OPTIMIZATION OF BIODIESEL PRODUCTION FROM WASTE COOKING OIL USING CALCINED PERIWINKLE SHELL AS CATALYST

BY

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A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING, FACULTY OF ENGINEERING, UNIVERSITY OF BENIN, BENIN CITY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR DEGREE IN CHEMICAL ENGINEERING

(B.ENG.)

FEBUARY, 2025

CERTIFICATION

This attests to the fact that **UTOBOR ELOHOR PRISCILIA** of the Chemical Engineering Department at the University of Benin in Benin City, Edo State, Nigeria, carried out the study of this work.

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DEDICATION

I want to dedicate this project to God Almighty, who has guided me through this important time in my life, providing me with various opportunities and the grace to successfully complete this study.

I also dedicate this study to my dad, Chief Dr. Gabriel Utobor, and my mom, Mrs. Evelyn Utobor, for their unwavering support and belief in me.

ACKNOWLEDGEMENT

I'd like to extend a heartfelt thank you to my project supervisor, Dr. C.A. Osagiede, for your invaluable mentorship and guidance throughout my research project. I also want to express my gratitude to the head of our department, Engr. Prof. (Mrs.) E.T. Akhihiero, as well as my project coordinator, Prof. S.E. Uwadia.

A huge shoutout goes to Engr. Prof. Andrew Amenaghawon for your significant impact on my academic journey.

I really appreciate the team at the Oben metering station NGIC for their constant support, both financially and emotionally, throughout my studies and during this project.

I'm especially thankful to Engr. Fred, the owner of Luco Research Laboratory, for generously sharing your expertise and providing crucial support that made my research possible.

I also want to recognize my project colleagues for their unwavering support and understanding throughout this research journey. A big thank you to my friends and classmates Ajiri, Nonye, Oghenehwosa Rukevwe, and Queen for all your help.

Finally, I sincerely thank my family. Their dedication, encouragement, and selflessness have truly been my guiding light. Their steadfast belief in me has inspired me to keep pushing forward.

ABSTRACT

With the increasing global demand for sustainable and renewable energy, biodiesel has become an essential alternative to traditional fossil fuels. This study looks into producing biodiesel from waste cooking oil (WCO) by using a unique catalyst made from calcined periwinkle shells.

The WCO was characterized to uncover its main properties using ASTM D6751 standard method and the catalyst was produced through calcination at 900°C. The transesterification process was optimized using Response Surface Methodology (RSM) with a Box-Behnken design, using factors like catalyst loading (1–10 **wt.**%), reaction time (30–150 minutes), temperature (40–80°C), and the molar ratio of alcohol to oil (3:1–10:1).

The result obtained from the characterization of the WCO are acid value of 6.17 mg KOH/g, a free fatty acid (FFA) content of 3.09%, a viscosity of 9.2 mPa.s at 30.08°C, a saponification value of 244.14 mg KOH/g, and a density of 956 kg/m^3. The analysis of the calcined periwinkle shell show that it contains a high amount of calcium oxide (CaO) of about 97.08%, as revealed by Energy Dispersive X-ray (EDX) analysis. Additionally, Fourier Transform Infrared Spectroscopy (FTIR) confirmed the existence of functional groups necessary for biodiesel production, while Scanning Electron Microscopy (SEM) showed a highly porous structure, which significantly improved its catalytic efficiency. With the optimized conditions, a biodiesel yield of over 90% was achieved. The final biodiesel product met industry standards and exhibited enhanced physicochemical properties.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of Study

Energy is one of the most important pillars for one's country economic and social development. Currently, a large share of the world energy demand is provided through non-renewable sources, which accounts for about 78% of the total share ((Erchamo *et al*., 2021). Petroleum plays a vital role in every economy in the world especially in transportation, industrial, and agricultural sectors as well as to the fulfillment of several other fundamental human requirements, Because of the depletion of fossil fuel supplies and the rapid consumption of mineral oils, the price of mineral-based fuel oil (i.e. petroleum, diesel, kerosene, natural gas, etc.) has been rising daily since 1970s. Additionally, using fuels derived from petroleum has a detrimental effect on the environment and releases pollutants such as CO_2, HC, NOx, and SOx (Borugadda & Goud, 2012). The rapid increase in the world population has led to a continuous increase in the consumption of fossil fuels. According to Suzihaque *et al*. 2022), the amount of diesel made from petroleum that is used globally has grown in just a decade, rising from 3.5 million tonnes in 2010 to 3.9 million tonnes in 2019, and the Asia-Pacific area, which includes nations like China, Japan, and Malaysia diesel consumption increased from 1.1 million tonnes in 2010 to 1.4 million tonnes in 2019. This is the reason that has led to the search and development of innovative renewable fuels, such as biodiesel (Suzihaque *et al*., 2022).

The idea of producing biodiesel is not new; the concept was first demonstrated by the French government at the Paris Exhibition in the 1800s when they used peanut oil as fuel, Biodiesel is a renewable fuel because it is made from an endless supply of plant and animal fats, making it easily accessible as long as supplies of vegetable or animal fats are available). However, in this context, waste cooking oil (WCO) is regarded as a promising feedstock ((Boey *et al.*, 2011). Biodiesel is made through a reaction between triglyceride and alcohol. Triglycerides are mostly found in plants and animals; The most common method of producing biodiesel is transesterification, which is inexpensive and has mild reaction conditions. Waste cooking oil was examined, along with the various variables of the transesterification process and some studies have been conducted on the variable of the transesterification process with the optimal condition of biodiesel production from waste cooking oil (Suzihaque et al., 2022)). Since biodiesel energy content and physicochemical (physical and chemical) characteristics are almost similar to those of conventional diesel fuel, it can be used alone or in combination (i.e. blend) with conventional diesel in existing conventional compression-ignition engines without requiring significant modifications (Farooq *et al.*, 2013).

Waste cooking oil refers to the used vegetable oil obtained from cooking. It is generated locally whenever food is cooked by frying with oil. These are derived from vegetable oil (i.e. soybean, cottonseed, groundnut, sunflower, rapeseed, sesame, corn, olive, palm, palm kernel, coconut, linseed, castor, and soy among a wide variety of plant sources) and animal fats/oils (i.e. butter, tallow, grease and fish oil)(Said *et al.*, 2015). Repeated frying for preparation of food makes the edible vegetable oil no longer suitable for consumption due to high free fatty acid (FFA) content (Raqeeb and Bhargavi, 2015). It is most times disposed into dustbin, soil or drainage system; their disposal creates many environmental issues. Instead of disposing waste cooking oil, it can be used as a feedstock for biodiesel production; Using waste cooking oil as a feedstock for biodiesel production will makes the process very economical, due to its low cost. In comparison to edible oils, waste cooking oil does not create food vs fuel crisis, it is easily available and does not cause any environmental issue. However, the only issue with waste cooking oil is that it has very high free fatty acid (FFA) and water content making its transesterification reaction very difficult; so the waste Cooking oil is given pretreatment or esterified with an acid first before its transesterification reaction (Monika *et al*., 2023)

1.2 Statement of the Problem

Increasing uncertainty about global energy production and supply, environmental concerns due to the use of fossil fuels, and the high price of petroleum products are the major reasons to search for alternatives to petrol diesel (Chhetri *et al*., 2008).

Research has shown that approximately 70-95% of the total cost for biodiesel production is associated with the cost of the raw materials. Therefore, the major problem faced in the production of biodiesel is that it requires a huge amount for production and commercialization of the biodiesel produced (Farooq *et al*., 2013). Also, large-scale production often relies on food crops, raising ethical and environmental concerns (Mardhiah *et al*., 2017). The traditional biodiesel production methods often rely on homogeneous catalysts, which can lead to several drawbacks, including catalyst separation difficulties, corrosion issues, and wastewater generation; the transformation of homogeneous catalyst into heterogeneous system has led to great attention by scientists**.** Heterogeneous catalysts, on the other hand, offer several advantages; however, the rate of reaction is lower as compared to homogeneous system, with higher reaction temperature and longer duration required. In contrary to the heterogeneous base catalyst, the reactivity of the process is higher, within a short period and lower temperature; but, this type of catalysts are sensitive to acid and water, and result to unfavorable side reaction that occur during biodiesel production, such as saponification (Mardhiah *et al*., 2017).

Waste Cooking oil (WCO) serves as a good feedstock for biodiesel production. But most of the waste cooking oil is disposed into dustbin or drainage system or into the soil. Their disposal creates many environmental issues; though if is a good feedstock for biodiesel production but the issue with waste cooking oil is that it has a very high FFA and water content making its transesterification reaction very difficult (Monika *et al*., 2023).

1.3 Aim and Objective

This study aims to optimize biodiesel production from waste cooking oil using calcined periwinkle shell as catalyst.

The specific objectives include:

1. Characterization of waste cooking oil.
2. Catalyst preparation from periwinkle shell.
3. Characterization of catalyst.
4. Investigate the influence of reaction parameters, including temperature, reaction time, catalyst loading, and alcohol-to-oil molar ratio, on biodiesel yield and product quality.
5. Optimization of the transesterification process using surface response methodology.
6. Biodiesel characteristics.

1.4 Scope of the Study

This study was conducted in a small laboratory scale.

- The collection of basic raw material needed for analysis of this study (i.e. waste cooking oil, periwinkles shell)
- Catalyst preparation
- Biodiesel production and optimization.

1.5 Relevance of the Study

This study offers an eco-friendly way to manage waste by recycling cooking oil that would otherwise be thrown away. Not only does this help cut down on pollution, but it also tackles larger environmental issues. Plus, developing biodiesel as a renewable energy source that can fulfill our energy needs without depending on limited petroleum supplies, this can fulfill our energy needs without depending on limited petroleum supplies.

The cost of raw materials plays a big role in the overall expenses of biodiesel production. By using waste cooking oil, we can significantly reduce these costs when compared to traditional edible oils. Additionally, using periwinkle shells as catalysts presents a cost-efficient and sustainable solution that further lowers production costs.

This study really highlights the idea of turning waste into energy by transforming used cooking oil and discarded periwinkle shells into valuable products. This not only helps cut down on waste but aligns with the principles of a circular economy.

By investigating the effectiveness of calcined periwinkle shell as a catalyst, this research enhances our knowledge of heterogeneous catalysis in biodiesel production. It also fine-tunes the transesterification process, which could lead to higher yields and more efficient biodiesel production. Enhancing biodiesel production methods can reduce our dependence on imported petroleum, strengthening local energy security and supporting domestic energy industries.

The findings from this study could benefit both small and large-scale biodiesel production sectors by identifying cost-effective raw materials and improving production processes. This could pave the way for the commercialization of biodiesel derived from waste cooking oil and alternative catalysts.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 The Biodiesel Production

Energy is seen globally as a key indicator of economic progress and is essential for human existence. It plays a crucial role in the sustainability of various sectors, including industry, transportation, and traditional thermal power plants that generate energy. Fossil fuels make up a significant share of the world's energy production, but experts warn that our oil and gas reserves are dwindling quickly. This situation highlights the urgent need to explore alternative energy sources for residential, industrial, and transport purposes. In response to concerns about supply instability and a growing awareness of the harmful environmental impacts and health risks tied to fossil fuel emissions, governments worldwide have started implementing stricter emission regulations and promoting the use of alternative energy (Abubakar *et al.*, 2016). The search for alternative energy sources by researchers and government agencies has led to the exciting discovery that biofuel can serve as a strong contender against fossil fuels in terms of efficiency and availability. One of the key reasons for promoting biodiesel as an alternative energy source is that it produces significantly lower emissions during combustion compared to fossil fuels. Biofuels like biogas, bioethanol, and biodiesel stand out as some of the most promising options for energy generation, while also helping to tackle the serious issue of greenhouse gas emissions, including sulfur and nitrogen compounds (Abubakar *et al.*, 2016).

