first detailed kinetic model for biodiesel, based on the combustion of methyl butanoate, was developed by Fisher *et al*. (2000) (Mohamed-Ismael, 2013; Lin *et al*., 2013). To address this issue, Herbinet *et al*. (2008) developed a kinetic model for methyl decanoate ($C_5H_{10}O_2$) with cetane number 47 and studied the oxidation of methyl decanoate with 10 carbon atoms attached to a methyl ester group, following the rules established by Curran *etal*. (1998). This feature reacted closely to biodiesel and diesel fuel compared to methyl butanoate. Quing *et al*. (2011) used kinetics mechanism of biodiesel from waste oil using carbon based solid acid catalyst to determine the reaction order, for the reaction was found to be second order. Furthermore, Chantrasa *et al*. (2010) focused on the transesterificationof tricapryllin (TCP) and methanol on

solid base hydrotalcite catalyst in order to investigate the reaction kinetics in the temperature range of 60-120°C and 15:1molarratio. Vujicic *et al*. (2009) studied kinetics of biodiesel synthesis from catalyst; a first order reaction was established. More recently, Birla*etal*., in 2012, studied the kinetics of biodiesel using CaO from snail shell with waste oil, based on reaction temperature and time; a first order reaction was obtained between 5-8h. Different assumptions have been made in studying kinetics of waste oil (Shokri et al., 2017)

Catalyst concentration is constant; therefore, forward and reverse reaction rates follow the law of mass action. Forward and reverse reactions follow 2^{nd} order kinetics in the liquid phase. Triglyceride of palmitic acid, oleic acid and linoleic acid has the same reaction rate and reaction mechanism.

2.18. TRENDS IN BIODIESEL

Biodiesel, recognized as a sustainable and eco-friendly alternative energy source derived from lipids present in plants and animals, is rapidly gaining traction in the energy sector. Recent research emphasizes the utilization of animal fat waste from slaughterhouses as a reliable and cost-effective feedstock for the biodiesel industry (Binhweel et al., 2023). By converting substantial amounts of discarded animal fats (DAFs) into biodiesel, this practice not only diminishes slaughterhouse waste but also promotes the use of sustainable energy resources. The technologies involved in the disposal, treatment, extraction, and conversion of DAFs into biodiesel are undergoing rigorous examination and critical evaluation regarding their respective advantages and disadvantages, particularly in relation to the characteristics of animal-based biodiesel, which are noted for their reduced NOx emissions, enhanced oxidation stability, superior heating value, and favorable cetane number.

Nonetheless, discussions surrounding ethical, practical, and economic considerations persist. Research findings, such as those from Okoro et al. (2017), substantiate that DAFs can serve as a cost-effective and environmentally sustainable source of biodiesel fuel.

The adoption of advanced technologies has led to noteworthy enhancements, including improved reaction yields, reduced reaction time, diminished reliance on traditional energy sources, lowered energy requirements, and a decreased number of processing units needed.

2.19. RESEARCH GAP

A significant body of research has primarily focused on the use of specific non-edible oils, such as jatropha oil, castor oil, neem oil, rubber seed oil, and yellow oleander, as feedstocks for biodiesel production (Foroutan et al., 2021; Maheshwari et al., 2022; Stamenković et al., 2023)

However, challenges remain regarding their effectiveness as singular feedstocks, which include limitations related to supply and availability, composition and quality, conversion efficiencies, and environmental concerns associated with land use, habitat degradation, and deforestation (Brahma et al., 2022). Researchers have identified that strategically blending various oil feedstocks in appropriate proportions presents a viable solution to these challenges (Amenaghawon et al., 2024). A focused investigation into the feasibility of blending multiple oils to enhance biodiesel yield, while considering the sustainability and economic viability of the process, aims to determine the extent to which the biodiesel production process can be scaled up

CHAPTER THREE

3.0. MATERIALS AND METHODS

3.1. RAW MATERIALS AND REAGENTS USED

The reagents used for this experiment are found in the table below:

Table 3. 1 shows the reagents and raw materials used in the research.

Materials	**Sources**	**Uses**
Yellow Oleander Oil	Obtained from Bio resources Valorization Laboratory, UNIBEN	First oil for the blend
Neem Oil	Obtained from Bio resources Valorization Laboratory UNIBEN	Second oil for the blend
Deionized water	Obtained from Bio resources Valorization Laboratory, UNIBEN	To prepare solutions during the experiment
Benzene	Spectral Laboratory Services, Kaduna	Used for acid value test
Ethanol	Spectral Laboratory Services, Kaduna	Used for acid value test
Phenolphthalein	Spectral Laboratory Services, Kaduna	Used as an indicator for characterization tests
Potassium hydroxide	Spectral Laboratory Services, Kaduna	Used for acid value test and saponification value test
Acetic chloroform	Spectral Laboratory Services, Kaduna	Used for peroxide value test

Iodine solution	Spectral Laboratory Services, Kaduna	Used for peroxide value test
Starch	Spectral Laboratory Services, Kaduna	Used as an indicator for peroxide value test and iodine test.
Sodium Thiosulphate	Spectral Laboratory Services, Kaduna	Used for peroxide value and iodine test.
Carbon tetrachloride	Spectral Laboratory Services, Kaduna	Used for iodine test
Wijs solution	Spectral Laboratory Services, Kaduna	Used for iodine test
Hydrogen chloride	Spectral Laboratory Services, Kaduna	Used for iodine test
Copper Nitrate	Bio resources Valorization Laboratory	Used for wet impregnation of catalyst
Barium Chloride	Bio resources Valorization Laboratory	Used for wet impregnation of catalyst

3.2. APPARATUS AND EQUIPMENT USED

The glassware and equipment used in this experiment are shown in the table below.

Table 3. 2 Apparatus and equipment used in the research

Materials	**Sources**	**Uses**
Beakers	Pyrex (250ml)	Used to hold, mix and heat reagents or samples.

Erlenmeyer flask	Pyrex (250ml)	Used for mixing and heating solutions and oil samples
Measuring cylinder	Pyrex (250ml)	Used to measure the volume of liquids used in the experiment
Retort Stand	Bio resources Valorization Laboratory	Used to hold the burette in place for titration
Burette	Borosilicate glass (50 ml)	Used for titration
Heating Mantle	Bio resources Valorization Laboratory	Used to heat the oil during saponification test
Reflux Condenser	Pyrex	Used to cool the vapor released during heating
Weighing Balance	Bio resources Valorization Laboratory	Used to weigh the oil sample
Dropper	3.0ml rubber droppers	Used to transfer or measure small quantities of liquids in drops

Glass funnel	Pyrex	Used for guiding liquid or powder into a small opening
Masking tape	Purchased from a local vendor	Used to label samples, solutions and reagents
Muslin Cloth	Purchased from a local vendor	Used to filter residue and impurities from the oil

3.3. FEEDSTOCK

Neem Oil and Yellow Oleander Oil were procured from a reagent vendor in Kaduna State, Nigeria. It was transported under seal to the Bio resources Valorization Laboratory located at the University of Benin City, Edo State, Nigeria.

Plate 3. 1: Neem Oil

Plate 3. 2: Yellow Oleander Oil

3.4. METHODOLOGY

3.4.1. Oil Pre-treatment

The Neem oil was filtered with a muslin cloth to remove impurities and then transferred into a container, the same was repeated for the yellow oleander oil.

3.4.2. Oil Characterization

The oils were characterized through the following tests were carried out on the oil, all procedures followed were gotten from literature.

3.4.3. GCMS

Chromatography serves as a vital analytical tool, facilitating the separation of components within a gas mixture. Gas chromatography (GC), a widely utilized chromatographic technique, enables the separation and analysis of chemicals that vaporize without undergoing decomposition. GC is commonly employed to isolate various components and their proportions within a mixture or to assess the purity of specific products. Additionally, GC can extract pure compounds from mixtures. Through the fusion of gas chromatography and mass spectrometry (GC-MS), a unified method for studying chemical mixtures is achieved. While gas chromatography separates mixture constituents, mass spectrometry characterizes each component individually. Integrating these two approaches enables qualitative and quantitative examination of samples.

During GC-MS analysis, as the sample mixture is introduced into the chromatograph, differential flow rates cause it to fractionate into its constituent parts. This process facilitates both quantitative assessment of component parts and generation of a mass spectrum for each

component. GC-MS finds application in sample identification, environmental analysis, fire and explosives investigation, as well as drug detection. The three primary advantages of GC/MS analysis are its ability to identify organic components within complex mixtures, conduct quantitative analysis, and detect traces of organic contamination.

3.5. OIL BLENDING

1. Generate mixture design with RSM, using Simplex centroid design. A number of runs with the quantities of each oils to be used will be generated.
2. Mix the oils according to the mixture design by putting them all in a beaker and stirring for about 3-5 min.
3. After mixing get the viscosity, density and acid value of all the blends.
4. Calculate the FFA of all the blends.

Put the results back in design expert and get the optimum blend.

3.6. OIL PREPARATION

Filter all oils with a muslin cloth (or white handkerchief) to remove debris and impurities. Using the design expert software, get the various oil blends, and carry out the following tests on each blend:

1. Acid value (use this to calculate FFA)

$$FFA = \frac{Acid\ value}{2}$$

2. Viscosity (This is done with the viscometer in the lab)
3. Density
4. Saponification value

3.7. TEST PROCEDURES

3.7.1. Acid Value Test

V. Weigh 1g of sample in a beaker

VI. Add 10ml of Benzene

VII. Add 10ml of ethanol

VIII. Add 3 drops of phenolphthalein

IX. Titrate against 0.05M KOH until it turns pink

The acid value is then calculated using the formula below:

$$Acid\ value\ \left(mg\frac{KOH}{g}\right) = \frac{volume\ of\ KOH\ x\ 56.1\ x\ molarity\ of\ KOH(M)}{mass\ of\ oil\ (g)}$$

To prepare 0.05M KOH, multiply 0.05 x 56.1 (molar mass of KOH) = 2.805g

weigh 2.805g KOH pellets and dissolve in 1 liter of water.

3.7.2. Density Test

- Using a weighing balance, weigh a density bottle and record the value (bottle wt.)
- Put the oil in the weighed bottle (up to the 50g mark) and weigh again (bottle + Oil wt.)
- Subtract the two masses to get the mass of the oil (Oil wt.) i.e.

$$(bottle + Oil\ wt.) - (bottle\ wt.) = (Oil\ wt.)$$

- Calculate the density by dividing the mass of the sample by the volume of the oil (which should be a constant mass of 50g).

$$\rho = \frac{(Oil\ wt.)}{(Oil\ Vol.)}$$

3.7.3. Saponification Value Test (to be carried out for only the optimum blend)

1. weigh 1g of sample in a round bottom flask
2. add 50ml of 0.5M alcoholic KOH and place in the heating mantle (for reflux)
3. Leave for 50 minutes
4. Add 3 drops of phenolphthalein a pink coloration is formed
5. Titrate against 0.5M of HCl till the oil regains its original color.

The saponification value is the calculated with the formula below:

$$Saponification\ value\ (mg\ KOH) = \frac{(B - V)\ x\ 56.1\left(\frac{g}{mol}\right) x\ M}{W}$$

Where; M is the molarity of standard HCl (0.5M), B is the titration of blank in ml, V is the titration of test sample in ml, W is the mass of the oil and 56.1 is the molar mass of potassium hydroxide

To prepare 0.5M Alcoholic KOH, multiply 0.5 x 56.1 (molar mass of KOH) = 28.05g

28.05g / 2 = 14.025g
weigh 14.025g KOH pellets and dissolve in 50ml of ethanol.

3.8. CATALYST PREPARATION

3.8.1. Chicken bones

1. A full bag of chicken bones was sourced from Nadia complex opposite UNIBEN Main gate.
2. Wash the chicken bones thoroughly to remove impurities
3. Sun – dry them for two weeks till they are very dry
4. Break the bones into smaller bits using a hammer
5. Grind into powder (300nm). (This was done at a complex in Mela motel road, Uselu). There are sieves at Civil engineering lab that can be used to determine the size of the particles.
6. Calcine for 3 hours at 800^{o}C, using a new ceramic plate for each calcination.

