

**ONE POT CONVERSION OF HIGH FREE FATTY ACID WASTE COOKING OIL
USING A BIFUNCTIONAL CATALYST DERIVED FROM PIG BONES AND PUMPKIN
STALKS: OPTIMIZATION VIA TAGUCHI APPROACH**

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BENIN CITY.

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**A project submitted to the Department of Chemical Engineering, Faculty of Engineering,
University of Benin, Benin City in partial fulfillment of the requirements for the award of
BACHELOR DEGREE in Chemical Engineering (B Eng.)**

SEPTEMBER, 2023.

CERTIFICATION

This is to certify that this project research work was carried out by OVIOSUN BOSE CHANTEL of the Department of Chemical Engineering at the University of Benin, Benin City, Edo State, Nigeria.

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DEDICATION

In gratitude to God Almighty, I am extremely grateful for His unlimited grace, consistent love, immeasurable faithfulness, great privilege, knowledge, wisdom, understanding and the enablement given to me to be able to start and complete my project research work. Therefore, I dedicate this research report to God Almighty.

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This project research work would not have been successful without the effort and sacrifice of the great people God brought my way.

I wish to extend my utmost gratitude to God Almighty for the privilege, grace and enablement to start and finish this undergraduate research project. It was not an easy journey, but God saw me through.

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I would be remiss if I did not mention my parents and siblings, especially my beloved late mother, Mrs. Izehiwa Oviosun. I am extremely grateful for her incessant prayers while she was alive. Her prayers have had a profound effect and will continue to have a lasting effect. I also wish to convey my thanks to my siblings and well-wishers. Their belief in me has kept my spirits high and my motivation strong throughout my entire undergraduate studies.

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ABSTRACT

This study investigated one-pot conversion of high free fatty acid waste cooking oil using a bi-functional catalyst derived from pig bones and pumpkin stalks and optimized it via the Taguchi approach. The pig bones underwent a calcination process at 900 °C for 6 hours, and the pumpkin stalks were subjected to carbonization at 450 °C for 3 hours. The bi-functional catalyst was then formed by wet impregnation of both the calcined pig bones and carbonized pumpkin stalks.

The bifunctional catalyst was subjected to characterization using Fourier Transform Infrared (FTIR), Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses, Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF), and Thermogravimetric Analyzer (TGA). The XRF analysis indicated that the bifunctional catalyst contained 63.397 % CaO within its overall composition. The bifunctional catalyst was successfully employed in the one pot conversion of high free fatty acid WCO into biodiesel. Utilizing the Taguchi L9 approach, the process was optimized. According to the ANOVA design, three significant variables influenced the process: the temperature of the reaction, length of the reaction, and molar ratio of methanol to oil. As a consequence, the numerical model projected an optimal biodiesel yield of 86.929 wt.%, accompanied by an acid value of 0.410 mg KOH/g. These favorable outcomes were attainable by employing specific reaction conditions: a 24:1 methanol-to-oil ratio, 1 wt.% catalyst loading, a reaction temperature of 65 °C, and a reaction time of 60 minutes. Notably, the projected biodiesel yields closely approximated the experimental result of 84.291 wt.%, which also exhibited an acid value of 0.405 mg KOH/g when these same optimal conditions were applied. A reusability study conducted on the bifunctional catalyst revealed the catalyst's economic advantage due to its effective catalytic activity. This led to a notable production of biodiesel from WCO over five consecutive runs, resulting in the following outcomes: 88.26 wt.% yield with an acid value of 0.435 mg KOH, 73.58 wt.% yield with an acid value of 0.518 mg KOH, 67.0 wt.% yield with an acid value of 0.684 mg KOH, 55.55 wt.% yield with an acid value of 0.710 mg KOH, and 44.63 wt.% yield with an acid value of 0.798 mg KOH, respectively. The physicochemical properties of the biodiesel produced from WCO using the bifunctional catalyst were assessed in accordance with ASTM D6751 and EN standards.

Based on the results of the reusability study, it could be inferred that the bifunctional catalyst synthesized from pig bones and pumpkin stalks is cost-effective. This catalyst can help lower the expenses of producing biodiesel, making it more affordable for commercial use.

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LIST OF ABBREVIATIONS

WCO – Waste Cooking Oil

ASTM – American Standard Test Method

EN – European Standard

L9 OA – Taguchi Orthogonal Array

CPPS – Carbonized Powdered Pumpkin Stalks

FAME – Fatty Acid Methyl Ester

UNBC – Unused Bifunctional Catalyst

UBC – Used Bifunctional Catalyst

ANOVA – Analysis of Variance

EU – European Union

ILUC – Indirect Land Use Change

BDs – Biodiesels

AV – Acid Value

FFA – Free Fatty Acid

CaO – Calcium Oxide

HAP – Hydroxyapatite

DOEs – Design of Experiments

BET – Brunauer-Emmet-Teller

BHJ – Barrett-Joyner-Halenda

IEA – International Energy Agency

EDXRF – Energy Dispersive X-ray Fluorescence

TGA – Thermogravimetric Analyzer

SEM – Scanning Electron Microscope

XRD – X-ray Diffractometer

FTIR - Spectrophotometer

GHG – Green House Gas

mg KOH/g – Milligrams of Potassium Hydroxide Per Gram

mg NaOH/g – Milligrams of Sodium Hydroxide Per Gram

BTLE – Biomass-To-Liquid Fuel

AL – Akyl Levulinales

NO_x – Nitrogen Oxide

SO_x – Sulphur Acid

KOH – Potassium Hydroxide

NaOH – Sodium Hydroxide

CI – Compression Ignition Engine

PRM – Polynomial Regression Method

CN – Cetane Number

TGS – Triglycerides

NGO – Non-Governmental Organization

GCMS – Gas Chromatography

SCFs – Superficial Fluids

THF – Tetrahydrofuran

BHA – Butyl – Hydroxyanisol

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF STUDY

Fatty acid alkyl esters are produced by subjecting vegetable or animal fats to a transesterification process with a low molecular weight alcohol, using a suitable catalyst. This process creates biodiesel, often referred to as 'green fuel', due to its numerous advantages such as biodegradability, renewability, reduced toxicity, higher cetane number, and flash point. Consequently, biodiesel has gained recognition as a potential substitute for conventional petroleum-based diesel (Baig and Ng 2010). In the majority of current biodiesel production methods, which employ homogeneous catalysis, refined vegetable oils serve as the primary raw materials. However, these refined oils come at a considerable expense. The cost of these feedstocks significantly affects the economic aspects of biodiesel production, as highlighted in a review conducted by Marchetti and Gebremariam, (Akhavue et al. 2020) discovered that the economics of biodiesel production are notably affected by the expense of feedstocks. Studies have indicated that the expenditure on raw materials for biodiesel production may make up as much as 88% of the total production expenses. Therefore, a substantial reduction in the production cost of biodiesel can be achieved through the utilization of non-edible oils or waste cooking oil (Haas et al. 2016). The elevated levels of free fatty acids (FFA) in waste cooking oil and various non-edible oils lead to saponification by the alkali catalyst, resulting in a reduced biodiesel yield due to the challenge of separating the product. Moreover, the purification process generates waste water, causing environmental pollution concerns, which require the treatment of waste water before disposal or reuse (Daud et al. 2015). This, in turn, adds to the cost of biodiesel production.

The majority of research has adopted a two-stage procedure to reduce the FFA levels in these oils to below 1%. Initially, there's a pretreatment phase, often referred to as esterification, which reduces the FFA content in the oil. Subsequently, the treated oil undergoes an alkaline-catalyzed transesterification process to produce biodiesel (Tariq et al. 2012). While this approach does improve the potential biodiesel yield from high-FFA oils, it proves to be economically impractical because it necessitates a greater number of purification steps to eliminate corrosive acids and because the catalyst cannot be reclaimed. In lieu of homogeneous catalysts for biodiesel synthesis, a new method has been introduced, involving a one-step process that combines esterification and transesterification, using heterogeneous catalysts (Policano et al. 2016; Ali et al. 2018; Mansir et al. 2018). The use of heterogeneous catalysts in the biodiesel production process not only reduces the volume of wastewater generated during purification but also offers the advantage of catalyst recovery for reusability. This could potentially lead to a reduction in the overall cost of biodiesel production when heterogeneous catalysts are adopted. Although previous studies have explored the use of heterogeneous catalysts for biodiesel production through transesterification, it's important to note that the catalysts employed in simultaneous esterification and transesterification processes are distinctive in nature, as they are bi-functional, exhibiting both acidic and basic properties (Akhavue et al. 2020).

The conversion of high free fatty acid waste cooking oil (WCO) into biodiesel in a single-step process, using a bi-functional catalyst derived from pig bones and pumpkin stalks, and the optimization through the Taguchi approach is a noteworthy subject in the biodiesel production field. Biodiesel, being a renewable and environmentally-friendly liquid fuel, presents a hopeful substitute for conventional petroleum-based diesel, which can aid in mitigating carbon dioxide (CO₂) and greenhouse gas emissions (Erchamo et al. 2021). Nonetheless, the significant expenses associated with production and the scarcity of essential resources present obstacles to the broad acceptance of biodiesel. To address this issue, it is crucial to investigate alternative catalysts and make use of waste cooking oil as a raw material. Waste cooking oil, which is readily available in substantial quantities from households and industries, has proven to be an appealing choice for biodiesel production due to its abundance and cost-effectiveness when compared to edible vegetable oils (Sahar et al. 2018). Employing waste cooking oil as a primary resource for biodiesel manufacturing accomplishes a dual objective: it not only lowers the overall expenses but also serves as an effective solution for the issue of improper waste disposal. Converting waste cooking

oil into biodiesel not only mitigates the environmental consequences of waste disposal but also plays a role in fostering a more sustainable and circular economy.

Conventional catalysts typically applied in the biodiesel manufacturing process, like alkali-homogeneous catalysts, are ill-suited for waste cooking oil due to its elevated levels of free fatty acids (FFA) and water content (Naeem et al. 2021a). In this project, pig bone and pumpkin leaf stalk are explored as bi-functional catalysts for biodiesel production via Taguchi optimization approach. These unconventional catalysts offer the advantage of addressing the challenges associated with waste cooking oil, such as high FFA content and soap formation (Mansir et al. 2018). The utilization of pig bone and pumpkin leaf stalk as catalysts is intended to enhance the efficiency and cost-efficiency of biodiesel production. While there is prior research on different catalysts and raw materials for biodiesel production, there is a scarcity of information regarding the specific use of pig bone and pumpkin leaf stalk as dual-purpose catalysts for converting waste cooking oil. Therefore, the main goal of this project is to investigate the one pot conversion of high free fatty acid waste cooking oil (WCO) using a bi-functional catalyst derived from pig bones and pumpkin stalks; and optimization via Taguchi approach. The project aims to assess the effectiveness of the catalyst, the efficiency of the conversion process, and the potential for reusing the catalyst, all with the goal of advancing the creation of eco-friendly and financially feasible methods for producing biodiesel.

1.2 PROBLEM STATEMENT

The production and utilization of biodiesel derived from waste cooking oil offer significant promise for reducing waste and promoting sustainable energy. Nevertheless, the cost-effective and efficient production of biodiesel using waste cooking oil faces several hurdles. The high levels of free fatty acids (FFA) and water content in waste cooking oil pose limitations for conventional biodiesel synthesis catalysts, such as alkali-homogeneous catalysts. These difficulties lead to the formation of soap, separation issues, and increased production expenses. Moreover, employing expensive edible vegetable oils as the starting materials significantly increases the expenses associated with biodiesel production, reducing its economic feasibility. This studies objective is to investigate the one pot conversion of high free fatty acid waste cooking oil (WCO) using a bi-

functional catalyst derived from pig bones and pumpkin stalks; and optimization via Taguchi approach. However, despite the potential of this novel catalyst, there is limited literature regarding its application. Therefore, a comprehensive investigation is needed to assess the efficiency and performance of this bi-functional catalyst in the transesterification process to produce biodiesel using waste cooking oil. Through this research, we aim to address the difficulties linked to using waste cooking oil as a raw material and create a novel and eco-friendly method for producing biodiesel. The results will play a significant role in refining the production process, enhancing conversion efficiency, cutting down expenses, and encouraging the use of waste materials. This, in turn, will boost the economic feasibility and environmental friendliness of biodiesel production from waste cooking oil.

1.3 AIM AND OBJECTIVES

The aim of this research study is to investigate the one-pot conversion of high free fatty acid waste cooking oil (WCO) using a bi-functional catalyst derived from pig bones and pumpkin stalks and to optimize it via the Taguchi approach.

The objectives are as follows:

1. Collection and pretreatment of wastes as raw materials; pig bones, pumpkin stalks and waste cooking oil (WCO).
2. Synthesizing the pig bones and pumpkin stalks to generate a bi-functional catalyst.
3. Waste cooking oil (WCO) characterization.
4. Biodiesel production utilizing the bifunctional catalyst.
5. Optimization of the produced biodiesel using Robust Design (Taguchi L9 Method)
6. Examining the impact of the following factors on the anticipated outcomes (biodiesel output and acidity level); the proportion of Methanol to oil, the quantity of catalyst, the duration of the reaction, and the temperature during the reaction.
7. Characterization of the unused and used bi-functional catalyst.
8. The reusability study of the bi-functional catalyst.
9. The produced biodiesel characterization.

1.4 SCOPE OF STUDY

The scope of studies entails the following:

1. Collection and pretreatment of pig bones and pumpkin stalks.
2. Collection and characterization of waste cooking oil (WCO).
3. Synthesizing the pig bones and pumpkin stalks to generate a bi-functional catalyst.
4. Using the synthesized bi-functional catalyst to achieve the one-pot conversion of waste cooking oil (WCO) into biodiesel.
5. Characterization of the unused and used bi-functional catalyst.
6. Optimization of the produced biodiesel via Robust Design (Taguchi L9 Method).
7. Determination of the reusability of the bi-functional catalyst.
8. Characterization of the yield of each sample of biodiesel produced.
9. Conclusion and recommendation

1.5 RELEVANCE OF STUDY

While there has been extensive research on various catalysts and feedstocks for biodiesel production, there is limited available information, specifically regarding the utilization of pig bones and pumpkin stalks as bi-functional catalysts in the conversion of waste cooking oil. Therefore, the objective of this project is to investigate the one-step conversion of high free fatty acid waste cooking oil (WCO) using a bi-functional catalyst derived from pig bones and pumpkin stalks and to enhance the process using the Taguchi method. In order to promote sustainable and economically viable biodiesel production processes, this study will evaluate catalytic performance, conversion efficiency, and reusability, all of which contribute to cost-effectiveness.

Therefore, this study's area of focus encompasses the following aspects:

1. Enhancing the efficiency of biodiesel production through the development of a bi-functional catalyst derived from waste materials.
2. Examining the catalytic performance and selectivity of such a bi-functional catalyst in the conversion of waste cooking oil into biodiesel.

3. Evaluating the long-term performance and stability of a sustainable bi-functional catalyst in the one-pot conversion of high free fatty acid waste cooking oil for biodiesel production.
4. Investigating how various process parameters and catalyst properties impact biodiesel production, aiming to optimize both output and quality.
5. Conducting a comparative analysis to assess the effectiveness and feasibility of using a bi-functional catalyst derived from solid waste materials in biodiesel production as opposed to a traditional catalyst, with a particular focus on reusability.
6. Assessing the environmental impact, advantages, and sustainability associated with producing biodiesel from waste materials and feedstock.
7. This approach contributes to reducing the volume of waste cooking oil that ends up in landfills and lowers waste disposal costs.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Since the onset of the industrial revolution during the late 18th and early 19th centuries, energy has played a crucial role in enabling humanity to sustain economic development and a high quality of life. Forecasts from the International Energy Agency (IEA) and research by Shahid and Jamal indicate that by 2030, the world will need 50% more energy than it presently consumes, with China and India contributing 45% to this escalating demand. Over the past three decades, the transportation sector has exhibited consistent growth, largely driven by the increasing global car population. This industry currently accounts for the majority of the world's oil consumption and is projected to experience the most rapid growth in energy demand in the future. Oil constitutes 97.6% of the fossil fuel energy utilized in transportation, with natural gas making up the remainder. Significantly, approximately three-quarters of the expected surge in oil demand between 2006 and 2030 is anticipated to originate from this sector, highlighting the imperative to seek alternative fuel sources (Atabani et al. 2012), hence the need to look for an alternative source of fuel.

The 1970 oil crisis led many nations to examine replacing fossil fuels with alternative fuels (Costa and Sodr  2011). Therefore, blending biofuel with conventional fuel could precisely cut down on usage and help combat the greenhouse effect. Biofuel is not always convenient to substitute fossil fuel in extreme heat and cold. However, biofuel can be utilized as a substitute fuel in a controlled setting with specialized combustion equipment. More biofuel than diesel fuel is consumed despite having a lower heating value. Additionally, it produces higher NO_x emissions, which harm the environment. The availability of raw materials for biofuel production is becoming a significant limitation for agricultural regions. Biofuel, in essence, represents a form of renewable energy harnessed from various sustainable sources. The most widely used biofuels are made from food plants that need fertile agricultural area to develop, such as biodiesel from vegetable seeds and ethanol from wheat, corn, and sugar beet (Demirbas 2010, 2011).

The world food supply is now dealing with important concerns. Fuel vs. food could be a problem since it could be risky to use crop acreage for the production of liquid biofuels, which would be bad for the world's food supply. Divergent opinions exist regarding how significant this could be, its influence, the harm it is causing, and what will be done about it. Recently, the rise in global oil prices led to a notable improvement in the manufacturing of biofuels worldwide. Products like corn, vegetable oil, and sugar cane will be utilized to make biofuels as well as feed and food. With a fuel energy value close to diesel fuel, seed oils are renewable and offer endless opportunities to obtain energy. Additionally, excessive use of vegetable oils has the potential to cause a number of significant problems, including a lack of food in poor nations (Sadeghinezhad et al. 2014). Starvation or the use of food as fuel are issues that have already sparked a contentious debate. The problem will undoubtedly become more complicated as oil demand rises in the near future. As of 2011, the Food and Agriculture Organization of the United Nations reported that 925 million people around the globe suffer from hunger. One approach to address this issue and reduce its consequences involves examining the potential use of recycled or surplus edible oils for biodiesel production. It is also widely acknowledged that the usage of used cooking oil for human consumption is unhealthy (Nurfitri et al. 2013). Utilizing waste-derived catalyst and oil could also mitigate environmental harm. Furthermore, extensive research conducted over the last five years has focused on the utilization of waste materials such as bones, rocks, ashes, and shells as catalysts for producing biodiesel. The exploitation of such waste products has become particularly alluring due to their abundance and low cost. One feedstock with two benefits is used cooking/frying oil waste. Using WCO as a feedstock will in addition prevent water pollution because it won't be released into the water bodies, as well as being an inexpensive raw materials for the manufacturing of biodiesel (Mansir et al. 2018).

In consideration of this, this paper presents a comprehensive examination of the utilization of feedstock and catalyst derived from waste sources. To align with a sustainable, environmentally friendly strategy for biodiesel production, the paper explores the development of waste cooking oil (WCO) feedstock and a bifunctional catalyst using heterogeneous solid wastes from pig bone and pumpkin leaf stalk. These choices are motivated by their significant advantages, notably the ease of separation, recyclability, and the potential for reuse. Additionally, it takes waste management into consideration.

2.2 BIODIESEL

Biodiesel serves as a sustainable substitute for conventional diesel fuel derived from petroleum. It is produced by transforming triglycerides found in various sources like plant and animal-based fats, including lipids and tallows, into fatty acid mono alkyl esters. This conversion process, known as transesterification, involves reacting triglycerides with an alcohol in the presence of a catalyst (Akhavue and Okwundu 2019). The Triacylglycerols, which make up the majority of vegetable oils and other materials, are transesterified with monohydric alcohols, most frequently methanol, to produce the matching mono-alkyl esters, which are then used to make biodiesel. Therefore, biodiesel is often called the fatty acid methyl esters (FAME) derived from vegetable oils, animal fats, or other substances containing triacylglycerols. As the least expensive alcohol, methanol has been commonly used to produce biodiesel. Consequently, the fatty acid composition of biodiesel mirrors that of the original oil or fat used for its production (Knothe and Razon 2017). The features of a fatty ester are influenced by both the fatty acid chain and the alcohol group. Hence, it's crucial to consider the attributes of the different alcohols that can be used to produce fatty acid alkyl esters (FAAE) for biodiesel production.

Furthermore, biodiesel is significantly more eco-friendly than conventional diesel due to its superior cetane rating and reduced emissions of NO_x, SO_x, carbon monoxide, hydrocarbons, and particulate matter. Additionally, when compared to standard fuel, biodiesel emissions contain fewer pollutants, including polycyclic aromatic hydrocarbons (Vijayan et al. 2018). Given its resemblance to diesel fuel in terms of properties and its clean combustion in compression ignition (CI) engines, biodiesel is considered the ideal substitute for diesel fuel. It is categorized into four generations based on the feedstocks used. The first generation of biodiesel is produced from edible feedstocks such as palm, sunflower, soybean, and so on. However, due to the high cost of these feedstocks and the competition between food and fuel production, the commercialization of biodiesel made from these sources faces significant challenges (Singh et al. 2021).