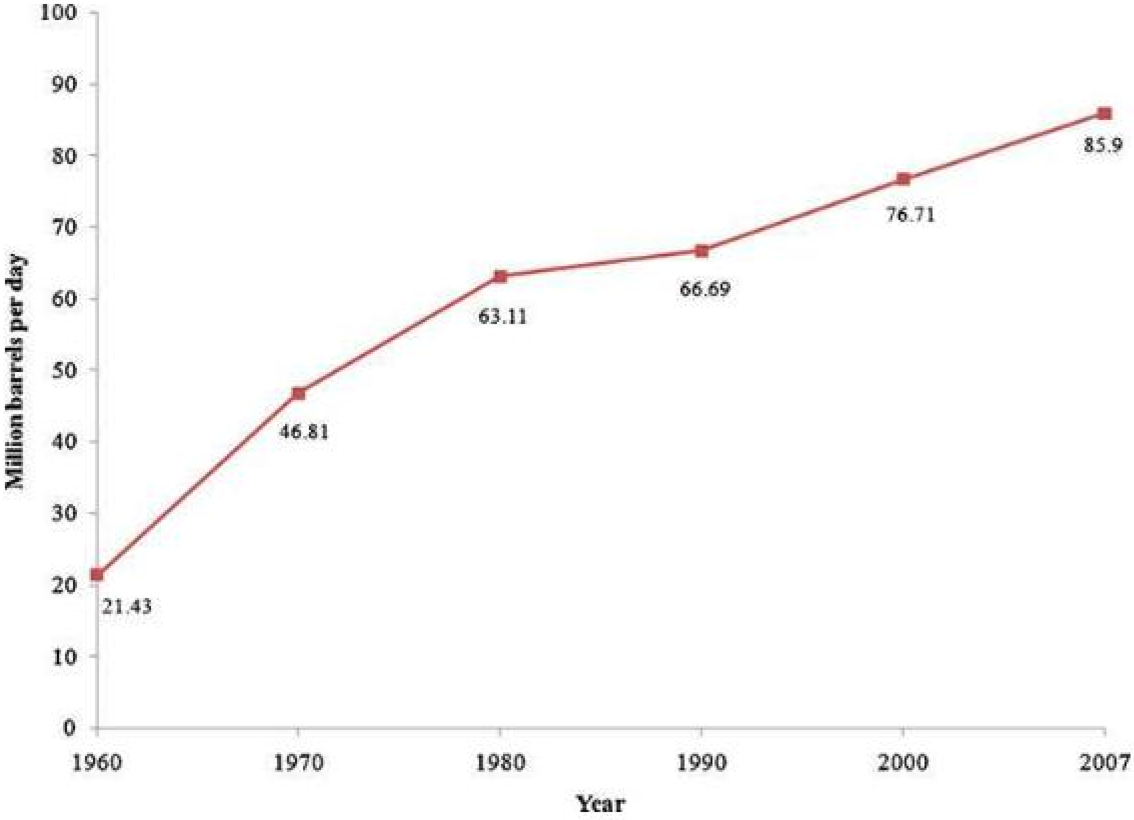


Figure 2. 1: World petroleum consumption from year 1960 to 2007 (Boey et al., 2011)

Today, there's a growing urgency to explore alternative fuel sources that are as renewable as traditional energy options. Most renewable energy sources rely heavily on nature, making them tricky to store, with the exception of bio-energy. Bio-energy comes from biomass, which includes materials like wood, agricultural waste, municipal waste, and biofuels such as alcohol and various vegetable oils. One notable advantage of liquid biofuels over solid fuels is their ease of transportation. Many types of vegetable oils have been tested globally to assess how well they perform in diesel engines. While straight vegetable oil (SVO) is indeed used as fuel, it turns out that esterified oils provide superior fuel properties. Research has shown that vegetable oil esters can be a viable alternative to diesel fuel. However, there are lot of work to be done to make biodiesel a commercially viable option for diesel engines ((Subramaniam *et al.,* 2013). These days, there hasn't been much effort put into using esters from non-edible oils as an alternative to diesel, aside from a few feedstocks. Research indicates that vegetable oils have a distinct chemical structure; they can link up to three fatty acids to a glycerin molecule through ester linkages. The fatty acids differ in both their carbon chain lengths and the quantity of double bonds. Among the most common saturated fatty acids are Palmitic (which has 16 carbon atoms) and Stearic (with 18 carbon atoms), and nearly every vegetable oil contains a small amount of both. Typically, vegetable oil is made up of about 97% triglycerides and 3% di- and mono-glycerides, as well as some fatty acids. The process that removes all glycerol and fatty acids from vegetable oil in the presence of a catalyst is known as transesterification (Subramaniam *et al.*, 2013).

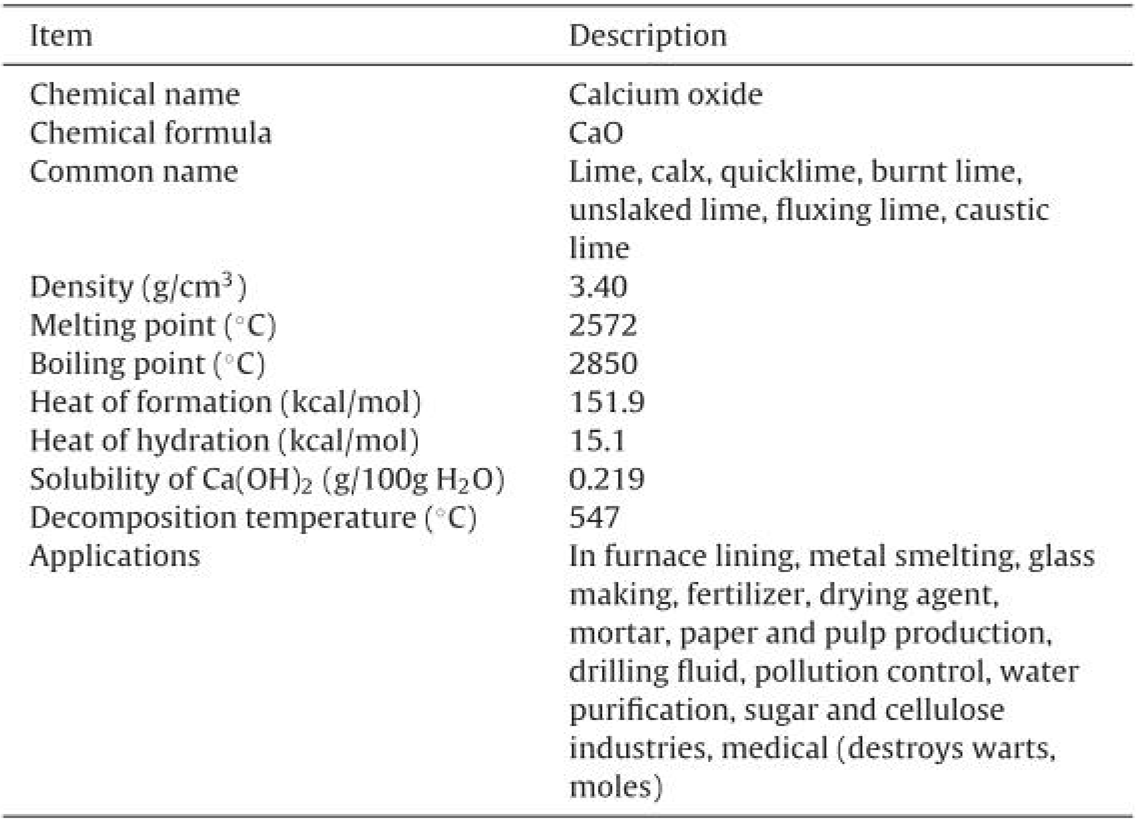
Transesterification is a term used for a significant category of organic reactions where one ester is converted into another by swapping the alkoxy part. This process entails removing glycerin from fatty acids using a catalyst like sodium or potassium hydroxide and replacing it with anhydrous alcohol, typically methanol. The resulting product undergoes centrifugation and gets rinsed with water to eliminate impurities. This yields biodiesel in the form of methyl or ethyl ester, along with a smaller quantity of glycerol, which is a valuable by-product used in making soaps, cosmetics, and various other items. There are three main methods for producing esters from oils/fats: base-catalyzed transesterification, acid-catalyzed esterification, and enzymatic catalysis, with base-catalyzed transesterification being the most widely used due to its economic efficiency(Refaat, 2009). The whole process usually includes three reversible steps: first, triglycerides transform into diglycerides, then into monoglycerides in the second step, and finally to glycerin from the monoglycerides (Latchubugata *et al.*, 2018).

Transesterifying oil or fat from renewable sources—especially leftover cooking oil—results in biodiesel, which is a liquid fuel and one of the most favored alternatives to fossil fuels derived from renewable sources (Erchamo *et al*., 2021). Waste cooking oil is a glycerol ester that consists of several important fatty acids which only dissolve in organic solvents. When disposed of improperly, it can be harmful both to the environment and to human health (Suzihaque *et al*., 2022). According to research by Suzihaque *et al*. (2022), in Malaysia, a significant amount of household oil waste makes its way into drains and soil, with estimates suggesting around 540,000 tonnes of waste cooking oil (WCO) from vegetable and animal fats being discarded annually, exacerbating environmental issues. However, using it as a raw material for biodiesel production presents an economic benefit—lower feedstock costs compared to using fresh cooking oil—and addresses the food versus fuel debate (Monika *et al*., 2023).

Monika *et al.* (2023)also point out that the presence of free fatty acids and water in waste cooking oil can complicate the transesterification process. These issues can be sidestepped through an esterification reaction or by adding an acid to the WCO before starting the transesterification. Traditionally, used cooking oil goes through a cleaning process that filters out food residue along with other impurities. Soluble impurities can be eliminated by washing the waste cooking oil with hot distilled water at around 80 °C. Silica gel is applied in further processing to remove any remaining water from the treated oil (Mahmood *et al.*, 2020). Biodiesel production using solid catalysts instead of traditional liquid ones could lower production costs significantly, thanks to the ability to reuse these catalysts. Plus, it allows both transesterification and esterification to happen at the same time. However, there’s still a lack of comprehensive studies on the kinetics and mechanisms of acid and base catalysts when using solid catalysts ((Semwal *et al.*, 2011). Research on heterogeneous catalysts has identified a range of materials, including metal hydroxides, metal complexes, and metal oxides like calcium oxide, magnesium oxide, and zirconium oxide, among others. These solid catalysts can address some of the limitations that come with using homogeneous catalysts. For instance, it was found that the activity levels among these alkaline earth oxide catalysts ranked as follows: BaO > SrO > CaO > MgO (Semwal *et al*., 2011).

According to a review by Marinkovi *et al*. (2016) calcium oxide can be produced by the thermal decomposition of limestone and by calcining raw materials that contain CaCO3, such as periwinkle shells, eggshells, snail shells, oyster shells, mussel shells, and goat bones. Each of these materials needs different temperatures to effectively produce CaO. There are four potential forms of calcium oxide (CaO) catalysts that can be used in transesterification: pure CaO, doped CaO, loaded CaO, and mixed CaO. Doped CaO occurs when alkaline chemicals are added to the CaO particles, increasing both the number of basic sites and the overall surface area, which enhances its catalytic activity. When it comes to mixed CaO catalysts, their effectiveness is further improved by combining CaO with metal oxides like lanthanum or cerium oxides as well as zinc. Additionally, various CaO-based catalysts have also been tested in transesterification reactions involving substances like di glyceroxide, calcium methoxide, and glycerolate. Despite the recent interest in nano-sized calcium oxide, commercially available pure calcium oxide remains the most widely used following thermal activation. To boost its catalytic efficiency, the surface area of neat CaO can be enhanced by reducing the particle size (Marinkovi et al., 2016).

Table 1. 1: Properties of calcium oxide (Boey et al., 2011).



Item	Description
Chemical name	Calcium oxide
Chemical formula	CaO
Common name	Lime, calx, quicklime, burnt lime, unslaked lime, fluxing lime, caustic lime
Density (g/cm^3)	3.40
Melting point (°C)	2572
Boiling point (°C)	2850
Heat of formation (kcal/mol)	151.9
Heat of hydration (kcal/mol)	15.1
Solubility of $Ca(OH)_2$ ($g/100g\ H_2O$)	0.219
Decomposition temperature (°C)	547
Applications	In furnace lining, metal smelting, glass making, fertilizer, drying agent, mortar, paper and pulp production, drilling fluid, pollution control, water purification, sugar and cellulose industries, medical (destroys warts, moles)

2.2 SOME COMMON NON-EDIBLE FEEDSTOCKS USED FOR BIODIESEL PRODUCTION.

There are a number of potential raw materials for producing biodiesel. However, using non-edible oils for biodiesel production is increasingly viewed as a promising alternative to edible oils, as the latter can compete with food needs (Verma & Sharma, 2016).

2.2.1 The Jatropha plant: The Jatropha plant, scientifically known as J. curcas, is a small tree from the Euphorbiaceae family. It thrives in various climates, enduring extreme heat as well as low and high rainfall. This seasonal, leaf-shedding tree can grow up to 5 meters tall and is native to India. Its seeds contain between 30% and 35% oil by weight, which can easily be transformed into biodiesel that meets industry standards. Jatropha is gaining recognition as a promising global source for biodiesel production. Typically, under good conditions, this plant produces 2 to 5 tons of dry seeds per hectare each year after about five years, depending on factors like genetic variety, climate, and management practices. Unfortunately, both the seeds and oil are not suitable for human consumption due to harmful toxins such as phytates, phorbol esters, lectins, and trypsin inhibitors. This makes Jatropha oil an appealing energy source since it can't be used for food without detoxification. The seeds also contain around 30% oil, which consists of a mix of saturated fatty acids (14.2% palmitic acid and 7.0% stearic acid) and unsaturated fatty acids (44.7% oleic acid and 32.8% linoleic acid). Jatropha is recognized not only as an oil plant but for its diverse uses and potential. It can help prevent and manage soil erosion, reclaim land, serve as a physical barrier, and be grown as a commercial crop. Both the fruit and wood of the Jatropha plant can be utilized for fuel, while the crop also has traditional medicinal uses. The oil extracted from the seeds can be used in soap making, cosmetics, and candle production, and can even substitute for diesel or paraffin. Factors like species and climate greatly affect Jatropha's oil content, with altitude playing a notable role. In India, it’s been identified as a significant source for biodiesel (Borugadda & Goud, 2012).

2.2.2 Waste Cooking Oil: Biodiesel production can also tap into various cooking or spent oils, which are both cost-effective and eco-friendly. These spent oils generally come from the food industry, non-food industry, or households and restaurants. Commonly used consumable oils include palm oil, soybean oil, rapeseed oil, and coconut oil, although they require extra processing to deal with high-temperature acids and eliminate residues. Got by-products from food factories can further contribute to biodiesel production. Waste oils from the non-food sector, such as those derived from plastic and tires, have also been utilized to create biodiesel through pyrolysis (Singh *et al.*, 2020).