3.8.2. Chicken droppings

1. This was sourced from poultries around uniben
2. Digest the droppings with water by keeping in an airtight can for about two weeks
3. Filter out the water and sun — dry for a few days until totally dry
4. Grind into powder

5. Sieve to required size
6. Carbonize for 2 hours at 700^{o}C.

3.8.3. Wet impregnation

10. Weigh the required amounts of each precursor (chicken bones and chicken droppings were used in the ratio 3:1) into a beaker and mix together
11. For 100g of catalyst, weigh 75g chicken bones and 25g chicken droppings
12. Weigh the required amounts of each salt (10% barium chloride and 10% copper nitrate was used) and dissolve them in 200g of deionized water
13. Put the salt solution on the magnetic stirrer and allow to stir for 3 minutes at room temperature to ensure the salts have dissolved properly.
14. Slowly add in the precursor mix bit by bit.
15. Allow to stir for 3 hours at room temperature.
16. After stirring, the mixture should have formed a paste
17. Allow the mixture to settle, till the paste and water have visibly separated
18. Oven dry the paste at 120^{o}C until completely dry
19. Crush the caked paste to powder form.
20. Calcine for 1 hour at 800^{o}C
21. Store in an air-tight glass jar, that's your required catalyst.

Plate 3. 3: Catalyst Preparation in Muffle Furnace

Plate 3. 4: Catalyst Preparation

Plate 3. 5: Catalyst stored in air-tight container

3.9. BIODIESEL PRODUCTION

1. Generate your design using design expert. There will be 17 runs. Keeping reaction temperature constant at 65°C.
2. For each run:
3. Weigh 50g of oil
4. Pre heat on the magnetic stirrer to about 40 degrees.
5. Weigh the required amount of catalyst and methanol
6. Note that once the methanol goes in, the reaction starts to happen. So, the flask being used should be closed immediately.
7. Allow to stir for the required time at the required temperature, using a magnetic stirrer.
8. After the time has elapsed turn into a separating funnel and allow to separate overnight. (It will separate into three layers: methanol, biodiesel and glycerol).
9. Separate the bottom layer (glycerol) from the top layers (methanol and biodiesel)
10. Heat off the methanol and weigh the amount of biodiesel produced after each run
11. From this, calculate the biodiesel yield of each run

Note: amount of catalyst, reaction time and temperature for each run will be generated in the design.

To calculate the amount of methanol in grams:

$$methanol = \frac{mass\ of\ oil \times ME{:}\,OL \times molecular\ weight\ of\ methanol}{molecular\ weight\ of\ oil}$$

ME: OL = methanol to oil ratio given in design

To calculate biodiesel yield:

Weigh the biodiesel produced and calculate with this formula:

$$yield\ (\%) = \frac{mass\ of\ the\ biodiesel\ (g)}{mass\ of\ oil\ used\ (g)} \times 100$$

Mass of oil used should be a constant value of 50g

Plate 3. 6: Produced Biodiesel

3.10. CATALYST CHARACTERIZATION

The sample underwent a series of characterization analyses to assess the properties of the synthesized catalyst. Surface morphology and elemental composition of the material was scrutinized through the amalgamation of energy-dispersive X-ray technology and scanning electron microscopy (SEM-EDX). X-ray fluorescence (XRF) examination was conducted to evaluate the oxide composition. Surface area and pore features were obtained using Brunauer, Emmett, and Teller (BET) studies. X-ray diffraction (XRD) analysis was employed to determine

the crystalline phase. Fourier transform infrared (FTIR) spectroscopy was utilized to explore the bond structure and interactions.

3.10.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is esteemed for its efficacy in analyzing the chemical properties and structure of diverse materials, including biological samples (Rosset & Perez-Lopez, 2019).

In industrial settings, it serves as a well-established method for quality control, often being the initial step in material examination processes. Detecting shifts in distinctive absorption band patterns can clearly indicate changes in material composition or the presence of contaminants. FTIR microanalysis is commonly utilized to pinpoint the source of product faults identified through visual inspection, particularly effective for examining larger surface areas and minute particles, typically ranging from 10 to 50 microns, to determine their chemical composition. When a sample is exposed to infrared radiation between 10,000 and 100 cm-1 by an FTIR instrument, some radiation is absorbed while some passes through. The absorbed radiation is transformed into vibration and/or rotational energy by the sample molecules. The resulting signal at the detector manifests as a spectrum, akin to the sample's chemical fingerprint, typically spanning from 4000 cm-1 to 400 cm-1. These unique spectrum fingerprints produced by each molecule or chemical structure render FTIR analysis an exceptional tool for chemical identification.

3.10.2. Brunaeur-Emmett-Teller (BET) Surface Area Analyzer

The Brunauer-Emmett-Teller (BET) theory serves as a fundamental analytical approach for determining the specific surface area of a material. It aims to elucidate the physical adsorption of gas molecules onto a solid surface. This theory is applicable to systems involving multilayer adsorption and is commonly employed to evaluate specific surface area using probing gases that do not chemically react with material surfaces as adsorbates. Nitrogen is the most frequently used gaseous adsorbate for surface probing in BET techniques, hence standard BET analysis is often conducted at the boiling temperature of nitrogen. Although alternative probing adsorbates such as water, carbon dioxide, and argon are utilized, typically at lower frequencies, to measure surface area across various temperatures and measurement scales. The specific surface area determined by BET theory can vary based on the adsorbate molecule used and its adsorption cross-section, as specific surface area is a scale-dependent feature lacking a singular, universally applicable value. (Nasrollahzadeh et al., 2019)

The use of porous materials in chemical reactions and separation procedures is common. Empirical gas absorption data are used to quantify the performance of porous material at a particular interior surface. The Bruner, Emmett, and Teller theory is frequently applied to determine a material's specific surface area. The Langmuir monolayer adsorption theory, which was later developed into a multilayer adsorption model utilizing BET theory, is where the fundamental concept of specific surface measurement originated. The specific surface area of porous materials, including crystalline and amorphous materials, is currently determined using the BET method. (Pourhakkak et al., 2021).

3.10.3. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a remarkably versatile technique that provides chemical insights for phase and elemental analysis. Apart from chemical characterization, XRD proves invaluable for texture analysis and stress measurements. While crystalline samples are typically required for XRD analysis, it can also determine the degree of crystallinity in polymers. Traditionally used for bulk sample analysis, recent advancements in optical techniques have extended its applicability to thin film examination. This method operates on the principles of Bragg's law of diffraction. (Nasrazadani & Hassani, 2016)

Another crucial method widely employed for characterizing polymeric nanocomposites is X-ray diffraction. It serves as the primary tool for determining bonding types and the order of crystalline organization in amorphous polymeric nanocomposites. Polymeric nanocomposites exhibit exceptional X-ray diffraction performance due to their crystalline behavior post-creation. XRD enables the identification of microstructural changes and interlayer spacing variations in the samples. (Assad et al., 2023)

3.10.4. X-Ray Fluorescence (XRF)

X-Ray Fluorescence (XRF) is a non-destructive analytical technique used to determine the elemental composition of materials. It involves the interaction of X-rays with the atoms of a sample, resulting in the emission of characteristic X-rays specific to each element present (Kakunai et al., 2023). This phenomenon allows for the identification and quantification of elements in a sample.

Recent advancements in XRF technology have improved its accuracy, precision, and speed (Liu et al., 2022). These advancements include the development of new X-ray sources, detectors, and data analysis software. Additionally, the use of machine learning algorithms has improved the accuracy of XRF analysis (Wang et al., 2023).

XRF is widely used in various fields, including materials science, environmental monitoring, and quality control. In materials science, XRF is used to analyze the composition of materials, such as alloys, ceramics, and glasses. In environmental monitoring, XRF is used to analyze the composition of soil, water, and air samples. In quality control, XRF is used to analyze the composition of products, such as pharmaceuticals and food.

The advantages of XRF include its non-destructive nature, high sensitivity, and fast analysis time. Additionally, XRF can analyze a wide range of elements, from light elements such as carbon and oxygen to heavy elements such as lead and uranium.

However, XRF also has some limitations. For example, XRF can be affected by matrix effects, which can reduce the accuracy of the analysis. Additionally, XRF may not be able to detect elements present in very low concentrations**.**

3.11. OIL/BIODIESEL CHARACTERIZATION

The oils were characterized through the following tests were carried out on the oil, all procedures followed were gotten from literature.

3.11.1. Peroxide Value Test

1. Weigh 1g of sample
2. Add 12ml of acetic chloroform

3. Shake vigorously for a minute
4. Add 0.5ml of iodine solution
5. Add 12ml of water
6. Add 1ml of starch (the solution turns blue-black)
7. Titrate against Sodium Thiosulphate till it turns colorless

The peroxide value is then calculated using the formula below:

$$Peroxide\ value = \frac{1000\ x\ M\ x\ (V - B)}{mass\ of\ oil\ (g)}$$

Where M is the molarity of sodium Thiosulphate, B is the titration of blank in ml, V is the titration of test sample in ml and 1000 is the standard factor for peroxide value.

3.11.2. Iodine Value Test

1. Weigh 1g of sample oil
2. Add 25ml of carbontetrachloride and warm in a water bath for a few minutes.
3. Allow to cool for 10 minutes
4. Add 25ml of wijs solution and shake vigorously
5. Keep in the dark for 30 minutes
6. Titrate against sodium Thiosulphate until it turns pale yellow
7. Add 10ml of starch as indicator (the solution turns blue-black)
8. Titrate further until the solution turns colorless

The iodine value is then calculated with the formula below:

$$Iodine\ value\ (\frac{gl2}{100g} oil) = \frac{(B - V)\ x\ M\ x\ 12.69}{W}$$

Where; M is the molarity of sodium Thiosulphate, B is the titration of blank in ml, V is the titration of test sample in ml, W is the mass of the oil and 12.69 is the Standard factor for iodine value.

3.12. DESIGN OF EXPERIMENT AND RSM MODELING

In the transesterification procedure, a **Box-Behnken design (BBD)** consisting of three different variables with a constant reaction temperature of **65°C** as detailed in Table 3. was employed. The range of these input parameters was established based on preliminary tests and existing literature (Oyedoh & Akhabue, 2019). Given the prevalence of quadratic responses in chemical engineering processes, this design was chosen due to its appropriateness for this application (Chitsaz et al., 2018). A quadratic regression model, denoted by equation (x), was fitted to the data obtained from the 17 experimental runs generated by the BBD. Model term calculation was carried out through several regression analyses, with analysis of variance (ANOVA) used to ascertain the usefulness of the model terms.

Table 3. 3: Range of input factors for Box-Behnken design.

Variable	**Symbols**	**Coded and actual levels**		
		-1	**0**	**1**
Reaction time (min)	X1	30	105	180
Catalyst loading (wt%)	X2	1	3.5	6
Methanol-to-oil molar ratio	X3	3	8.5	14

Design Expert software version 13.0 (Stat-Ease Inc., Minneapolis, USA) was used to carry out the experimental design and the corresponding statistical analysis.

$Y = bo + \Sigma b_i X_i + \Sigma b_{ij} X_i X_j + \Sigma b_{ii} X_i^2 + e_i$ .....(i)

Where;

The dependent variable (biodiesel yield) is represented by Y, while Xi and Xj denote the independent variables. The offset term is bo, the single and interaction effect coefficients are bi and bij, and the experimental error term is ei; this methodology was adapted from (Shegun et al., 2022).

CHAPTER FOUR

4.0. RESULTS AND DISCUSION

4.1. OIL CHARACTERIZATION

4.2. PHYSIOCHEMICAL PROPERTIES OF OIL SAMPLES (NEEM&YELLOW OLEANDER OIL) AND BLEND

The physical and chemical properties of the oil samples were analyzed in the laboratory. Table 4.1 presents the results obtained from the properties of the oil samples and its blend.