2.3 HISTORY OF BIODIESEL

Rudolf Diesel invented the diesel engine, also referred to as a compression ignition engine, with the capability to operate on a range of fuels, including heavy mineral oil, vegetable oil, and a

mixture of coal dust and water. Initial efforts to develop a diesel engine faced considerable challenges. In 1900, Diesel successfully demonstrated his engine, which ran exclusively on peanut oil, at the Paris World Exhibition (Mishra and Goswami 2018). In 1900, vegetable oil was initially employed as a fuel, but the term "biodiesel" was not coined until 1988. Rudolf Diesel, a German engineer, had foreseen in 1893 the potential use of pure vegetable oils as fuel for agricultural machinery. At the 1900 Paris World's Fair, the French Otto Company unveiled a diesel engine powered by peanut oil. The process of transesterification for producing biodiesel from vegetable oils was introduced by Belgian scientist George Chavanne in 1937, providing the first-ever description of biodiesel production (Dewangan et al. 2018).

In 1940, the first experiments using methyl and ethyl esters of vegetable oils were conducted in France. Belgian researchers were also utilizing palm oil ethyl ester as a bus fuel at the same time. Research on fats and oils as alternative fuels was slow until the late 1970s and early 1980s, when worries about rising petroleum prices spurred significant testing (Friedrich 2004; Balat and Balat 2014). Early in the 1990s, widespread manufacturing of biodiesel, also known as mono alkyl ester, began. Since then, output has continuously increased. In order to combat the decline of rural areas and meet the rising levels of energy demand, biodiesel was promoted in the European Union (EU) throughout the 1980s. However, it wasn't until the second part of the 1990s that it really started to take off. With the increasing demand for petroleum and the environmental advantages it offers, experts are currently placing their emphasis on biodiesel production. The most widely adopted and efficient method for biodiesel production involves the transesterification of vegetable oils and animal fats. This method is not a recent innovation; it was originally proposed by Duffy and Patrick as far back as 1853. Since then, numerous research with various oils have been conducted (Mishra and Goswami 2018).

2.4 GROWING INTEREST IN BIODIESEL

Exploration of alternative energy sources is gaining traction due to increasing environmental and energy resource challenges. There is a growing fascination with alternative fuels like biodiesel as a potential replacement for conventional diesel oil in internal combustion engines, addressing the ever-expanding global energy demands. Given that they are renewable and have comparable

qualities to diesel oil, biodiesels present a very viable substitute. The projected decline of conventional fuels and environmental concerns have drawn much attention to this possible alternative fuel (Oladeji and Adedipe 2012). Utilizing liquid fuels such as biodiesel produced from waste cooking oil using a process called transesterification is considered one of the most encouraging approaches to replacing conventional fossil fuels. Nevertheless, due to the competition between biodiesel production from edible vegetable oils and animal fats with food resources, it has faced significant opposition in recent times. Supporting the utilization of vegetable oils for purposes like biodiesel production is challenging, especially considering the significant recent surge in their demand for food. Additionally, there is a potential for increased costs associated with using these oils as fuel. Therefore, it becomes imperative to explore alternative sources, such as waste materials from the edible oil industry and non-edible plant oils like soapnut and jatropha, as the primary feedstock for biodiesel production (Ramavathu et al. 2015).

A significant portion of the costs associated with biodiesel production is attributed to the acquisition of raw materials. Hence, opting for more affordable raw materials rich in fatty acids, such as animal fats, non-edible oils, used cooking oil, and byproducts from vegetable oil refining, can effectively reduce the expenses involved in biodiesel production (Gashaw and Teshita 2014). The recent emphasis has shifted towards utilizing waste cooking oil as the primary source material for biodiesel manufacturing. This change is driven by the reduced production expenses, concerns regarding potential competition between biodiesel feedstock and food resources, and the aim to mitigate environmental pollution.

2.5 DEBATE SURROUNDING BIODIESEL

There is increasing concern that farmers will be compelled to cultivate more crops for fuel and that there will be less land available for food due to the biodiesel industry's rapid growth. The "food vs. fuel" debate gained momentum in 2008 as global prices began to rise (Pradhan and Malani 2022). Following a dispute centered on a matter known as "indirect land use change" (ILUC). The study of the indirect and unintentional effects on carbon emissions brought on by the development of feedstock for biofuels is known as ILUC. For example, wetlands or forests elsewhere in the world might be turned into agriculture if additional cropland is set aside for biofuel feedstocks.

There is an atmospheric release of carbon as a result of this land alteration. Certain biofuels may have contributed to greater atmospheric carbon emissions than their fossil fuel equivalent due to indirect land use changes, according to some experts (Frank Vogelgesang, Uttaya Kumar 2018).

2.6 GROWTH OF THE BIODIESEL INDUSTRY

Petroleum-based fuels serve as the predominant energy source for the global economy. However, due to market fluctuations, it is shifting toward a sustainable bio-based economy, as fossil sources are expected to run out by 2050. Besides the excessive exploitation of petroleum reserves, the pursuit of sustainable alternatives like biodiesel has been spurred by climate change and the adverse environmental impacts caused by exhaust emissions (Bhattacharya et al. 2016). Biodiesel presents an appealing choice due to its non-toxic and easily degradable nature. It results from the transesterification of animal or plant oils with methanol in the presence of a catalyst, forming fatty acid methyl ester molecules (Akhavue and Ewah 2021). Typically, a substantial amount of glycerol is generated as a byproduct from the production of biodiesel. For every 100 pounds of biodiesel produced through the transesterification of animal fats or vegetable oils, about 10 pounds of crude glycerol are obtained. However, the remarkable expansion of the biodiesel industry has led to an oversupply of glycerol, resulting in a dramatic tenfold decrease in the prices of crude glycerol in recent years. This price decline has created challenges for both glycerol production and refining companies, as well as the economic sustainability of the biodiesel sector (Binhayeeding et al. 2017).

The escalation in biodiesel production could lead to higher prices for edible vegetable oil, giving rise to the fuel-versus-food dilemma. To address these concerns, researchers have explored and implemented alternative sources like non-edible plant oils, microbiological resources, and the recycling of waste cooking oil. Although the cost of biodiesel production currently exceeds that of fossil-based diesel, its global expansion is driven by the environmental advantages it offers. One alternative strategy to increase biodiesel production capacity is to reduce waste byproduct generation and valorize waste created (Kosamia et al. 2020). Many biodiesel companies have begun to treat crude glycerol as a waste rather than refining it for commercial use. Crude oil is also utilized as a direct ingredient in animal feed. While crude glycerol may appear to be a burden for

many biodiesel producers, it has considerable potential for usage as a starting material for value-added bio-chemicals in the biorefining process. Such value-added chemicals can increase revenue for existing biodiesel firms while also making the process more sustainable.

2.7 FUTURE OF BIODIESEL

Climate change, characterized by shifts in weather patterns, poses the most critical environmental threat to ecosystems worldwide at present. If the global average temperature surpasses a threshold of 2°C, it could lead to the potential extinction of about one million species. The predominant factor contributing to global warming, as widely acknowledged, is the utilization of fossil fuels. Therefore, there is a pressing need to transition from fossil fuels to renewable and biodegradable energy sources to mitigate the release of CO₂ and greenhouse gases (Karmakar and Halder 2019). Aside from recognizing that the rise in carbon dioxide emissions is responsible for climate change, the depletion of fossil fuel reserves has sparked enthusiasm for promoting biofuels as a significant source of renewable energy. Sustainable biofuel production plays a crucial role in the fight against climate change, the enhancement of local economies, especially in underdeveloped regions, and the improvement of global energy security. Biodiesel has become a primary focus for renewable transportation fuels.

Biodiesel is notably appealing for several reasons. It exhibits strong biodegradability, low toxicity, and versatility in various applications, including boilers and internal combustion engines, with minimal adjustments needed. Additionally, it shows only a marginal decrease in performance and emits virtually no sulfates, aromatic compounds, or other environmentally detrimental chemicals. Biodiesel releases fewer pollutants, possesses a higher flash point, offers improved lubrication, and boasts a higher cetane number compared to traditional diesel fuel. It shares very similar physicochemical characteristics, enabling its use either in its pure form (as B100) or when blended with petroleum-based diesel fuel (typically in the range of 5 to 20%, B5 to B20) with minimal technical modifications or, in some cases, no adjustments at all (Atabani et al. 2017). Numerous nations, such as the Germany, United States, Indonesia, Malaysia, Italy, Brazil, France, and various European countries, have adopted biodiesel, indicating substantial potential for both its production and utilization.

2.8 PROPERTIES OF BIODIESEL

2.8.1 DENSITY

A crucial fuel property that directly influences an engine performance characteristic is density. The air-fuel ratio is influenced concurrently with the quantity of fuel supplied to the combustion chamber. This is so that fuel injection pumps may measure gasoline by volume rather than mass, since denser fuel has a higher mass per unit volume. Consequently, because the mass of gasoline injected varies, alterations in fuel density will have an impact on the engine's power output. The selection of vegetable oil significantly influences the density of biodiesel, with its primary dependence on the content of esters and the residual alcohol level in the fuel (Encinar et al. 2011).

Density is another crucial characteristic of diesel fuels that has an impact on the fuel injection system, which is typically tested at 15 °C. The specific gravity of a liquid is the ratio of its density to the density of water, whereas the density of biodiesel is the weight of a unit volume of fluid. The fuel is measured volumetrically by the fuel injection system, and high densities result in high fuel consumption. Biodiesel is observed to exhibit densities ranging from 0.860 g/cm³ to 0.897 g/cm³ at 15 °C. These density values are notably higher than those of petroleum diesel. However, it can be argued that this elevated density serves to offset the lower volumetric energy content of the biodiesel fuel (Alnuami W., Buthainah A., Etti C. J., Jassim L. I. 2014).

2.8.2 VISCOSITY

This is a measurement of the friction between molecules and the resistance of oil to motion when forced to flow. As a result of the length of their triglyceride molecules, the viscosity of oils decreases somewhat as their degree of unsaturation increases, and oils with low molecular weight fatty acids are slightly less viscous than oils with high molecular weight fatty acids and an identical degree of unsaturation.

Viscosity, which reflects a liquid's resistance to flow due to internal friction, is a vital property of diesel fuel. It plays a pivotal role in the engine's fuel injection system, especially in cold conditions. Diesel fuel with high viscosity leads to inadequate atomization, resulting in decreased engine performance and the emission of smoke. Although slightly viscous, biodiesel has viscosities that

are comparable to petroleum diesel. In comparison to its source oils, biodiesel has this advantage (Alnuami W., Buthainah A., Etti C. J., Jassim L. I. 2014).

2.8.3 KINEMATIC VISCOSITY

Kinematic viscosity is a vital consideration in the design of fuel injectors for diesel engines. If the fuel has a high degree of viscosity, it can lead to improper injector function. Biodiesel frequently possesses a higher viscosity when compared to standard diesel fuel (Ramkumar and Kirubakaran 2016). Consequently, the atomization characteristics are compromised, potentially leading to larger fuel droplets in comparison to diesel fuel.

Elevated kinematic viscosity levels lead to issues such as inadequate fuel atomization, inefficient combustion, and the accumulation of carbon on the injectors. Therefore, it's imperative to keep the viscosity of biodiesel low. While biodiesel blends often exhibit enhanced lubricity, their increased viscosity tends to produce larger droplets upon injection, resulting in inefficient combustion and increased exhaust emissions. Moreover, this heightened viscosity contributes to operational challenges like challenging engine starts, erratic ignition, and reduced thermal efficiency. One approach to reducing the viscosity of vegetable oils is transitioning to biodiesel (Lakachew 2014). Maintaining the viscosity of fatty acid methyl esters within an acceptable range is essential to avert detrimental impacts on the performance of the fuel injector system. Consequently, the viscosity of biodiesel should closely match that of diesel fuel to ensure proper functioning.

2.8.4 MOISTURE CONTENT

During transesterification, water results in undesirable results. It results in soap formation and depletes the catalyst, reducing its effectiveness. Furthermore, the presence of gels and foams can obstruct the glycerol separation process in biodiesel, leading to a decrease in the methyl ester concentration. In comparison to previous approaches, water has been found to have less of an impact on the supercritical methanol method (Rekhate and Prajapati 2019).

2.8.5 SPECIFIC GRAVITY

Specific gravity is defined as the mass to water equivalent volume ratio. Specific gravity is a measurement of a substance's density relative to another substance's density. Determining the specific gravity of oil involves weighing it in relation to water under specific temperature and pressure conditions, where one unit of oil is compared to one unit of water. This specific gravity measurement is essential for understanding the consistency of oils and fats, aiding in the design of processing equipment specific to these substances. As a result, specific gravity has no dimensions because it is a ratio of two densities.

Specific gravity is typically used as a measurement when comparing the density of water to that of biodiesel fuel. By measuring the specific gravity of the biodiesel fuel, one may ascertain its density and chemical make-up. The performance of biodiesel in combustion systems and engines may be impacted by the density of the fuel, which can vary depending on the feedstocks and manufacturing processes utilized. It's an important factor and can be used to assess the composition and quality of biodiesel. Changing densities can be a sign of impurities, the mixing of biodiesel with other compounds, or adjustments to the manufacturing process.

Higher specific gravity biodiesel might be denser and possibly have more energy, whereas lower specific gravity biodiesel might be less dense and potentially have greater contaminants. For instance, a substance is denser than water if its specific gravity is more than 1, in which case it will tend to sink in liquids. In contrast, if biodiesel is lighter than water, it tends to float if the specific gravity is less than 1.

2.8.6 SAPONIFICATION VALUE

The saponification value is the quantity of potassium hydroxide (KOH) or sodium hydroxide (NaOH) required to react with and neutralize the unbound fatty acids within a given quantity of biodiesel feedstock or product. It is the process of dissolving triglycerides (fats and oils) into their individual fatty acid and glycerol molecules by reacting them with an alkaline solution.

The saponification value, often expressed in milligrams of potassium hydroxide (mg KOH) or sodium hydroxide (mg NaOH) required to neutralize one gram of the biodiesel sample, plays a

pivotal role in assessing the quality of both the raw materials used in biodiesel production and the final product. Lower saponification values indicate a reduced presence of free fatty acids in the feedstock, which could potentially impede the transesterification process converting triglycerides into biodiesel. This lower saponification value is generally preferred for optimal biodiesel generation. Conversely, higher concentrations of free fatty acids can lead to the formation of soap during the reaction, hindering the separation and purification of the biodiesel.

2.8.7 REFRACTIVE INDEX

A physical characteristic, the refractive index, can be utilized to evaluate the quantity and purity of the biodiesel or its feedstock (vegetable or animal fats). The refractive index calculates how much light is distorted or bent as it travels through a material, such as a liquid. It is affected by things which includes the substance's chemistry, density, and molecular structure.

A refractometer, an optical device that measures the angle of refraction of light flowing through a sample, is commonly used to determine the refractive index. The dimensionless refractive index is typically represented by the letter "n".

2.8.8 IODINE VALUE

The iodine number is the key factor that gauges the total level of unsaturation in a combination of fatty substances. Its value is solely influenced by the origin of the vegetable oil, and biodiesel produced from the same type of oil is expected to demonstrate similar iodine values (Encinar et al. 2011). This pertains to the chemical makeup of the fuel. A higher iodine value suggests that the fats and oils are more unsaturated. The EN 14214 specification for biodiesel in Europe specifies an iodine value of 120. The typical biodiesel composition standards for linolenic acid methyl ester composition set restrictions on this requirement. The restriction on unsaturated fatty acids is required because heating more unsaturated fatty acids causes glycerides to polymerize. This may cause deposits to accumulate or the lubricating property to deteriorate. If fuel drips down the cylinder's sides and enters the crankcase, it's prone to solidify, potentially resulting in the accumulation of thick residues in the engine's sump (Basumatary 2013).

2.8.9 ACID VALUE

The fuel's acid content is gauged by its "acid number." These acids come from two sources: oxidation-induced breakdown and acids used in the synthesis of biodiesel that are not entirely eliminated after manufacturing. This quantity of base is necessary to reach a specific endpoint during titration, which serves as an assessment of the free fatty acid content in biodiesel. An excessive presence of free fatty acids within the fuel can lead to corrosion and might suggest issues like water contamination, improper production, or oxidation-induced degradation. Elevated levels of free fatty acids in the fuel can hinder the transesterification process and lead to the formation of soap. The acid number in biodiesel blends undergoes modifications over time as a result of the natural oxidation process. It's crucial to keep an eye on changes in the acid number for biodiesel blends that won't be used promptly, as this can serve as an indicator of fuel degradation. High acid values can lead to harm to gasoline pumps and filters (Basumatary 2013). Table 2.1 displays the weight percentages of fatty acid distributions in various biodiesel feedstocks, such as waste cooking oil, jatropha oil, palm oil, and soybean oil.

Table 2.1: Fatty acid distributions (% by weight) of some biodiesel feedstocks (Alnuami W., Buthainah A., Etti C. J., Jassim L. I. 2014).

| S/N | Fatty acid | Waste Cooking Oil | Soybean Oil | Jatropha Oil | Palm Oil |
|-----|-------------|-------------------|-------------|--------------|----------|
| 1. | Palmitic | 16.0 | 11.4 | 14.1-15.3 | 44.3 |
| 2. | Arachidic | 52.9-65.8 | 0.2 | 0.3 | - |
| 3. | Palmitoleic | 4.8-8.8 | 0.1-1.0 | 1.3 | - |
| 4. | Linoleic | 40.8 | 54.9 | 29-44.2 | 10.5 |
| 5. | Myristic | 4.7-14.5 | 0.1 | 0.1 | 15.6 |
| 6. | Stearic | 5.2 | 3.2 | 3.7-9.8 | 4.6 |
| 7. | Behenic | 15.4-20.7 | 0.3-2.4 | 0.2 | - |
| 8. | Oleic | 34.3 | 21.8 | 34.3-45.8 | 38.7 |

2.8.10 FLASH POINT

At a typical pressure of 101.3 kPa, the flash point, often denoted as FP, represents the minimum temperature at which vapor becomes adequately emitted to trigger spontaneous ignition when there is air and an external heat source, like a spark or flame, present. The temperature at which enough vapor is produced to raise the concentration of combustible vapor above the lower flammability limit is known as the flammability threshold. Lighter compounds hence have lower flash points with higher vapor pressure (Santos et al. 2020).

Due to its propensity for ignite, flash point is regarded as a significant characteristic for the safe handling of flammable goods, especially in high-temperature settings. According to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), inflammable liquid (FP < 93 °C) is divided into four categories and is found in Section 9 of the Material Safety Data Sheet (MSDS) (Santos et al. 2020).

Numerous research studies addressing the prediction of flash points for both individual substances and mixtures can be located in existing literature, as flash point data plays a vital role in the safe storage, handling, and transportation of inflammable materials. FP is typically defined to comply with insurance and fire standards because of its significant importance in relation to legal requirements and safety. For example, diesel fuel and biodiesel must meet American Society of Testing and Materials standards by maintaining a minimum flash point of 311 K and 360 K, respectively. Considering that biodiesel is both environmentally friendly and non-harmful, boasts a low carbon footprint, excellent lubricating properties, and a higher flash point compared to diesel, it is increasingly regarded as a practical alternative to conventional petroleum-based diesel (Costa do Nascimento, Natália Daniele Dorighello Carareto, Antonio Marinho Barbosa Neto, Vincent Gerbaud 2020).

2.8.11 PEROXIDE VALUE

Biodiesel exhibits greater chemical reactivity compared to diesel due to its heightened susceptibility to oxidation. The physiochemical characteristics of the biodiesel deteriorate as a result of this oxidative instability. Additionally, sediment made up of goopy gels, viscous colloids,

and other contaminants can form and then be removed from the biodiesel. This could result in an engine stalling or even breaking down if the gasoline nozzle, injection pump, and fuel filter are damaged or clogged. In order to determine whether biodiesel is suitable for use as a diesel substitute, one of its crucial properties is oxidation stability. One of the important markers of oxidative deterioration, the peroxide value quantifies the degree of lipid peroxidation. A higher peroxide value indicates that hydroperoxides are produced more frequently via the peroxidation chain mechanism (Qi and Lee 2014).

2.8.12 OXIDATION STABILITY

The quality of biodiesel is significantly influenced by its oxidative characteristics. Oxidation stability serves as a crucial indicator, revealing the extent of oxidation, potential reactivity with air, and the need for antioxidants. This increased susceptibility to oxidative deterioration in biodiesel can be attributed to the presence of double bonds and unsaturated fatty acid chains in its parent molecules, which readily interact with oxygen upon exposure to air. As a result of their chemical composition, biodiesel fuels are more prone to oxidative degradation when compared to fossil diesel fuels (Atabani et al. 2012).