2.2.3 Neem oil: Neem, known scientifically as Azadirachta indica, is a fast-growing evergreen tree that can reach heights of about 15 to 20 meters. It may shed its leaves entirely or most of them during severe droughts. Neem can flourish in very poor soils that are rocky, shallow, dry, or saline. Its dense crown, which is round or oval, can have a diameter of up to 15 to 20 meters in mature specimens. The fruit is a drupe with a smooth olive texture and can vary from egg-shaped to nearly spherical. Neem seeds yield about 35% to 45% oil, which ranges in color from light to dark brown and has a bitter taste. The primary component of neem oil is Azadirachtin, which can vary between 300 and 2500 ppm depending on the extraction process and the quality of the crushed seeds. Neem has numerous health benefits and is used to manage pests in agriculture. It's commonly featured in Ayurvedic medicine, particularly for treating skin disorders. Neem products, including neem gum and neem leaf paste, have various uses, serving as bulking agents, special foods for diabetics, and treatments for acne. Neem oil is also known for being an effective mosquito repellent (Borugadda & Goud, 2012).

2.3 Methods of Biodiesel Production

2.3.1 Direct Use and Blending (Dilution) with Diesel Fuel: This approach primarily involves using vegetable oil mixed with diesel to lower viscosity and enhance engine performance. Essentially, a fuel mix is a combination of diesel and other substances. In the domestic diesel market, you can find rich blends of biodiesel. For instance, B20 denotes diesel fuel that contains 20% biodiesel, whereas pure biodiesel is marked as B100. Generally, B20 blends can be used directly in diesel engines. There are various methods to combine B100 with petroleum diesel. This blending can happen as biodiesel and petroleum diesel are mixed directly into the tank, at the production site before dispatch, typically in the tanker truck, or by simultaneously combining both components inline into the tanker truck (Perumal, 2023).

2.3.2 Micro-emulsion (Supercritical): This process consists of mixing oils with a suitable solvent like methanol, ethanol, or other alcohols to create emulsions. The micro-emulsion technique helps mitigate the negative aspects of vegetable oils by utilizing alcohol as a solvent. The results of these ionic or nonionic micro-emulsions mirror those of diesel fuel. Alongside evaporation, the improved atomization characteristics lead to better overall combustion properties of the biofuel. However, this method also has its downsides, such as heavy carbon particles, increased viscosity, issues with needle pinching, and partial combustion (Perumal, 2023). Additionally, it can cause carbon buildup in the engine and lead to incomplete combustion.

2.3.3 Thermal Cracking (Pyrolysis): Pyrolysis refers to the thermal decomposition of biomass in the absence of oxygen. The term comes from the Greek words “pyro,” meaning fire, and “lysis,” meaning to break down into its basic components. Pyrolysis technology is known for producing bio-fuel with high fuel-to-feed ratios, making it an increasingly popular method for converting biomass into bio-fuel in recent decades. The primary aim of this technology is to create high-value bio-oil that can compete with and ultimately replace non-renewable fossil fuels. Nevertheless, the next hurdle for pyrolysis researchers is the advancement of technologies to reach this objective (Jahirul *et al.*, 2012).

2.4 Various Method of Transesterification Of Waste Cooking Oil

The process of Transesterifying spent cooking oil can be accomplished either with or without a catalyst.

2.4.1 Non-Catalytic Transesterification: One promising approach to biodiesel production is the supercritical process, which is known for being fast and catalyst-free. Some production facilities in Europe have adopted this technology. However, because it requires high temperatures and pressures, it leads to increased capital costs that limit its commercial use (Semwal *et al.,* 2011).

2.4.2 Catalytic Transesterification: Typically, transesterification is performed using a catalyst, which can be either a base, acid, or enzyme. These catalysts can be grouped into homogeneous and heterogeneous types ((Liu *et al.*, 2008). Homogeneous catalysts exist in the same liquid phase as the reaction mixture, and in transesterification, the base-catalyzed method is much quicker than the acid-catalyzed alternative. That said, it requires a significant amount of water to separate the catalysts from the organic phase after the reaction, making it more expensive to isolate the catalyst from the resulting mixture. On the other hand, heterogeneous catalysts are in a different phase (often solid) compared to the reaction mixture. They're non-corrosive, eco-friendly, and can be reused multiple times, making them a more cost-effective option for biodiesel production (Said *et al.*, 2015).

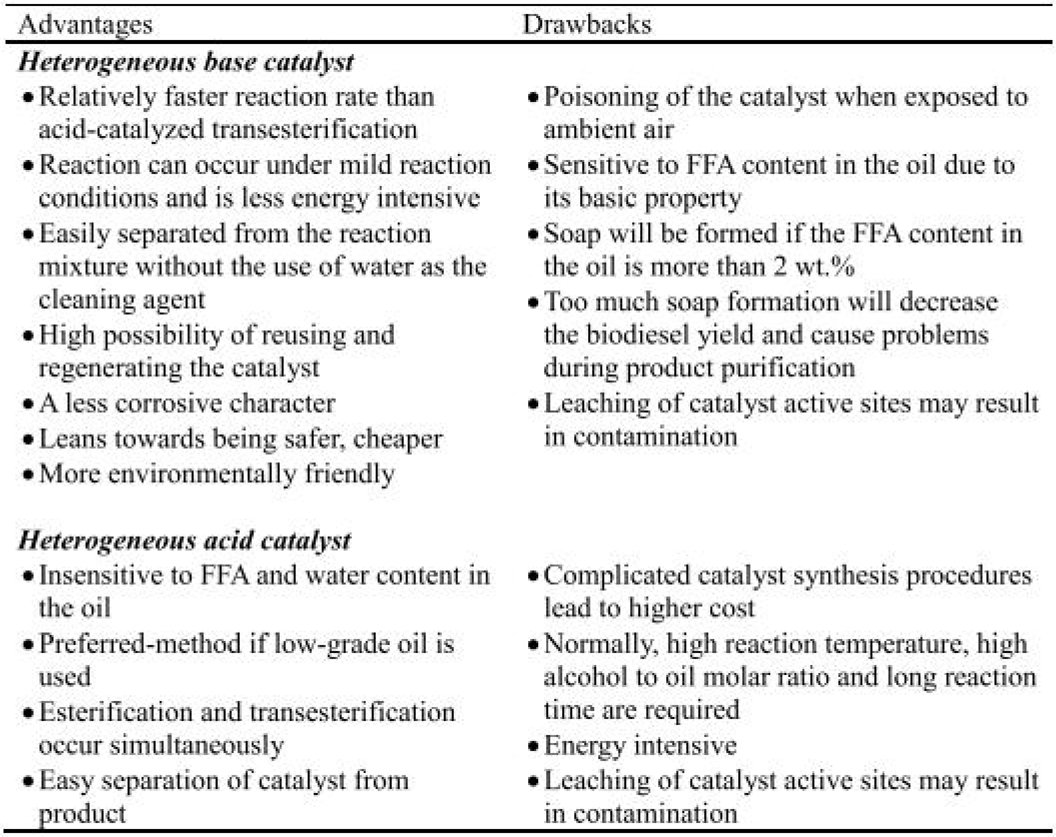
2.4.3 Homogeneous Alkali-Catalyzed Transesterification Methods: The common alkali process for transesterification typically uses catalysts such as hydroxides, potassium, sodium carbonates, and alkaline metal alkoxides. These alkaline catalysts have several benefits, including shorter reaction times and the ability to operate at lower temperatures with minimal amounts of catalyst, all while not significantly darkening the oil's color. They are very effective at producing high-quality vegetable oils. However, a major issue arises when the oils contain a considerable amount of free fatty acids (FFAs), which do not convert to biodiesel. Instead, these FFAs can react with the base catalyst to form soaps, complicating the separation of biodiesel, glycerin, and water (Maitera *et al*., 2019)

2.4.4 Heterogeneous Alkali-Catalyzed Transesterification Methods: The use of heterogeneous catalysts is seen as a beneficial approach for biodiesel production due to its cost-effectiveness and minimal environmental impact. These solid catalysts can simplify both production and purification processes under milder conditions. Many types of heterogeneous alkali catalysts have been developed, including basic zeolites, alkaline earth metal oxides, and hydrotalcites. These solid base catalysts are easy to regenerate, less corrosive, and promote safer, cheaper, and more environmentally friendly operations. However, they are best used when the FFA content in the raw materials doesn't exceed 1%. By replacing homogeneous catalysts with heterogeneous ones, many of the challenges associated with the former can be avoided (Borugadda & Goud, 2012).

2.4.5 Homogeneous Acid-Catalyzed Transesterification: This method represents a traditional approach to biodiesel production. It involves mixing triglycerides with alcohol, but instead of using a base, an acid most commonly sulfuric acid is employed (Marchetti *et al.*, 2007). While acid catalysts can yield high ester production, the reaction typically takes a long time, often exceeding one day. They are particularly effective when oils contain high levels of FFAs and water, as they can tackle both the esterification of FFAs and the transesterification of triglycerides simultaneously. However, this process demands a high alcohol-to-oil ratio, considerable acid catalyst concentration, and extended reaction times, all while presenting challenges related to the corrosive nature of acid catalysts (Marinkovi *et al.,* 2016).

2.4.6 Heterogeneous Acid-Catalyzed Transesterification Methods: Current research is concentrating on finding new sustainable solid acid catalysts for transesterification. Solid acid catalysts are believed to hold significant potential to replace their liquid counterparts due to several advantages, including: (1) insensitivity to FFA content, (2) simultaneous esterification and transesterification, (3) eliminating the need for biodiesel washing, (4) ease of catalyst separation from the reaction medium, which lowers the contamination levels of the product, (5) simple regeneration and recycling of the catalyst, and (6) reduced corrosion concerns, even in the presence of acidic substances (Chouhan & Sarma, n.d.).

Table 1. 2 The advantages and drawbacks of heterogeneous base catalysts and heterogeneous acid catalysts used in the transesterification of WCOs (Said et al., 2015)



Advantages	Drawbacks
Heterogeneous base catalyst	
• Relatively faster reaction rate than acid-catalyzed transesterification • Reaction can occur under mild reaction conditions and is less energy intensive • Easily separated from the reaction mixture without the use of water as the cleaning agent • High possibility of reusing and regenerating the catalyst • A less corrosive character • Leans towards being safer, cheaper • More environmentally friendly	• Poisoning of the catalyst when exposed to ambient air • Sensitive to FFA content in the oil due to its basic property • Soap will be formed if the FFA content in the oil is more than 2 wt.% • Too much soap formation will decrease the biodiesel yield and cause problems during product purification • Leaching of catalyst active sites may result in contamination
Heterogeneous acid catalyst	
• Insensitive to FFA and water content in the oil • Preferred-method if low-grade oil is used • Esterification and transesterification occur simultaneously • Easy separation of catalyst from product	• Complicated catalyst synthesis procedures lead to higher cost • Normally, high reaction temperature, high alcohol to oil molar ratio and long reaction time are required • Energy intensive • Leaching of catalyst active sites may result in contamination

2.5 Factors Affecting Transesterification Process Of Biodiesel Production

2.5.1 Effect of Molar Ratio of Alcohol: When it comes to the transesterification process, the ratio of alcohol to oil plays a critical role. Biodiesel can be made using several types of alcohols, like methanol, ethanol, isopropyl alcohol, propanol, pentanol, and butanol. Studies show that methanol is the top choice for producing biodiesel, mainly because it’s cheaper than longer-chain alcohols. Plus, methanol doesn't form an azeotrope with water, which simplifies the recycling process during biodiesel production (Suzihaque *et al.,* 2022). The amount of alcohol used is essential for achieving good biodiesel yields; usually, you need about 3 moles of alcohol for every mole of triglycerides. This reaction yields 3 moles of fatty acid esters and 1 mole of glycerol. Using a bit more alcohol can speed up the conversion of fats into esters, leading to better biodiesel yields, but only up to a point. If you keep increasing the alcohol concentration beyond that threshold, it won't necessarily result in higher yields and could actually raise the costs of recovering the alcohol (Mathiyazhagan & Ganapathi, 2011).

2.5.2 Temperature and Pressure: The temperature at which transesterification occurs is crucial for how quickly the reaction takes place. While it's possible for the reaction to happen at room temperature given enough time, it's usually performed near the boiling point of methanol when done at atmospheric pressure (Banerjee & Chakraborty, 2009). A study by Latchubugata *et al.* (2018) showed a significant increase in %FAME yield during a 240-minute reaction time with a 15:1 methanol to palm oil molar ratio. However, raising the temperature often leads to lower biodiesel conversion rates. This decrease in yield might happen because at 70°C, which is above methanol's boiling point of 64.7°C, methanol tends to vaporize unless the reaction is pressurized and the condenser temperatures are kept low. When there's insufficient methanol, it causes more interaction with the liquid-phase oil and the solid catalyst CaO, which diminishes the %FAME yield.