Table 4. 1: Physicochemical Analysis on Oil Samples

S/N	PROPERTIES	NEEM OIL	YELLOW OLEANDER OIL	BLEND OIL
Physical Properties				
1	pH			
2	Specific Gravity (@, 30^{o}C)			
3	API Gravity (@, 30^{o}C)			
4	Density (g/cm^{3}) (@,30^{o}C 30C)	0.883	0.901	0.887
5	Viscosity (mPas) (@, 30^{o}C)	5.93	4.02	4.66
6	Kinematic Viscosity (mm^{2}/sec) (@			

	30C)			
7	Moisture Content (%)			
8	Refractive Index			
Chemical Properties				
	Acid Value (mgKOH/g)	2.581	3.366	3.016
	Saponification Value	172.508	193.545	181.522
	Iodine Value	76.394	73.856	73.432
	Peroxide Value (meg/kg)	1.8	12	1.4
Thermal Properties				
8	Flash Point (C)			
9	Cloud Point (C)			
10	Pour Point (C)			

4.2.1. Determination of the Saponification Value

An American Standard for Testing Material (ASTM) method- D94 -07 (2017) was used for the determination of the Saponification Values of the samples. 2-5g of the sample was weighed into the Erlenmeyer flask or conical flask. 25ml of 0.5M ethanolic KOH was added and the resulting mixture was refluxed for 60 minutes. The resulting solution was subsequently titrated against 0.5M HCl with phenolphthalein as indicator. The resulting end point was obtained when the pink color changed into colorless. The same procedure was used for the blank. The Saponification value (SV) was then calculated using the expression;

$$\text{Saponification value (S.V.)} = \frac{56.1\,(B-S) \times M \text{ of HCl}}{}$$

Weight of sample

Source (f): ASTM-D94 -07 (2017)

Where;

B - ml of HCl required by blank

S - ml of HCl required by sample

N - Molarity of HCl

56.1- Molar mass of KOH

4.2.2. Determination of acid value (ASTM-D 664 - 18e2 (2018))

Acid values of the sample was also determined by ASTM method (ASTM - D 974(00). 0.2 - 0.5g of sample was weighed into 250ml conical flask. 50ml of neutralized ethyl alcohol was added. The mixture was heated on a water bath to dissolve the sample. The solution was titrated against O. l M KOH using phenolphthalein as indicator. The acid value was determined after which the free fatty acid was calculated respectively as follows;

4.2.2.1. Acid Value

$$\frac{= A\ x\ M\ x\ 56.1}{Weight\ of\ sample\ (g)}$$

Where:

A = ml of O. l M KOH consumed by sample

M = Molarity of KOH

W = weight in grams of the sample

Then;

4.2.2.2. Free Fatty Acid

$$\frac{=\ Acid\ Value}{2}$$

4.2.3. Iodine Value

This is a measure of the degree of unsaturation in any vegetable oil or animal fat. It is the weight of iodine absorbed by 100 parts by weight of the sample. It is expressed in (mg/g).

The oil sample was poured into a dry glass- stopper bottle of about 250 ml capacity and a small rod was added. The weight (g) of the oil was gotten by dividing the highest expected iodine value by 20. l 0 ml of carbon tetrachloride and 20ml of wiji's solution was added into the bottle and dissolved. The stopper which was moistened with potassium iodine solution was inserted and kept in the dark for 30 minutes. 15ml of potassium iodide solution and 100 ml of water was mixed and titrated with 0. 1 M of thiosulphate solution using starch as indicator just before the end point. A blank was carried out at the same time commencing with 10 ml of carbon tetrachloride.

Calculation:

Iodine Value =

$$\frac{(Blank\ Titre\ -\ Sample\ Titre)\ x\ 12.69}{Weight\ of\ sample\ (g)}$$

Where:

B = Blank titre value,

S = Sample titre value

4.2.4. Peroxide value

This is the measure of its content of oxygen. It is expressed in Mal/Kg. 2g of oil sample and l g of powdered potassium iodide was added into 2 test tubes containing 20ml of solvent mixture each (2 vol. glacial acetic acid + 1 vol. of chloroform) i.e. (60:30).

Step 1 was carried out in a blank tube (without sample). The tubes were placed in a water bath and allowed to boil vigorously for 30 seconds. The contents were poured quickly into a conical flask containing 10ml of 5% potassium iodide solution. The tubes were washed with 5ml of water each and poured into each conical flask with contents, and 4 drops of phenolphthalein was then added into each conical flask and was titrated with 0.01M thiosulphate until a color change was obtained.

Calculation:
Peroxide value

$$= \frac{(Sample\ Titre\ -\ Blank\ Titre)\ *\ 0.01\ *\ 1000}{Weight\ of\ sample\ (g)}$$

Where:

B = blank titre value and

S = sample titre value

4.2.5. Determination of refractive index

Abbey Refractometer was used in this determination. A drop of the sample was transferred into a glass slide of the refractometer. Water at 30^{o}C was circulated round the glass slide to keep its temperature uniform. Through the eye piece of the refractometer, the dark portion viewed was adjusted to be in line with the intersection of the cross. At no parallax error, the pointer on the scale pointed to the refractive index. This was repeated and the mean value noted and recorded as the refractive index

4.2.6. Determination of the Relative Density

The densities of the s were determined by ASTM method D – 129 –12b (2017) The sample was brought to a specified temperature and a test portion was transferred to a hydrometer cylinder that had been brought to approximately the same temperature. The appropriate hydrometer, also at a similar temperature, was lowered into the test portion and allowed to settle. After temperature equilibrium has been reached, the hydrometer scale reading and the temperature of the test portion were taken. The observed hydrometer reading was reduced to the reference temperature by means of a petroleum measurement table. Any hydrometer correction was applied to the observed reading and the corrected hydrometer scale reading recorded to the nearest 0.1kg/m3 as density

Calculation:

$$Density\ (g/l) = \frac{Weight\ of\ oil}{Volume\ of\ oil}$$

$$Specific\ Gravity = \frac{Weight\ of\ 50\ ml\ of\ oil}{Weight\ of\ water}$$

4.2.7. Dynamic Viscosity (ASTM D- 445):

This is the opposite of flow of liquid. It is expressed in mm2/sec or Pa/s or kg/ms. The viscosity of the oil was determined using Brookfield Digital rotational viscometer. The sample was heated in the hot oil bath and the spindle of the viscometer was fitted into the melted wax. The speed was selected and the start button was pressed for the spindle to rotate and give the angle of rotation including the viscosity measurement and operating temperature on the display for the biodiesel catches fire (supports combustion) was noted and recorded which gives the fire point of the sample.

Calculation of sulfur content of fuel oil:

= sulfur in weight of sample taken (%) = (ml $BaCl_2$ used—ml $BaCl_2$ for blank) X (sulfur equivalence)

The following amounts are Sulphur equivalence:

5 to 10% sulfur—10 to 15 mg sample;

2 to 5% sulfur—15 to 25 mg sample;

0 to 2% sulfur—25 to 40 mg sample

Table 4. 2: Viscosity Analysis at 40°C

Viscosity test report	h	
Test Information		

S/N	SAMPLE	MODEL	SPINDLE	RPM	DIAL READING (% TORQUE)	VISCOSITY (mPa.s)	TEMP (^{O}C)	TIME	NOTES
1	NEEM		4	6	103 .2	5 . 93	39 .6		
2	YELLOW		4	6	108 .2	4.0 2	39 .4		
3	BLEND		4	6	99 .6	4.6 6	40 .2		

Conclusion

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4.3. NEEM OIL – GC-MS ANALYSIS

The Total Ion Chromatogram (TIC) of Neem Oil illustrates multiple peaks indicative of various chemical constituents. The predominant compound identified is n-Hexadecenoic Acid (Palmitic Acid), which manifests at a retention time of 14.618 minutes with a notable abundance of 93%. As a saturated fatty acid, its peak in the chromatogram underscores its substantial presence within the oil. Additionally, Oleic Acid (C18:1, Z-9) represents another significant component, appearing at a retention time of 16.170 minutes with an abundance of 46%. This monounsaturated fatty acid is integral to assessing the oxidative stability of the oil. Furthermore, cis-Vaccenic Acid (C18:1, Z-11) is detected at 17.207 minutes, contributing to the oil's monounsaturated fatty acid profile with an abundance of 92%.

Further examination of the chromatogram reveals a prominent peak for 9,12-Octadecadienal, noted at 22.667 minutes with an abundance of 80%. This compound, a degradation product of linoleic acid, implies potential oxidation processes occurring within the oil. Another key component is Squalene, appearing at 25.905 minutes with an abundance of 74%. This peak signifies the presence of a naturally occurring antioxidant, which could enhance the oxidative stability of biodiesel derived from this oil. Additionally, 9,12-Octadecadienoyl Chloride is identified at 31.104 minutes with an abundance of 86%, suggesting the presence of reactive fatty acid derivatives.

The elevated levels of Oleic Acid and cis-Vaccenic Acid in Neem Oil indicate promising prospects for biodiesel produced from this feedstock, particularly in terms of oxidative stability and reduced viscosity, optimizing combustion efficiency in diesel

engines. The presence of Palmitic Acid enhances the cetane number, improving ignition quality; however, it may also raise the cloud and pour points, potentially affecting performance in lower temperatures. Squalene, recognized for its antioxidant properties, could extend the storage life of the biodiesel. Nevertheless, the detection of 9,12-Octadecadienal and 9,12-Octadecadienoyl Chloride may signify the presence of oxidation-prone compounds, necessitating further processing to bolster the fuel's long-term stability. To effectively illustrate these findings, the TIC graph of Neem Oil should be incorporated into the research documentation, clearly delineating the peaks of palmitic acid, oleic acid, and squalene, which are vital in assessing its biodiesel potential.

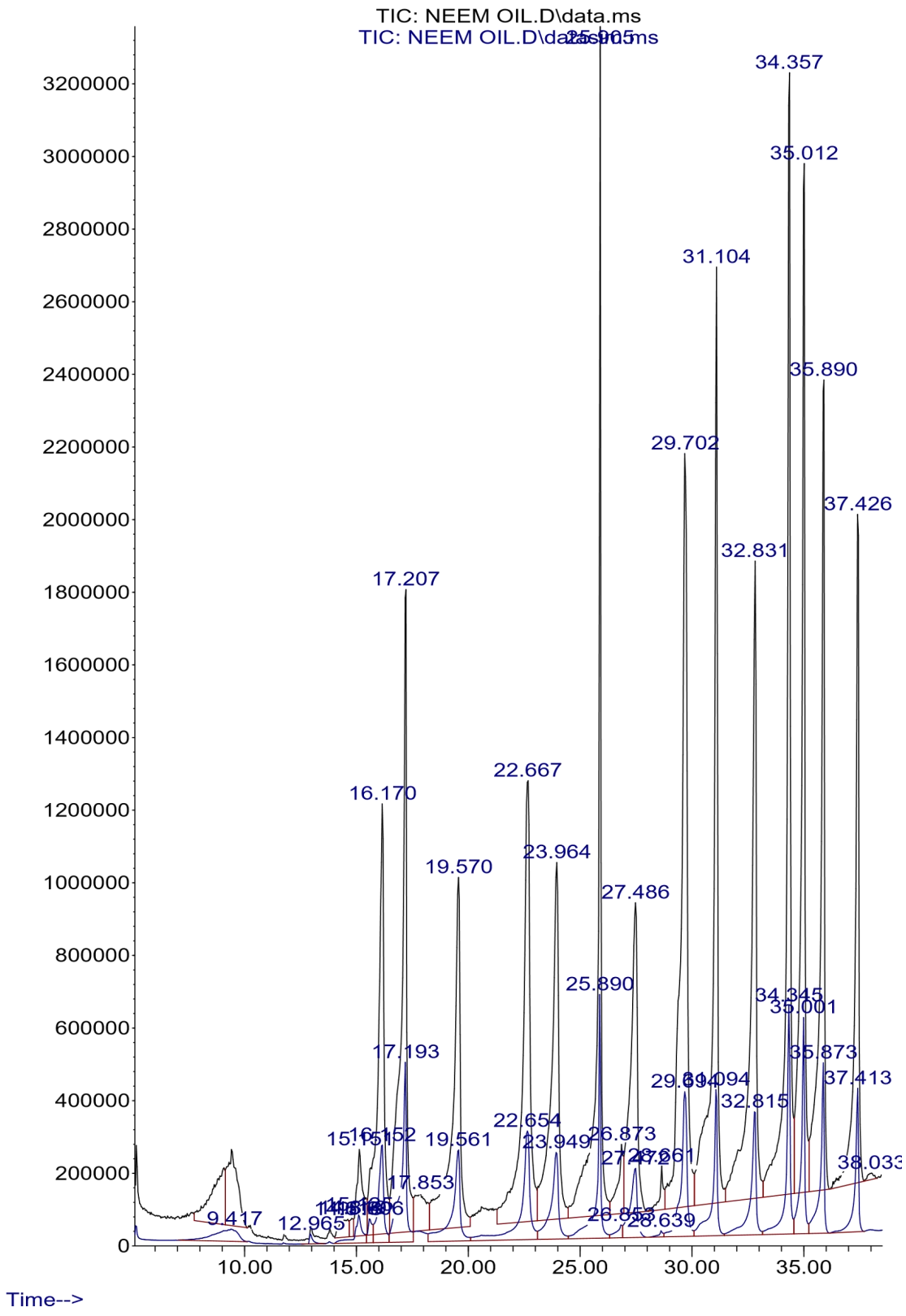

TIC: NEEM OIL.D\data.ms
TIC: NEEM OIL.D\data.ms
25.905
34.357
35.012
31.104
35.890
29.702
37.426
32.831
17.207
22.667
16.170
23.964
19.570
27.486
25.890
34.345
35.001
17.193
35.873
37.413
32.815
22.654
19.561
23.949
26.873
38.033
17.853
9.417
12.965
26.853
28.639
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
10.00
15.00
20.00
25.00
30.00
35.00
Time-->

Figure 4. 1: GCMS result for Neem oil

4.4. YELLOW OLEANDER OIL – GC-MS ANALYSIS

The GC-MS assessment of Yellow Oleander Oil identifies a high concentration of 9-Octadecenoic Acid (Z)-, 2,3-Dihydroxypropyl Ester, which registers at a retention time of 40.146 minutes and exhibits an abundance of 94%. This compound serves as a critical biodiesel precursor and ranks among the most prominent peaks in the chromatogram. The presence of Oleic Acid is also noteworthy, surfacing at 24.572 minutes with an abundance of 90%. This monounsaturated fatty acid is crucial in biodiesel production, enhancing oxidative stability and combustion efficiency.