Given its susceptibility to oxidation, which can result in fuel degradation, biodiesel's oxidation stability is vital since it indicates the substance's resistance to the chemical changes brought on by oxidation reaction. The oxidation stability of biodiesel is notably influenced by the types of fatty acids it contains and the degree of unsaturation. In comparison, polyunsaturated fatty acid alkyl esters (FAAEs) exhibit a reactivity to auto-oxidation that is at least twice as high as that of monounsaturated FAAEs, whereas saturated FAAEs display greater stability when compared to their unsaturated counterparts. Due to the lower molar concentration of double bonds, FAAEs with a longer chain or greater molecular weight would be less susceptible to auto-oxidation for the same number of double bonds per molecule. Ethyl ester has demonstrated greater oxidation stability compared to that of methyl ester as an illustration of this phenomena. Aside from the level of unsaturation, the positioning of double bonds within an unsaturated molecule plays a vital role in assessing the oxidation stability of biodiesel. According to a study, omega-3 fatty acids oxidize more quickly than omega-6 fatty acids (Issariyakul and Dalai 2014).

2.8.13 CETANE NUMBER

A crucial element in assessing the quality of biodiesel lies in the cetane number (CN), a dimensionless parameter that characterizes the ignition characteristics of the fuel within an engine cylinder. This factor influences the engine's starting performance, noise levels, and emissions. Improved combustion is achieved with a lower ignition delay time or a higher cetane number (Miraboutalebi et al. 2016).

It is a measure of ignition characteristics and indicates the ability of gasoline to immediately self-ignite after injection. Elevated CN values consistently indicate superior fuel ignition characteristics and represent one of the most critical considerations when deciding which methyl esters to select for biodiesel use. Increase in fatty acid chain length and saturation lead to an increase in cetane number. A higher cetane number suggests a shorter time between ignition and the commencement of fuel injection into the combustion chamber. As biodiesel possesses a greater CN compared to conventional diesel fuel, it leads to more efficient combustion (Atabani et al. 2012).

2.8.14 LUBRICITY

Insufficiently lubricated gasoline can lead to the malfunction of critical engine components like fuel pumps and injectors. Fuels with lower lubricity need additives or blending with fuels with sufficient lubricity to restore the lubricity. Biodiesel has greater lubricity to traditional petroleum diesel. The lubricity of biodiesels can be significantly influenced by the fatty acid compositions and alcohols (Gopinath et al. 2015).

Lubricity is a term that describes the decrease in frictional resistance between two solid machine components in relative motion. The details of the entire lubricity are provided by two common types of lubrication, namely hydrodynamic and boundary lubrication. With the aid of a liquid film between them, such as the fuel in the injector, hydrodynamic lubrication is employed to lessen wear between the machine's solid parts. A liquid film, such as the diesel fuel in a fuel injector, keeps two surfaces from coming into touch during hydrodynamic lubrication. Compounds are used in boundary lubrication to adhere to machine parts and form a thin coating that shields them from wear. Boundary lubrication becomes useful when the hydrodynamic lubricant splits or emerges

from the machine parts. Superior quality lubrication is necessary in the fuel injection mechanism of a diesel engine to reduce wear. Frequently, the fuel utilized in the injector serves as a lubricant. Proper lubrication is crucial in today's fuel injection system. Multiple injections after each cycle, high pressure, and injection rate shaping have made determining the level of lubrication a challenging process. Generally speaking, lubricity effectiveness declines in the following order: O > N > S > C (Singh et al. 2019).

2.8.15 FIRE POINT

At this temperature, there are sufficient amounts of volatile substances present to allow for sustained burning. The oil's smoke flash point and fire point increase with the amount of volatile stuff it contains. Biodiesel is a safer option than petroleum diesel due to its increased flash and fire points, reducing its flammability. However, it is important to note that biodiesel is more vulnerable to oxidation compared to petroleum diesel, leading to degradation over time when exposed to air (Alnuami W., Buthainah A., Etti C. J., Jassim L. I. 2014). The biodiesel standards outlined by ASTM and EN can be found in Table 2.2.

Table 2.2: Biodiesel ASTM and EN specifications (Atabani et al. 2012).

| Properties of Fuel | Biodiesel | | Diesel |
|--|-----------|-----------|-----------|
| | ASTM | EN | |
| Oxygen (wt.%) | 11 | 0-0.31 | 0-0.31 |
| Boiling point °C | 315-350 | 180-340 | 180-340 |
| Carbon (wt.%) | 77 | 84-87 | 84-87 |
| Acid value (Mg KOH/g) | Max 0.50 | 0.062 | 0.062 |
| Cloud point °C | -3 to 15 | -35 to 5 | -35 to 5 |
| Density Ib/gal (kg/m ³) | 7.3 (880) | 7.3 (880) | 7.1 (850) |
| Cetane number | 46-65 | 40-55 | 40-55 |

| | | | |
|--------------------|------------|----------|------------|
| Sulfur (wt.%) | 0.0015 max | 0.02 max | 0.0-0.0024 |
| Oxidation | - | 3 min | 3 min |
| Flash point °C | 100-170 | 100-170 | 60-80 |
| Viscosity at 40 °C | 1.9-6.0 | 3.5 | 2.6 |
| Hydrogen (wt.%) | 12 | 12 | 12-16 |
| Pour point °C | -5 to 10 | -5 to 10 | -35 to -15 |

2.9 PRODUCTION OF BIODIESEL

Three fundamental approaches exist for generating biodiesel from oils and fats. These processes encompass the transesterification of oil through any of the following methods:

1. Base-catalyzed transesterification
2. Direct acid catalyzed transesterification
3. Transforming oil into fatty acids, with the ultimate goal of producing diesel fuel.

The process of base-catalyzed transesterification is the preferred method for producing the majority of biodiesel due to its cost-effectiveness, yielding a conversion rate of 98% with the added advantages of operating at low temperatures and pressures.

2.9.1 TRANSESTERIFICATION PROCESS

Transesterification entails the basic action of substituting the ester's alcohol with a different substance. It is similar to hydrolysis except that hydrolysis uses water whereas transesterification uses alcohol. The high viscosity of triglycerides has frequently been reduced using this method. Transesterification is the chemical process in which a triglyceride, found at the core of fats and oils, undergoes a reaction with alcohol to generate esters and glycerol. A triglyceride comprises glycerin linked to three long-chain fatty acids, and the type of fatty acids attached to glycerin determines the properties of the fats. Furthermore, the composition of these fatty acids can impact the features of biodiesel as well. A catalyst, typically a potent alkaline substance like sodium

hydroxide, is present when a triglyceride reacts with an alcohol during the esterification process. The formation of monoalkyl ester, which is biodiesel, along with crude glycerol occurs when alcohol reacts with fatty acids. Typically, methanol or ethanol is utilized as the alcohol (methanol produces methyl esters, while ethanol yields ethyl esters), and either potassium hydroxide or sodium hydroxide serves as the alkali catalyst in the majority of production processes. The process of transesterification plays a pivotal role in biodiesel production. This chemical reaction, involving the triglyceride and methanol, results in the formation of biodiesel as it is commonly recognized. Methanol is the preferred choice for producing biodiesel due to its cost-effectiveness and wide availability. However, when it comes to ethyl ester biodiesel production, potassium hydroxide has been found to be a more effective catalyst, even though both bases can be used to produce methyl ester biodiesel. The equation for this reaction can be found in Figure 2.1, while the transesterification process is illustrated in Figure 2.2.

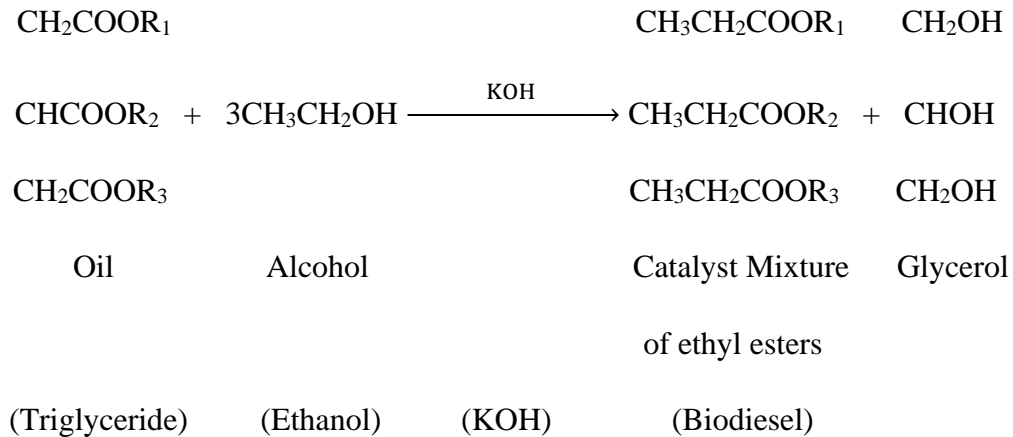


Figure 2.1: General representation of the transesterification process (Sahu et al. 2018).

The transesterification reaction, however, faces two significant obstacles. First, the reaction system's heterogeneity creates problems with mass transfer restrictions. Secondly, because the transesterification reaction can be reversed, a higher molar ratio of alcohol to oil is needed. This leads to increased operational expenses and greater energy consumption, ultimately reducing the overall efficiency of biodiesel production. Alternative techniques for producing biodiesel, such as

reactive distillation, ultrasonication, microwave methods, non-catalytic supercritical approaches, the biox process, and membrane technology, can also be considered. In the absence of a catalyst, the non-catalytic supercritical approach sidesteps the disadvantages associated with catalytic procedures. These drawbacks include the requirement to address free fatty acids (FFAs) and triglycerides (TGs) at different points during the reaction, the negative impact of water molecules in the mixture, catalyst deactivation, the need to separate the catalyst from the product mixture, low glycerol purity, and the generation of wastewater. Even though it requires elevated operating temperatures (553-673 K), substantial pressures (10-30 MPa), and a significant methanol-to-triglycerides molar ratio of up to 42:1, this method is energy-intensive and financially impractical (Aransiola et al. 2014). Tetrahydrofuran (THF) serves as one of the co-solvents in the biox process, facilitating the dissolution of methanol and expediting the reaction. THF is favored for its similar boiling point to methanol (339 K compared to methanol's 337.7 K), allowing for the convenient removal of excess solvents in a single step once the reaction is completed. This approach is commonly employed for producing biodiesel from oil feedstock with elevated free fatty acid (FFA) levels, exceeding 10%, and it can be conducted at ambient temperature and pressure. The tight similarity between the boiling points of the co-solvent and methanol presents a cost-related challenge and complicates the separation of the resulting substances (Badday et al. 2012). Furthermore, given the co-solvent's toxicity and hazardous nature, it is imperative to ensure its thorough removal from both glycerol and biodiesel (Tan et al. 2019).

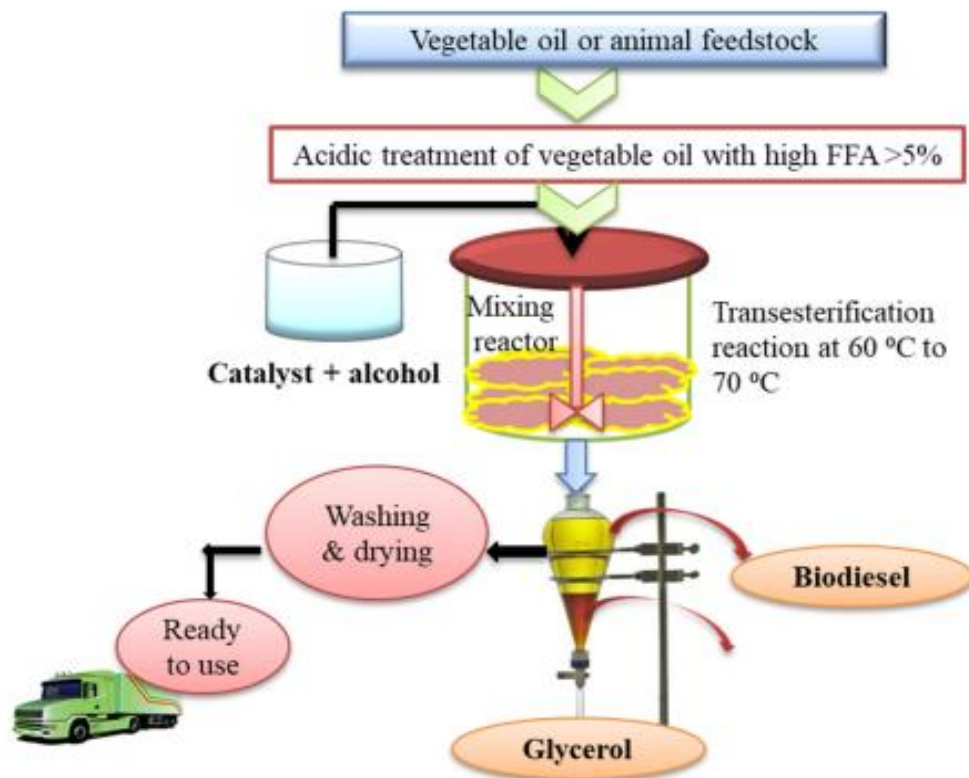


Figure 2.2: The process of transesterification (Ganesan et al. 2021).

2.9.2 SEPARATION

Glycerin and biodiesel are the two main byproducts after the reaction is finished. The surplus methanol that was consumed in the process is present in significant amounts in each. If necessary, the reactive mixture is occasionally neutralized at this stage. Given that glycerin is much denser than biodiesel, the two can be separated by gravity with the glycerin being simply drained from the lower section of the settling tank. Alternatively, in certain situations, a centrifuge can be employed for a quicker separation of these two components.

2.9.3 ALCOHOL REMOVER

After the separation of glycerin and biodiesel phases, any surplus alcohol in each phase is removed through either flash evaporation or distillation. In some procedures, the alcohol is extracted, and

the mixture is neutralized before separating glycerin and esters. Regardless of the approach chosen, the alcohol is recovered and reused after undergoing the distillation process. It is important to take precautions to make sure that water doesn't collect in the stream of recovered alcohol.

2.9.4 GLYCERIN NEUTRALIZATION

Unused catalyst and soaps are included in the glycerin by-product, which is neutralized with an acid and then transported to storage as crude glycerin. The salt might occasionally remain in the glycerin. To create 80–88% pure glycerin that is prepared for sale as crude glycerin, water and alcohol are removed. Glycerin is distilled to 990/0 purity or higher and marketed into the cosmetic and pharmaceutical industries in more complex procedures.

2.9.5 WASHING

When the biodiesel has been separated from the glycerin, it may be cleaned by being gently washed in warm water to remove any remaining catalyst or soaps before being dried and put away. This step is not required in every procedure. An amber-yellow liquid that is transparent and has a viscosity similar to petrodiesel is often produced at this point in the production process. Some methods add a distillation phase to the biodiesel production process to remove trace levels of colorants and create colorless biodiesel. Figure 2.3 displays the visual representation of the biodiesel production process flowchart. The biodiesel may still have some water traces in it once the cleaning operation is finished. In order to dry the biodiesel, retained water traces are removed by heating it to 110 °C (Gashaw and Teshita 2014).

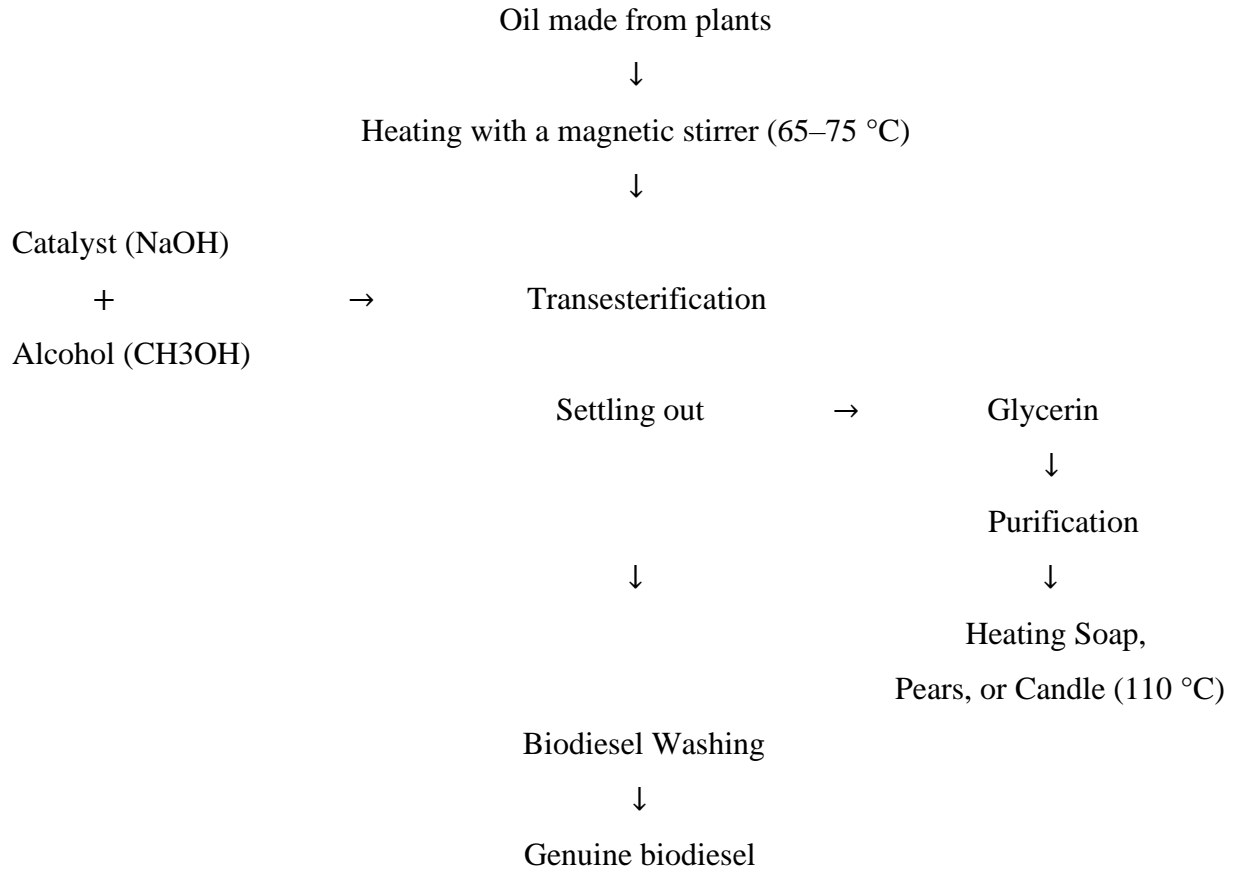


Figure 2.3: Flow chart of Biodiesel production process (Gashaw and Teshita 2014).

2.10 FACTORS INFLUENCING BIODIESEL YIELD

2.10.1 REACTION TEMPERATURE

A crucial element that will influence the biodiesel output is reaction temperature. For example, increasing the reaction temperature can expedite the reaction and shorten the reaction duration by lowering the oil's viscosity. Conversely, surpassing the optimal temperature can lead to decreased biodiesel yield as it accelerates triglyceride saponification and decreases methanol yield (Anitha and Dawn 2010).

To prevent the loss of alcohol through evaporation, it's generally recommended to maintain a transesterification reaction temperature below the alcohol's boiling point. The optimal temperature for the reaction can vary between 50°C and 60°C, depending on the specific oils or fats being used

(Mathiyazhagan and Ganapathi 2011). Hence, multiple sources endorse the use of a reaction temperature near the boiling point of alcohol to expedite the conversion process. This indicates that methyl esterification of FFAs can be achieved to a notable extent at ambient temperature but may necessitate a prolonged reaction duration. At room temperature, approximately 78% conversion is achieved after 60 minutes. Notably, temperature plays a more substantial role in accelerating reactions, particularly in the case of butyl esterification. This is because temperature boosts the energy of the molecules involved and enhances the blending of the alcoholic polar medium with the non-polar oily phase (Gashaw and Teshita 2014).

2.10.2 REACTION TIME

An increase in the conversion of fatty acid esters becomes evident as the reaction time is extended. This is due to the gradual combination and dispersion of alcohol and oil, which initially results in a slow reaction. Subsequently, the reaction progresses more rapidly. However, the highest ester conversion is achieved in approximately 90 minutes. Further prolonging the reaction time does not lead to an increase in the yield product, which is biodiesel or mono alkyl ester. On the contrary, an extended reaction period results in a reduction in biodiesel production because transesterification is a reversible reaction, leading to the loss of esters and the formation of soap (Mathiyazhagan and Ganapathi 2011; Jagadale et al. 2012).

2.10.3 TYPE AND AMOUNT OF CATALYST

The catalyst's concentration also plays a role in influencing the production of biodiesel. Typically, sodium hydroxide (NaOH) or potassium hydroxide (KOH) are the two commonly used catalysts for biodiesel production (Mathiyazhagan and Ganapathi 2011). The type and amount of catalyst required for the transesterification process are typically contingent on the quality of the feedstock and the specific transesterification method employed. When dealing with a purified feedstock, it is possible to use any catalyst for the transesterification process. However, for feedstocks with elevated moisture and free fatty acid levels, it is advisable to avoid homogenous transesterification. This is because there is a significant risk that saponification, rather than transesterification, may

occur. Furthermore, it's important to note that an increase in catalyst concentration usually leads to a higher yield of fatty acid alkyl esters. The reason for this lies in the fact that the transesterification process employs a greater amount of catalyst, leading to an increased number of active sites. However, using a larger quantity of catalyst might not be economically advantageous due to its cost. Consequently, much like the optimization of the oil-to-alcohol ratio, it is crucial to determine the optimal amount of catalyst required for the transesterification process (Jagadale et al. 2012).