2.5.3 The Effect of Reaction Time: Generally speaking, extending the reaction time tends to improve the conversion rate. transesterification experiments was performed on different oils—like peanut, cottonseed, sunflower, and soybean—using a 6:1 methanol to oil ratio, a 0.5% sodium methoxide catalyst, and a temperature of 60°C. They managed to achieve around an 80% yield for soybean and sunflower oils after just 1 minute. After an hour, the conversion rates for all the oils were quite similar, sitting between 93% and 98%. In another study, the reaction time needed for Transesterifying beef tallow with methanol. They observed that in the first minute, the reaction was pretty slow because the methanol hadn't fully mixed with the beef tallow yet. However, there was a sharp increase in yield from 1 to 5 minutes, peaking around the 15-minute mark. Interestingly, the levels of di- and monoglycerides rose initially but then began to drop, with final results showing that there were more monoglycerides than diglycerides (Ma & Hanna, 1999).

2.5.4 Amount of FFA in the Oil: The characteristics of the oil feedstock, particularly the free fatty acids (FFAs) and moisture content, play a crucial role in determining biodiesel yield. When FFAs and water are present, they can impede the catalyst's effectiveness by causing soap to form, which ultimately has a negative effect on yield. This issue is especially pronounced with waste cooking oil (WCO) that contains moisture (Mahmood *et al*., 2020). As a result, treating WCO beforehand is necessary to ensure successful transesterification. In this research, the pretreated WCO showed a moisture level of 0.12 wt% and an FFA concentration of 0.69%. To address the difficulties associated with non-edible vegetable oils that have high FFA levels, a two-step transesterification method is implemented. Initially, a homogeneous acid pretreatment is employed to esterify the oil until the FFA content decreases to below 0.5%. Following that, a base-catalyzed transesterification finishes off the process (Genene Demisu, 2021).

2.5.5 Effect of Catalyst Loading: Researchers have looked into how the amount of catalyst influences the transesterification process of waste cooking oil (WCO), testing concentrations between 1% and 4% by weight. They ran experiments using a 1:6 oil to methanol molar ratio at a temperature of 60°C. The findings showed that increasing the catalyst from 1% to 3% significantly boosted biodiesel yield from 36% to 93%. However, when the catalyst concentration was raised further from 3% to 4%, there was no notable increase in yield. This indicates that a catalyst level of 3% by weight seems to be the sweet spot for effectively converting waste cooking oil with methanol. The initial surge in yield can be attributed to improved catalyst activity, but beyond that optimal point, adding more catalyst doesn’t enhance yield. This underscores the need to avoid using too much catalyst, as it could complicate the separation process later on (Pukale *et al*., 2015).

2.5.6 Agitation/Mixing: Proper agitation is key to the reaction, and the speed at which you mix can have a big impact on the final product. If you stir too quickly, you might end up with soap, while not stirring enough could lead to lower yields. So, picking the right mixing speed is really important (Mathew *et al.,* 2021). Oils and alcohols don’t mix completely, which means the transesterification reaction only happens at the liquid-liquid interface, making it a rather slow process. That’s why good mixing is essential for transesterification. We need to ensure that these two feedstocks mix well to boost the chances of effective transesterification. One common approach for this reaction is mechanical mixing. Depending on what the transesterification process requires, you might need to adjust the mixing intensity. Generally, to achieve an even and thorough mix of the feedstocks, you'll want to increase the blending intensity. If the feedstock is very thick and viscous, exclusive mechanical mixing becomes necessary to help combat the negative effects of viscosity on how well the oil and alcohol transfer. The speed of agitation is vital for biodiesel production since mixing the oil and catalyst speeds up the reaction. For example, when other factors are kept constant, mixing at speeds of 200 rpm, 400 rpm, 600 rpm, and 800 rpm for 60 minutes showed that a greater conversion of the end product was achieved at 400 rpm. Slower stirring speeds generally result in less product. Conversely, if you stir too fast, you encourage soap formation because transesterification is a reversible process (Monika *et al.,* 2023).

2.5.7 Type of Alcohol: To carry out the transesterification of one mole of feedstock oil, you'll need three moles of alcohol. Methanol and ethanol are the go-to choices for this reaction, mainly because they're affordable. When methanol is used, the resulting biodiesel is known as fatty acid methyl ester (FAME), while using ethanol gives you fatty acid ethyl ester (FAEE). Generally, FAME tends to offer better engine performance compared to FAEE. In terms of cost and reactivity, methanol has the upper hand over ethanol. Plus, FAME is more volatile than FAEE, but it's worth noting that FAEE is thicker and more viscous. For transesterification, methanol is the most efficient option. Choosing methanol for biodiesel production can lead to significant cost savings, making it an excellent choice for commercial operations. However, it's crucial to use the right amount of methanol. Too little can slow down the reaction, whereas using too much can complicate the separation of the byproduct, glycerin (Banga & Pathak, 2023).

2.6 Physiochemical Properties Of Biodiesel

2.6.1 Flash Point: The flash point is essentially the lowest temperature (at a standard atmospheric pressure of 101.3 kPa or 760 mm Hg) at which the vapors from a substance can ignite when they encounter an ignition source under specific testing conditions. For biodiesel, we usually measure the flash point using the ASTM D93 test method. It's worth mentioning that biodiesel has a flash point that is higher than that of regular diesel, typically above 130 ºC, making it safer to handle and store. To ensure a minimum flash point, biodiesel specifications put a cap on the alcohol content. If any alcohol from the production process is left in the biodiesel, it can seriously lower the flash point and negatively impact how well the fuel burns. Moreover, having too much methanol can harm engine seals and elastomers, as well as lead to corrosion in metal parts. For these reasons, the allowable alcohol content in biodiesel is limited to a maximum of 0.24 mg/kg (G.Lakshmi Narayana Rao, 2010)

Having a high flash point is really important to prevent fires during storage, handling, and transportation. There's a direct relationship here: the more solvents and leftover alcohol present in biodiesel, the lower its flash point tends to be. (Suherman *et al.*, 2023).

2.6.2 Kinematic viscosity: Kinematic viscosity is basically the measure of how much a liquid resist flowing. When we stack it up against petroleum diesel, biodiesel usually has a higher kinematic viscosity because of its heavier molecular structure. This greater viscosity can really impact how the fuel atomizes during combustion, which might lead to slower intake strokes and delays in ignition when the fuel mixes with air in the combustion chamber. In fact, biodiesel's viscosity can be around 10 to 15 times thicker than diesel, which can lower thermal efficiency. Plus, a higher kinematic viscosity may cause deposits to build up in the engine's chambers, while a lower viscosity could affect engine lubrication. There's also a link between kinematic viscosity and acid value. Usually, we assess fuel quality by checking out the increases in both kinematic viscosity and acid values in samples, since these aspects are tied to acid formation that happens during oxidation.

2.6.3 Cold Flow Properties: One major challenge with biodiesel is its performance in cold temperatures, specifically its tendency to flow poorly. This issue is highlighted by its relatively high cloud points (CP) and pour points (PP). The cloud point is usually higher than the pour point; it indicates the temperature at which the biodiesel starts to become cloudy due to crystals forming as saturated fats solidify. As the temperature drops, these crystals can grow and cluster together, leading to blockages in fuel lines and filters, causing serious operational problems.

When the temperature continues to fall and more solids form, the biodiesel gets closer to its pour point, which is the lowest temperature at which it can still flow. Saturated fatty compounds melt at significantly higher temperatures than unsaturated ones and when combined, they generally crystallize at warmer temperatures than the unsaturated fats. The cloud point is affected by both the type and amount of saturated fatty compounds present. So, biodiesel made from fats or oils that have a high level of saturated fatty compounds will show higher cloud and pour points because saturated fats have much higher melting points than unsaturated ones. For the latest insights on the melting points of fatty compounds, check out Knothe. (2016).

2.6.4 Pour point: The pour point is the lowest temperature at which biodiesel can flow freely, as below this temperature it tends to form a gel-like consistency. This characteristic is vital for the cold flow properties of the fuel, since biodiesel is generally considered effective if its pour point is above this threshold. Typically, biodiesel has a higher pour point than regular diesel, which isn't ideal. We really want those pour point numbers to be as low as possible, especially under zero degrees, because this ensures the fuel can keep moving even in chilly weather. On the flip side, if the pour point is too high, it can cause all sorts of problems in the engine, like reducing the fuel’s ability to reach the engine properly or even clogging up the filters.

2.6.5 Cetane Number and Combustion: The Cetane Number (CN) is an important indicator of diesel fuel quality because it determines how quickly the fuel ignites. To put it simply, a higher CN means that fuel ignites faster after being injected into the engine cylinder. Generally, shorter ignition delays are preferred. Interestingly, research often highlights compounds with lower CNs especially those rich in unsaturated fatty acids more than those with higher CNs. This difference stems from the nonlinear connection between ignition delay times and CN (Knothe et al., 2003).

In essence, even minor changes in shorter ignition delay times can significantly impact CN, unlike what we see with longer ignition delays (Knothe, 2016).

2.6.6 Density: Fuel density plays a vital role in how well an engine performs. Since fuel injection pumps measure fuel by volume rather than by mass, the quantity of fuel injected is directly affected by its density. This impacts the air-fuel ratio and the energy content within the combustion chamber as well. Generally, biodiesel fuels have slightly higher densities than petroleum diesel, and as the blend of biodiesel increases, so does its density. As shown in Fig. 4b, the density of fatty acid methyl esters (FAME) is notably influenced by the degree of unsaturation—more unsaturation leads to a higher density. It's important to point out that in this study, density and specific gravity are used interchangeably, even though specific gravity is usually the preferred term in most research. Table 11 shows the correlation coefficient between specific gravity and average unsaturation, which is 0.65. Additionally, it's been observed that the density of biodiesel is affected by the length of the carbon chain, with longer chains generally resulting in lower densities (Hoekman et al., 2012).

2.7 BIODIESEL OPTIMIZATION PRODUCTION

Improving biodiesel production yields can be greatly enhanced by leveraging statistical analysis tools like Mini Tab or Design-Expert (versions 6.0.8 and 9). There are several methods available, including response surface methodology (RSM), factorial design, fractional factorial, crossed design, and mixture design. These techniques are all designed to help analyze and interpret the yields we get from our experiments. (Uk, 2015).

2.7.1 Response Surface Method (RSM): Response Surface Methodology (RSM) encompasses a set of statistical and mathematical techniques that are valuable for developing, enhancing, and optimizing processes (Carley et al., 2004). This technique allows us to examine how various reaction parameters influence the process and helps predict the ideal conditions for achieving the best results, all while minimizing the number of experiments required. (Uk, 2015). One of the most common uses of Response Surface Methodology (RSM) occurs in scenarios where multiple input variables can affect a certain performance metric or quality attribute of a process. This performance metric or quality attribute is referred to as the response. The input variables, often known as independent variables, can be manipulated by the scientist or engineer in charge. (Carley et al., 2004). There are variety of methods used in Response Surface Methodology (RSM), including central composite design (CCD), Box-Behnken design, 3-level factorial, hybrid design, 1-factor design, pentagonal and hexagonal designs, as well as D-Optimal methods, distance-based designs, modified distance designs, and even user-defined strategies based on historical data. However, the two most common types of RSM are Central Composite Design (CCD) and Box-Behnken Design, each featuring its own unique structure. This method is straightforward and relies on a linear function, making it one of the preferred techniques for statistical analysis, particularly in biodiesel optimization. The main aim of RSM is to reveal how various process variables interact, using experimental data to generate a 3-D response surface and contour plot grounded in a regression model. This way of designing experiments not only effectively handles uncertainty but also enables conclusions to be drawn with minimal simulations. (Uk, 2015). This report we will concentrate on the second strategy: statistical modeling to develop an appropriate approximating model.

The first-order model is likely a great option if you're trying to get a good approximation of the true response surface over a small section of the independent variable space, particularly in areas where the function, f, remains fairly straight. When working with two independent variables, you can represent the first-order model by using coded values.

………………………………………………………………………………………… (1.0)

$$\eta = \beta_o + \beta_1 x_1 + \beta_2 x_2 ;$$

The first-order model represented in Equation (2.1) is often referred to as main effects model. This is because it only takes into account the main effects of the two variables, x and 2x1 ……………………………………………… (1.1) If there's an interaction between these variables, you can easily add it to the model like this. $\eta = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 ;$

This is the first-order model that includes an interaction term. By adding this interaction, we introduce some curvature to the response function. However, in many cases, the actual curvature in the true response surface is so pronounced that the first-order model, even with the interaction term, falls short. In such situations, a second-order model will probably be necessary. When dealing with two variables, the second-order model is

$$\eta = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 ; \quad \text{..................} \quad (1.2)$$

This model is probably quite helpful as a way to approximate the actual response surface within a fairly limited area. The second-order model is commonly employed in response surface methodology for a number of reasons: flexible (i.e It can take on a wide variety of functional forms, so it will often work well as an approximation to the true response surface), estimate the parameters (the β's) , solving real response surface problems.

In general, the first-order model is

$$\eta = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_k x_k \quad \text{..................} \quad (1.3)$$

and the second-order model is

$$\eta = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i<} \sum_{j=2}^{k} \beta_{ij} x_i x_j \quad \text{.......} (1.4)$$

2.7.1.1 Box Behnken design: This design is a rotatable second-order setup that relies on three level incomplete factorial designs. The unique way the Box–Behnken design is structured lets us boost the number of design points in sync with the number of polynomial coefficients. Take three factors, for instance; we can create the design using three blocks of four experiments. This approach includes a complete two-factor factorial design, where the level of the third factor is fixed at zero. (Aslan & Cebeci, 2007).