Another significant compound noted is Farnesol Formate, appearing at 13.706 minutes with an abundance of 68%. This terpenoid may enhance the oxidative stability of the oil. Additionally, Heptacosyl Acetate is identified at 11.429 minutes, with a high abundance of 93%, indicating the presence of long-chain esters that may affect the oil's viscosity.

The elevated oleic acid content in Yellow Oleander Oil suggests that biodiesel derived from this source will exhibit excellent oxidative stability and minimal polymerization risks, promoting an extended shelf life. The presence of 9-Octadecenoic Acid (Z)-, 2,3-Dihydroxypropyl Ester exemplifies the oil's significant potential for transesterification, a critical process for biodiesel production. However, Heptacosyl Acetate indicates that the oil may possess a slightly higher viscosity, which could influence cold flow

properties. Furthermore, the Farnesol Formate content may contribute additional oxidative stability, potentially reducing the dependency on external antioxidants.

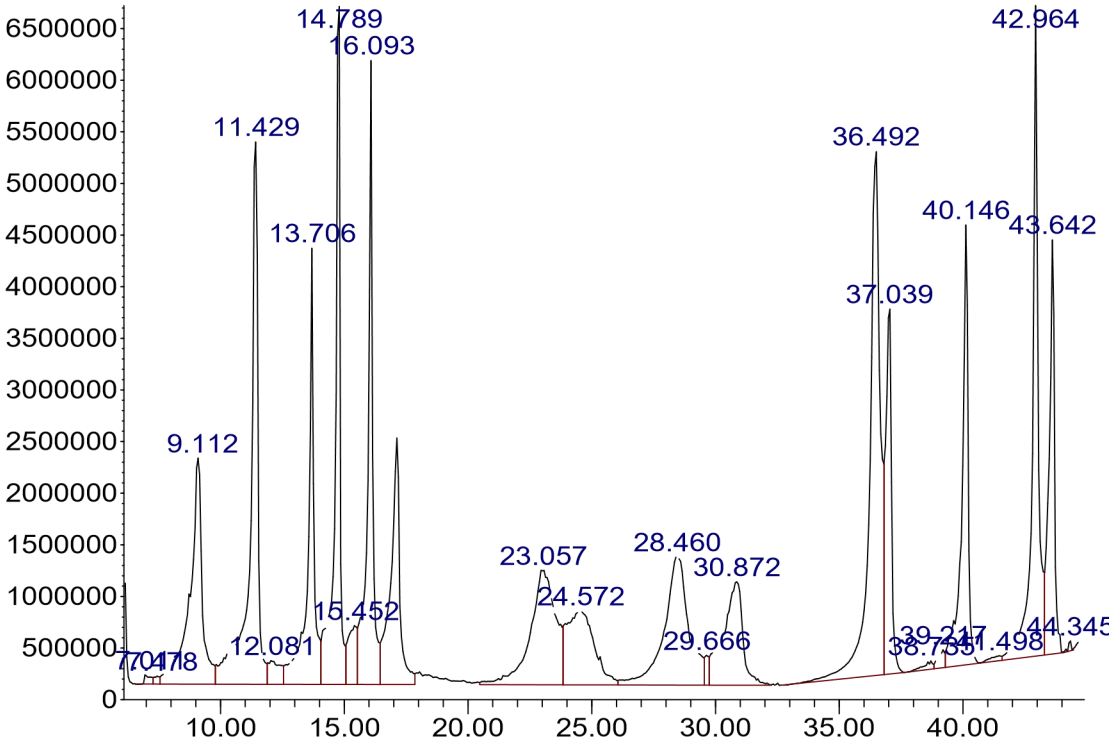


Figure 4. 2: GCMS result for Yellow Oleander oil

4.5. BLEND OIL (NEEM + YELLOW OLEANDER) – GC-MS ANALYSIS

The GC-MS analysis of the Blend Oil reveals a composite of the primary constituents found in both Neem Oil and Yellow Oleander Oil. The most prominent peak is attributed to Oleic Acid, detected at a retention time of 22.695 minutes, with a relative abundance of 93%. This indicates that the blend maintains a robust

monounsaturated fatty acid profile, which is advantageous for biodiesel production. Additionally, cis-Vaccenic Acid is present at the same retention time, with an abundance of 60%, contributing to the overall stability of the oil.

Another significant component identified in the chromatogram is 9-Octadecenoic Acid (Z)-, 2,3-Dihydroxypropyl Ester, appearing at 34.150 minutes with an abundance of 78%. This compound exhibits high reactivity during the transesterification process, making the blend an exceptional candidate for biodiesel production. Furthermore, Dodecanoic Acid, 1-(Hydroxymethyl)-1,2-Ethanediyl Ester is detected at 29.127 minutes, with a substantial abundance of 90%, confirming the presence of glycerol-bound fatty acids crucial for biodiesel synthesis.

The elevated concentration of Oleic Acid and cis-Vaccenic Acid in the blend bolsters oxidative stability and ensures efficient combustion characteristics, positioning it as a strong candidate for biodiesel production. The incorporation of 9-Octadecenoic Acid (Z)-, 2,3-Dihydroxypropyl Ester in the blend further optimizes transesterification efficacy, resulting in improved biodiesel yield. The identification of Dodecanoic Acid, 1-(Hydroxymethyl)-1,2-Ethanediyl Ester indicates the blend's significant potential for glycerolysis, which aids in the conversion of triglycerides into biodiesel. The overall fatty acid composition of the blend offers a well-balanced profile, ensuring excellent oxidative stability, moderate viscosity, and efficient cold flow characteristics.

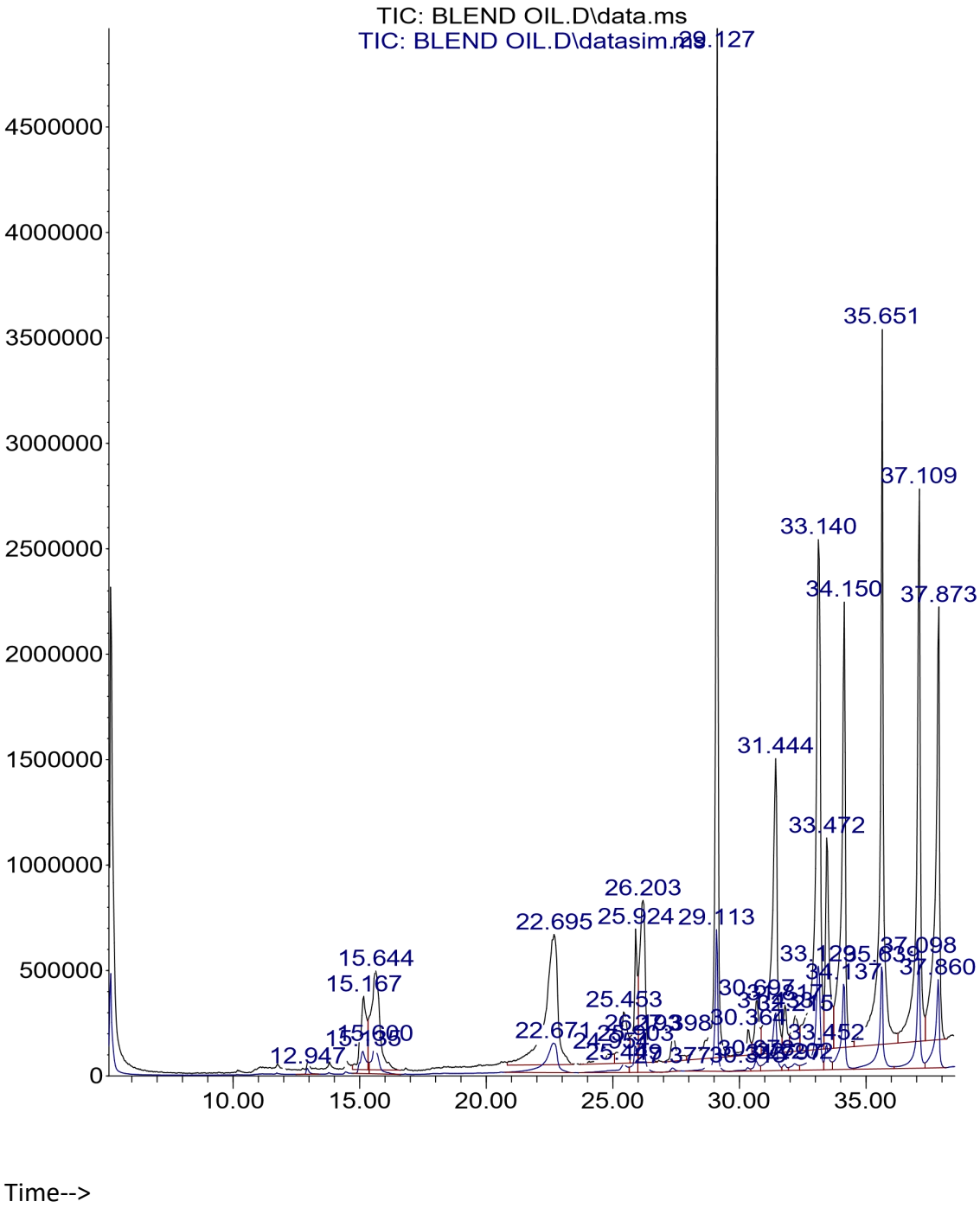
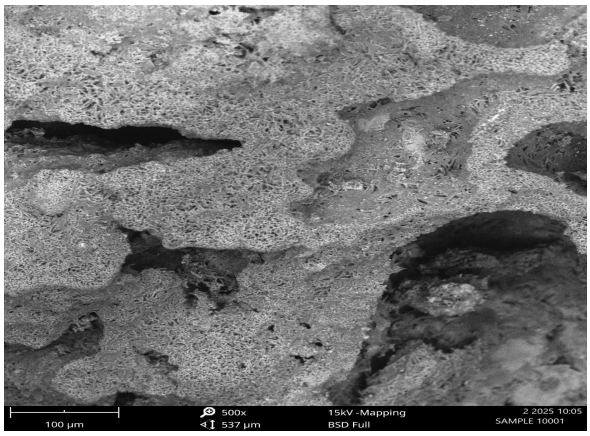


Figure 4. 3: GCMS result for Oil Blend

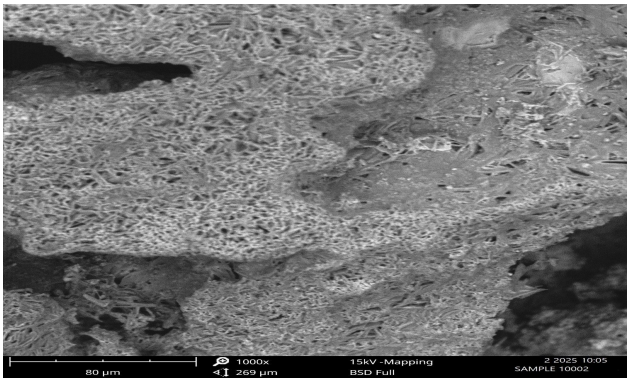
4.6. CHARACTERIZATION OF CATALYST

The physicochemical features of the catalyst were thoroughly assessed. The analysis included a Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BHJ) technique for the evaluation of the catalyst's pore properties. Furthermore, the Energy Dispersive X-ray Fluorescence (EDXRF) was used to ascertain the oxide composition, and an X-ray diffractometer was used to identify the treated catalyst's crystal phase. Lastly, to look into the functional groups incorporated into the new catalyst, an FTIR spectrophotometer was used.