2.10.4 METHANOL TO OIL RATIO

The molar ratio of alcohol to triglycerides stands as one of the most influential factors affecting biodiesel production. From a stoichiometric perspective, the process of transesterification necessitates 3 moles of alcohol, 1 mole of triglyceride, and 1 mole of glycerol to yield 3 moles of fatty acid methyl/ethyl esters and 1 mole of glycerol. This ratio typically falls in the range of 5.6 to 7.8:1 for both catalyst systems. To enhance biodiesel production, an excess of methanol can be introduced to shift the equilibrium in the desired direction (Anitha and Dawn 2010).

Methanol is the more commonly employed alcohol in the transesterification process, primarily due to its cost-effectiveness and the advantageous physical and chemical properties it offers (being a polar and the shortest-chain alcohol) compared to other options such as ethanol, propanol, butanol, and amyl alcohol. Although ethanol is also a suitable choice for transesterification and has some environmental benefits over methanol, it is not as widely used. Researchers have investigated the influence of methanol and ethanol volumetric ratios to oil in this context. The findings indicate that the optimal biodiesel yield is achieved with a 1:6 ratio of oil to methanol. In contrast, the quantity of biodiesel produced increases consistently as the methanol molar ratio rises (Gashaw and Teshita 2014).

2.10.5 FREE FATTY ACID AND MOISTURE CONTENT

The suitability of vegetable oils for use in the transesterification process hinges primarily on two key factors: the level of free fatty acids and the moisture content. The presence of moisture in oil

leads to an increase in the concentration of free fatty acids. For this reaction to proceed effectively, the oil should ideally contain less than 3% of free fatty acids. In the production of biodiesel through the base-catalyzed transesterification process, it is imperative to use raw materials that are both moisture-free and possess a low acid value. When oil samples exhibit a high free fatty acid content (exceeding 1%), additional alkali catalyst is required to neutralize these free fatty acids. It's worth noting that the presence of water is more detrimental to the process than free fatty acids, as it can result in the formation of soap and foam, thereby increasing viscosity. The separation of glycerol from biodiesel faces additional challenges due to the formation of gels and foams. Undesirable outcomes typically arise when free fatty acids and water are present during the transesterification process. This leads to the formation of soap, catalyst consumption, and a reduction in the effectiveness of the catalyst, ultimately resulting in diminished methyl ester production. To address this issue, the supercritical methanol approach has been proposed as a solution. It's worth noting that water plays a less significant role in the supercritical methanol approach (Mathiyazhagan and Ganapathi 2011).

The moisture levels in the collected waste chicken fats exhibit significant variations, with some samples containing as much as 18% (Jagadale et al. 2012). Because of this, turning these oils into biodiesel requires more than one procedure. One of the drawbacks of biodiesel is the negative correlation between its oxidative stability and its cold flow properties. Although they increase the fuel's cloud point, saturated molecules are less likely to oxidize than unsaturated ones. As FFAs and alcohol react, water is also produced, which prevents glycerides from being transesterified. This occurs due to the formation of water when free fatty acids (FFAs) react with alcohol to produce esters. The concurrent behavior of the curves implies that the primary obstacle preventing the completion of the acid-catalyzed esterification process with FFAs is the generation of water.

2.10.11 MIXING INTENSITY

Due to the limited solubility of oils and alcohols, the reaction can only occur at the interface where the two liquid phases meet, making transesterification a relatively sluggish process. Consequently, effective mixing is of paramount importance in the transesterification process. It is imperative to ensure proper blending of these two feedstocks to promote their interaction, thereby increasing the

occurrence of transesterification reactions. In the process of transesterification, mechanical agitation is commonly used. The intensity of this mixing can be adjusted based on the requirements of the transesterification process. Generally, increasing the degree of mixing is necessary to ensure effective and uniform blending of the feedstock. When vegetable oils with high kinematic viscosity are used as the feedstock, extensive mechanical mixing is essential to counteract the negative impact of viscosity on the mass transfer between oil, alcohol, and catalyst (Jagadale et al. 2012).

The speed of agitation plays a pivotal role in the production of the final product, whether it's mono alkyl ester or biodiesel, as it accelerates the reaction between the oil and catalyst. For instance, when keeping other parameters constant, mixing intensities of 200 rpm, 400 rpm, 600 rpm, and 800 rpm were employed for a duration of 60 minutes. The highest conversion of the end product was achieved at 400 rpm. A lower stirring speed results in reduced product output. Conversely, higher stirring speeds promote the formation of soap, primarily due to the reversible nature of the transesterification reaction (Gashaw and Teshita 2014).

2.11 BIODIESEL BLENDS

In this procedure, conventional fuel is blended with biodiesel. Biodiesel can be seamlessly integrated into existing diesel engines with minimal to no adjustments, allowing for its use in various ratios alongside petroleum-based fuels. These fuel combinations are referred to as biodiesel blends. While biodiesel is capable of being used independently in its pure form, it is more commonly mixed or combined with petroleum-based fuels. The most widely used blend of biodiesel fuel is known as B20 and contains 80% petroleum diesel and 20% biodiesel by volume. In the retail diesel fuel market, the typical products in use consist of different combinations of standard petroleum diesel and biodiesel fuel. Globally, the "B" factor system is employed to designate the proportion of biodiesel in any given fuel mixture. B100, for instance, stands for 100% biodiesel, whereas B20 refers to fuel mixes that contain 20% biodiesel. In line with this, 5% biodiesel is designated as B5 and 2% biodiesel as B2. The greater the usage of biodiesel fuel, the more ecologically responsible the resultant fuel becomes. Standard diesel engines can also accommodate B20 blends, which consist of 20% biodiesel and 80% petroleum diesel. B100 biodiesel fuel is either pre-blended with petroleum diesel during the production phase before being

loaded onto tanker trucks, or it is mixed in the tanker truck through a splash-blending process. The two components are mixed in-line and reach the tanker truck simultaneously. The transfer pump then draws from two locations, and the blending is finished when the pump exits. The use of additives can be made more efficient and practical by blending to levels up to 20% (B20) (Ajmal Kasim, Sunil Kumar 2017).

Although biodiesel can be used in its undiluted form, known as B100, certain modifications to the engine are necessary to prevent maintenance and performance issues (Balat and Balat 2010). In place of petroleum-based fuels, biodiesel can be used in locomotives, aircraft, heating oil, engines, and other applications. The elevated kinematic viscosity and density of biodiesel, coupled with its diminished oxidation stability and heating value, make it unsuitable for use as a standalone fuel in diesel engines. To enhance these properties, biodiesel is combined with diesel fuel, as it can be completely mixed with diesel (Wakil et al. 2015). However, because diesel has a lower cetane number and flash point than B100, blending would lower these values; corrosion, acid value, sulphated ash, carbon residue, and kinematic viscosity are all decreased.

2.11.1 BIODIESEL AS AN ADDITIVE, 1-2% (B2)

Biodiesel is a very powerful lubricity enhancer, according to tests on lubricity. A very low lubricity gasoline can be transformed into a usable fuel with as little as 0.25% additive. Although these concentrations are too low to have any effect on the engine's emissions or the fuel's cetane number. The lubricity offers a major benefit at affordable pricing.

2.11.2 BIODIESEL AS PURE FUEL (B100)

The pure form of biodiesel, sometimes referred to as clean diesel or B100, can be utilized. The method that most effectively reduces carbon monoxide, unburned hydrocarbons, and exhaust particles is this specific one. When biodegradability and non-toxicity are crucial, it is also the best way to use biodiesel. B100 might be useful for marine applications. Despite the fact that clean biodiesel should not be expected to cause any operational issues, its solvent properties will be more intense and could lead to issues with the liquefaction of varnish deposits in fuel tanks, the

deterioration of fuel lines, and the removal of paints from close to where fuel is filled. If exposed to biodiesel over an extended period of time, concrete may also deteriorate. Additionally, B100 will have the worst cold flow characteristics issues. In cars, biodiesel will deteriorate the natural rubber hoses and gaskets. (Commonly found in automobiles built before 1992), even though these have a tendency to wear out naturally and were probably already replaced with vitron, which is not reactive to biodiesel.

2.11.3 BIODIESEL BLENDS (USUALLY 20% - 50%)

It is a common practice to use blends that consist of 20% to 50% biodiesel combined with 80% to 50% No. 2 diesel fuel, primarily because biodiesel can be blended with petroleum-based diesel fuel in a wide range of ratios. Blends keep part of the emissions savings while reducing the financial effect of biodiesel. The amount of biodiesel used tends to have the greatest impact on emissions reduction, and when blends are utilized, the cold flow and solvency issues with B100 are less of an issue. As biodiesel "cleans" the engine process, if a sudden switch to 100% biodiesel is performed, fuel filters may become clogged with particulates. Therefore, it is advised to replace the fuel filter 600–800 miles after making the changeover to "biodiesel blend".

2.12 BIODIESEL USE AND APPLICATION

Biodiesel's potential as a long-term source of fuel for transportation has been studied by researchers (Al Hatrooshi et al. 2020). Vehicles that use biodiesel instead of regular diesel fuel emit fewer greenhouse gases and support environmental sustainability. Biodiesel has been researched for its uses in power generation in addition to transportation. Biodiesel can be used in internal combustion engines, contributing to a cleaner energy generation process with a reduced environmental impact. One of its primary advantages is its adaptability to various feedstocks, including waste cooking oil and non-edible vegetable oils (Awogbemi et al. 2021). This versatility in feedstock choice increases biodiesel's viability and sustainability in many geographical areas. With uses in transportation, electricity production, and the ability to lower carbon emissions, biodiesel has maintained its reputation as a renewable and environmentally benign fuel.

2.13 BIODIESEL HANDLING AND STORAGE

Water from the air may be absorbed during the handling and storage of biodiesel, and trace metals from automotive materials and container corrosion may be incorporated into the biofuel. These two processes combine to speed up the oxidative degradation of biodiesel, which causes the accumulation of gums and sediments inside the engine. The inclusion of antioxidants such tert-butyl-hydroquinone (TBHQ), butyl-hydroxytoluene (BHT), butyl-hydroxyanisol (BHA), pyrogallol (PY), and propyl gallate (PG) is a typical method to boost the oxidation stability of biodiesels. A number of different antioxidants have been compared, and TBHQ has been found to be among the most effective antioxidants for B100 (pure biodiesel) (Santos et al. 2014).

The handling and storage of biodiesel are essential for preserving its quality and safety over the course of its life. The right storage containers constructed of appropriate materials, maintaining a consistent temperature, and safeguarding against water contamination are crucial factors (O'Connery 2013; Christensen and McCormick 2014). Antioxidants can be added to biodiesel to assist prevent oxidation and assure its stability when it needs to be kept for a long time. Safety measures include adequate labeling, fire safety procedures, and following rules are also crucial. Maintaining fuel integrity calls for routine testing for microbiological contamination, water content, and fuel quality (Steiman et al. 2015). To avoid obstructions and guarantee a steady flow of gasoline, frequent maintenance of pumps and filters is also required.

2.13.1 HANDLING

Along with the primary process equipment, a biodiesel plant also requires supporting facilities like a steam generator (boiler), an electrical source, and water supply facilities. The biodiesel factory is supported by a number of storage tanks for handling raw materials and store finished goods for a predetermined amount of time. Based on the capability for producing biodiesel, this facility's capacity is determined. To carry out a transesterification or esterification reaction in most biodiesel production facilities, methanol is blended with either an alkaline or acid catalyst. The quantity of methanol utilized in the reaction generally rises in correlation with the quantity of free fatty acids contained in the vegetable oil. Any unreacted methanol is later retrieved through an evaporation or distillation process. Methanol, due to its low boiling point and reactivity, is considered one of

the more volatile and hazardous substances. The safe and sustainable manufacture of biodiesel will therefore be supported by knowledge of methanol handling and application (Paryanto et al. 2013). In addition to incorporating safety design considerations, there are additional factors to consider when managing and running a biodiesel plant to enhance safety and prevent losses. These factors include the identification and assessment of hazards, their control, and the limitation of risk/loss. For the proper and safe usage and handling of biodiesel and other chemicals, it is also vital to understand the qualities and traits of the chemicals and raw materials used in the synthesis of biodiesel. A greater flash point would allow for safer gasoline management. Biodiesel possesses a flash point that is three times higher than that of mineral diesel. Handling biodiesel is therefore far safer than handling diesel (Kassem and Çamur 2018).

2.13.2 STORAGE

The first investigation into the storage stability of biodiesel was conducted by du Plessis et al. in 1985, who tracked the development of acids, peroxides, and aldehydes as well as the rise in viscosity and decrease in Rancimat induction time over a 90-day period. They discovered that while biodiesel degraded quickly when exposed to heat and air, it remained stable when stored at 20 °C in tightly sealed containers or after being given an antioxidant. Additional studies on the stability of biodiesel for 180 days in storage revealed that exposure to metals exacerbated breakdown rates and that higher temperatures in pro-oxidizing environments sped up loss of stability. While the storage conditions do play a crucial role in maintaining the stability of biodiesel, the production and purification processes can also exert a substantial influence on its long-term stability. By adding citric acid to the water used to purify biodiesel following esterification, Serrano et al. have demonstrated a considerable increase in the stability of the fuel, which they attribute probably to the chelation of low concentration metals. (Christensen and McCormick 2014).

According to Yang et al., Acid value (AV) of Biodiesels (BDs) made from animal, soybean, and canola fat increased significantly after being stored for a year. Due to the presence of polyunsaturation, soybean BD among all BDs had the greatest increase in AV when compared to samples with a high abundance of cis-9, C18:1. The effects of holding biodiesels made from

canola, palm, soybean, and sunflower oils at three constant temperatures (15, 22, and 40 °C) for a full year were periodically evaluated by Moser. All studied biodiesels showed a rise in AVs after a year of storage; however, the increase was more evident at higher temperatures. As the AVs of tested BDs continued to be well within the specifications after a year in storage, storing biodiesel at a lower temperature can be an effective strategy to combat the effects of oxidation. Over the course of 52 weeks, Leung et al. examined the features of biodiesel degradation in twelve samples stored under various settings. As a result of biodiesel breakdown, the acid value increased, according to the results. The cause is the breakdown of fatty acid methyl ester molecules during degradation, which raises the ester's apparent volatility (AV). It was demonstrated in a different study that the PSB and POB test samples' acid values rose gradually in the first half of the experiments before rising sharply in the second (Kumar 2017).

In order to keep the fuel stable, longer-term storage of biodiesel for low-use uses of diesel fuel, like backup generators, will call for a bigger oxidation reserve than usual. For fuel stored for more than six months, the ASTM standards for B100 and biodiesel blends incorporate guidelines for monitoring stability. For storage periods longer than 12 months, advice is provided for petroleum diesel fuel. To make sure the fuel has not degraded prior to use, it is advised that acid value and particle matter be checked on a regular basis (Christensen and McCormick 2014).

2.14 WASTE COOKING OIL (WCO)

Waste cooking oil (WCO) is defined as previously used oil employed in deep frying and is no longer fit for human consumption. It falls within the category of used vegetable oils (UVOs), which are considered hazardous waste. WCOs are the primary representatives of this family, as the culinary and catering industries produce the majority of the UVOs that have been collected. WCOs are widely produced and geographically distributed since frying is the most common cooking method utilized worldwide (Mannu et al. 2020). Each year, more than 190 million metric tons of used vegetable oils are generated, and the European Union (EU) accounts for approximately 1 million tons of this total. By using waste cooking oil (WCO) as a feedstock for biodiesel, it is possible to reduce water pollution and the need for additional efforts to clear clogs in drainage systems. The utilization of waste cooking oil is vital for reducing the cost of biodiesel production,

potentially lowering it by 60 to 90% (Talebian-Kiakalaieh et al. 2013). The increase in household and restaurant waste cooking oil (WCO) production is raising significant concerns about its environmental impact. Waste cooking oil (WCO) can be readily gathered from restaurants and households through the installation of dedicated "recycle bins." However, public awareness campaigns may be required to promote and facilitate the collection process. NGO volunteers in Malaysia ran a campaign to raise awareness about the harm that WCO's direct discharge into the drainage system does to the environment. These volunteers inform the local community about the risks associated with improper disposal of waste cooking oil, such as the potential for contaminating soil and water, as well as the disruption of the aquatic ecosystem, whether it's done through drainage systems or landfills. Additionally, they warned residents about the drawbacks of utilizing recycled WCO as a cooking medium while preparing food. In order to collect the WCO, the NGO will set up a collecting center and make arrangements for the community to designate a representative. The On a monthly basis, the waste cooking oil (WCO) will be collected, and compensation will be provided to the community fund. Subsequently, the factory and diesel manufacturer will receive the accumulated WCO (Yaakob et al. 2013).

Waste cooking oils (WCOs) have recently seen a sharp increase in demand as raw materials. It stands out among the limited list of possible waste-based raw resources, which, if appropriately handled, can result in a variety of product classifications. A large part of what is causing this trend is the rise in WCO applications along with the definition of new waste management legislation in several nations. From an industrial standpoint, WCOs' straightforward chemical makeup makes them appropriate as valuable chemical building blocks in the manufacturing of fuel, materials, and lubricants. Proper recycling practices are closely tied to the sustainability of such applications (Mannu et al. 2020). Table 2.3 provides the common chemical and physical characteristics of waste cooking oil (WCO). This table includes the standard values for properties such as acid value, kinematic viscosity, iodine value, density, saponification value, peroxide value, water content, and sodium content (Yaakob et al. 2013; Mohammed Abdul Raqeeb and Bhargavi R 2019).

Table 2.3: WCO's primary characteristics (Yaakob et al. 2013; Mohammed Abdul Raqeeb and Bhargavi R 2019).

| Property | Units | Value |
|--------------------------------|-----------------------|------------|
| Saponification value | mg KOH/g | 188.2-207 |
| Acid value | mg KOH/g | 1.32-3.6 |
| Iodine number | gI ₂ /100g | 83-141.5 |
| Kinematic viscosity (40 °C) | mm ² /s | 36.4-42 |
| Water content | wt. % | 1.9 |
| Sodium content | mg/kg | 6.9 |
| Density | g /cm ³ | 0.91-0.924 |
| Peroxide value | mg/kg | 23.1 |

2.14.1 PROPERTIES OF WASTE COOKING OIL

The GCMS test, which stands for gas chromatography mass spectrometry, is employed as one of the chemical tests to analyze and identify chemical compounds within uncharacterized waste cooking oil. Waste cooking oils exhibit distinct physicochemical attributes, especially concerning factors like density, kinematic viscosity, and moisture content, in comparison to refined and crude oils (Banani et al. 2015; Azahar et al. 2016). The physical and sensory qualities of vegetable oils are altered during the frying process. The breakdown of free fatty acids (mono- and polyunsaturated) is to blame for this. Free fatty acids are extremely sensitive to high temperatures and are subject to chemical changes including oxidation reaction, polymerization, and hydrolysis. The hydrolysis of triglycerides is accelerated by heat and water, increasing the amount of FFA in the oil. Moreover, the formation of dimeric and polymeric acids and glycerides in waste cooking oils leads to an increase in the oil's viscosity. The composition of waste cooking oil was determined using gas chromatography coupled with mass spectrometry (GCMS), as conducted in the study by Banani and colleagues in 2015 (Banani et al. 2015). Table 2.4 presents the typical fatty acid composition found in waste cooking oil.

Table 2.4: Average composition of fatty acids in waste cooking oil (Banani et al. 2015).

| Fatty acid (trivial name/rational name) | Methyl ester (trivial name / rational name) | Formula | Common acronym | Acid Composition |
|--|--|-------------------|---------------------------|-----------------------------|
| Palmitic acid/ Hexadecanoic acid | Methyl Palmitate/Methyl Hexadecanoate | $C_{16}H_{32}O_2$ | $C_{16:0}$ | 15,86% |
| Oleic acid / 9(E)- Octadecenoic acid | Methyl Oleate/ Methyl 9(E) Octadecenoate | $C_{18}H_{34}O_2$ | $C_{18:1} (E)$ | 29,83% |
| Linolenic acid/ 9(Z),12(Z),15(Z)- Octadecatrienoic acid | Methyl Linoleate /Methyl 9(Z),12(Z),15(Z)- Octadecadienoate | $C_{18}H_{30}O_2$ | $C_{18:3} (Z,Z,Z)$ | 2,49% |
| Stearic acid / Octadecanoic acid | Methyl Stearate/Methyl Octadecanoate | $C_{18}H_{36}O_2$ | $C_{18:0}$ | 4,87% |
| Linoleic acid / 9(Z),12(Z) Octadecadienoic acid | Methyl Linoleate /Methyl 9(Z),12(Z) Octadecadienoate | $C_{18}H_{32}O_2$ | $C_{18:2} (Z,Z)$ | 28,85% |

2.15 CATALYST

A catalyst is a substance that accelerates a chemical reaction without actively participating in it. There are two main categories of catalysts employed in transesterification processes. These catalysts exist in both homogeneous and heterogeneous forms. The production of biodiesel has utilized heterogeneous solid acid and base catalysts made from biomass, zeolites, alkali earth

metals, and zinc aluminates. An advantage of heterogeneous catalysts over homogeneous ones is their potential for recovery and reusability (Akhabue and Ewah 2021). In the biodiesel production process, catalysts primarily fall into three categories: alkalis, acids, and enzymes. Alkali and acid catalysts are the more commonly employed catalyst types in biodiesel synthesis, as compared to enzyme catalysts. Catalysts that are homogenous and those that are heterogeneous were then separated out. However, enzyme catalysts have recently gained popularity since they may prevent the creation of soap and the purifying procedure is straightforward. The lengthier reaction times and higher expense, according to Leung et al. (2010), prevent their commercial application. In recent years, some researchers created new biocatalysts to cut costs. The fact that these biocatalysts do not require purification is advantageous (Talha and Sulaiman 2016).