Box–Behnken design requires an experiment number according to

N= k2 + k + cp, ……………………………………………………………………… (1.5)

In this context, (k) refers to the factor number, and (cp) indicates the number of replicates for the central point. The Box–Behnken design is essentially a spherical, rotational design. If you imagine it as a cube (see Fig. 2.2 (a)), it comprises a central point along with the midpoints of its edges. Alternatively, it can be seen as three interconnected 2^2 factorial designs with an added central point (refer to Fig. 2.2 (b)). This design has proven useful in optimizing a variety of chemical and physical processes.

The model is of the following form

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad \text{…………………………………………..} (1.6)$$

In this equation, y represents the predicted response. The term b_0 is the constant of the model, while x1, x2, and x3 are the independent variables. The coefficients b_1, b_2, and b_3 are linear, and the coefficients b_{12}, b_{13}, and b_{23} indicate the interactions between variables. Lastly, b_{11}, b_{22}, and b_{33} are the quadratic coefficients

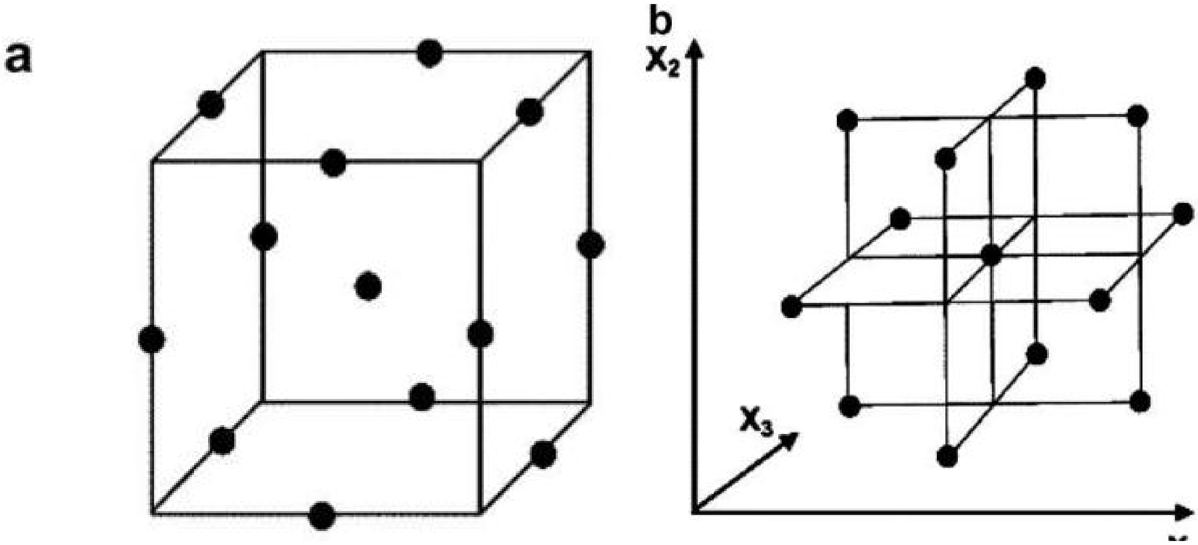


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Figure 2. 2 Box Behken Design

CHAPTER THREE

3.0 MATERIAL AND METHODS

3.1 Materials

Table 3. 1: List of Material and Their Uses.

Materials	**Uses**
Absolute Ethanol	For acid value test titration
Benzene	For acid value test titration
Chloroform	For peroxide test
Glacial acetic acid	For peroxide test
Sodium hydroxide (NaOH)	For saponification value test
Sodium thiosulphate ($Na_2S_2O_3$)	For peroxide test titration
Periwinkle shell	Used for the Catalyst preparation
Warm water	Used in washing the produced biodiesel
Potassium iodide	For iodine value test

Table 3. 2: the reagent used for this study

REAGENT	**USE**
BENZENE	To test for acid value
KOH (0.5 M)	The base used in titrating for the acid value
PHENOLPHTHALEIN	Indicator for titration

Table 3.2: Equipment, Apparatus and their Uses

Equipment and Apparatus	**Uses**
Beakers	They are used for pouring, mixing and keeping reagents for use
Burette	For titration of acid value test
Conical flask	It is used as the reactor for laboratory biodiesel synthesis and for acid value test titration
Digital viscometer	For measuring the kinematic viscosity of oil
Density bottle	Used to evaluate the density of oil
Heating mantle	Used to heat water for biodiesel washing and

	saponification value
Magnetic stirrer and stirring bar	This is the machine that supplies heat to the reaction. It has a rotating magnetic element that causes the stirring bar to create an agitated motion in the reactor
Retort stand and separating funnel	These are used to hold up the reacted mixture so as to allow separation by gravity.
Muffled furnace	Used to calcine the Grasscutter bones catalyst at high temperature
Round bottom flask	It is used as the reactor for esterification process and to heat water for biodiesel washing
Steel containers	The catalyst to be calcined were placed in steel container before being put into the muffled furnace
Volumetric cylinder	To measure a given volumetric quantity of reagent
Weighing balance	Used to evaluate the mass of a substance

3.2 Method

3.2.1 Feedstock (waste cooking oil) Pretreatment.

The waste cooking oil was collected from a nearby shop that makes bean cakes (akara) in Ekosodin Ugbowo, Edo. We filtered the oil to get rid of any food particles. After that, the oil was placed in a tightly sealed 10-liter gallon and stored at room temperature to avoid oxidation.

Plate 3. 1: waste cooking oil

3.2.2 Catalyst Preparation

Periwinkle shells were obtained from the Luco laboratory. These shells were placed in a furnace pan and inserted into the furnace, where they underwent calcination at 900°C for two hours. After calcination, the shells were reduced to a smaller size and then passed through a 75µm standard mesh. The sieved sample was then put into several crucibles and subjected to another round of calcination at 900°C for an additional two hours. This process helped to thermally activate the shells while effectively removing any carbonaceous and volatile materials. The activated periwinkle shells were stored in an airtight container and later utilized as a catalyst in the transesterification process.

*Plate 3. 2***:** *calcined periwinkle shell*

plate 3. 3 calcined periwinkle shell

3.2.3 Catalyst Characterization

Series of experimental method were carried out on the catalyst (calcined periwinkle shell) to examine the composition and properties of the synthesized catalyst. The surface morphology and surface structure of the sample was examined through Scanning Electron Microscopy (SEM). While the Elemental composition of the material was evaluated using Energy-Dispersive X-ray (EDX) analysis. Fourier Transform Infrared Spectroscopy (FTIR) was used to investigate the bond structure and molecular interactions. To check the crystal size and structure of the materials, X-ray Diffraction (XRD) was used with Cu-K radiation. The catalyst's surface area and pore volume were estimated with the Brunauer-Emmett-Teller (BET). Differential Thermal Analysis (DTA) was used to assess its thermal stability. X-ray Fluorescence (XRF) analysis was used to quantify the oxide composition, and the Barrett-Joyner-Halenda (BJH) was employed to measure pore volume and diameter.

3.2.4 Waste Cooking Oil Characterization

3.2.4.1 Determination of Acid Value and Free Fatty Acid of Waste Cooking Oil

In a conical flask, 1 gram of the oil sample was weighed. Next, 10 milliliters of both ethanol and benzene were measured out and added to the flask. To serve as an indicator, three drops of phenolphthalein was dropped in. the solution was titrated with 0.05M potassium hydroxide (KOH), continuing until the color changed from pink to colorless. Finally, I took note of the volume in the burette.

The acid value was calculated with the formular below

$$A.V. = \frac{56.1 X (S - B) x M}{W}$$

Where

s = oil sample titrate value

b = blank sample titrate value

m = molarity of KOH.

W = mass of oil

The Free Fatty Acid (FFA) of the oil was calculated with the formular below, which shows the the relationship between FFA and AV.

$$FFA = \frac{ACID\ VALUE}{2}$$

3.2.4.2 Determination of Density

- The electric weighing balance was zero.
- Then an empty 50ml density bottle was placed on it and weighed, and the mass recorded.

- The empty bottle was fill with waste cooking oil and weighed again, and the value recorded.

The density was calculated with the formular below

$$\text{DENSITY} = \frac{\text{MASS}}{\text{VOLUME}} = \frac{(W_2 + W_1)}{V}$$

Where:

W2 = mass of empty density bottle

W2= mass of density bottle and oil

V= volume of density bottle

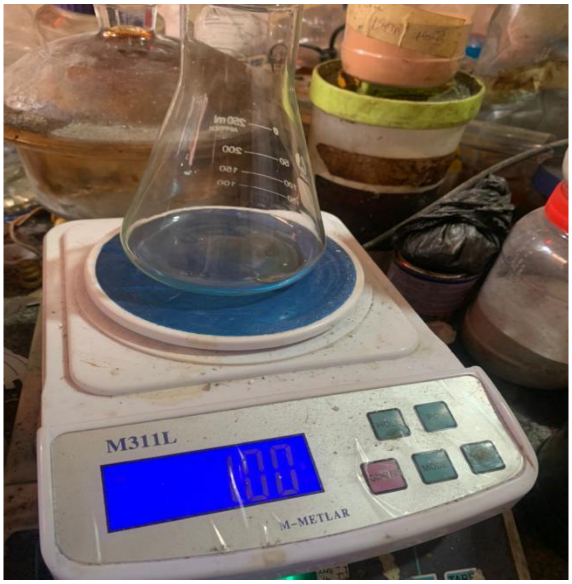


Plate 3. 4 weighed conical flask

3.2.4.3 Determination of Peroxide Value

- 2.5g of the oil sample was weighed with a conical flask.
- 30 milliliters of Acetic Acid-Chloroform mixture was added and shaken to mix properly.

- 2 milliliters of saturated potassium iodide solution was added to the mixture and it was stirred for one minute.
- 1 milliliters of starch indicator was added then was stirred until the mixture turned dark.
- 30 milliliters of distilled water was added to the mixture and shaken once more for a minute.
- 0.1N sodium thiosulfate was filled in a burette.
- The mixture was then titrated and vigorously shaken until all traces of the black colour turned white and the final burette reading was recorded.

The peroxide value was calculated with the equation below

$$\text{PEROXIDE VALUE} = \frac{(S - B)\, N \times 100}{M}$$

Where:

S= oil Sample titrate value

B= blank sample titrate value

M= mass of oil sample

N = Normality of $Na_2S_2O_3$

Plate 3. 5 blank sample after titration

3.2.4.4 Determination of Saponification Value

2.5 g of oil was mixed with 25mL of alcoholic after which a separate layer of oil sample at the bottom was observed.

The mixture was heated and shaken using a water bath at 80 to 85 for 30 minutes (till no separate layer of oil was seen, indicating end of saponification.

Also, a blank solution containing just the reagents was heated and shaken at same temperature for 30 minutes.

Phenolphthalein was added and titrated against 0.5M HCl until it became clear.

Take note of the final burette reading.

The oil's saponification value was calculated using

$$\text{Sap Value} = \frac{56.1\ X\ (V_S - V_B)\ x\ M}{}$$

V_B = Volume of blank

V_S = Volume of sample

W_S = Weight of sample

Plate 3. 6 experimental setup for saponification

3.2.5 design of experiment and modeling.

Design Expert software version 13.0 was utilized to conduct the experimental design and simulation, along with the necessary statistical analysis. The Box–Behnken Design (BBD), a method under Response Surface Methodology (RSM), was employed to optimize the process and assess how various process parameters influence biodiesel production. This approach helped generate the number of experimental runs needed and aimed to maximize the yield of Fatty Acid Methyl Esters (FAME). A selection of factors was based on previous literature, detailed in Table 3.3. The choice of Box–Behnken Design over Central Composite Design (CCD) was made because it requires far fewer experimental runs, resulting in a total of 29 experimental runs.

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

FACTORS	SYMBOL	CODED AND ACTUAL		
		-1	0	1
CATALST LOAD (Wt%)	A	1	5.5	10
REACTION TIME (MIN)	B	30	90	150
TEMPERATURE (o C)	C	40	60	80
MOLE RATIO	D	3	6.5	10

3.2.6 Biodiesel Optimization Production and Characterization

The biodiesel was produced using waste cooking oil, methanol and a heterogenous catalyst which was synthesized from periwinkle shell. The waste cooking oil was first filter to remove particles, the oil was weighed with a conical flask using an electrical weighing balance and the catalyst and methanol was added as stated by the optimizing condition. It is then placed on the magnetic stirrer and set to the various optimizing temperature. The reaction takes place producing the biodiesel which is placed in a centrifuge to separate the glycerol, biodiesel and catalyst before putting it into a separating funnel. It is then left for some time inside the separating funnel before being separated and washed with warm water.