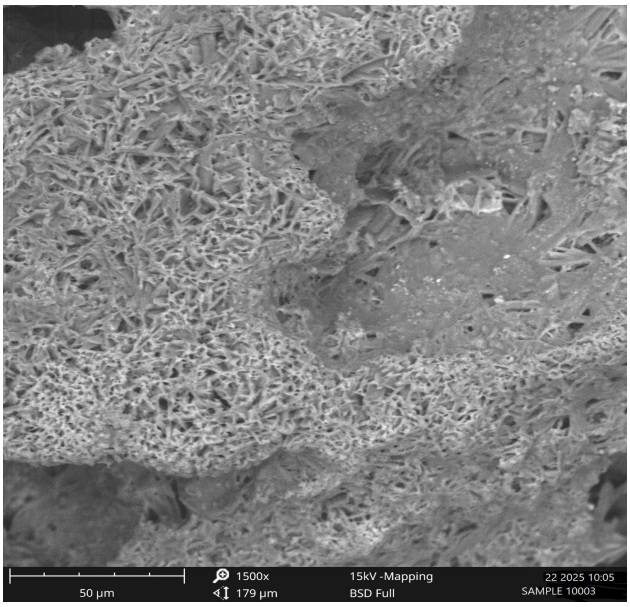
4.6.1. Scanning Electron Microscopy (SEM) Analysis



a) 500x



b) 1000x



c) 1500x

Figure 4. 4: SEM analysis of prepared catalyst (a) 500x (b) 1000x (c) 1500x

4.6.1.1. Discussion

1. **Morphology:** The images display a sophisticated and diverse surface morphology, suggesting a network of interconnected particles or grains. High magnification images (1500x, 1000x) provide a more intricate structure, potentially correlating to the active sites or support structure of the catalyst**.**

2. **Porosity:** The catalyst is characterized by high porosity, which is essential for catalytic performance as it enhances the available surface area for reactions. This porous structure allows for efficient access of reactants to the active sites and facilitates the diffusion of products away from these sites**.**

3. **Particle Size and Distribution:** A variation in particle size is observed. An even dispersion of the active catalytic phase is beneficial for enhancing catalytic efficiency**.**

4. **Backscattered Electron (BSE) Imaging:** The images were captured using backscattered electron (BSE) mode. In BSE imaging, contrast is determined by the average atomic number of the elements in the sample, where brighter areas correspond to heavier elements and darker areas to lighter elements. This method may be advantageous for a identifying the distribution of various components within the catalyst material, particularly if it is a composite**.**

4.6.1.2. Analysis for Catalysis

1. **Surface Area and Active Sites:** The high porosity and complex surface morphology indicate a substantial surface area. In catalysis, extensive surface area is preferable, as it provides numerous active sites for the reaction process. Features observed at higher magnification might delineate the arrangement of catalytically active components**.**

2. **Mass Transport:** The pore structure is pivotal for mass transport during reactions. The dimensions and interconnectivity of pores can affect the diffusion rates of reactants and products, which subsequently influences the overall reaction rate. It is crucial to have pores sufficiently large to permit easy access for reactants, while maintaining a structure that prevents the active components from being unreachable**.**

3. **Support Material:** If the catalyst comprises an active phase supported on a carrier material, the images may reveal insights regarding the dispersion of the active phase on the support. A uniform distribution of the active phase is typically sought to ensure optimal catalytic activity. The support material contributes mechanical stability, thermal durability, and helps maximize the effective surface area of the active catalytic components**.**

4. **Elemental Composition (Inferences from BSE):** With knowledge of the elemental components in the catalyst, BSE images can be utilized to deduce their distribution. For example, if the catalyst includes a heavy metal oxide as the active ingredient, one would anticipate observing bright regions in areas where this oxide is concentrated**.**

4.6.2. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The FTIR spectrum for the catalyst, recorded in the wavenumber range of 3495.26–499.96 cm^{-1}, offers critical insights into the functional groups present. A broad and pronounced absorption band at 3495 cm^{-1} is indicative of O-H stretching vibrations, suggesting the presence of hydroxyl groups.

These hydroxyl groups may originate from surface-bound water molecules or hydroxyl-functionalized metal oxides, which directly influence the material's basicity and catalytic activity.

A prominent peak identified in the 1400–1600 cm^{-1} range is associated with C=O stretching vibrations, typically related to carbonate or phosphate groups. This observation corroborates the Chlorapatite ($Ca_{10}(PO_4)_6F_{0.5}Cl_{1.14}$) phase recognized in the X-ray Diffraction (XRD) analysis, thereby confirming the presence of calcium phosphate compounds. While carbonate functional groups can enhance structural stability, they may also lead to CO_2 generation at elevated reaction temperatures, potentially impacting the catalyst's efficiency.

In the lower wavenumber region (below 1000 cm^{-1}), peaks attributing to Ca-O, Si-O, and P-O vibrations are distinctly observable. These findings validate the presence of metal oxides and phosphates, which are essential to heterogeneous catalysis. The phosphate vibrations correlate with the Chlorapatite phase, contributing to thermal stability and resistance to leaching.

Overall, FTIR results affirm that the catalyst contains hydroxyl, carbonate, and phosphate groups, which enhance reactivity, durability, and methanol adsorption in transesterification reactions. The presence of these functional groups indicates that the catalyst possesses active basic sites vital for the conversion of triglycerides into biodiesel.

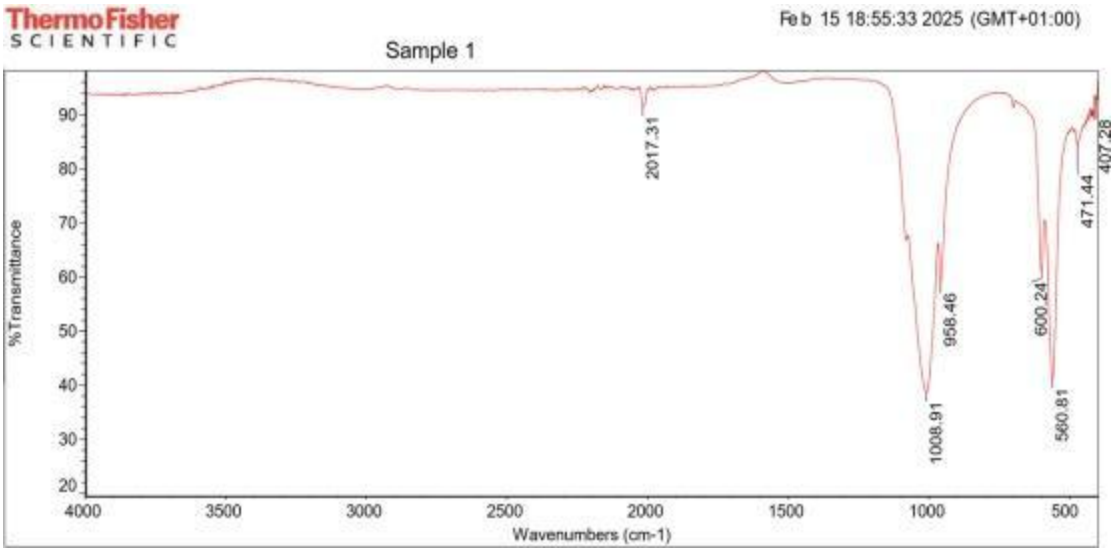


Figure 4. 5: FTIR Spectrum for the processed catalyst

4.6.3. X-ray Diffraction (XRD) Analysis

The XRD results obtained from XRD-1, XRD-2, and XRD-new provide valuable insights into the crystalline phases present within the catalyst.

These findings are paramount in assessing the thermal stability, durability, and catalytic efficiency of the material.

4.6.3.1. Major Phases Identified in XRD:

IX. Chlorapatite ($Ca_{10}(PO_4)_6F_{0.5}Cl_{1.14}$)

This phase is identified at 25.90°, 28.41°, 31.48°, 32.13°, 32.53°, and 46.41° (2θ positions). Chlorapatite contributes to structural stability and contains calcium and phosphate functional groups, thus enhancing catalyst durability.

The presence of fluoride (F^-) and chloride (Cl^-) further improves thermal resistance and minimizes leaching losses, ensuring sustained catalyst activity.

X. **Hatrurite (Ca_3SiO_5)**

Detected at 29.25° and 31.48° (2θ positions).

This phase, commonly found in cementitious materials, plays a role in enhancing thermal durability and mechanical strength. The calcium silicate structure introduces basic sites that improve transesterification efficiency.

XI. Lime (CaO)

Identified at 32.13° and 53.44° (2θ positions). This constituent is the primary catalytic component responsible for facilitating transesterification.

As a strong base, CaO assists in activating methanol and promotes the conversion of triglycerides into biodiesel.

XII. **Quartz (SiO_2)**

Recognized at 39.47° and 63.96° (2θ positions). While silica is catalytically inactive, its presence enhances the mechanical stability of the catalyst and helps prevent structural collapse at elevated temperatures.

The XRD results confirm that the catalyst exhibits high crystallinity, characterized by well-defined peaks indicative of structural stability and robust durability. The predominance of calcium-based phases (CaO and Chlorapatite) supports its efficacy in heterogeneous catalysis for biodiesel production.

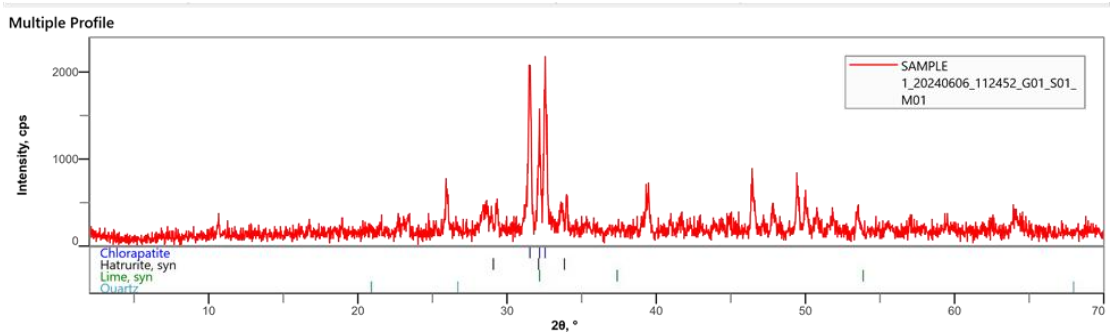


Figure 4. 6: XRD General Information

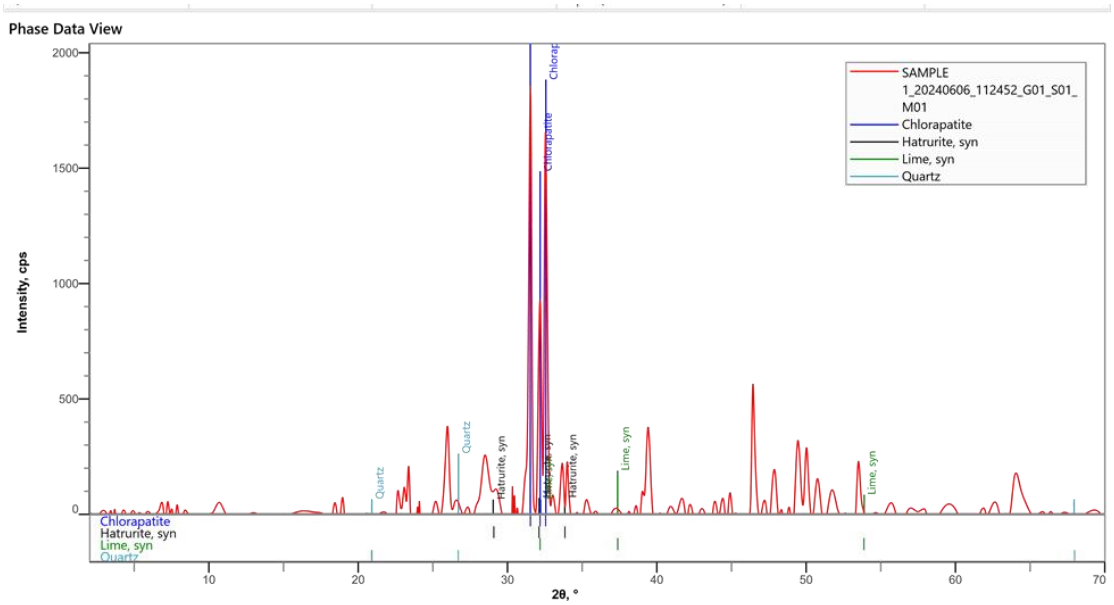


Figure 4. 7: XRD Phase Data View

4.6.4. X-ray Fluorescence (XRF) Analysis

The XRF results provide a detailed elemental composition of the catalyst . The data confirms the presence of major oxides, minor oxides, and trace elements, which influence the catalytic efficiency, stability, and reusability of the material.