Catalysts can be either of a chemical or biological nature, and both can initiate the transesterification process. Chemical catalysts encompass various types, including homogeneous agents such as alkalis or acids, as well as heterogeneous agents like solid acid or solid alkali catalysts, heterogeneous nanocatalysts, and supercritical fluids (SCFs). While the reaction demands a substantial amount of energy and necessitates a rigorous purification step to obtain the final purified product, these catalysts prove effective in successfully concluding the process (Thangaraj et al. 2019). The most appropriate biological catalyst is represented by immobilized lipases. Figure 2.4 illustrates the different techniques for catalytic transesterification used in biodiesel production.

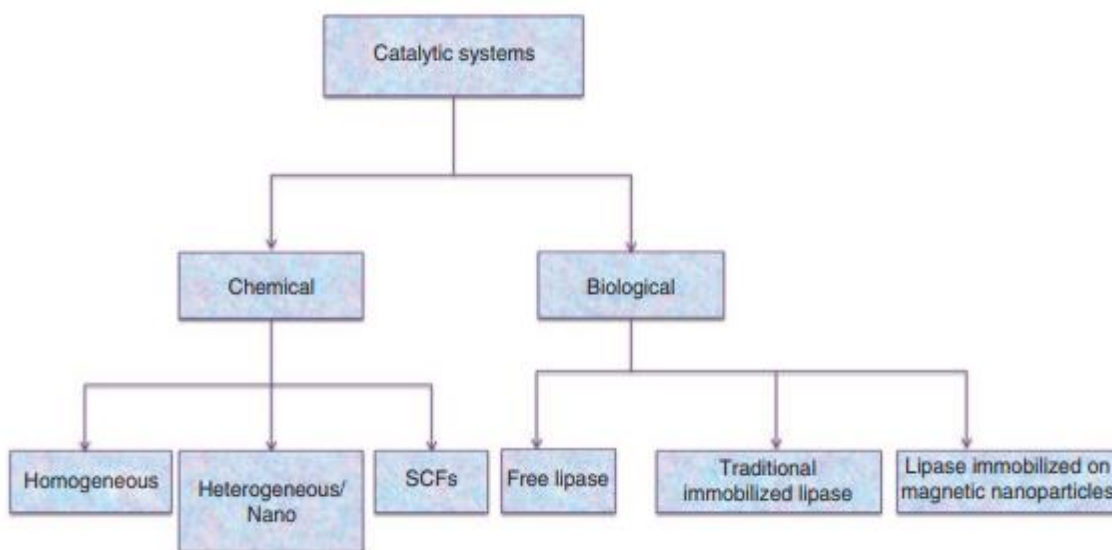


Figure 2.4: The various transesterification catalytic systems (Thangaraj et al. 2019).

2.15.1 HOMOGENEOUS CATALYST

Homogeneous catalysis involves the use of a chemical substance that shares the same phase as the reaction system, thus facilitating a series of reactions. Homogeneous catalysts are the most commonly employed catalysts in biodiesel synthesis due to their user-friendliness and shorter reaction times. This category encompasses both basic and acidic catalysts, with homogeneous catalysts typically being dissolved in a solvent that is in the same phase as all the reactants (Rizwanul Fattah et al. 2020). Vegetable oils featuring low water content and free fatty acid (FFA) values below 2% can be transformed with the assistance of homogeneous or same-phase catalysts. These catalysts are considered advantageous due to their straightforward operational procedures, minimal investment needs, rapid reaction kinetics, and higher product yields (more than twice that of heterogeneous catalysts). However, their suitability for large-scale industrial use is hindered by challenges associated with product separation, catalyst regeneration, and the formation of soap by NaOH at the conclusion of the reaction (Tandale 2017). In the initial studies, base catalysts like potassium and sodium methoxides were employed in combination with various Bronsted acids, including H₂SO₄, HCl, H₃PO₄, RSO₃H, NaOH, KOH, and CH₃KO.

When deciding between bases and acids, the preference leans towards NaOH and sulfonic acids. Several studies suggest that use NaOH rather than KOH, and these studies are supported by the latter's simple solvation, absence of impurities, and low molecular weight. However, when using methanol and NaOH as a catalyst for biodiesel production, it leads to the formation of sodium methoxide, which in turn results in the generation of water and reduced compatibility with other fuels. In a study conducted by Efavi et al. (2018), performed transesterification of *Citrullus vulgaris* seed oil using 0.13 g of NaOH, and the result was a 70% biodiesel yield. Various NaOH loadings and a 5:1 methanol to oil ratio were tested to assess the reaction's behavior. The density of the biodiesel complied with EN ISO 12185 standards, and it exhibited a safe flash point of 142°C, which is higher than that of conventional diesel fuel. Aslan and Eryilmaz (2020) employed the polynomial regression method (PRM) to examine the conversion capabilities of base catalysts NaOH and KOH when applied to black mustard seeds (*Brassica nigra* L.). KOH shown greater results with 97% biodiesel, and PRM is chosen as the optimum optimization strategy. Mango seed oil yielded 92.67% FAME (Fatty Acid Methyl Ester) when subjected to a treatment involving 1% by weight of NaOH at a temperature of 60°C and a methanol-to-oil ratio of 6:1 (Hiwot 2018). To

obtain 94.6% biodiesel from *Pongamia pinnata*, which has a substantial level of free fatty acids (FFA), a deep eutectic solvent was employed. This solvent consisted of choline chloride, acetic acid, oxalic acid, and urea (Kadapure et al. 2017). Esmaeili and Foroutan (2018) achieved a high level of conversion when processing goat tallow with the use of NaOH and KOH catalysts, and they subsequently assessed its fuel characteristics, which included flash, fire, pour, and cloud points. When combined with regular diesel, the fuel established an excellent capacity in C/I engines. Hariprasath and colleagues (2019) investigated the biodiesel yield obtained from used animal tallow using a NaOH catalyst, which they reported as 62%. In the conversion of used cooking oil into biodiesel, NaOH demonstrated superior performance compared to KOH and CH₃ONa, resulting in a 97% higher biodiesel production (Ganesan et al. 2021).

The factors contributing to higher yields in homogeneous catalysis include brisk media stirring, a uniform mixture of alcohol and catalyst, and the presence of turbulence instead of paddles. Acids can act as catalysts for both esterification and reactions because, unlike basic catalysts, they are not influenced by the presence of free fatty acids (FFA). It's important to note that acids have reaction rates that are 4000 times slower than bases (Gad et al. 2018). As a result, research utilizing acid catalysis is currently restricted and is exclusively applied for the transesterification of oils with high free fatty acid (FFA) content following esterification. Notably, there is a clear focus on animal fats and waste oils in this field, with the incorporation of ultrasonic technology as well.

2.15.2 HETEROGENEOUS CATALYST

Heterogeneous catalysts exist in a distinct phase or state compared to the reactants. These catalysts are known for consistently generating active sites for their reactants during a reaction. Heterogeneous catalysts can be categorized into two types: acid and base catalysts (Rizwanul Fattah et al. 2020). Heterogeneous catalysts, which typically take the shape of solids, function at a different phase in the liquid reaction mixture compared to homogeneous catalysts. Due to its many benefits, including its fast reaction rate, quick processing time, and great accessibility of catalysts, the homogeneous catalyst is widely used in the biodiesel business (Faruque et al. 2020). Conversely, using a homogeneous catalyst in esterification and transesterification reactions has a number of challenges, including the need for expensive post-separation procedures. Several studies

have presented results to investigate the effects of diverse heterogeneous materials in addressing the various challenges associated with the utilization of homogeneous bases and liquid acids, including alcoholysis catalysts (Galadima and Muraza 2014). Utilizing heterogeneous catalysts can substantially reduce processing expenses due to their ease of recovery, separation, and reusability. Heterogeneous catalysts are characterized by their adjustable attributes, such as acidic or basic properties, porosity, and surface area, which can significantly broaden the range of feedstocks applicable for the esterification and transesterification processes (Guldhe et al. 2017). The use of heterogeneous catalysts allows for a reduction in free fatty acid (FFA) content without requiring additional pretreatment. Additionally, these catalysts can readily catalyze the production of biodiesel from high-acid oil.

2.15.3 BIO-BASED BIFUNCTIONAL CATALYST

Bio-based or green catalysts are catalysts derived from biomass as their feedstock. Currently, for the production of biodiesel from vegetable oil, calcium and carbon sourced from natural and biological origins are being explored as potential options for heterogeneous catalysts. Adopting active bio-based solid catalysts will improve the process's viability and sustainability even further, and they can be made using biomass, which is abundant and very cheap (Naeem et al. 2021b). While there are still several challenges to address before achieving large-scale implementation, the importance of biomass in the production of biodiesel and bio-based chemicals is a relatively new and highly significant area of focus. Non-edible oils, such as those derived from the *Jatropha curcas* L. plant, often contain high levels of free fatty acids (FFA) and can readily undergo saponification in the presence of a base catalyst. To address these challenges, bifunctional catalysts that possess both acid and base active sites might offer a more efficient alternative to the time-consuming and costly two-step conversion process, which involves initial esterification of FFAs with acids followed by the transesterification of oils using bases (Anwar et al. 2018; Wahidin et al. 2018). This approach would facilitate the production of biodiesel from non-edible raw materials by simultaneously conducting transesterification and esterification reactions in a single reaction vessel. Lewis's acids can work in conjunction with Bronsted acids to catalyze the transesterification of carboxylic esters, while Bronsted acids are considered highly effective for esterifying carboxylic acids. To achieve concurrent catalytic impacts on biodiesel synthesis, the

development of bifunctional catalysts containing both Bronsted and Lewis acidic sites with adjustable Bronsted/Lewis's acid ratios is of particular interest. Bifunctional solid catalysts have the potential to integrate highly selective catalytic processes, reaction engineering, and product separation into a single reactor. Solid catalyst materials with both acid-base or Bronsted-Lewis acid sites can expedite the conversion of non-edible crude oils into biodiesel, eliminating the need for time-consuming product isolation and purification steps. Bifunctional heterogeneous catalysts are proficient in catalyzing the transformation of biomass resources into the desired product through tandem or sequential reactions conducted within a single reactor, particularly for the production of Alkyl levulinates (AL), specifically ethyl levulinates (EL) (Zhang et al. 2019). Figure 2.5 illustrates the prevailing trends in the catalytic processes for biodiesel production.

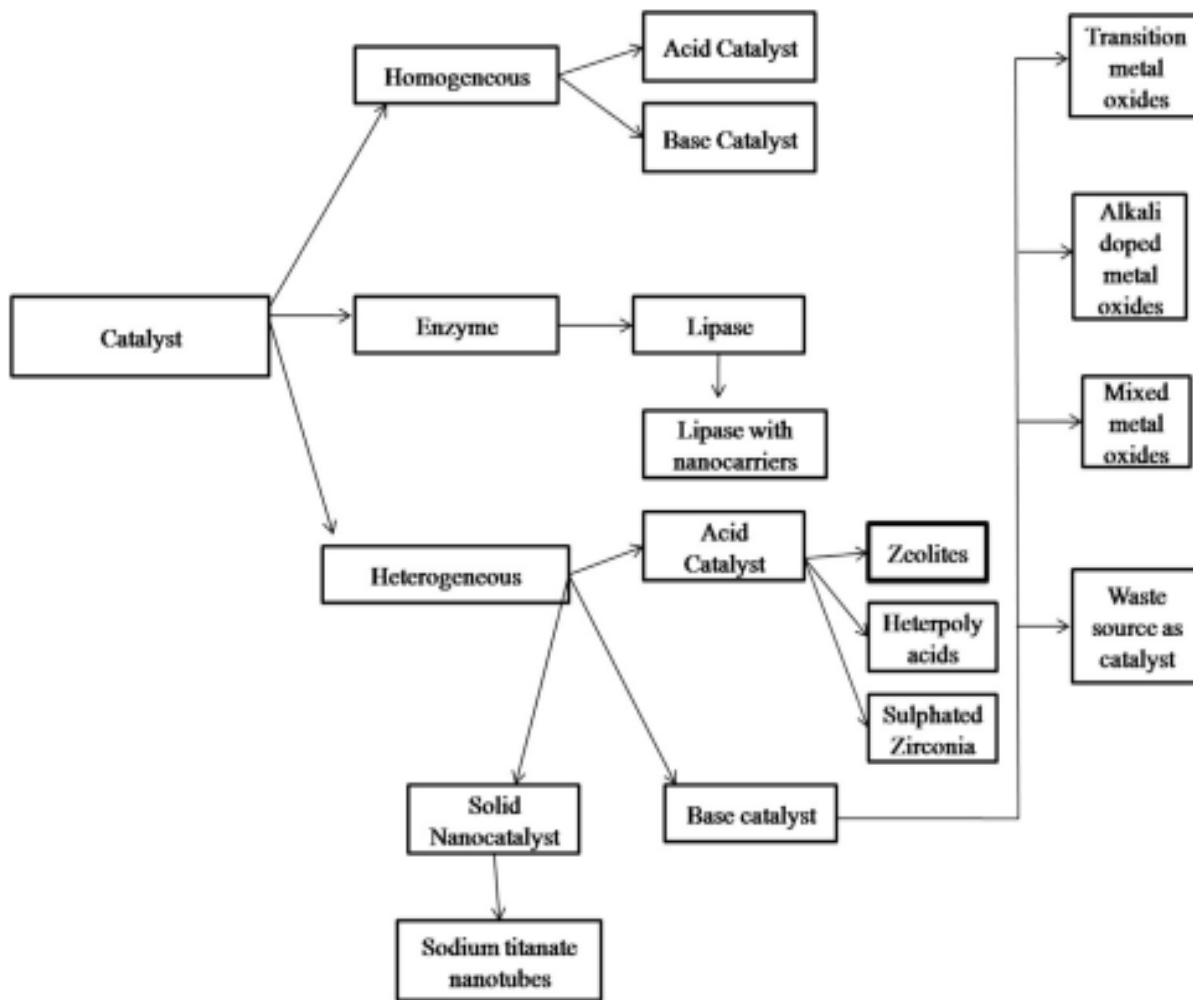


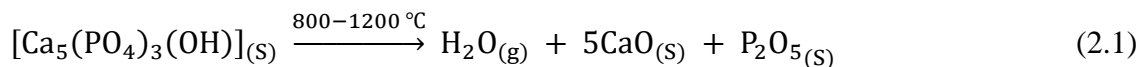
Figure 2.5: Catalytic trends in the production of biodiesel (Baskar and Aiswarya 2016).

2.16 PIG BONE

Animal bone is an organic-inorganic composite made up of organic protein, collagen fibers, inorganic ions, and the inorganic mineral hydroxyapatite. 90% of the organic material in bone is collagen, followed by 5% proteins and 2% lipids. The inorganic components of bone powder are P, Ca, Mg, B, Fe, Mn, K, Cu, and Zn. In many different applications, inorganic elements serve as structural, catalytic, and electrochemical components. Due to the rich content of bones, the biomedical and food sectors employ them. They are utilized in agriculture and plant development due to their elevated concentrations of inorganic components such as calcium (Ca) and phosphorus (P). Due to their accessibility, abundance, and ongoing production, animal bones make the best feedstocks for the manufacturing of calcium-based catalysts (Nasrollahzadeh et al. 2020). Few research investigations have explored the utilization of pig bones as a source of animal-derived alkaline catalyst in the production of solid biodiesel catalysts (Chen et al. 2015).

Pig bones represent a readily available form of waste from China's meat production industry. Hydroxyapatite (HAP) [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$], constituting 30% of pig bones, serves as their primary component and is considered an ideal dispersing support due to its robust ion-exchange properties, capacity to adapt to acidic and alkaline conditions, lack of toxicity, adsorption capabilities, and thermal stability. HAP has been used as a support in a number of studies to produce heterogeneous catalysts (Zhang et al. 2013). HAP served as an excellent solid substrate for conducting solvent-free Knoevenagel condensation reactions, according to Sebt and colleagues. Sun et al. (2010) detailed the effective application of HAP as a supportive catalyst for ruthenium in the achievement of quinolone hydrogenation. It is important to note that pig bones, similar to those of other mammals, consist of a combination of organic and inorganic constituents (Yan et al. 2016). The essential elements are: organic substances which includes collagen, proteins and lipids. Inorganic substances which include hydroxyapatite (HAP) [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$], Calcium carbonate (CaCO_3), Magnesium (Mg), sodium (Na), Potassium (K), Trace elements like strontium (Sr), copper, and zinc (Zn). These elements work together to shape and form pig bones. The bones' hardness and strength are due to the inorganic components, particularly hydroxyapatite, while their flexibility and structure are due to the organic components, particularly collagen. Pig age, food, and general health can all affect the precise make-up of its bones. To get CaO from the Pig bone, the cleansed pig bone, which is mostly made up of HAP, is heated at high temperatures in a regulated setting,

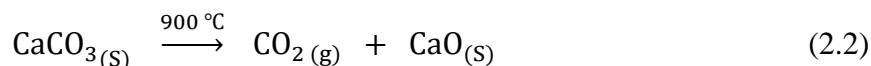
usually between 800°C and 1200°C. Researchers call this process calcination. The following chemical processes illustrated by Equation (2.1) occur during calcination:



2.17 CALCIUM OXIDE, CaO

Currently, the transesterification reaction used to make biodiesel uses homogenous base catalysts like KOH or NaOH dissolved in methanol. The significant limitation associated with homogeneous catalysts is that they are depleted during the process and cannot be recycled or rejuvenated (Farooq et al. 2013). Furthermore, the separation of products from the catalyst is a complex and costly process, which escalates production expenses. To address these challenges, the adoption of heterogeneous catalysts represents a promising solution. These catalysts can effectively prevent unwanted saponification reactions and are easier to isolate from reaction byproducts. Solid catalysts offer the advantage of reusability, enabling both transesterification and esterification to occur simultaneously during biodiesel synthesis, thus contributing to reduced production costs. Numerous types of heterogeneous catalysts, including supported catalysts, alkaline earth oxides, and hydrotalcites, have been the subject of research. Among these, CaO has garnered significant attention due to its prolonged catalytic lifespan, high activity rate, and the ability to operate under mild reaction conditions (Lani et al. 2017).

As stated in a report, CaO can be synthesized through the calcination of CaCO₃ or Ca(OH)₂ at temperatures exceeding 800 degrees Celsius, resulting in the formation of an oxide characterized by a limited surface area. However, it is difficult to make CaO at the nanoscale using this method. However, the thermal breakdown of CaCO₃ can be used to create microscale CaO (above 100 nm). This claim is substantiated by research conducted by Kasselouri and colleagues (Zul et al. 2021). The researchers illustrated that the disintegration of limestone, a mineral composed of CaCO₃, resulted in the formation of minute CaO particles. CaCO₃ must be converted into CaO at calcination temperatures greater than 900 °C, which is illustrated by Equation (2.2).



In closed systems operating at extremely high temperatures, exceeding 900 °C, the endothermic reaction is significantly influenced by the partial pressure of the gas phase (PCO_2). In theory, the decomposition temperatures for carbonate minerals commonly present in limestones, like calcite and magnesite, typically fall in the range of 900 °C and 400–550 °C, respectively. As a result, the calcination temperature of limestone varies and is easily controlled by the size of the grains or the $CaCO_3/MgCO_3$ ratio (Baziotis et al. 2011). In the 1980s and 1990s, certain studies indicated that it is more advantageous to produce CaO through the decomposition of calcium hydroxide rather than by calcining limestone. This method yields CaO with a greater surface area. As the size of the catalyst decreases, the active surface area of the catalyst increases. Consequently, smaller particle sizes require less quantity in the process, leading to improved catalytic activity and a higher surface-to-volume ratio (Zul et al. 2021). Figure 2.6 provides an illustrative depiction of the process for creating CaO from natural waste materials.