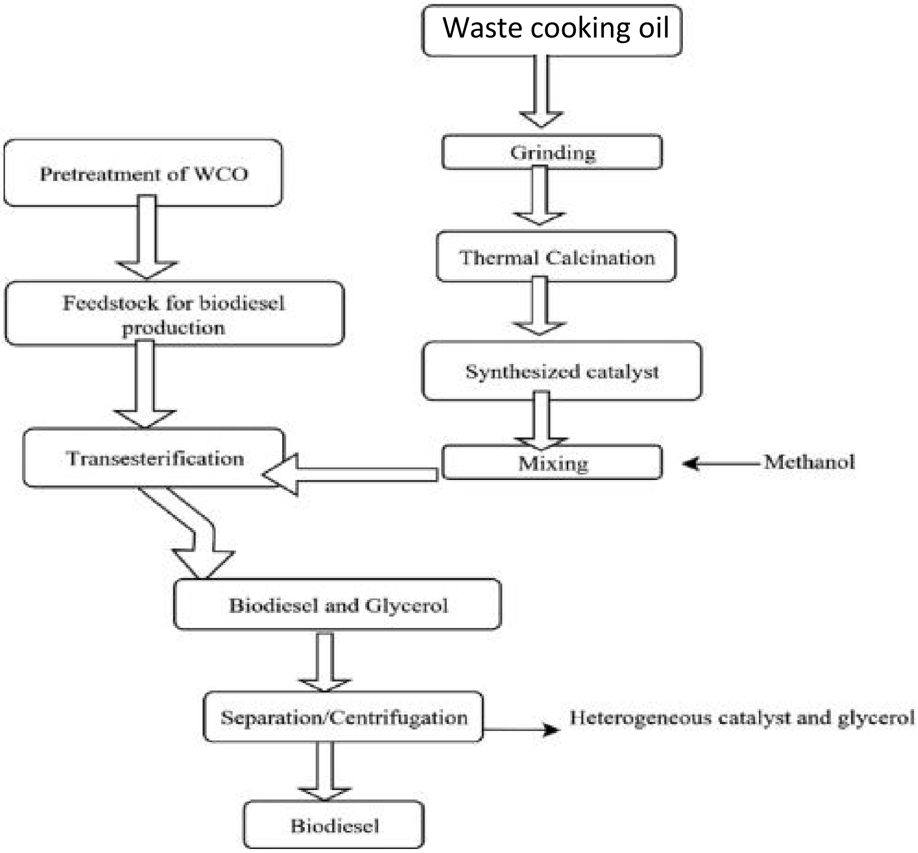


Figure 3. 1:diagrammatic representation of the biodiesel manufacturing process using ostrich bone derived heterogenous catalyst (Mahmood et al., 2020).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Physiochemical Properties of Waste Coking Oil

Table 4. 1: properties of the waste cooking oil for biodiesel production (wco)

Property	**Value**
Acid value (mg KOH/g oil)	6.17
FFA (%)	3.09
viscosity @ 30.08 ^{o}C (mPa.s)	9.23
Peroxide value	3.95
Saponification value (mg KOH/g oil)	244.14
Average molecular weight (g/mol)	707.65
Density (kg/m^3)	956

Table 4.1 outlines the properties of the waste cooking oil (WCO) used in biodiesel production. The acid value for the WCO was measured at 6.17 mg KOH/g oil, while the free fatty acid (FFA) content stood at 3.09%. This is considered high, especially according to ASTM D664 and ASTM D94 guidelines (FFA content greater than 1%), which could affect the efficiency of its conversion to biodiesel. However, studies have shown that heterogeneous catalysts can effectively process oils with high FFA levels (between 6-15%) without requiring any pre-treatment, achieving yields over 90% (Uk, 2015). The viscosity of the oil is recorded is 9.23 mPa.s at 30.08°C, which is very high for biodiesel feedstock, and might affect flow during processing. Additionally, a peroxide value of 3.95 indicates some level of oxidation; this could

influence the stability of the fuel. The saponification value, sitting at 244.14 mg KOH/g oil, provides insight into the average molecular weight of the triglycerides, which corresponds with the measured molecular weight of 707.65 g/mol. Lastly, the density of 960 kg/m³ aligns with expectations, highlighting its potential as a suitable candidate for biodiesel production.

4.2 Characterization of the heterogenous catalyst.

4.2.1 Fourier Transform Infrared (FTIR) Spectroscopy

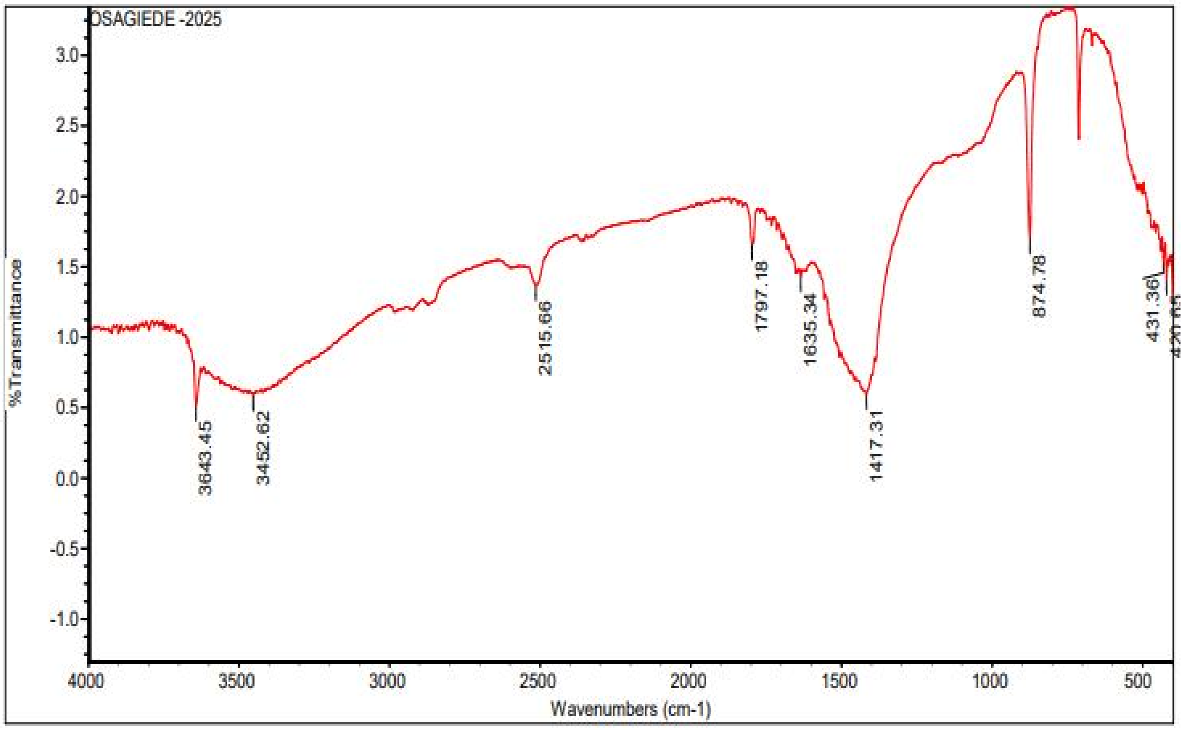


Figure 4. 1: FTIR spectra of waste cooking oil (WCO)

The FTIR spectrum displayed in Figure 4.2 reveals some noteworthy changes across different wavenumber ranges. It highlights several distinct absorption peaks at specific wavenumbers, which indicate the presence of various functional groups. For instance, the broad peak around 3429.62 cm⁻¹ suggests that hydroxyl (-OH) groups are present. The peak at 3963.45 cm⁻¹ might be associated with overtone bands or a weaker stretching vibration of another functional group. This particular absorption band points to the existence of thiol (-SH) groups, commonly found in sulfur-containing organic compounds. Additionally, the C=O stretching observed at 1797.18 cm^{-1} and 1653.54 cm^{-1} identifies the stretching vibration of a carbonyl (C=O) functional group, which is typically seen in esters.

4.2.2 Energy Dispersive X-ray

TABLE 4. 2:

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
20	Ca	Calcium	97.08	97.63
26	Fe	Iron	0.42	0.58
13	Al	Aluminum	0.81	0.55
14	Si	Silicon	0.51	0.36
15	P	Phosphorus	0.46	0.35
12	Mg	Magnesium	0.39	0.24
25	Mn	Manganese	0.08	0.11
11	Na	Sodium	0.17	0.10
16	S	Sulfur	0.09	0.07
19	K	Potassium	0.00	0.00
22	Ti	Titanium	0.00	0.00
17	Cl	Chlorine	0.00	0.00

Elemental composition of synthesized catalyst from EDX

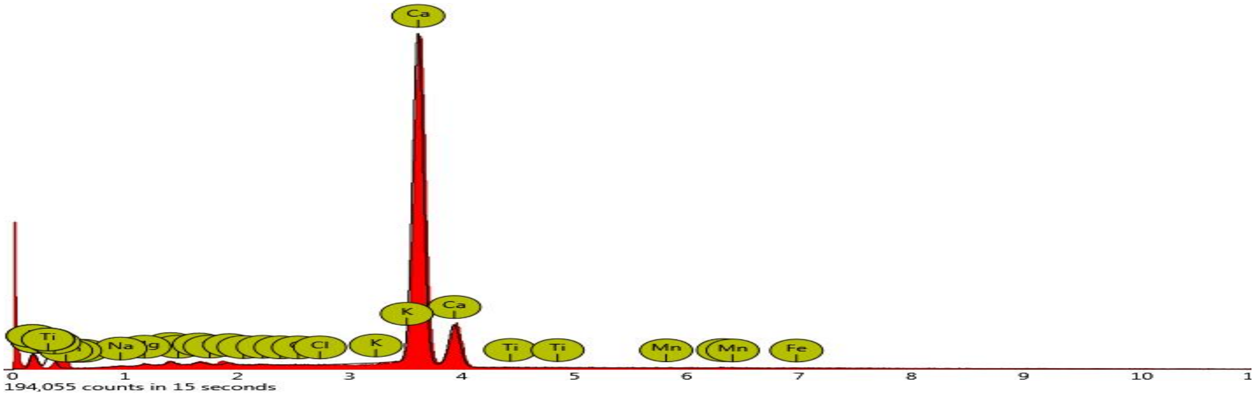
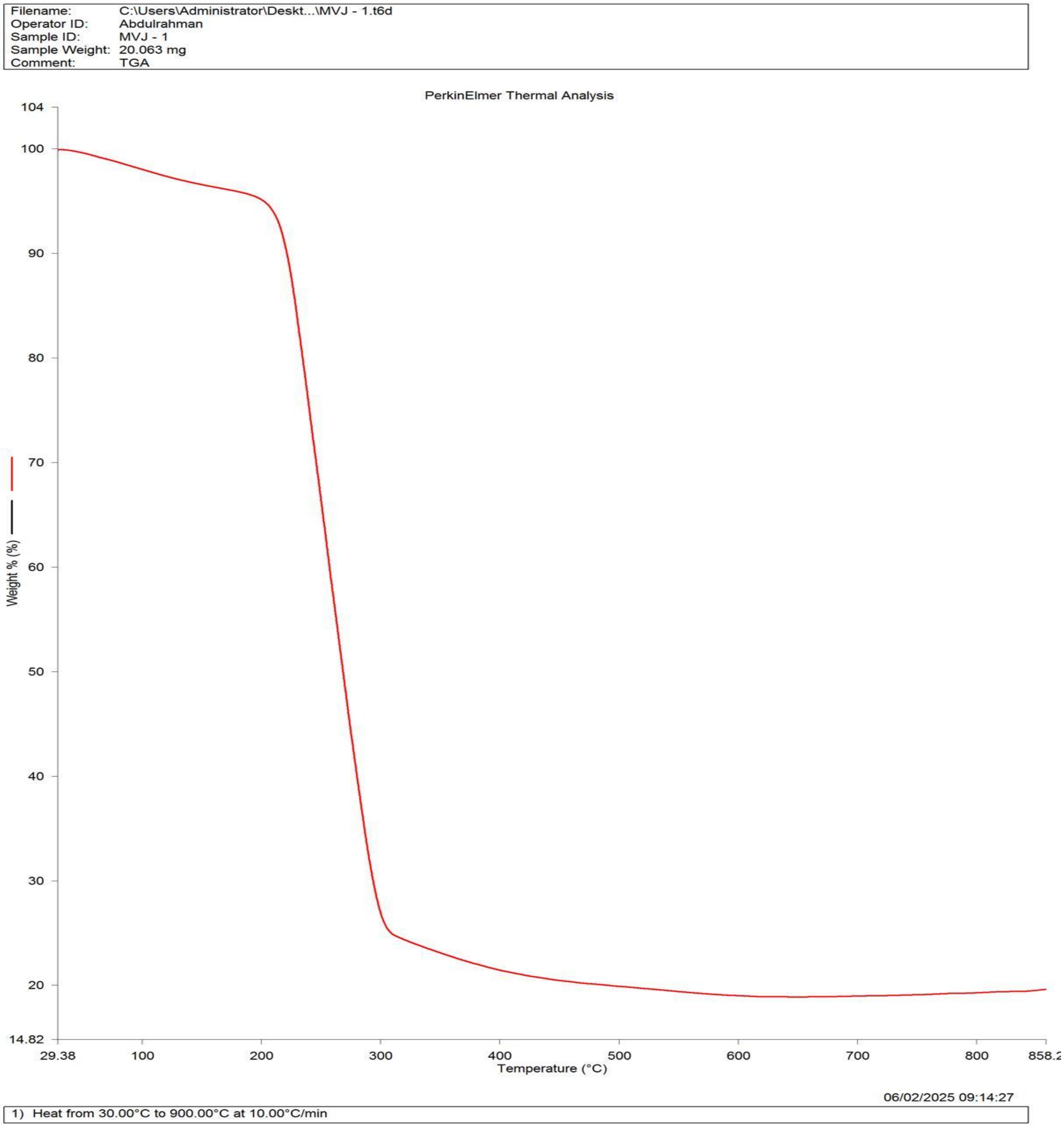


Figure 4. 2 EDX pattern of synthesized catalyst

The results from the elemental composition displayed in Table 4.2 reveal that there are several elements present, with calcium (Ca) standing out as the most significant. In fact, calcium accounts for about 97.08% of the atomic concentration and 97.63% of the weight concentration. The other elements that were identified are found in much smaller amounts, including iron (Fe), aluminum (Al), silicon (Si), phosphorus (P), magnesium (Mg), manganese (Mn), sodium (Na), sulfur (S), potassium (K), titanium (Ti), and chlorine (Cl). The particularly high levels of calcium suggest that the sample primarily consists of calcium-based compounds. The trace amounts of other elements like iron, aluminum, silicon, and phosphorus could either be impurities or naturally occurring elements in the sample. Additionally, the presence of silicon and phosphorus might indicate the mineral content or how environmental factors have impacted the material.