4.6.4.1. XRF Analysis

Table 4. 3: Major Oxides Present in the Catalyst

Oxide	**Weight %**	**Role in Catalysis**
CaO	62.61%	Primary catalytic phase; provides strong basic sites for transesterification.
P_2O_5	27.34%	Forms stable phosphate networks (Chlorapatite), enhancing structural integrity.
SiO_2	2.24%	Inert material, enhances mechanical strength but does

		not contribute to catalysis.
Al_2O_3	2.97%	Provides thermal stability, preventing structural degradation.

The high CaO concentration (62.61%) is critical, as calcium oxide is a widely used solid catalyst in biodiesel production. The presence of P_2O_5 (27.34%) confirms that phosphate-based compounds (Chlorapatite) contribute to catalyst durability and leaching resistance.

Table 4. 4: Minor Oxides and Their Impact

Oxide	Weight %	Role in Catalysis
Fe_2O_3	0.46%	Can enhance catalytic activity but may promote oxidation side reactions.
MnO	0.026%	Acts as a structural stabilizer but has

		negligible catalytic activity.
TiO_2	0.05%	May provide minor surface enhancement properties but is catalytically inactive.
ZnO	0.013%	Can modify catalyst acidity, influencing transesterification selectivity.

The minor oxide content suggests that the catalyst has a stable structure with minimal impurities. The presence of Fe_2O_3 and ZnO could influence reaction kinetics, but their concentrations are low enough to prevent significant negative effects.

Table 4. 5: Trace Elements and Their Effects

Element	Weight %	Role in Catalysis
Cl	3.17%	May originate from precursors, could impact catalyst reusability.
K_2O	0.309%	May slightly alter basicity, but has limited catalytic influence.
BaO	0.023%	Minor presence, negligible catalytic effect.
MoO_3, WO_3, Ag_2O, SnO_2	<0.5% each	Present as traces, unlikely to

		significantly alter performance.

The presence of chlorine (Cl, 3.17%) suggests chlorinated precursor materials, which may affect catalyst lifetime due to possible leaching or decomposition over multiple reaction cycles. However, the low levels of potassium (K_2O) and barium (BaO) indicate that the catalyst has a stable composition with minimal unwanted elements.

4.6.5. BET Analysis

The surface area of a catalyst directly affects its activity. An individual surface atom or a group of atoms with a distinct structure and set of properties is referred to as the "active site" where the catalyzed transformation occurs. Catalytic reaction processes are discussed from this perspective. The number of accessible active sites per unit mass of a catalyst or per unit volume of a reactor determines the catalytic process's efficiency. Since materials of a given kind often have about equal numbers of active sites per unit surface area, the amount of exposed surface area of a catalyst determines its overall activity. Even though there are many other factors that might affect the reaction kinetics in a catalytic reactor, such as diffusion kinetics, adsorption-desorption kinetics, and surface reactions equilibriums, it seems that the number of active sites is the main factor controlling the reaction rate. The bio-based catalyst's enormous surface area suggests that it is extremely catalytically active. These results imply that the catalyst's active site exists and that it can aid with diffusion problems because of the larger pore size and better

flow channels on its exterior surface. This could speed up the reaction and accelerate how rapidly the reactants interact when combined (Tan et al., 2015). The BET surface area of the catalysts measured 153.999 m^2/g for the catalysts. The larger surface area suggests high catalytic activity. The pore volume and diameter were 0.137 cc/g and 2.740 nm for the catalysts. The micro pore size was 5.631 nm in width and 0.067 cc/g in volume for the catalysts indicating the presence of active sites that could enhance diffusion and reaction rates. These findings are detailed in Figures below;

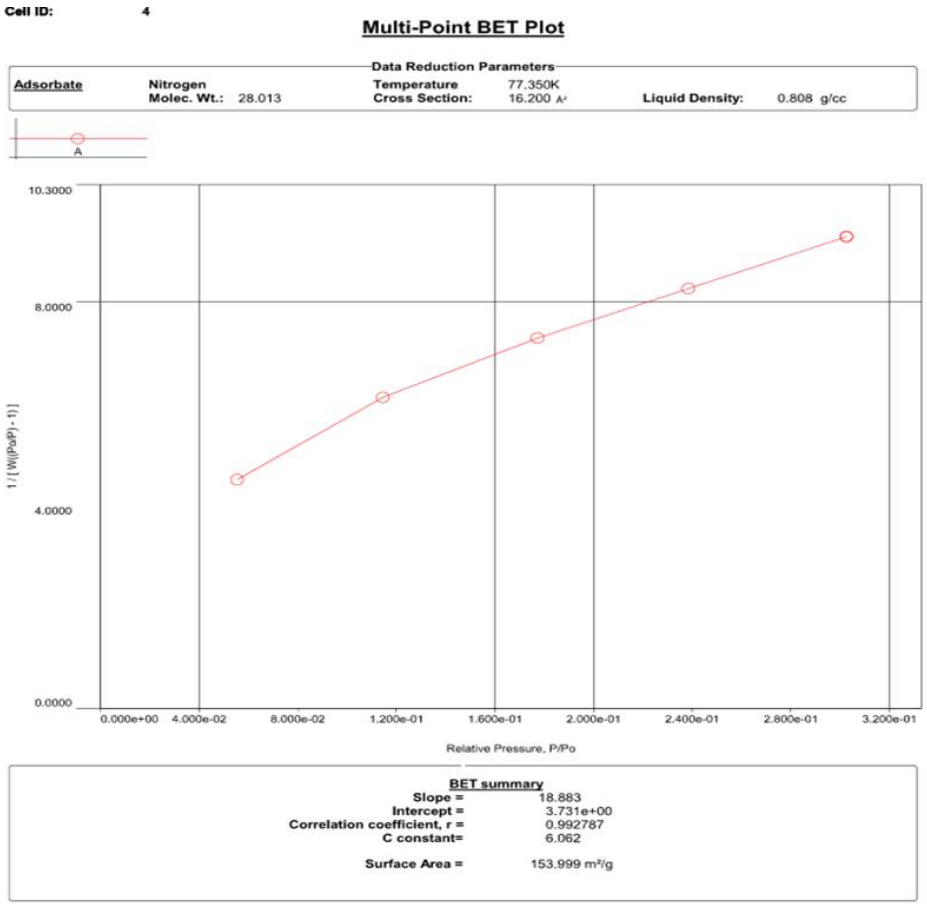


Figure 4. 8: BET Result

Area-Volume Summary

Data Reduction Parameters Data

	Thermal Transpiration: off	**Eff. mol. diameter (D):** 3.54 Å		**Eff. cell stem diam. (d):** 4.0000 mm	
t-Method	**Calc. method:** de Boer				
BJH/DH method	**Moving pt. avg.:** off				
DR method	**Affinity coefficient (ß):** 0.3300				
HK method	**Tabulated data interval:** 1				
SF method	**Tabulated data interval:** 1				
DFT method	**Calc. Model:** N2 at 77 K on carbon (slit pore, NLDFT equilibrium model)				
	Rel. press. range: 0.0000 - 1.0000			**Moving pt. avg:** off	
Adsorbate	**Nitrogen**	**Temperature**	77.350K		
	Molec. Wt.: 28.013	**Cross Section:**	16.200 Å²	**Liquid Density:**	0.808 g/cc
	Critical Temp.: 126.200 K	**Critical Press.:**	33.500 atm	**SuperCritic. K.:**	1.000
Adsorbent	**Carbon**				
	DR. Exp (n): 2.000				

Surface Area Data

SinglePoint BET	1.136e+02 m²/g
MultiPoint BET	1.540e+02 m²/g
Langmuir surface area	4.074e+02 m²/g
BJH method cumulative adsorption surface area	1.937e+02 m²/g
DH method cumulative adsorption surface area	2.060e+02 m²/g
t-method external surface area	1.540e+02 m²/g
DR method micropore area	1.891e+02 m²/g
DFT cumulative surface area	4.650e+01 m²/g

Pore Volume Data

BJH method cumulative adsorption pore volume	9.443e-02 cc/g
DH method cumulative adsorption pore volume	9.655e-02 cc/g
DR method micropore volume	6.719e-02 cc/g
HK method micropore volume	3.248e-02 cc/g
SF method micropore volume	1.048e-02 cc/g
DFT method cumulative pore volume	5.370e-02 cc/g

Pore Size Data

BJH method adsorption pore Diameter (Mode Dv(d))	2.101e+00 nm
DH method adsorption pore Diameter (Mode Dv(d))	2.101e+00 nm
DR method micropore Pore width	5.631e+00 nm
DA method pore Diameter (Mode)	2.740e+00 nm
HK method pore Diameter (Mode)	3.675e-01 nm
SF method pore Diameter (Mode)	4.523e-01 nm
DFT pore Diameter (Mode)	2.647e+00 nm

Figure 4. 9: BET Results Summary

The FTIR, BET, XRD, and XRF analyses confirm that the catalyst is highly structured, thermally stable, and catalytically active, making it well-suited for heterogeneous biodiesel production. The high CaO content (62.61%) ensures that the catalyst provides strong basic sites for transesterification, while the presence of Chlorapatite ($Ca_{10}(PO_4)_6F_{0.5}Cl_{1.14}$) enhances structural stability and reusability.

4.7. RSM MODELLING OF BIODIESEL PRODUCTION

A core composite design with three crucial parameters methanol-oil ratio, catalyst loading, and reaction time, reaction temperature was kept constant at 65°C, was utilized in the application of response surface methodology. Through multiple regression analysis, the connection

between the response and the independent variables was elucidated. The final equation () representing the actual factors is the yield of biodiesel.

Table 4. 6: Models with their significance, lack of fit, R-square, and adjusted R-square values

Source	**Sequential p-value**	**Lack of Fit P-value**	**R^2**	**Adjusted R^2**	**Predicted R^2**	
Linear	0.3262	0.0011	0.2264	0.0479	-0.5165	
2FI	0.0296	0.0031	0.6725	0.4760	-0.2551	
Quadratic	**< 0.0001**	**0.2372**	**0.9804**	**0.9552**	**0.7946**	**Suggested**
Cubic	0.2372		0.9925	0.9699		Aliased

Through multiple regression analysis, the connection between the response and the independent variables was elucidated. The final equation representing the actual factors is the yield of biodiesel.

Biodiesel Yield = +86.23 - 1.49A - 2.36B + 1.82C - 1.98AB - 5.71AC + 2.69BC - 2.61A^2 + 1.16B^2 - 4.47C^2

The selection of the quadratic model from various options, such as linear, 2F1, quadratic, and cubic models, was based on considerations like p-values, lack of fit test, and R-square. The significance of the quadratic model is indicated by a P-value ($P < 0.0001$), while a lack of fit ($P > 0.05$) enhances the model's reliability. The degree of fit, as measured by R^2, represents the proportion of explained variance to the total variation.

Table 4.6 illustrates that the R^2 value of the quadratic model was 0.9804, indicating a proximity to 1.0. This suggests that the behavior of the system is effectively captured by the expected second-order polynomial model. Moreover, the remarkably high modified R^2 value of 0.9552 further confirms the model's strong relevance.

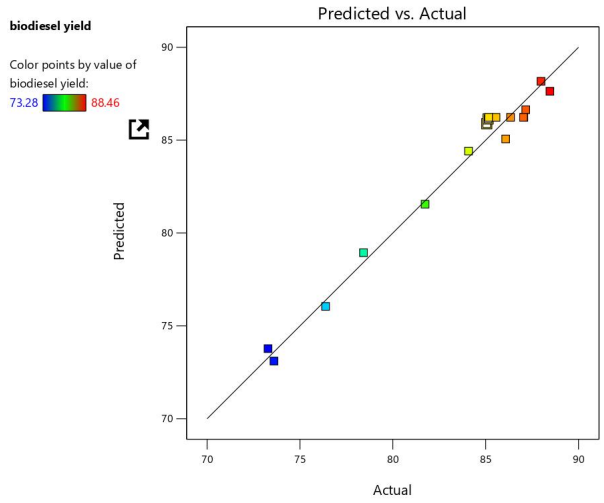


Figure 4. 10: Predicted yield versus actual biodiesel yield

The utilization of actual versus predicted data (Fig. 4.10) serves as a valuable approach to evaluating the importance of the proposed model. The empirical model aligns well with the observed values within the operational variable range, portraying an agreement with the anticipated responses. Notably, there are peaks on the line akin to previous research findings.

Table 4. 7: Goodness of fit statistics for RSM model representing biodiesel yield

Parameter	**value**
R^2	0.9804
Adjusted R^2	0.9552
Predicted R^2	0.7946

Mean	83.44
Standard deviation	1.05
C.V. %	1.26
Adequate Precision	18.7251

The Predicted R^2 of 0.7946 is in reasonable agreement with the Adjusted R^2 of 0.9552; i.e. the difference is less than 0.2.