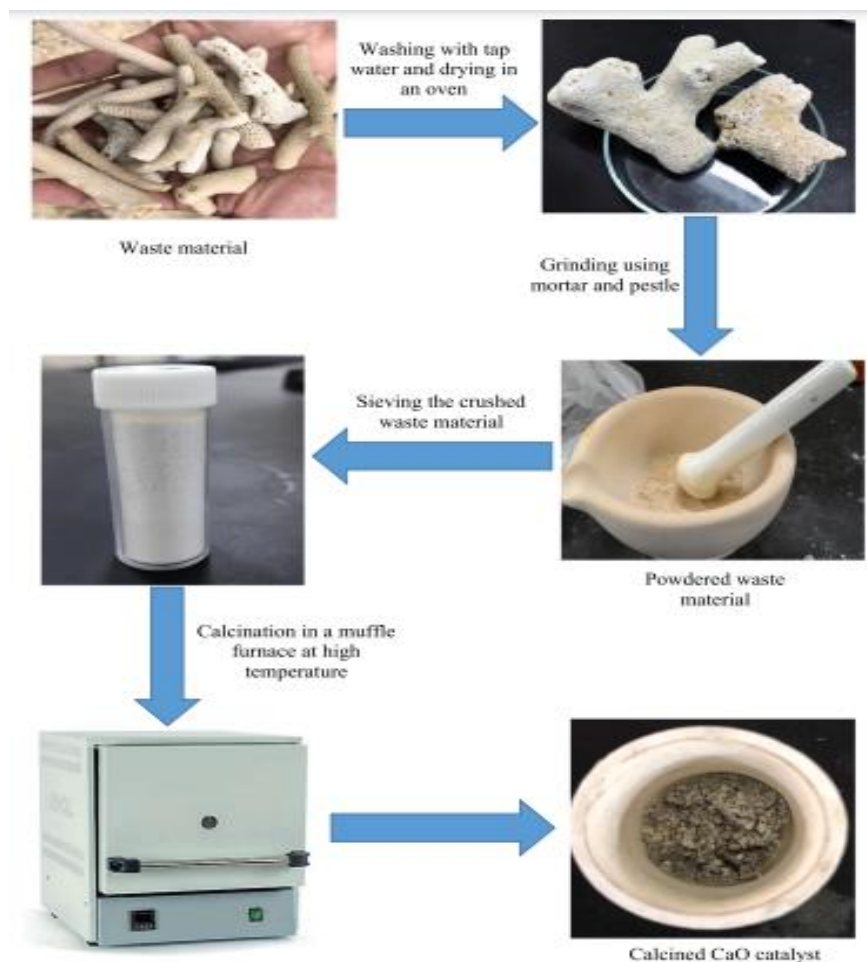


Figure 2.6: Preparation of CaO from natural waste materials (Zul et al. 2021).

2.17.1 CHARACTERISTICS OF CATALYSTS BASED ON CaO

Calcium oxide is typically created through the thermal breakdown of minerals like calcite and limestone, as well as from calcium hydroxyapatite (HAP) $[\text{Ca}_5(\text{PO}_4)_3(\text{OH})]$ and calcium carbonate (CaCO_3) found in natural sources including animal bones, seashells, and eggshells. This is achieved by subjecting raw materials containing $[\text{Ca}_5(\text{PO}_4)_3(\text{OH})]$ or CaCO_3 to elevated temperatures, causing the release of a carbon dioxide molecule and resulting in the formation of quicklime. The specific calcination temperature necessary for the production of CaO varies depending on the raw materials used. According to experimental findings, the temperature at which CaO forms is substantially influenced by the rate of heating (Bilton et al. 2012). Due to its inherent instability, quicklime will undergo a spontaneous conversion into CaCO_3 and $\text{Ca}(\text{OH})_2$ when it comes into contact with CO_2 and moisture from the atmosphere. Table 2.5 lists the primary chemical and physical characteristics of CaO. The presence of active sites and their spatial distribution, influencing their accessibility, form the foundation of CaO's catalytic role in transesterification. In the 1970s, the basicity of CaO was established at $0.57 \text{ mmole g}^{-1}$ using a titration method after calcination in air at approximately 773 K. The active sites on the surface of CaO exhibit rapid reactivity with nearby CO_2 and H_2O . As a result, the strength of CaO's basic properties varies, ranging from a minimum value of $9.8 < \text{H}_- < 12.2$ for commercially deactivated CaO, increasing to $15.0 > \text{H}_- > 18.4$ for CaO that has likely been exposed to air, and surpassing $\text{H}_- > 426.5$. Recent findings indicate that the activation process and the initial precursor employed play a pivotal role in determining CaO's basicity, alongside its other textural and structural characteristics (Marinković et al. 2016).

Table 2.5: Physicochemical characteristics of calcium oxide (CaO) (Marinković et al. 2016).

| Characteristic | Description |
|--------------------|--|
| Chemical Name | Calcium Oxide |
| Common Name | Lime, caustic lime, unslaked lime, fluxing lime, quicklime, calx, burnt lime |
| Chemical formula | CaO |
| Molar mass (g/mol) | 56.0774 |

| | |
|---|---|
| Odour | Does not have odour |
| Melting point (K) | 2886 |
| Density (g/cm ³) | 3.34 |
| Heat of formation (kJ/mol) | 635.55 |
| Solubility in water (mg CaO/ml) | 1.19 (298 K), 0.57 (373 K), exothermic reaction |
| Boiling point (K) | 3123 |
| Solubility in biodiesel + methanol + glycerol (mg CaO/ml alcohol phase) | 0.4 (298 K), 0.6 (333 K) |
| Solubility in alcohols Methanol (mg CaO/ml) | 0.1–0.2 (298 K), 0.03-0.04 (333 K), exothermic reaction |
| Glycerol (mg CaO/ml) | 1.6 (0.5 h contact, 298 K) |
| Heat of hydration (kJ/mol) | 63.18 |
| Glycerol + methanol (mg CaO/ml) | 5.7 (2 h contact, 298 K) ~ (333 K) |

2.17.2 LOADED / DOPED CaO

Suggesting the incorporation of specific catalytically active substances into a CaO support to enhance the inherent reactivity of the pure CaO catalyst. Among the substances commonly used for this purpose, alkaline earth metals and their oxides are the most frequently employed. By calcining them at high temperatures, they are created from comparable predecessors, porous materials that are thermally unstable. Many researchers have utilized these doped CaO-based catalysts for the transesterification of feedstocks containing FFAs by using the impregnation approach to manufacture a catalyst in nano form (Banković-Ilić et al. 2017).

Some researchers have effectively introduced alkali earth metals such as lithium, potassium, and zinc into CaO. This reliable approach promotes the generation of alkaline sites. The doped CaO functions as both a catalyst and a substrate for an active component, (Marinković et al. 2016). As an example, Boro et al. (2014) conducted an assessment of the efficacy of lithium-doped CaO derived from eggshells for the transesterification of Nahor oil (a non-edible feedstock) into biodiesel. The eggshell underwent calcination at 800°C and was exposed to varying lithium

concentrations (ranging from 1% to 5% by weight) for a duration of two hours. The experimental results revealed that with the increase in Li loading (up to 2% by weight), the catalyst's alkalinity increased while the surface area decreased. However, in comparison to pure CaO, the Li-doped catalyst exhibited a smaller surface area. While the surface area was significant, it was the level of basicity that had a more pronounced influence on the catalytic performance. When utilizing a 2% by weight loading of Li, a methanol/oil ratio of 10:1, and a 5% by weight catalyst concentration, the doped catalyst exhibited excellent performance in the transesterification reaction. After a 4-hour reaction period at 65°C, it achieved an impressive approximately 94% conversion of biodiesel. Furthermore, research has explored the creation of a nanocatalyst, comprising lithium-ion impregnated calcium oxide, for the production of biodiesel from Karanja and Jatropha oils. This investigation included the adjustment of reaction temperature, free fatty acid content, the quantity of impregnated lithium-ion, catalyst amount, and the molar ratio of alcohol to oil (Kaur and Ali 2011).

2.17.3 NEAT CaO

The choice between utilizing pure (neat) or impure (crude) calcium oxide (CaO) as a catalyst in biodiesel production hinges on various factors, which encompass the desired biodiesel quality and cost considerations. When making high-purity biodiesel, pure CaO, which is refined and of high purity, is frequently employed. Although more expensive, it can deliver a more constant and predictable catalytic performance. Reddy et al. (2006) initially investigated the methanolysis of soybean oil and chicken fat using nanocrystalline CaO as a solid catalyst. The catalyst was in the form of powder, pellets, and granules, and the reaction took place at ambient room temperature. They discovered that both feedstocks may provide a high biodiesel yield (about 100%). Despite the need for a high methanol/oil molar ratio of 27:1, the enhanced reactivity and reaction kinetics of nano CaO were facilitated by its increased surface area, owing to the smaller crystallite size. It was discovered that the catalyst's granular form provided better recycling than the powdered version. Additionally, due to its ease of handling, the pelletized version of the catalyst would be more appealing for commercialization. Tetrahydrofuran, functioning as a co-solvent, expedited the blending of oil and methanol as reactants and played a substantial role in reducing the reaction time by 50%. Nevertheless, employing the exact conditions without a co-solvent and using

commercial laboratory-grade CaO did not result in the successful production of biodiesel, as evidenced by the remarkably low TAG conversion rate, which only reached 2%. Reddy et al. (2006) also looked into the effectiveness of Mg, Zn, Al, Ti, and Ce oxides as well as other nanocrystalline metal oxides for oil transesterification. With the exception of MgO powder, which only achieved 6% conversion, no reaction could be seen in the presence of the other nano-oxide catalysts (Banković-Ilić et al. 2017).

2.18 PUMPKIN STALK

The fluted pumpkin, also known as *Telfaria Occidentalis* Hook F or "Ugu leaf" among Nigerians, is a leafy vegetable with significant commercial value. It originates in tropical West Africa and is a member of the curcubitaceae family. Despite being grown as an annual crop, it is a herbaceous perennial crop, particularly in West Africa's traditional agricultural practices. It makes tendrils that hold immature, drupe-like pods, which typically have both male and female seeds. These seeds are reported to contain 29% and 30%, respectively, of oil and protein. In West African nations, fluted pumpkin is mostly farmed for its leaves, which are a significant part of the indigenous food. The leaves are harvested by farmers for either personal use or for sale. The nutrient content of pumpkin seeds with flutes has been reported by several researchers (Goodhead T.O., Wami E.N. 2021). Less than 200 g of leaves are produced each stem, which weighs 1.2 kg in total. leaving a waste stem of more than 1 kg. According to research, they are not very effective in some areas of the country and as a result, they have a negative impact on the environment. In order to turn these wastes into other goods, numerous research projects are now conducted. After a month of germination, the leaves and shoots, which are utilized as food and pasture, are available for harvest. Subsequent harvests take place every 2-4 weeks (Igbozulike 2015). It has a large number of applications in conventional medicine, particularly as a hematopoietic agent. According to Kayode & Kayode (2011), the plant's antioxidant and antibacterial capabilities, high protein content, and mineral and vitamin content (particularly iron and vitamin A and C) may all contribute to the plant's ability to fight off several ailments. Activated carbon may be produced from stem waste (O.A. and JNR 2011). Among the well-known and popular tropical leafy vegetables (TLVs) grown in South-Eastern Nigeria, it comes in first place in terms of net revenue. Table 2.6 summarizes the nutritional values and composition of ugu seed and leaf. Ugu is a dark green leafy vegetable

(DGV), and DGVs have antioxidant properties due to their carotenoids, vitamins, and minerals. Additionally, certain forms of cancer can be prevented from progressing by substances found in DGVs (Kelechi and Dorothy 2015). Ugu thus offers a lot of advantages to man.

The results of proximate analysis of the functional qualities, chemical make-up, and lipid/oil fatty acid composition of fluted pumpkin seeds revealed a high percentage of crude fat ($42.17 \pm 0.27\%$), moderate percentages of crude protein ($17.50 \pm 0.12\%$), carbohydrates ($17.96 \pm 0.35\%$), ash ($5.67 \pm 0.10\%$), and low moisture content ($6.67 \pm 0.01\%$). The mineral composition of the seed flour showed that potassium (1824 mg/100g wet sample), magnesium (535 mg/100g wet sample), and sodium (280 mg/100g wet sample) are the three main minerals present. The oil has the following physiochemical characteristics: a refractive index of 1.471, an acid value of 3.56 ± 0.45 , a saponification value of 188.24 ± 2.12 , an iodine value of 78.26 ± 1.24 , and a free fatty acid value of 4.5 ± 0.15 (Eloka-Eboka et al. 2017).

Table 2.6: Ugu seed and leaf nutritional values and composition (Igbozulike 2015).

| Nutrient | Leaf | Seed |
|-------------------|-------------|-------------|
| Calories | 47.0 | 543.0 |
| Fat (g) | 1.8 | 45.0 |
| Fibre (g) | 2.2 | 1.7 |
| Phosphorus (mg) | 0.0 | 572.0 |
| Water (ml) | 86.0 | 6.0 |
| Protein (g) | 2.9 | 20.5 |
| Carbohydrates (g) | 7.0 | 23.0 |
| Calcium (mg) | 0.0 | 84.0 |

2.19 TAGUCHI OPTIMIZATION APPROACH

When traditional experimental design methodologies were used for industrial testing throughout the past four decades, there were restrictions. The orthogonal array design method, created by Japanese engineer Dr. Genichi Taguchi, gives conventional experimental design a fresh perspective. 'Labc' stands for Taguchi's Design of Experiments (DOEs), where 'La' stands for orthogonal arrays of variables or the design matrix, 'b' for levels of variables, and 'c' for the number of variables. The DOE's widely accepted Taguchi approach has been shown to provide high-quality items at a very cheap cost. The automotive, electronics, and other processing sectors frequently use this technique. The Taguchi method's goal is to find the ideal input parameter values while ignoring fluctuation brought on by uncontrollable or noise-related elements. Here, the term "factor" refers to an experimental input variable that allows for the manipulation of the experiment's state (Kondapalli et al. 2015). One of the most effective techniques for multifactor optimizing conditions is the Taguchi orthogonal array (L9 OA). To get the best result under the examined removal conditions, it is employed. Additionally, it creates an experiment process that enables the independent assessment of components using a limited number of trials (Maazinejad et al. 2020).

The Taguchi technique is a statistical and quality tool that guarantees a set of data's mean with the least amount of fluctuation. Additionally, the dependent variable's optimization in relation to the independent variables is conceivable. This is accomplished by observing the signal-to-noise (S/N) ratio, which is actually comparable to the ratio of expected signal to unexpected noise in a system. The S/N concept has two effects: it reduces variance and refines mean. The S/N is also related to how factors affect the answers. Nominal is the best, smaller is better, and larger is better qualities are the three potential optimization principles. These ideas are described in Equations (2.3) - (2.5) (Mia 2018).

Smaller is the better principle
$$\frac{S}{N} = -10 \log \frac{1}{n} (\sum x^2) \quad (2.3)$$

Nominal is the best principle
$$\frac{S}{N} = 10 \log \frac{\bar{x}}{S_x^2} \quad (2.4)$$

Larger is the better principle
$$\frac{S}{N} = -\log \frac{1}{n} \left(\sum \frac{1}{x^2} \right) \quad (2.5)$$

where x represents the experimental data of the dependent variables (specific cutting energy and surface roughness), \bar{x} is the mean of x , S_x^2 represents the variance of x , and n represents the number of experimental observations. The goals of this study are to reduce surface roughness values to enable better surface quality of manufactured parts and to reduce the specific cutting energy needed owing to sustainable manufacturing establishment. As a result, for both responses, the smaller-is-better principle, as specified in Equation 2.4, is applied (Mia 2018).

CHAPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 RAW MATERIALS

The components employed in this investigative research encompass:

1. Pig bones (Basic precursor)
2. Pumpkin stalks (Acidic precursor)
3. Waste cooking oil, WCO (Feedstock)

3.1.2 CHEMICALS AND REAGENTS

Table 3.1 enlists the chemicals and reagents that were utilized for this study.

Table 3.1: Raw materials and reagents utilized in this study.

| Substances | Origin/Producer | Uses |
|-------------------------|--|--|
| Waste Cooking Oil (WCO) | Obtained locally from food Restaurants within the University of Benin campus in Benin City, Edo State. | Feedstock for biodiesel production |
| Pig bones | Slaughter house at Ring Road, Benin City, Edo State. | The raw material used as the basic precursor in the bifunctional heterogeneous catalyst. |

| | | |
|--|---|--|
| Pumpkin stalks | Obtained from Vegetable Sellers at Ring market, Ring Road, Benin City, Edo State. | The raw material used as the acidic precursor in the bifunctional heterogeneous catalyst. |
| Acetic acid | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used to carry out the Peroxide value of WCO and produced biodiesel. |
| Potassium hydroxide (KOH) | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Employed in the pre-treatment of both the basic precursor and the acid values of the Waste Cooking Oil (WCO) and the biodiesel produced. |
| Benzene | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used to carry out the acid values of WCO and the produced biodiesel. |
| Sulphuric acid (H ₂ SO ₄) | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Utilized in the pre-treatment of the acidic precursor. |
| Chloroform (CHCl ₃) | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Utilized for assessing peroxide and iodine values in both Waste Cooking Oil (WCO) and the produced biodiesel. |
| Distilled water (H ₂ O) | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used to prepare standard solutions and the washing of produced biodiesel. |

| | | |
|--|---|--|
| Potassium iodide (KI) | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used to carry out the iodine and peroxide values of WCO and the produced biodiesel. |
| Methanol (CH ₃ OH) | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | To promote WCO's simultaneous esterification and transesterification into biodiesel. Also used to carry out the acid and saponification values of WCO and the produced biodiesel. |
| Phenolphthalein indicator | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used as an indicator for titration. |
| Starch indicator | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | For determining iodine and peroxide values for both the WCO and the produced biodiesel. |
| Ethanol (C ₂ H ₅ OH) | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | To ascertain the acid and saponification values in both the WCO and the biodiesel produced. |
| Alcoholic KOH | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used as an added reagent to carry out the saponification values of both the WCO and the produced biodiesel. |
| Wij's solution | Laboratory for Chemical Engineering at the University | Used to carry out the iodine value test. |

| | | |
|--|---|---|
| | of Benin, located in Benin City, Edo State. | |
| Sodium thiosulphate (Na ₂ S ₂ O ₃) | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used to determine peroxide and iodine values in Waste Cooking Oil (WCO) and the produced biodiesel. |
| Hydrochloric acid (HCL) | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used to determine saponification values in both Waste Cooking Oil (WCO) and the produced biodiesel. |

3.1.3 APPARATUS USED

Table 3.2 contains details of the equipment employed in this study, along with their respective functions.

Table 3.2: Apparatus used in this study and their functions.

| Equipment | Source/Manufacturer | Functions |
|--------------------|---|---|
| Soxhlet extractor | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | To warm up distilled water. |
| Long air condenser | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used for reflux during the determination of the saponification value. |
| Burette | Pyrex (50 ml) | Used for titration |
| Weighing balance | Laboratory for Chemical Engineering at the University | To determine mass. |

| | | |
|-------------------------------|---|--|
| | of Benin, located in Benin City, Edo State. | |
| Separating funnel | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used for separating produced biodiesel from glycerol, and for washing the separated biodiesel. |
| Beakers | Pyrex (250 ml) | for storing substances. |
| Magnetic Stirrer | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used for ensuring that the reactants are continually stirred. |
| Volumetric measuring cylinder | Pyrex (500ml) and (50 ml) | To measure solvent volumetrically |
| Oven | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used for drying and also to determine the moisture content of the WCO |
| Muffle furnace | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | For calcination of pig bones and carbonization of pumpkin stalks. |
| Volumetric flask | Pyrex (1000ml) | Solvent volumetric measurement. |
| Syringe | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used to measure an accurate amount of starch solution as an indicator for titration. |
| Round bottom flask | Pyrex (1000 ml) | Used for reflux during the determination of the saponification value and also |

| | | |
|--------------------------|--|--|
| | | used for the production reaction of biodiesel. |
| Stirring bar | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used to induce the stirring of the content in the conical flask when placed on the magnetic stirrer. |
| Bama bottles | Obtained locally from food Restaurants within the University of Benin campus in Benin City, Edo State. | Used as an air-tight container for storing calcined catalyst |
| Crucible | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | To determine the moist content of WCO and the produced biodiesel. |
| Centrifuge | Luco Chemical Laboratory Limited. | for separating the reaction-produced biodiesel mixture. |
| Viscometer | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | To determine the viscosity of WCO and the produced biodiesel. |
| Pet bottles | Uselu market, Ugbowo, Benin City, Edo State. | Used for storing produced, washed and dried biodiesel. |
| Desiccator | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used for cooling and condensing calcined catalysts |
| Wooden mortar and pestle | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used to ground catalyst to finer powder. |

| | | |
|------------------|---|--|
| Grinding Machine | Grinding mill at Uselu market, Ugbowo, Benin City, Edo State. | For pulverizing the Pig bones. |
| Conical flask | Pyrex (250ml) | Acts as a reactor. |
| Retort stand | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | To hold the burette and separating funnel. |
| Fine mesh | Laboratory for Chemical Engineering at the University of Benin, located in Benin City, Edo State. | Used for sieving grounded catalyst to finer powder. |
| Pet bottles | Uselu market, Ugbowo, Benin City, Edo State. | Used for storing produced, washed and dried biodiesel. |

3.2 METHODS

3.2.1 OIL CHARACTERIZATION

3.2.1.1 ACID VALUE TEST

The objective of this examination was to assess the acidity of Waste Cooking Oil (WCO) both before and after the concurrent esterification and transesterification processes. The acid value, denoted by the quantity of potassium hydroxide in milligrams needed to neutralize the free fatty acids in one gram of fat, was utilized for this comparison. Free fatty acids serve as an indicative measure of rancidity, typically generated during the decomposition of triglycerides. This metric indicates the extent to which fatty acids have been released from glycerides through hydrolysis caused by factors such as moisture, temperature, and/or the action of the lipolytic enzyme lipase.