4.2.3 Thermogravimetric Analysis (TGA) And Differential Thermogravimetry (DTG)



Filename: C:\Users\Administrator\Deskt...\MVJ - 1.t6d
Operator ID: Abdulrahman
Sample ID: MVJ - 1
Sample Weight: 20.063 mg
Comment: TGA

1) Heat from 30.00°C to 900.00°C at 10.00°C/min

Figure 4. 3: Thermogravimetric Analysis of the Catalyst

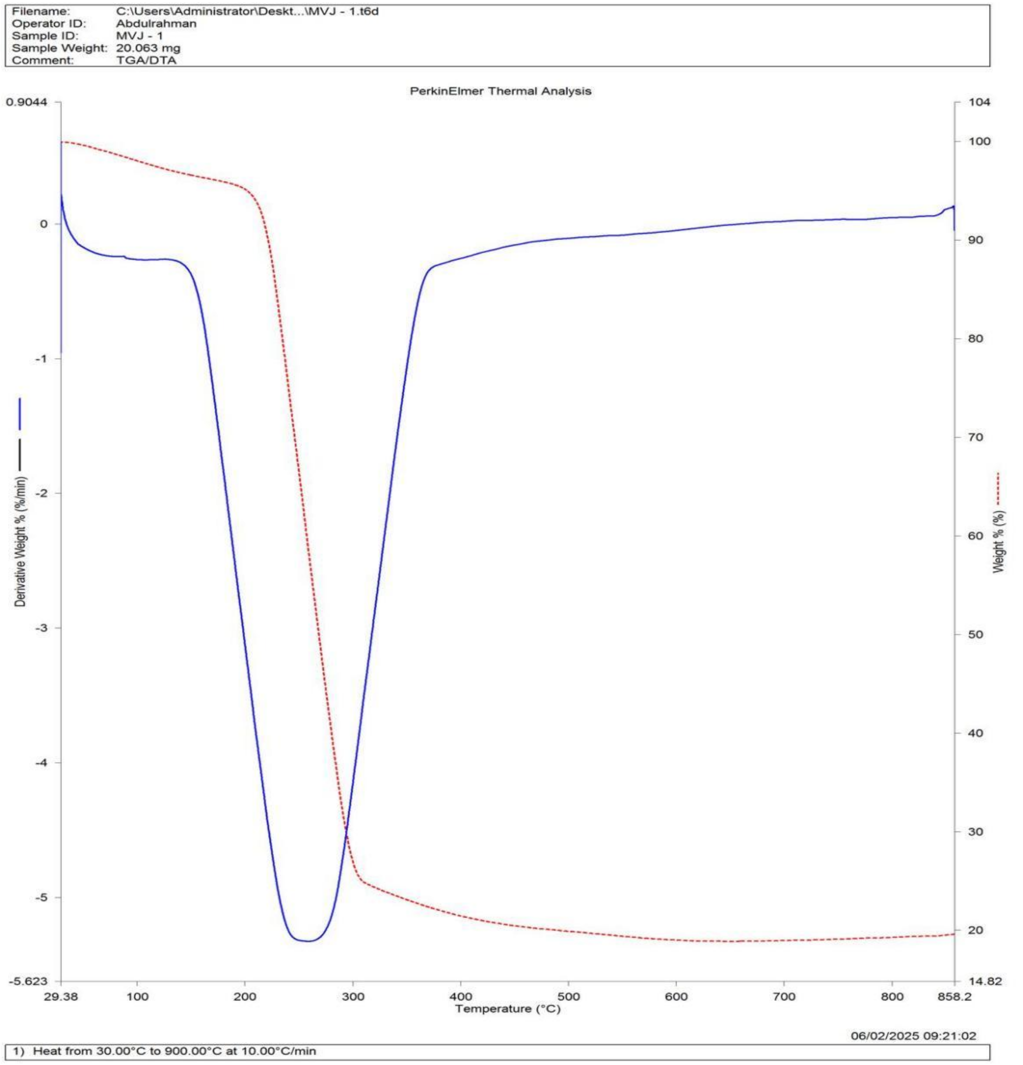


Figure 4. 4: Thermogravimetric Analysis (TGA) with Differential Thermogravimetry (DTG) on the Catalyst

The Thermogravimetric analysis curve in Figure 4.4 reveals that the catalyst maintains its weight stability up to about 150°C. During this phase, the catalyst shows only a slight weight loss, indicating that there aren't any significant amounts of moisture or volatile substances present at these lower temperatures. However, when the temperature increases from around 150°C to 300°C, there's a noticeable drop in weight, which points to a breakdown or major thermal decomposition of the main component in the sample. Once it reaches 300°C, the weight loss starts to stabilize, suggesting that most of the volatile components have already decomposed. Looking at the results from the Thermogravimetric Analysis (TGA) alongside Differential Thermogravimetry (DTG) shown in Figure 4.5, the Blue Line representing Derivative Weight % versus Temperature (the DTG Curve) displays a prominent peak in the 150–300°C range. This indicates a single-step decomposition process. The temperature at the peak of the DTG signifies the maximum rate of decomposition, which is useful for identifying the material's composition.

4.2.4 Scanning Electron Microscopy (SEM)

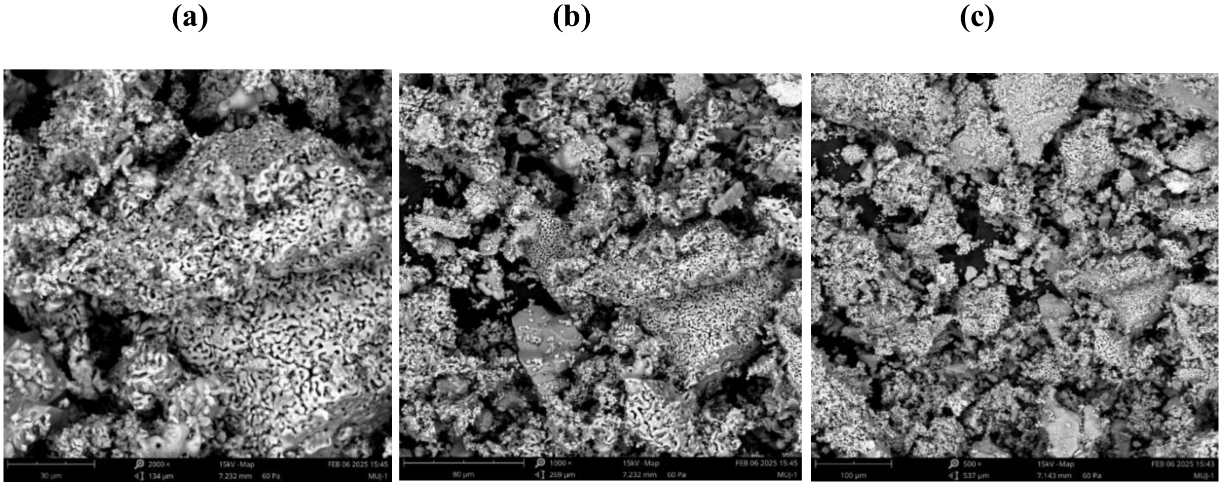


Figure 4. 5: SEM analysis of prepared catalyst at (a) x2000 (b) x1000 (c) x500

The SEM images shown in Figure 4.6 illustrate the micrograph taken at magnifications of 2000×, 1000×, and 500×. They reveal a structure that is both highly porous and rough. The irregular voids and interconnected channels are indicative of material burnout, thermal degradation, or phase separation. It's clear that heat caused a considerable change in the microstructure, likely resulting in the formation of a carbonaceous network or an inorganic framework. This transformation is primarily attributed to the sintering effect of the catalyst particles at elevated calcination temperatures, which results in the aggregation of these catalyst particles.

4.3 RSM Modelling of Biodiesel Production

The Box-Behnken design, utilizing response surface methodology, focused on four key factors: the methanol-to-oil (mtOH/oil) ratio, temperature, reaction time, and catalyst loading, to optimize biodiesel production from waste cooking oil. This approach involved a multiple regression analysis that produced 29 different experimental runs, as detailed in Table 4.4. The quadratic statistical model for the actual variables can be found in Table 4.5. You can calculate the biodiesel yield using Equation (1) provided below.

$$\text{Biodiese yield } \% = +94.94 +8.48A +4.81B +3.04C +10.08D -13.43AB -13.87AC -9.93AD -6.82BC +0.5600BD +1.0000CD -15.22A^2 -21.27B^2 -4.32C^2 -16.24D^2 \ldots\ldots\ldots\ldots(1)$$

The equation indicates that the yield of biodiesel is influenced by a variety of individual factors and their interactions, with some of these factors needing to remain within a specific range for best results. The presence of negative quadratic terms points to the idea that pushing certain factors to extremes can actually reduce the yield. Essentially, this means there’s a sweet spot we should strive for to optimize production.

Run Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residuals	Externally Studentized Residuals	Cook's Distance	Influence on Fitted Value DFFITS	Standard Order
1	54.94	54.68	0.2650	0.583	0.084	0.081	0.001	0.096	13
2	62.84	71.80	-8.96	0.583	-2.843	-4.215⁽¹⁾	0.755	-4.987⁽²⁾	10
3	78.10	75.55	2.55	0.583	0.810	0.800	0.061	0.946	2
4	77.68	73.05	4.63	0.583	1.469	1.539	0.201	1.821	20
5	77.70	77.94	-0.2417	0.583	-0.077	-0.074	0.001	-0.087	14
6	74.50	72.88	1.62	0.583	0.516	0.502	0.025	0.594	24
7	50.58	50.02	0.5617	0.583	0.178	0.172	0.003	0.203	17
8	46.66	43.09	3.56	0.583	1.131	1.144	0.119	1.353	21
9	55.48	51.59	3.89	0.583	1.234	1.260	0.142	1.490	22
10	95.98	94.94	1.04	0.200	0.237	0.229	0.001	0.115	28
11	61.04	58.30	2.74	0.583	0.869	0.860	0.070	1.018	4
12	95.98	94.94	1.04	0.200	0.237	0.229	0.001	0.115	25
13	30.90	35.00	-4.10	0.583	-1.301	-1.337	0.158	-1.582	9
14	86.54	88.50	-1.96	0.583	-0.623	-0.609	0.036	-0.721	8
15	64.68	70.38	-5.70	0.583	-1.808	-1.989	0.305	-2.354⁽²⁾	16
16	29.24	31.74	-2.50	0.583	-0.792	-0.781	0.059	-0.924	1
17	65.90	68.21	-2.31	0.583	-0.734	-0.722	0.050	-0.854	3
18	95.98	94.94	1.04	0.200	0.237	0.229	0.001	0.115	29
19	69.74	66.34	3.40	0.583	1.079	1.086	0.109	1.285	6
20	88.66	83.84	4.82	0.583	1.529	1.615	0.218	1.910	19
21	63.44	62.14	1.30	0.583	0.413	0.401	0.016	0.474	23
22	64.46	62.26	2.20	0.583	0.699	0.686	0.046	0.812	5
23	90.10	94.94	-4.84	0.200	-1.110	-1.120	0.021	-0.560	27
24	69.22	74.41	-5.19	0.583	-1.647	-1.767	0.253	-2.091	15
25	70.78	72.11	-1.33	0.583	-0.423	-0.410	0.017	-0.485	12
26	77.26	80.42	-3.16	0.583	-1.003	-1.003	0.094	-1.187	7
27	78.54	75.01	3.53	0.583	1.120	1.131	0.117	1.338	11
28	95.08	94.71	0.3717	0.583	0.118	0.114	0.001	0.135	18
29	96.68	94.94	1.74	0.200	0.398	0.385	0.003	0.193	26

Table 4. 3 Box Behnken optimized result for biodiesel production

Table 4. 4 Analysis of variance for a quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	9137.50	14	652.68	27.39	< 0.0001	significant
A-Calyst load	861.91	1	861.91	36.18	< 0.0001	
B-Reaction time	277.44	1	277.44	11.64	0.0042	
C-Temperature	111.02	1	111.02	4.66	0.0487	
D-Mole Ratio	1219.68	1	1219.68	51.19	< 0.0001	
AB	721.46	1	721.46	30.28	< 0.0001	
AC	769.51	1	769.51	32.30	< 0.0001	
AD	394.02	1	394.02	16.54	0.0012	
BC	186.32	1	186.32	7.82	0.0143	
BD	1.25	1	1.25	0.0527	0.8218	
CD	4.00	1	4.00	0.1679	0.6882	
A^2	1502.49	1	1502.49	63.06	< 0.0001	
B^2	2935.81	1	2935.81	123.22	< 0.0001	
C^2	121.03	1	121.03	5.08	0.0408	
D^2	1711.68	1	1711.68	71.84	< 0.0001	
Residual	333.55	14	23.83			
Lack of Fit	303.85	10	30.39	4.09	0.0934	not significant
Pure Error	29.70	4	7.42			
Cor Total	9471.05	28				

The Model F-value of 27.39 suggests that the model is statistically significant. There's just a 0.01% likelihood that an F-value this high could be a fluke caused by random noise. When we look at P-values, any value below 0.0500 shows that those model terms are significant. In this case, the terms A, B, C, D, AB, AC, AD, BC, A^2, B^2, C^2, and D^2 are all significant. On the flip side, values above 0.1000 indicate that the model terms aren't significant. If you end up with a lot of insignificant terms (excluding those necessary for maintaining hierarchy), simplifying your model might be beneficial. As for the Lack of Fit F-value, which is 4.09, it indicates there's a 9.34% chance that such a value could arise from noise. Lack of fit is something we want to avoid since we aim for a good model fit. This probability, being relatively low (under 10%), is definitely concerning.