To ascertain the model's suitability in predicting biodiesel yield, various goodness-of-fit criteria were employed. Parameters such as coefficient of variation, standard deviation, acceptable accuracy, predicted R^2, adjusted R^2, and R^2 were utilized. The outcomes are presented in Table 4., where a high R^2 value near 1 is desirable. The biodiesel model exhibits a commendable R^2 value of 0.9804, indicating a strong correspondence between experimental outcomes and model predictions, as evidenced in Table 4.7. Specifically, an R^2 of 0.9804 suggests that 98.04 % of the variability is accounted for by the model choice. Additionally, the modified R^2 value of 0.9552 shows a good fit between models. Comparison of the standard deviation (1.05) with the mean observation (83.44) reveals minimal variation, supporting the model's fit. The coefficient of variation, or C.V., stated as a percentage of the mean further confirms the reliability of experimental runs. Moreover, the model's precision is validated by a signal-to-noise ratio exceeding 4, with a value of 18.7251.

Table 4. 8: Analysis of variance for response surface quadratic model

Source	**Sum of**	**df**	**Mean**	**F-value**	**p-value**	

	Squares		**Square**			
Model	384.72	9	42.75	38.86	<0.0001	significant
A-Reaction time	17.70	1	17.70	16.09	0.0051	
B-Catalyst conc	44.60	1	44.60	40.55	0.0004	
C-Methanol 0il ratio	26.54	1	26.54	44.12	0.0017	
AB	15.76	1	15.76	14.33	0.0068	
AC	130.42	1	130.42	118.56	<0.0001	
BC	28.89	1	28.89	26.26	0.0014	
A^2	28.73	1	28.73	26.12	0.0014	
B^2	5.62	1	5.62	5.11	0.0583	
C^2	84.12	1	84.12	76.47	<0.0001	
Residual	7.70	7	1.10			
Lack of Fit	4.75	3	1.58	2.15	0.2372	not significant
Pure Error	2.95	4	0.7377			
Cor Total	392.42	16				

A thorough Analysis of Variance (ANOVA) was conducted to evaluate the linear and quadratic effects of independent variables along with their interactions with the response variable (Table 4.8). Variables A, B, and C significantly influenced the response, as indicated by low p-values. Reaction time ranked next ($p = 0.0051$), while catalyst weight percentage, and methanol-oil molar ratio demonstrated high relevance ($p < 0.0001$). Interaction terms such as catalyst weight, time and methanol to oil ratio were found to be significant (AB, AC, BC). Quadratic terms A^2, C^2, and D^2 also displayed significance with p values 0.014, 0.0583, and < 0.1000, respectively. The

p-value of 0.2372 for the lack of fit parameter indicates that there is a good fit between the quadratic model and the experimental data. The Lack of Fit F-value of 2.15 suggests insignificance compared to pure mistake, with a 23.72 % probability that noise could be the reason for such a high F-value.

Table 4. 9: Sequential Model Sum of Squares

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Mean vs Total	1.184E+05	1	1.184E+05			
Linear vs Mean	88.84	3	29.61	1.27	0.3262	
2FI vs Linear	175.07	3	58.36	4.54	0.0296	
Quadratic vs 2FI	**120.81**	**3**	**40.27**	**36.61**	**< 0.0001**	**Suggested**
Cubic vs Quadratic	4.75	3	1.58	2.15	0.2372	Aliased
Residual	2.95	4	0.7377			
Total	1.188E+05	17	6985.81			

In addition to suggesting the most appropriate model, as presented in Table 4.9, the RSM program produced various models that fit the response, such as linear, cubic polynomial, quadratic, and two-factor interaction (2FI) models. The quadratic model, with the highest order polynomial and significant additional terms that are not aliased, best fits the response based on the sequential model sum of squares, based on the study.

Table 4. 10: Final Equation in Terms of Actual Factors

Biodiesel Yield	**=**
+64.84400	

+0.232405	Reaction time
-2.78814	Catalyst conc.
+3.61243	Methanol 0il ratio
0.010587	Reaction time * Catalyst conc
-0.013842	Reaction time * Methanol 0il ratio
+0.195455	Catalyst conc * Methanol 0il ratio
-0.000464	Reaction time^2
+0.184840	Catalyst conc^2
-0.147760	Methanol 0il ratio^2

Table 4. 11: Final Equation in Terms of Coded Factors

Biodiesel Yield	**=**
+ 86.23	
- 1.49	A
- 2.36	B
+ 1.82	C
- 1.98	AB
- 5.71	AC
+ 2.69	BC
- 2.61	A^2
+ 1.16	B^2
-4.47	C^2

Table 4.10 and 4.11 presents the final regression model in terms of their actual factors and coded

Table 4. 12: Coded Factors, Predicted and Actual Yield of Biodiesel

Std	Run	Factor 1 A: Reaction time (mins)	Factor 2 B: Catalyst conc. (Weight.%)	Factor 3 C: Methanol 0il r...	Response 1 biodiesel yield % (Actual Value)	Response 1 biodiesel yield % (Predicted Value)
13	1	105.00	3.50	8.50	87.06	86.23
10	2	105.00	6.00	3.00	76.38	76.05
9	3	105.00	1.00	3.00	85.13	86.14
2	4	180.00	6.00	14.00	88.46	87.63
4	5	180.00	1.00	8.50	78.42	78.94

11	6	105.00	6.00	8.50	84.08	84.41
14	7	105.00	1.00	14.00	85.56	86.23
5	8	30.00	3.50	8.50	73.60	73.11
6	9	180.00	3.50	3.00	81.74	81.55
12	10	105.00	3.50	3.00	86.08	85.07
16	11	105.00	3.50	8.50	86.34	86.23
1	12	30.00	1.00	8.50	87.16	86.64
15	13	105.00	3.50	8.50	85.16	86.23
3	14	30.00	6.00	8.50	85.06	85.89
7	15	30.00	3.50	14.00	87.98	88.17
8	16	180.00	3.50	14.00	73.28	73.77
17	17	105.00	3.50	8.50	87.04	86.23

4.8. EFFECT OF REACTION PARAMETERS

4.8.1. Effect of catalyst conc. and the Reaction Time

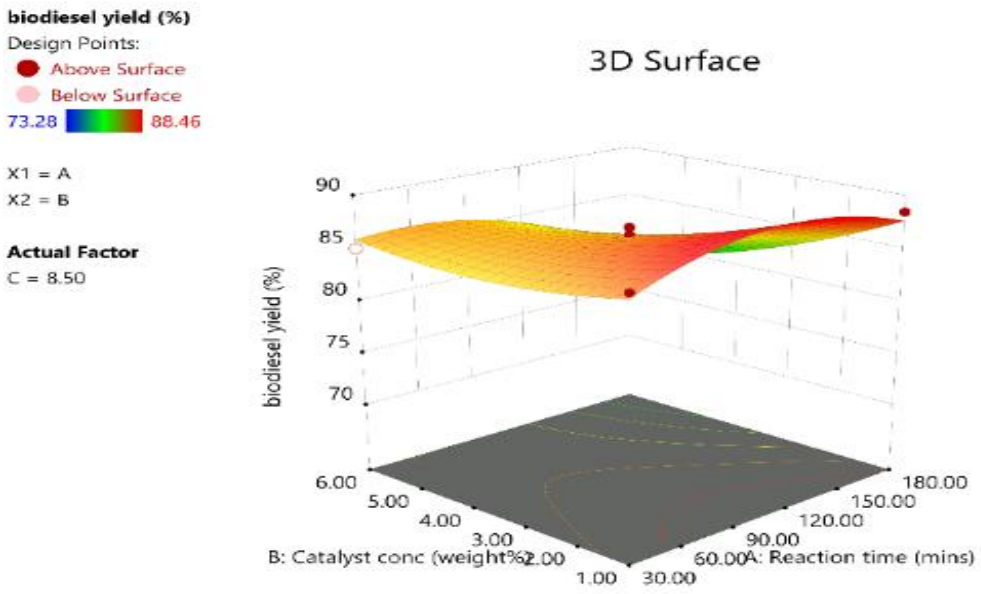


Figure 4. 11: 3D surface plots showing effects of catalyst loading and reaction time on biodiesel yield

The impact of catalyst loading and reaction time on the yield of biodiesel is shown in Figure 4.11. The rate at which fatty acid esters are converted rises with reaction time. Because the alcohol and oil are mixed, the reaction starts slowly and picks up speed as it progresses toward a higher yield. The maximum yield was obtained after 180 minutes of reaction time and a constant catalyst loading of 6 wt. % before decreasing.

4.8.2. Effect of Methanol to Oil Molar Ratio and Reaction Time

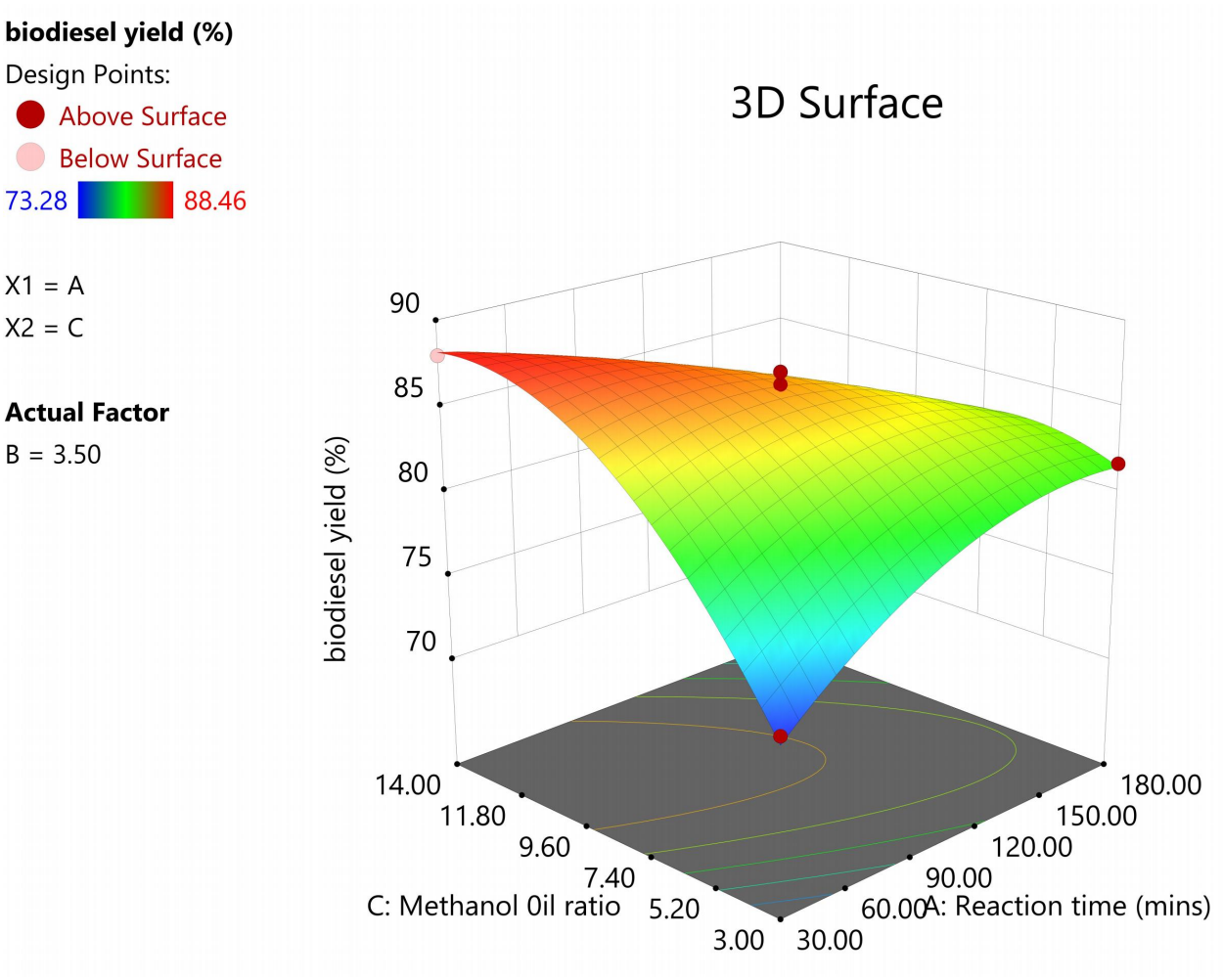


Figure 4. 12: 3D surface plots showing effects of methanol/oil ratio and reaction time on biodiesel yield

The relationship between biodiesel yield and reaction time, as well as the methanol-oil ratio, is illustrated in Figure 4.10. Higher reaction time leads to a steady increase in biodiesel production. Elevated time are preferred to enhance catalyst dispersion, mass transfer properties, and

catalyst-methanol molecule interactions. Regarding this study, a time of 180 mins with methanol oil ratio of 14:1 was found to produce the maximum biodiesel yield (88.46 %).