The acid value of the Waste Cooking Oil (WCO) was determined through titration in an alcoholic medium using a standardized 0.05 N potassium hydroxide (KOH) solution. The 0.05 N KOH

solution was prepared by dissolving 2.805 g of potassium hydroxide pellets in a 1000 mL volumetric flask filled with distilled water. Afterward, the solution was transferred to a burette for the titration process. Into a conical flask, 1 g of WCO was weighed, and 10 mL each of benzene and ethanol, measured with a 50 mL measuring cylinder, were added. Three drops of phenolphthalein indicator were introduced using a dropper. The contents of the conical flask were titrated against the 0.05 N potassium hydroxide solution in the burette until a faint pink color persisted for 15 seconds. Subsequently, the acid value was calculated using Equation (3.1).

$$\text{Acid Value} = \frac{(T_V - T_B) \times \text{KOH Normality} \times 56.1}{\text{Weight of WCO (g)}} \quad (3.1)$$

Where:

T_B = Titrated value of blank solution

T_V = Titrated value of WCO

3.2.1.2 FREE FATTY ACID (FFA)

Equation (3.2) is employed to ascertain the free fatty acid content (FFA), representing the weight percentage of fatty acids within the oil.

$$\text{Free Fatty Acid (FFA)} = \frac{\text{Acid Value}}{2} \quad (3.2)$$

3.2.1.3 MOISTURE CONTENT

Initially, the weight of an empty crucible was measured and recorded. Subsequently, 10 g of Waste Cooking Oil (WCO) was weighed inside the crucible, and the combined weight, including its initial weight, was also recorded. The crucible containing the 10 g of WCO was then placed in an oven set at 105 °C and heated for a period of 3 hours. Following this, the crucible with the WCO was taken out of the oven, reweighed every hour, and returned to the oven for the next three hours to monitor any fluctuations in weight until it stabilized, resulting in two identical weights. Equation (3.3) was used to calculate the moisture content.

$$\text{Moisture Content} = \frac{\text{Initial weight of WCO} - \text{Final weight of WCO}}{\text{Initial weight of WCO}} \times 100\% \quad (3.3)$$

3.2.1.4 DENSITY

The weight of a 30 mL density bottle, which was empty, was measured and its weight noted. The bottle was then filled with WCO and reweighed, and this weight was also recorded. The difference between these two values was used to calculate the change in weight, and the mass/weight of the oil was recorded. The oil's density was determined by dividing the mass by the volume of the density bottle, and the outcome was documented in kilograms per cubic meter (kg/m³). Equation (3.4) was used to calculate the density.

$$\text{Density} = \frac{\text{Weight of bottle with WCO} - \text{Weight of empty bottle}}{\text{Volume of WCO}} \quad (3.4)$$

3.2.1.5 SPECIFIC GRAVITY (S.G)

The method using a density bottle was also used to compute the specific gravity of Waste Cooking Oil (WCO). A 30 mL density bottle, which had been thoroughly cleaned, dried, and weighed (W_0), was filled with WCO. The stopper was then securely positioned, and the weight was measured once more to provide (W_1). The bottle was subsequently cleaned and dried again, but this time it was filled with water instead of WCO. It was then weighed to obtain (W_2). Equation (3.5) provides the expression used to calculate the specific gravity, denoted as S.G.

$$\text{Specific gravity, S. G} = \frac{\text{Density of fluid}}{\text{density of water}} = \frac{W_1 - W_0}{W_2 - W_0} \quad (3.5)$$

Where:

W_1 = The empty bottle weight + WCO

W_0 = The empty bottle weight

W_2 = The empty bottle weight + Water

3.2.1.6 SAPONIFICATION VALUE

The purpose of this test was to compare the saponification value of WCO before and after the oil underwent simultaneous esterification and transesterification. The saponification value is described as the quantity of potassium hydroxide in milligrams required to fully react with all the reactive groups in one gram of the sample. It is obvious that alkalis are needed to saponify all of the sample's triglycerides, diglycerides, and monoglycerides as well as to neutralize all of the sample's free fatty acids and other reactive ester-like compounds like lactones.

1 gram of waste cooking oil (WCO) was placed into a round-bottom flask, and 50 mL of alcoholic KOH was introduced. The mixture underwent reflux for one hour. Following this period, it was allowed to cool and then transferred into a conical flask. Three drops of phenolphthalein indicator were included, and the surplus alkali was titrated with 0.5 M Hydrochloric acid (HCL) until the color shifted from the initial purple to a pale, colorless endpoint. Simultaneously, a blank determination was conducted using the same amount of KOH solution, following the same procedures. Equation (3.6) outlines the formula for calculating the saponification value in mg KOH/g of the sample.

$$\text{Saponification Value, S. V} = \frac{M \times 56.1 \times (T_B - T_W)}{\text{Weight of WCO (g)}} \quad (3.6)$$

Where:

T_W = Value of WCO's titration

M = Molarity of HCL

T_B = Value of blank titration

56.1 = Equivalent weight of base.

Equation (3.7) provides the expression for calculating the average molecular weight:

$$M_W = \frac{168300}{SV - AV} \quad (3.7)$$

Where:

M_W = Molecular weight of WCO

AV = Acid Value

SV = Saponification Value

3.2.1.7 IODINE VALUE

This is one of the best methods for analyzing the unsaturation levels of fats and oils. In order to interact with the double bond, the principle entails introducing halogen to an unsaturated connection.

1 gram of Waste Cooking Oil (WCO) was measured into a 250 mL conical flask, and 25 mL of acetic chloroform was introduced. The mixture was gently warmed and left to cool for 10 minutes. Following this, 25 mL of Wij's solution was added, stirred vigorously, and the blend was placed in a dark area to avoid sunlight-induced reactions. After 30 minutes, it was taken out of the dark area, and 25 mL of potassium iodide (KI) solution was incorporated into the mixture. The contents were blended meticulously and titrated with 0.1 N sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) from the burette until a yellow color emerged. At this juncture, 10 mL of starch was introduced as an indicator via a syringe, causing the color to shift to a dark indigo/blue hue. The titration persisted against $\text{Na}_2\text{S}_2\text{O}_3$ until the blue color vanished, signifying the attainment of an endpoint. The identical process was replicated without the utilization of oil, serving as the blank. Equation (3.8) provides the expression for determining the iodine value.

$$\text{Iodine Value} = \frac{12.69 \times N \times (V_1 - V_2)}{\text{Weight of WCO (g)}} \quad (3.8)$$

Where:

V_1 = Value of Sodium thiosulphate blank titration

12.69 = Constant value

N = Normality of Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$)

V_2 = Value of Sodium thiosulphate required when used with 1 g of WCO

3.2.1.8 PEROXIDE VALUE

The presence of peroxides causes unsaturated fats and oils to get rancid in the first stage. The peroxide value (1 mm = 2 meq) refers to the millimoles of peroxide or milliequivalents of oxygen present per 1000 g of fat.

One gram of Waste Cooking Oil (WCO) was measured into a 250 mL conical flask. To this flask, 12 mL of acetic chloroform was added, and the mixture was shaken for 1 minute. Subsequently, 0.5 mL of saturated potassium iodide (KI) solution was introduced and shaken. Following this, 12 mL of distilled water was added and shaken to release iodine from the chloroform layer. Finally, 1 mL of starch solution was included as an indicator and shaken. The entire content in the 250 mL conical flask underwent titration against 0.1 N Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) until the blue-gray color in the aqueous upper layer vanished. The same procedure was replicated without the oil, acting as a blank. Equation (3.9) provides the expression used to calculate the peroxide value.

$$\text{Peroxide value} = \frac{10 \times (N_1 - N_2)}{\text{Weight of WCO (g)}} \quad (3.9)$$

Where:

N_1 = The volume of titration for the blank solution of sodium thiosulphate

N_2 = The volume of sodium thiosulphate used with 1 gram of Waste Cooking Oil (WCO)

3.2.1.9 KINEMATIC VISCOSITY

A capillary viscometer, calibrated following the ASTM D445 standard, was employed to ascertain the kinematic viscosity of Waste Cooking Oil (WCO). 250 mL of WCO was measured in a beaker and heated to 40 °C. The heated sample was subsequently transferred to a clean, dry capillary viscometer for measurement, with timing conducted between the lower and upper meniscus. The kinematic viscosity of the resulting biodiesel was also determined using the identical method. Figure 3.1 illustrates the viscometer along with its displayed readings.



Figure 3.1: Viscometer with displayed readings.

3.2.2 CATALYST PREPARATION

Pig bones and pumpkin stalks were combined to create the bi-functional catalyst used in this study. The basic ingredients of these catalysts are waste materials that can pollute the environment and cause irritation. This section describes the preparation of the catalysts.

3.2.2.1 OBTAINING FEEDSTOCK

The pig bones and pumpkin stalks, which were the waste materials utilized in this experimental study, were sourced from Ring Road, Oba Market, Benin City, Edo State. Waste Cooking Oil (WCO) was sourced from a restaurant located within the University of Benin (UNIBEN) in Benin City, Edo State.

3.2.2.2 PREPARATION OF THE BASIC PRECURSOR USING PIG BONES

The pig bones, collected from the slaughterhouse at Ring Road, were washed with distilled running tap water and cleaned to remove debris. They were then sundried for 2 days to remove moisture. When they had dried to a reasonable extent, they were further taken to the oven and dried at 600 °C for 24 hours. Afterward, they were taken to the grinding mill at Uselu Market, Uselu, Benin City, Edo State, and pulverized into a fine powder. Figures 3.2 – 3.4 display the dried pig bones before and after being pulverized.

The pulverized pig bones were then treated with a 1 M standard solution of KOH, forming a slurry. The slurry was stirred and heated using a heating mantle until it dried. Afterward, the resulting substance was covered and left for 48 hours. After 48 hours, the substance underwent a cleansing process with distilled water, underwent filtration using a filtering net, and subsequently underwent a 24-hour oven-drying period at 50 °C. Afterward, it underwent a calcination process in a muffle furnace at 900 °C for a duration of 6 hours (Akhabue et al. 2020). After calcination, the sample (base precursor) was left in the muffle furnace to cool. Before reaching room temperature, it was removed and placed in the desiccator to further cool, preventing the escape of volatile particles and condensing them back into bulk particles. After complete cooling, the samples were taken out of the desiccator and finely ground using a wooden mortar and pestle to create a finer powder. This step was necessary to address the caking that occurred during calcination and desiccation. The resulting powder was then sieved with a 0.225 fine mesh size. To prevent the samples from absorbing moisture and reacting with it, they were stored and maintained in an airtight container, awaiting further use.



Figure 3.2: Pig Bones before they were crushed.



Figure 3.3: Crushed Pig Bones.

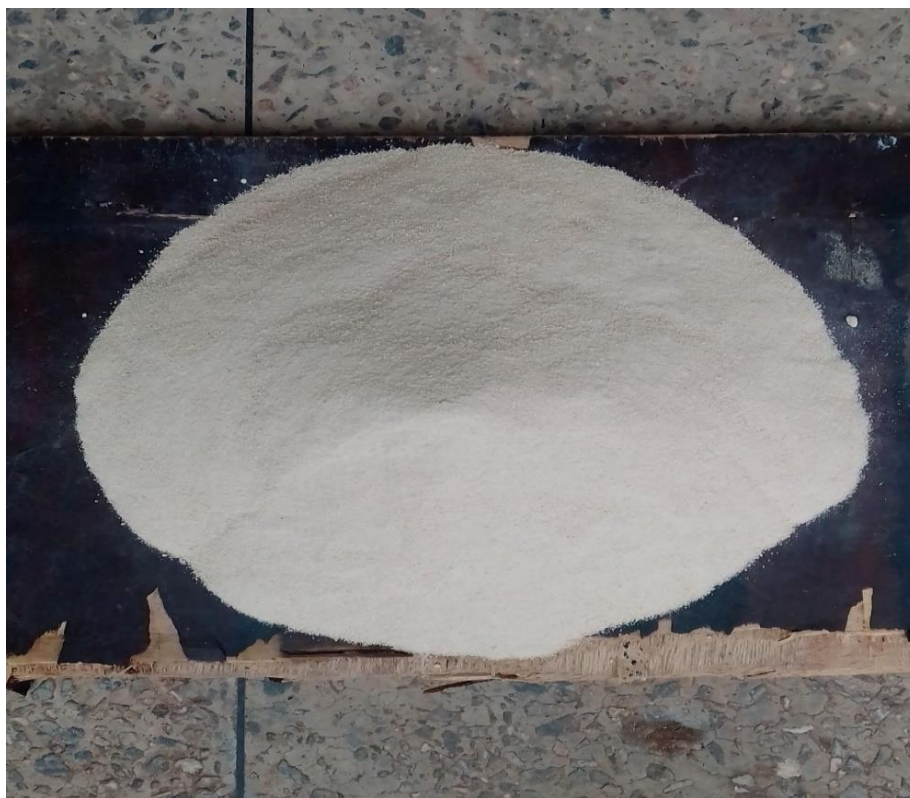


Figure 3.4: Pulverized Pig Bones.

3.2.2.3 PREPARATION OF THE ACIDIC PRECURSOR USING PUMPKIN STALKS

After collecting the pumpkin stalks from the vegetable sellers at Ring Road, they were selected and cleaned to remove the bad or rotten ones. Figure 3.5 displays waste pumpkin stalks. They were then sun-dried for 2 days. Subsequently, the pumpkin stalks, which had been dried, underwent carbonization at 450 °C for a duration of 3 hours in a muffle furnace. After the carbonization process, the stalks were cooled, crushed, and ground into a powder using a wooden mortar and pestle. The resulting powder was then filtered through a mesh with a pore size of 0.225 mm.

The carbonized powdered pumpkin stalks (CPPS) were then sulphurated with 1 M sulfuric acid (H₂SO₄). This process involved mixing 2000 g of CPPS with a 0.5 M standard solution of H₂SO₄ in a 2:4 ratio inside a 2000 mL beaker. The mixture was stirred continuously and subjected to heating at 150 °C for a duration of 2 hours using a heating mantle. Subsequently, the blend was covered and left for 48 hours before undergoing a washing and filtration process using distilled water and a filtering net to eliminate impurities and free ions that may be present. The washed and sulfurized CPPS was then subjected to an 8-hour drying process in an oven at 180 °C. After drying, it was ground again using a wooden mortar and pestle and filtered through a mesh size of 0.225 mm pore. Finally, it was stored in an airtight container awaiting further use.



Figure 3.5: Waste pumpkin stalks.

3.2.2.4 PREPARATION OF BIFUNCTIONAL CATALYST THROUGH WET IMPREGNATION

A wet impregnation process was used to create a bifunctional catalyst. Sufficient amount of distilled water was added to thoroughly mix calcined pig bones and sulphurated pumpkin stalks in a 3:2 weight ratio. After blending, the resultant mixture underwent a 3-hour drying phase at 180 °C in an oven to ensure complete water evaporation. Subsequently, the mixture was moved to a desiccator following a 3-hour calcination at 700 °C in a muffle furnace. After cooling to room temperature within the desiccator, it was sealed in an airtight container for subsequent analysis and use. Figure 3.6 displays the obtained bifunctional catalyst.

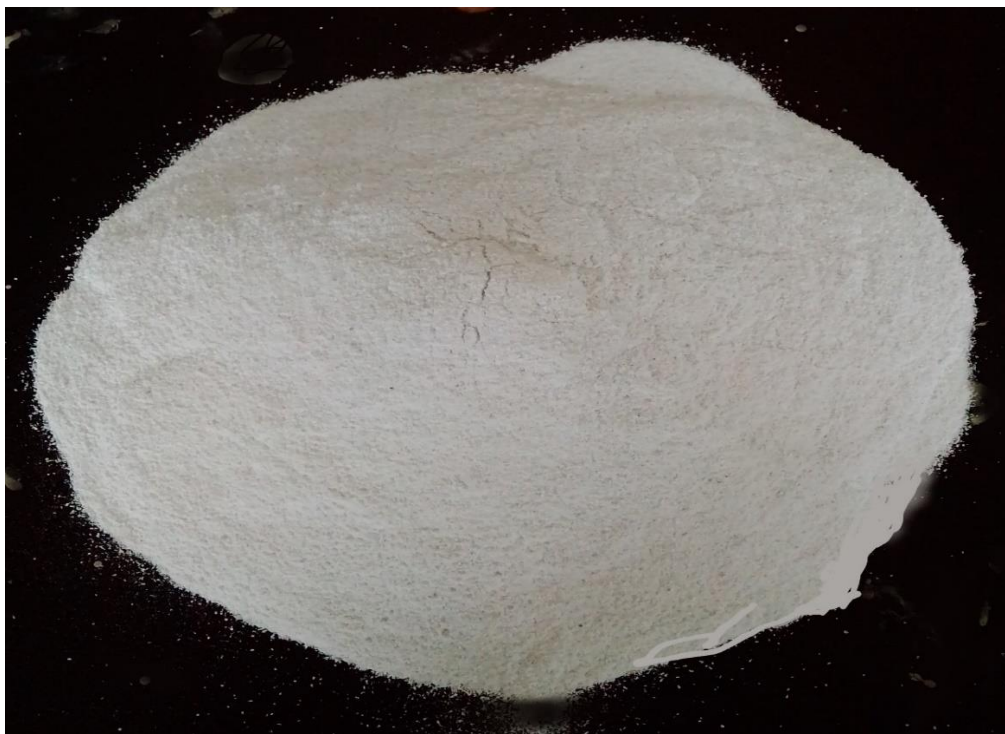


Figure 3.6: Bifunctional catalyst.

3.2.3 WCO PRETREATMENT AND CHARACTERIZATION

A clean and fine filter cloth was used to filter the waste cooking oil (WCO) to remove food residue and other contaminants. The filtered WCO was then stored in a container, awaiting further use and analysis. Following standard procedures, the following characteristics were analyzed: density, acid

value, moisture content, viscosity, saponification value, FFA content, peroxide value, and iodine value.

3.2.4 BIFUNCTIONAL CATALYST CHARACTERIZATION

The bifunctional catalyst was characterized both when it was used for biodiesel production and when it was not used for biodiesel production. These two states were referred to as the 'used' and 'unused' bifunctional catalysts.

3.2.4.1 UNUSED BIFUNCTIONAL CATALYST (UNBC) CHARACTERIZATION

The physicochemical characteristics of the Unused bifunctional catalyst (UNBC) were determined through six characterizations. The scanning electron microscope (SEM) was employed to scrutinize the surface morphology of the UNBC, while its pore characteristics were assessed through the Brunauer Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. The thermal properties of the UNBC were explored using a thermogravimetric analyzer (PerkinElmer TGA4000). The Energy Dispersive X-ray Fluorescence (EDXRF) technique was utilized to determine the oxide composition of the UNBC. Additionally, an X-ray diffractometer (XRD) was employed to identify the crystalline phases present in the UNBC. Finally, the functional groups within the UNBC were evaluated using an FTIR spectrophotometer.

3.2.4.2 USED BIFUNCTIONAL CATALYST (UBC) CHARACTERIZATION

The physicochemical characteristics of the Used bio-based bifunctional catalyst (UBC) were also determined. Two characterizations were conducted on the UBC. The Energy Dispersive X-ray Fluorescence (EDXRF) technique was used to identify the oxide composition present in the UBC. Additionally, an FTIR spectrophotometer was employed to analyze the functional groups present in the UBC.

3.2.5 UTILIZING TAGUCHI L9 MATRIX IN THE EXPERIMENTAL DESIGN

The process of esterification and transesterification in oils is found to be influenced by various factors, including the molar ratio of methanol to oil, reaction duration, catalyst concentration, agitation rate, heating intensity, reaction temperature, and others (Karmakar et al. 2018; Akhabue et al. 2020; Fadara et al. 2021). In the present investigation, the Taguchi Design was employed to model the concurrent esterification and transesterification of WCO. The chosen methodology was the L9 (3^4) orthogonal array. Table 3.3 presents four specific factors, each with three varying levels, including the methanol to oil molar ratio, catalyst loading, reaction temperature, and time. Using Design Expert 11.0, the Taguchi experimental design was carried out. Equation (3.10) provides the total number of trials that must be conducted and is based on the number of components and levels.

$$N = (L - 1) F + 1 \quad (3.10)$$

Where:

L = Number of levels

F = Number of factors

N = Total number of experiments

The yield of WCO produced biodiesel and the acid value, AV were employed in this example as the responses, and the mathematical model that correlates the components to the responses was created using the regression analysis technique.