Table 4. 5: Models with their significance, lack of fit, R-square, and adjusted R-square values

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.1099	0.0010	0.1376	-0.0113	
2FI	0.3215	0.0010	0.1912	-0.0577	
Quadratic	**< 0.0001**	**0.0934**	**0.9296**	**0.8103**	**Suggested**
Cubic	0.5129	0.0433	0.9297	-0.7223	**Aliased**

The R2 values in Table (4.6) were used to assess how well the polynomial model fits the data compared to other models. To evaluate the model's terms, we can refer to the F-value and P-value listed in Table (4.5). The Model F-value of 27.39 suggests that the model is significant. There's only a 0.01% chance that an F-value this high could just be due to random noise, and since the P-values are below 0.0500, it indicates that the terms in the model are indeed significant. Specifically, A, B, C, D, AB, AC, AD, BC, A^2, B^2, C^2, and D^2 are all significant terms in the model. On the other hand, values greater than 0.1000 suggest that those model terms aren't significant. If there are numerous insignificant terms (excluding those necessary for maintaining hierarchy), you might want to consider reducing the model for better results. The Lack of Fit F-value of 4.09 indicates that there’s a 9.34% chance that a Lack of Fit F-value this large could occur because of noise. Since lack of fit is undesirable—we want our model to fit well—this relatively low probability (<10%) is concerning.

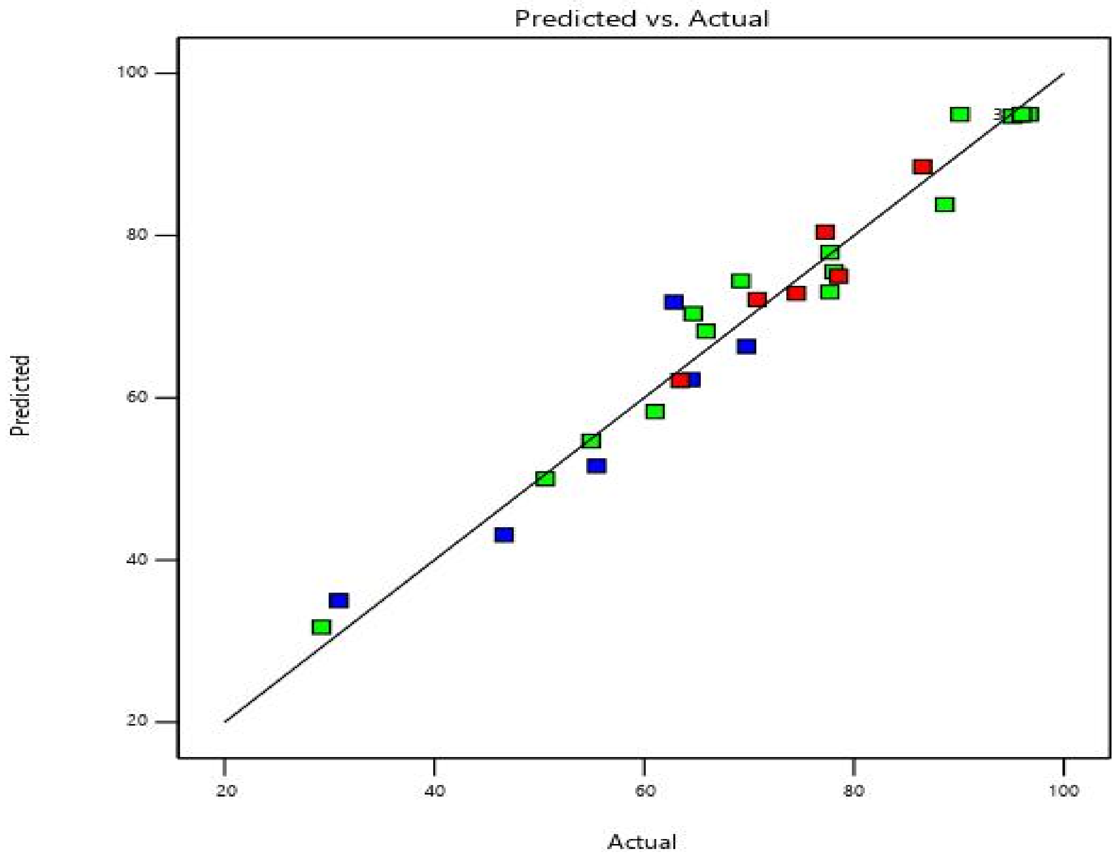


Figure 4. 6: Predicted vs. Actual plot.

The Predicted vs. Actual plot (figure 4.7) clearly shows a linear trend, indicating that the model's predictions closely match the actual values. The black diagonal line marks a perfect scenario where the predicted values correspond exactly to the actual ones. Points that are near this diagonal line signify a high degree of accuracy in the model. On the other hand, any points that stray far from the line reveal areas where the model's accuracy falls short. The use of multiple colors—red, green, and blue—suggests that there are different categories of data, which might correspond to various experimental conditions, parameter settings, or validation datasets. Between the actual values of 20 and 40, the predicted values seem to slightly overestimate (you'll notice the blue points are above the line). In the range of 60 to 80 actual values, most predicted points align closely with the actual values, showcasing a high level of accuracy. However, for actual values between 80 and 100, there are a few red points indicating slight underprediction, even though the majority of predicted values remain accurate.

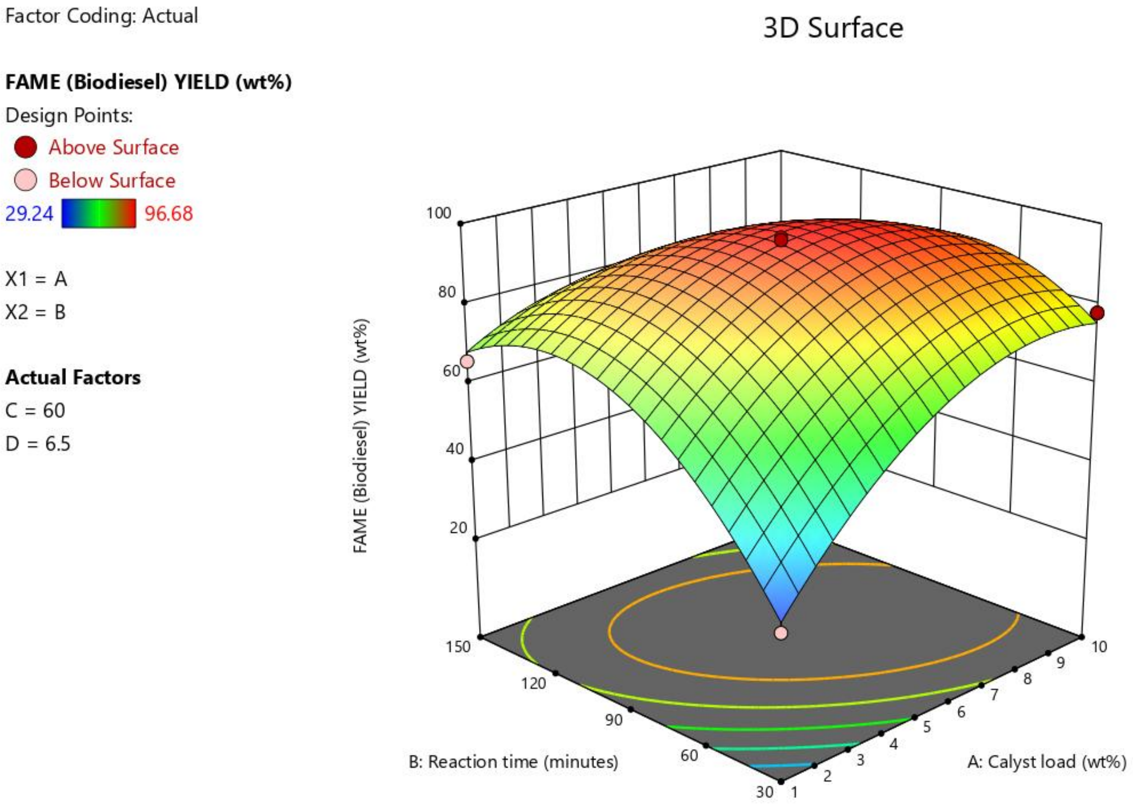


Figure 4. 7: 3D surface plot illustrates the variation in FAME (Fatty Acid Methyl Ester) yield as a function of reaction time (minutes) and catalyst load (wt%).

The plot illustrates a curved surface that shows a non-linear connection between reaction time, catalyst load, and biodiesel yield. The peak biodiesel yield, which is around 96.68 wt%, is achieved at a moderate catalyst load along with an ideal reaction time. This optimal area is highlighted in the red and yellow shades at the curve's top. On the flip side, the lowest biodiesel yield, approximately 29.24 wt%, occurs when both reaction time and catalyst load are kept at their minimum. This is shown by the blue and green areas at the bottom of the plot. As reaction time increases, the yield goes up initially but then levels off, indicating that after a certain point, longer reaction times don't significantly boost biodiesel production. A similar pattern is observed with catalyst load. While increasing the catalyst load initially drives the reaction forward, once you exceed an optimal level, further increases can lead to unwanted side reactions or even catalyst deactivation, which ultimately lowers the yield.

Table 4. 6: Properties of waste cooking oil used for biodiesel production

Property	**Value**
Acid value (mg KOH/g oil)	2.595
FFA (%)	1.2975
Moisture content (%)	0.02
Dynamic viscosity @ 40 ^{o}C (mPa.s)	29.50
Saponification value (mg KOH/g oil)	300.135
Average molecular weight (g/mol)	565.638
Density @ 40 ^{o}C (kg/m^3)	903.0
Specific gravity	0.9127

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study successfully showcased the potential of calcined periwinkle shells as a heterogeneous catalyst for producing biodiesel from waste cooking oil (WCO). The analysis of WCO's physicochemical properties revealed an acid value of 6.17 mg KOH/g, a free fatty acid (FFA) content of 3.09%, a viscosity of 6.62 mPa.s at 30.08°C, a peroxide value of 3.95, a saponification value of 244.14 mg KOH/g, and a density of 956 kg/m³. These measurements affirmed that WCO could serve as a suitable feedstock for biodiesel, although its elevated FFA content necessitated careful catalytic processing.

The catalyst was created by calcining periwinkle shells at 900°C and showed an impressive calcium oxide (CaO) content of 97.08%, as verified through Energy Dispersive X-ray (EDX) analysis. Fourier Transform Infrared Spectroscopy (FTIR) confirmed the presence of vital functional groups necessary for catalytic activity, while Scanning Electron Microscopy (SEM) revealed a highly porous structure that boosted catalytic efficiency.

Using Response Surface Methodology (RSM) with a Box-Behnken design, the transesterification process was optimized, identifying the best conditions for biodiesel production: a catalyst loading of 5.5 wt.%, a reaction temperature of 60°C, a reaction time of 90 minutes, and an alcohol-to-oil molar ratio of 6.5:1. Under these optimal conditions, the biodiesel yield surpassed 90%, demonstrating the effectiveness of the CaO catalyst derived from periwinkle shells.

The end product of the biodiesel met industry standards and displayed favorable physicochemical properties, highlighting its potential as a sustainable alternative to fossil diesel.

This research emphasizes the economic and environmental advantages of using waste-derived catalysts and contributes to the progress of cost-effective and renewable biodiesel production. However, further research into the catalyst's reusability and its application on a larger, industrial scale is suggested to improve its commercial viability.

5.2 Recommendation

industrial trials should be carried out to see how these periwinkle shell-based CaO catalysts perform in real-world situations, away from the lab. This kind of assessment will give us valuable insights into their potential for commercial application and how scalable they actually are.

To enhance the catalyst's performance, we could consider tweaking its makeup by mixing it with other metal oxides or using surface treatments. This might help us speed up reaction times and push biodiesel yield beyond the impressive 90% noted in this study.

Since the waste cooking oil has a free fatty acid (FFA) level of 3.09%, it makes sense to explore more effective pre-treatment methods. Approaches like esterification with a suitable acid catalyst could improve the transesterification process and minimize unwanted side reactions.

The efficacy of periwinkle shell-derived CaO against other waste-based catalysts, such as those from eggshells, snail shells, and animal bones should be compared to help pinpoint the best alternatives for biodiesel production.

7.0 REFERENCE

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