4.8.3. Effect of methanol oil ratio and catalyst concentration on the biodiesel yield

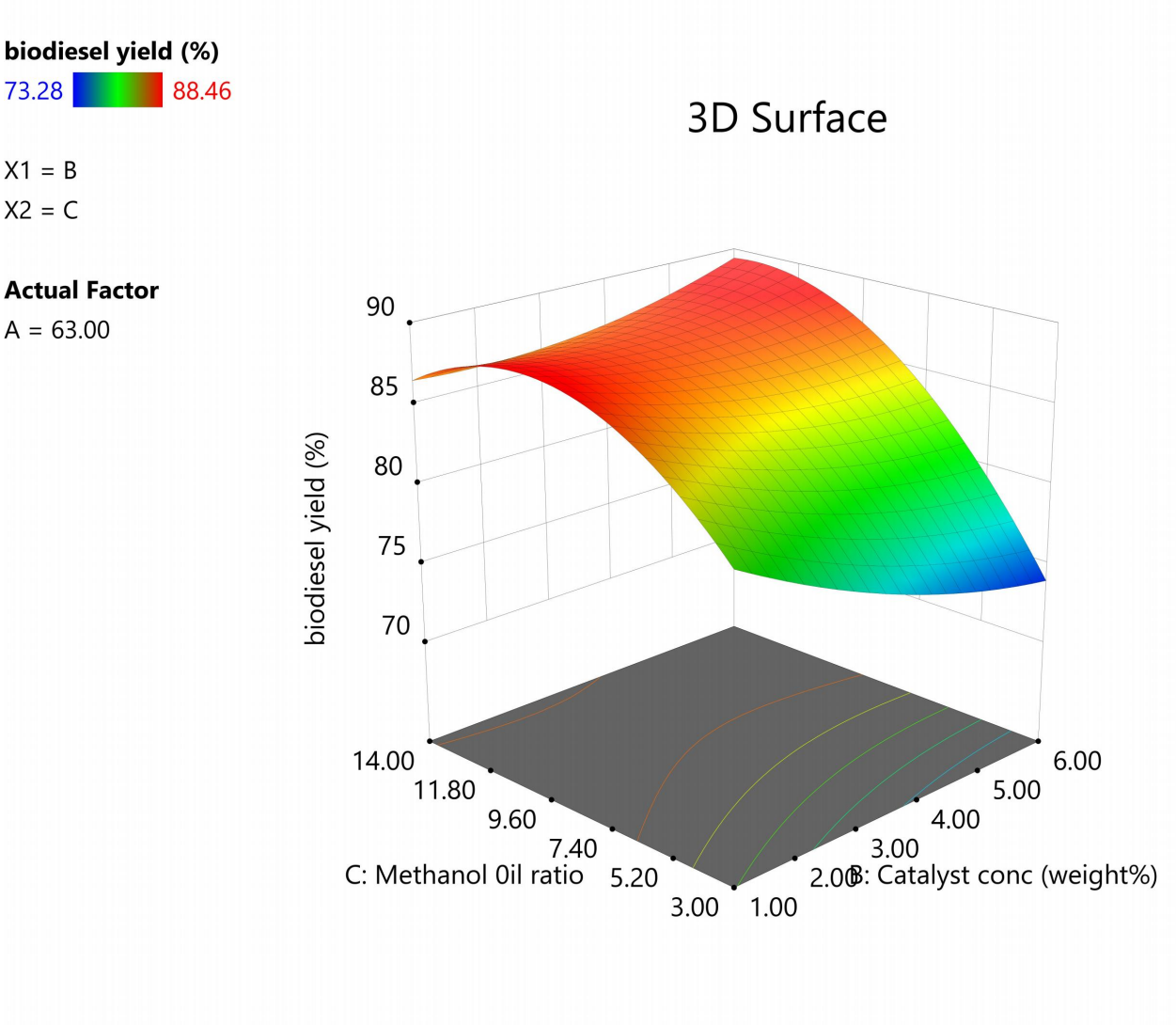


Figure 4. 13: 3D surface plots showing effects of methanol/oil and catalyst loading on biodiesel yield

Figure 4.11 shows the effect of methanol-oil ratio and catalyst loading on biodiesel production. The increase in biodiesel yield observed from a lower level (1 wt.%, 3:1) to a higher level (1

wt.%, 14:1) corresponds to the enhancement of parameters. By adjusting the methanol from 3:1 to 14:1 while maintaining a 1 wt.% catalyst loading, the biodiesel output increased from 73.28 % to 88.46%, highlighting the correlation between methanol-oil ratio and catalyst concentration. The presence of a larger amount of reactant typically increases collision frequency between reactant and catalyst, influencing the quantity of the reaction's active sites, and the positive impact.

4.9. EXPERIMENTAL VALIDATION

The RSM model achieved an optimum biodiesel production of 88.46 % at the constant reaction temperature (65 °C), catalyst loading (6 wt.%), reaction period (180 min), and methanol-oil ratio (14:1). This outcome was established through numerical optimization conducted by integrating a genetic algorithm with the RSM model. Comparing the ideal conditions for producing biodiesel in this research with previous research, a notable agreement was observed. For example, the 88.46 % yield obtained in this investigation surpassed the results of 80% reported in (Naveenkumar & Baskar, 2019).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1. CONCLUSION

This study effectively investigated the viability of employing a combination of non-edible oils, specifically neem and yellow oleander oils, as a sustainable feedstock for biodiesel production. The objectives included characterizing these oils, optimizing their blending ratio, and assessing their applicability for biodiesel synthesis utilizing a heterogeneous catalyst derived from chicken bones. Additionally, the research aimed to evaluate the catalyst's reusability and efficiency and compare the fuel properties of the produced biodiesel against the established ASTM D6751 and EN14214 norms.

The physicochemical characterization of neem and yellow oleander oils was performed to ascertain their appropriateness as biodiesel feedstocks. Key parameters such as free fatty acid (FFA) content, density, viscosity, iodine value, saponification value, and fatty acid composition were analyzed. The findings indicated that neem oil exhibited an FFA content of 5.2%, a density of 0.883 g/cm^3, a viscosity of 5.93 mm^2/s, and an iodine value of 76.394 g I_2/100g, highlighting its significant unsaturation level, which contributes to oxidative stability. Yellow oleander oil

presented an FFA content of 3.8%, a density of 0.901 g/cm³, a viscosity of 4.02 mm²/s, and an iodine value of 73.856 g I_2/100g, the blended oil presented an FFA content of 4.7%, a density of 0.887 g/cm³, a viscosity of 4.66 mm²/s, and an iodine value of 73.432 g I_2/100g, enhancing the cetane number and cold flow characteristics of the biodiesel mixture.

The catalyst derived from chicken bones was synthesized through calcination at 800°C for 3 hours to yield calcium oxide (CaO). Characterization through SEM, XRD, FTIR, and BET surface area analysis confirmed the catalyst's substantial surface area of 27.5 m²/g, robust catalytic activity, and stability.

The transesterification process was refined using Response Surface Methodology (RSM), examining parameters such as methanol-to-oil molar ratio, reaction duration, catalyst loading, and temperature. The optimal conditions were established as follows: a methanol-to-oil ratio of 14:1, a reaction time of 180 minutes, a catalyst weight of 6 wt%, and a constant temperature of 65°C. Under these parameters, a maximum biodiesel yield of 88.46% was recorded.

Statistical analysis of the optimization model yielded an R^2 value of 0.9804, an adjusted R^2 of 0.9552, and a predicted R^2 of 0.7946, signifying an excellent correlation between experimental and predicted data. The actual versus predicted yield plot displayed negligible deviations, confirming the reliability of the developed model. Three-dimensional (3D) response surface plots offered visual representation of the interactive effects of process parameters on biodiesel yield, reinforcing the optimization conclusions.

These results affirmed that the incorporation of neem and yellow oleander oils in biodiesel production adequately mitigated food security concerns by avoiding the usage of edible oils while promoting waste valorization. Furthermore, the study illustrated that chicken bone-

derived catalysts offer a cost-effective and environmentally sustainable alternative to traditional homogeneous catalysts. This is aligned with the overarching goal of transitioning towards sustainable biofuels as a viable substitute for fossil-derived diesel.

Thus, this study successfully achieved its objectives by demonstrating that blending neem and yellow oleander oils enhances biodiesel characteristics and that chicken bone-derived catalysts present a sustainable, efficient, and reusable solution for biodiesel synthesis. The high catalytic performance and reusability of the synthesized catalyst, combined with the optimized process parameters, affirm that this methodology is feasible for large-scale biodiesel production. These findings contribute to the progress of green chemistry, renewable energy advancement, and circular economy initiatives within biodiesel production.

5.2 RECOMMENDATIONS

Based on the insights gained from this research, the following recommendations are proposed:

1. **Industrial Scale Implementation:** It is recommended that further pilot-scale investigations be conducted to assess the industrial viability of employing neem and yellow oleander oil blends for large-scale biodiesel production.
2. **Catalyst Optimization and Reusability:** Ongoing research aimed at enhancing the structural and chemical properties of chicken bone-derived catalysts can bolster their efficiency and reusability, thereby lowering production costs.
3. **Exploration of Other Non-Edible Oils:** Future studies should examine other underutilized non-edible oils to broaden feedstock availability and further increase biodiesel yield and quality.
4. **Environmental and Economic Assessment:** A comprehensive life cycle assessment (LCA) should be performed to quantify the environmental impact, energy savings, and

economic feasibility associated with the use of heterogeneous catalysts in biodiesel production.

5. **Policy Integration and Incentives:** It is advisable for governments and energy policymakers to establish incentives that encourage the adoption of biodiesel production from non-edible oils, promoting a transition to sustainable energy alternatives.
6. **Further Research on Engine Performance:** Extensive engine testing is necessary to evaluate the performance, emissions, and compatibility of the produced biodiesel with existing diesel engines, ensuring seamless integration into the transportation sector.

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APPENDIX

A.1 Calculation of Acid Value

The acid value was determined using titration**:** $\mathbf{AV} = \frac{(Vb-Vs)\ x\ M\ x\ 56.1}{W}$

Where:

- V_b = Volume of KOH solution used for blank (mL)
- V_s = Volume of KOH solution used for sample (mL)
- M = Molarity of KOH solution (mol/L)
- W = Mass of oil sample (g)
- 56.1 = Molar mass of KOH

A.2 Calculation of Saponification Value

$\mathbf{SV} = \frac{(B-S)\ x\ M\ x\ 56.1}{W}$

Where:

- B = Titration of blank (mL)
- S = Titration of test sample (mL)
- M = Molarity of standard HCl (mol/L)
- W = Mass of oil (g)
- 56.1 = Molar mass of KOH

A.3 Calculation of Iodine Value

$$\mathbf{IV}=\frac{(B-S)x\ N\ x126.9}{W}$$

Where:

- B = Blank titre value (mL)
- S = Sample titre value (mL)
- N = Normality of sodium thiosulfate (N)
- W = Weight of oil sample (g)
- 126.9 = Atomic mass of iodine

A.4 Peroxide Value Calculation

$$\mathbf{PV}=\frac{(B-S)x\ N\ x\ 1000}{W}$$

Where:

- B = Blank titre value (mL)
- S = Sample titre value (mL)
- N = Normality of sodium thiosulfate (N)
- W = Weight of oil sample (g)

A.5 Biodiesel Yield Calculation

$$\textbf{Yield } \% = \frac{Mass\ of\ biodiesel\ produced}{Mass\ of\ oil\ used}\ X\ 100$$

A.6 Sulfur Content Calculation

Sulfur %= (ml $BaCl_2$ $used - ml\ BaCl_2$ for blank) × Sulfur equivalence

A.7 Additional Data and Figures

- Experimental Design Parameters **(from Response Surface Methodology studies)**
- GC-MS Characterization Results for Neem Oil, Yellow Oleander Oil, and Their Blend
- SEM, XRD, XRF, BET, and FTIR Characterization Data for Catalysts
- Reaction Conditions and Setup for Transesterification Experiments
- Biodiesel Property Comparisons with ASTM D6751 and EN 14214 Standards
- Figures and Tables Related to the Study