The acquired outcomes underwent analysis of variance (ANOVA) to assess the influence of different parameters. With only the parameters having a significant impact taken into account, mathematical models for the biodiesel yield and the FFA conversion were created using the regression analysis technique. Fitted statistical tests were used to analyze how well the developed model fit with the experimental data and the predicted data. Various tests, such as the coefficient of determination (R^2), adjusted R^2 , anticipated R^2 , standard deviation (SD), and coefficient of variation (CV), were conducted on the model.

Table 3.3: Different process factor values at various levels.

| S/N | Factors (unit) | Level 1 | Level 2 | Level 3 | Responses |
|-----|------------------------------------|---------|---------|---------|--------------------------|
| 1 | Methanol to Oil Ratio (mol/mol) | 6:1 | 24:1 | 24:1 | Yield (%) |
| 2 | Catalyst Loading (wt.%) | 1 | 1 | 5 | Acid Value (mg KOH/g) |
| 3 | Reaction Temperature (°C) | 55 | 65 | 65 | |
| 4 | Reaction Time (min) | 60 | 60 | 120 | |

3.2.6 ONE POT CONVERSION OF HIGH FREE FATTY ACID WCO

In a one-pot conversion, high free fatty acid WCO underwent processing in a 250 mL conical flask catalyzed by UNBC. Initially, 50 g of high free fatty acid WCO was placed in the flask, along with a stirring bar. The flask was then positioned on a magnetic stirrer, with the temperature set to 60 °C. Once the stirrer reached 60 °C, a predetermined quantity of methanol was introduced into the flask based on the methanol-to-oil molar ratio. Concurrently, a specified amount of catalyst, determined by the catalyst loading, was also introduced. The conical flask was securely sealed to prevent methanol from escaping and to enable a controlled reaction. The reaction commenced when the magnetic stirrer reached the designated temperature of 60 °C. A stopper was then set for 60 minutes to allow sufficient time for the reaction to take place. After one hour, the conical flask, containing the reacted mixture, was taken off the magnetic stirrer, and the mixture underwent centrifugation to separate the catalyst from the entire reaction mixture. The resultant mixture from centrifugation was subsequently transferred to a separating funnel, which was securely clamped to a retort stand. The mixture in the separating funnel was left to separate for several hours, even overnight, to ensure sufficient time for complete separation. Following this, two distinct layers became clearly visible in the separating funnel. The upper layer contained the crude biodiesel, the main product, while the lower layer held the glycerol, a byproduct, as shown in Figure 3.7. The

glycerol was separated from the crude biodiesel and discarded as waste. The biodiesel remaining in the separating funnel underwent several washes with distilled water heated to 50 °C until the washed biodiesel became visibly clear. Following this, the cleansed biodiesel was moved from the separating funnel to a beaker for the drying process. A stirring bar was placed inside the beaker to aid the drying process, which was carried out using a temperature-controlled magnetic stirrer set at 80 °C. The drying process was crucial to eliminate any water molecules that could have been retained in the biodiesel produced. The acid value (AV) of the dried biodiesel underwent analysis through titration, employing the same procedure utilized to determine the acid value of WCO. The sole distinction lies in the replacement of WCO with the produced biodiesel in this instance. Equations (3.11) and (3.12) present the expressions employed to calculate the yield and acid value of the produced biodiesel, respectively.

$$\text{Biodiesel Yield (wt. \%)} = \frac{\text{Mass of dried biodiesel}}{\text{Mass of WCO}} \times 100 \quad (3.11)$$

$$\text{Acid Value, A. V (mgKOH/g)} = \frac{v \times 56.1 \times M}{m} \quad (3.12)$$

Where:

v = Value obtained from titration

m = Mass of dried biodiesel used

M = Concentration of KOH

56.1 = Molecular weight of KOH.

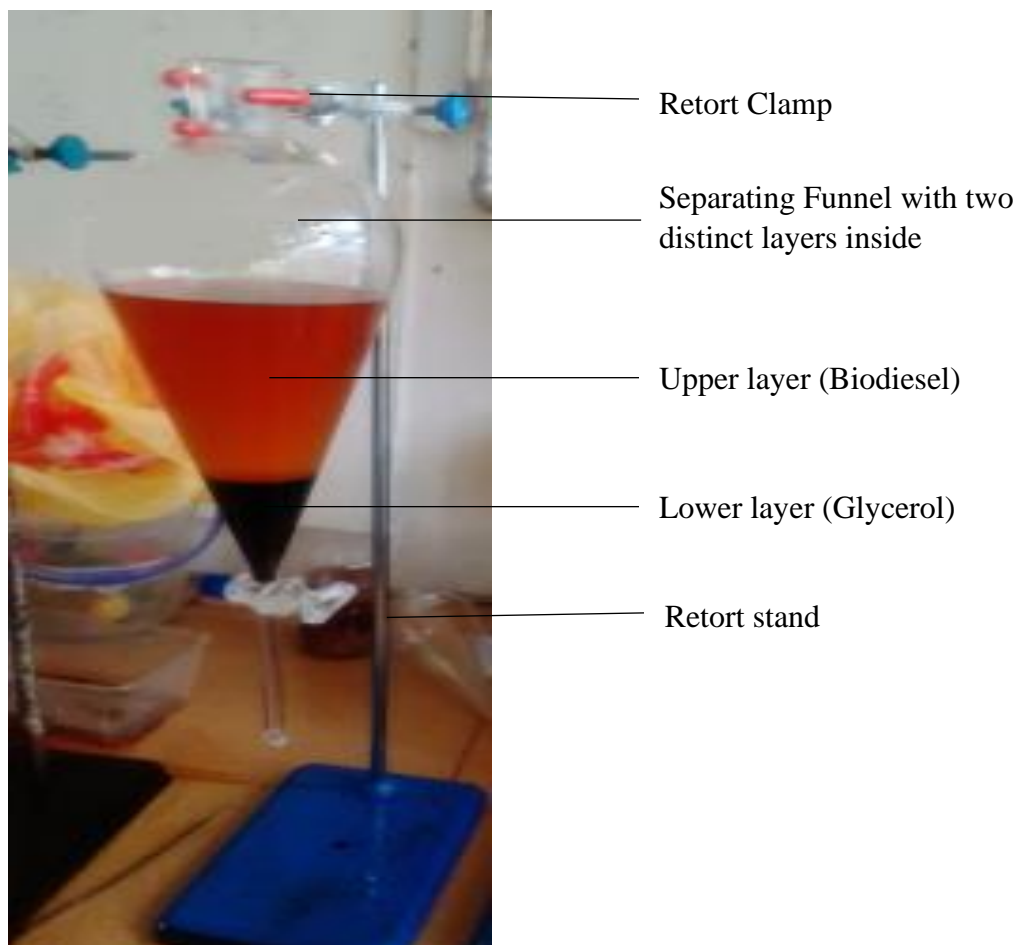


Figure 3.7: Separating funnel containing biodiesel and glycerol with distinct layers.

The expression in Equation (3.13) provides the conversion of free fatty acids (FFA) in the produced biodiesel.

$$\text{FFA (\%)} = \frac{AV_{\text{WCO}} - AV_{\text{Biodiesel}}}{AV_{\text{WCO}}} \times 100 \quad (3.13)$$

3.2.7 OPTIMIZATION OF THE PRODUCED BIODIESEL FROM WCO

The optimization of the one-pot conversion of high free fatty acid WCO was conducted using the Taguchi L9 technique, which involved 4 variables with 3 levels and 2 responses. The experimental design employed a 3-level, 4-factor Taguchi L9 design for the one-pot conversion of high free

fatty acid WCO. The variables considered as independent factors were temperature (in degrees Celsius), time (in minutes), catalyst loading (in weight percentage), and the methanol-to-oil ratio (in mole-to-mole ratio). The modeling aimed to optimize these factors, maximizing biodiesel yield and minimizing acid value (AV) through numerical optimization. The discovered optimal parameters were then applied in the laboratory to investigate the reusability of the bifunctional catalyst.

3.2.8 CHARACTERIZATION OF THE PRODUCED WCO BIODIESEL

The fuel properties of the biodiesel derived from WCO under optimal conditions were analyzed to assess its physicochemical characteristics. Adhering to the prescribed ASTM D6751 biodiesel standards, the biodiesel produced at the optimum condition underwent characterization for various properties such as peroxide value, density, moisture content, kinematic viscosity, acid value, iodine value, and others.

3.2.9 BIFUNCTIONAL CATALYST REUSABILITY STUDY

The capacity of the bi functional catalyst for reuse and the recovery rate after each consecutive run were investigated. The optimal reaction conditions, determined through the optimization design of the one-pot conversion of high free fatty acid WCO, were applied for multiple iterations of biodiesel production. These optimal conditions consisted of a methanol-to-oil molar ratio of 24:1, a 1% catalyst loading by weight, a reaction temperature of 65 °C, and a reaction time of 60 minutes. Following each consecutive run of biodiesel production under these optimal conditions, the catalyst was separated from the mixture through centrifugation. The catalyst underwent washing with an adequate amount of methanol, oven-dried at 180 °C until it was dry enough, and its weight was recorded before reuse in another round of biodiesel production. This procedure was repeated five times using 500 g of high free fatty acid WCO, 300 g, 250 g, 200 g, and 150 g, respectively, with the biodiesel yield decreasing after each successive run. In summary, the investigation into the reusability of the bifunctional catalyst showed that it could be utilized for a total of five cycles. Figures 3.8 to 3.10 illustrate the sequence of biodiesel reusability studies and the resulting yields.



Figure 3.8: Analysis on reusability studies.



Figure 3.9: Yields on reusability studies.



Figure 3.10: Yields of WCO produced biodiesel.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 PHYSIOCHEMICAL CHARACTERISTICS OF WCO

Table 4.1 presents the physicochemical attributes of waste cooking oil (WCO), which were assessed following the ASTM standard, as detailed in the preceding chapter.

Table 4.1: Physiochemical characteristics of WCO.

| Properties | Unit | Value |
|-------------------------------|-------------------|--------------|
| Density | Kg/m ³ | 833 |
| Viscosity at 40 °C | mPa.S | 12 |
| Saponification Value | mg KOH/g oil | 204.765 |
| Acid Value | mg KOH/g oil | 14.867 |
| Molecular Weight | g/mol | 886.265 |
| Free Fatty Acid Content (FFA) | mg KOH/g oil | 7.434 |
| Specific Gravity | - | 0.906 |
| Iodine Value | mg KOH/g oil | 62.562 |
| Moisture Content | % | 1 |
| Peroxide Value | mol/kg | 7 |

4.2 BIFUNCTIONAL CATALYST CHARACTERIZATION

4.2.1 UNUSED BIFUNCTIONAL CATALYST (UNBC) CHARACTERIZATION

4.2.1.1 COMPOSITION OF OXIDES IN THE UNBC USING XRF ANALYSIS

The oxides and their compositions in the UNBC were identified through the application of XRF analysis, as illustrated in Table 4.2. In the UNBC, CaO, a basic oxide, constituted the most significant portion, representing 63.397 % of the total composition. Other basic oxides found in the UNBC included K₂O (2.386 %), CuO (0.053 %), MnO (0.050 %), and BaO (0.019 %). There was no trace of magnesium oxide (MgO). Additionally, acid oxides, such as SO₃ (0.569%) and P₂O₅ (27.773 %), were detected in the UNBC. Two examples of amphoteric oxides, Fe₂O₃ (0.226 %) and Al₂O₃ (1.521 %), with both acidic and basic properties, were also present in the UNBC. Table 4.2 gives more details on the chemical oxides and their compositions.

Table 4.2: Percentage of Oxides in the UNBC.

| Oxides | (%) |
|--------------------------------|--------|
| SiO ₂ | 2.495 |
| V ₂ O ₅ | 0.014 |
| MnO | 0.050 |
| Fe ₂ O ₃ | 0.226 |
| CuO | 0.053 |
| CaO | 63.397 |
| SO ₃ | 0.569 |
| P ₂ O ₅ | 27.773 |
| ZnO | 0.005 |
| K ₂ O | 2.386 |
| BaO | 0.019 |
| Al ₂ O ₃ | 1.521 |
| TiO ₂ | 0.076 |
| SnO ₂ | 0.518 |

4.2.1.2 THE UNBC'S SURFACE CHARACTERISTICS

The surface area of a catalyst directly affects its activity. Discussions of the catalytic reaction processes revolve around the idea of active sites, which refers to a single surface atom or group of such atoms with unique structure and features where the catalyzed transformation takes place. The efficiency of the catalytic process is determined by the concentration of accessible active sites per unit volume of a reactor or per unit mass of a catalyst. The quantity of a catalyst's surface that is exposed impacts its overall activity since materials of a certain kind often include roughly equal numbers of active sites per unit surface area (Alaei et al. 2018). The primary factor influencing the reaction rate seems to be the quantity of active sites, despite the potential influence of various other parameters on reaction kinetics in a catalytic reactor. These additional factors encompass diffusion kinetics, adsorption-desorption kinetics, and equilibria in surface reactions. The Brunauer-Emmett-Teller (BET) surface area of the unused bifunctional catalyst was determined to be 569.182 m²/g, with the Barrett-Joyner-Halenda (BJH) adsorption surface area of the pores measuring 623.319 m²/g. The considerable surface area suggests the potential catalytic activity of the UNBC, as outlined by Alaei et al. (2018), who suggest that reactants exhibit enhanced interaction with the catalyst's active sites when there is a larger surface area. The pore volume and diameter were measured at 0.310 cm³/g and 2.141 nm, respectively. Additionally, the micropore surface area was calculated to be 601.965 m²/g, while the average micropore volume and width were determined to be 0.514 cm³/g and 6.399 nm, respectively. These findings suggest that the catalyst's active site is present and that it can help with diffusion issues because the catalyst's external surface has a high pore size and improved flow channels. This might hasten the process, making the mixture for the reaction one in which the drug and alcohol interact more quickly. Figure 4.1 displays a plot BET/BJH.

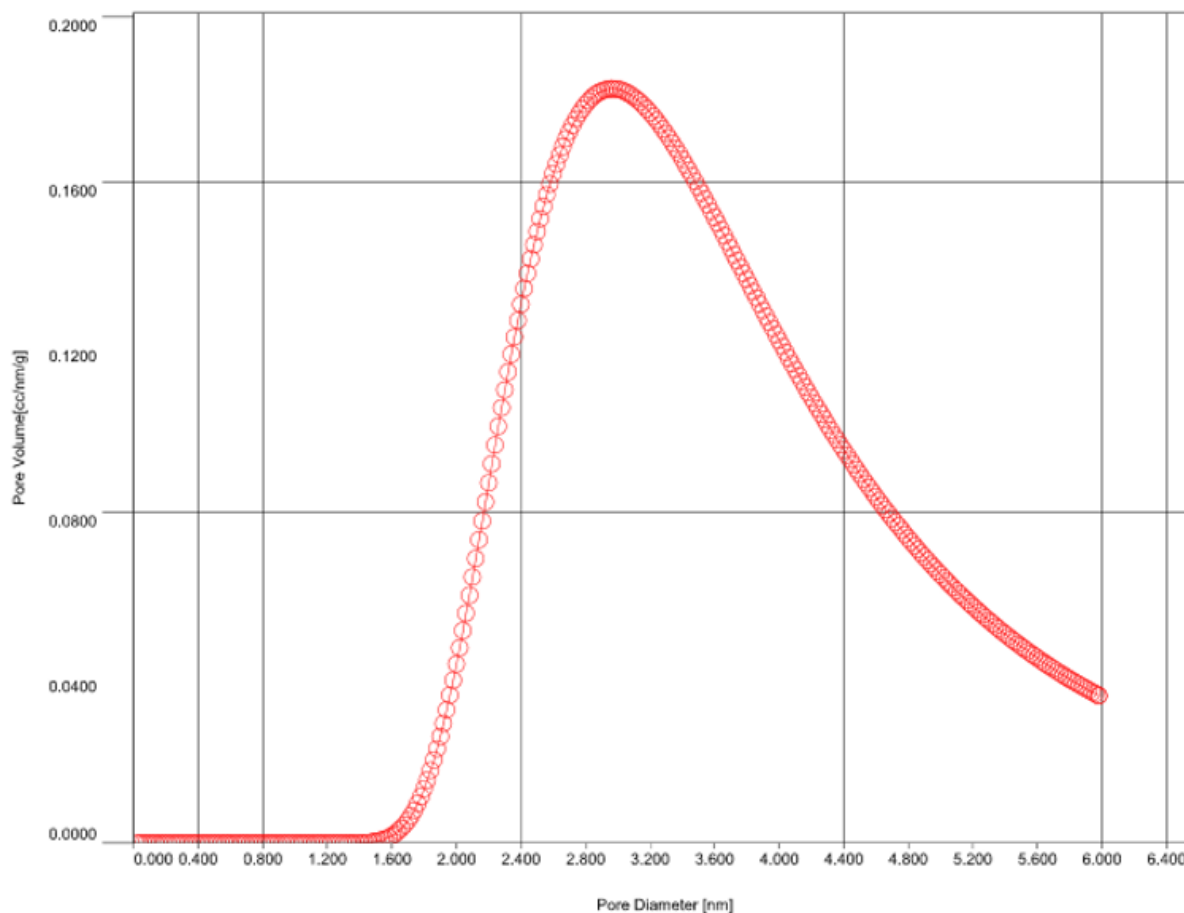


Figure 4.1: BET/BJH plot for the unused bifunctional catalyst.

4.2.1.3 THERMAL CHARACTERISTICS OF THE UNBC

Thermogravimetric analysis (TGA) and differential thermal analysis (DTGA) were employed to explore the thermal properties of the unused bifunctional catalyst when subjected to heat. The findings, presented in Figure 4.2, indicated three distinct phases in the TGA plot, each correlating with different weight reductions of the catalyst. The initial weight reduction period took place between 100 and 300 °C. Moisture must have been removed from the catalyst during this time. During the second stage, which lasted between 300 and 400 °C, more moisture was removed. About 83 % of the catalyst's weight was lost during this time. Beyond 600 °C, a minimum weight loss was noted. The weight is seen to be practically constant above 800 °C, and the catalyst at this point underwent thermal breakdown.

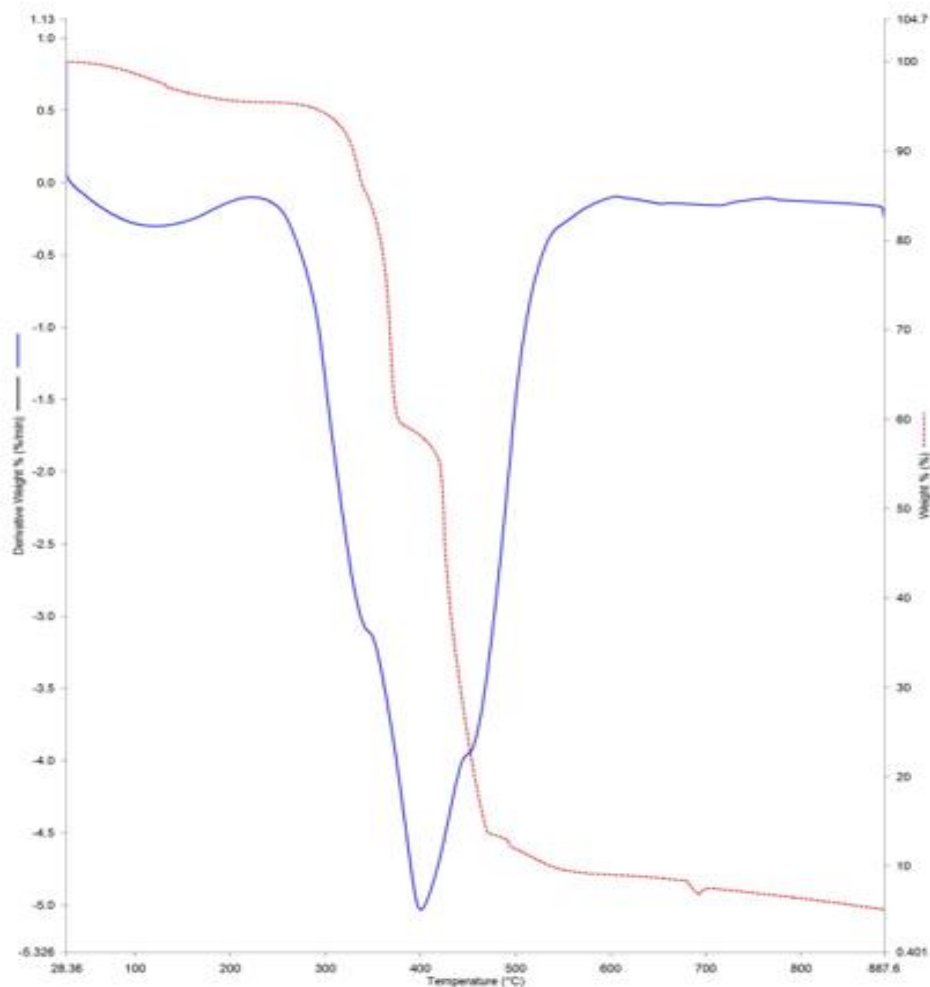
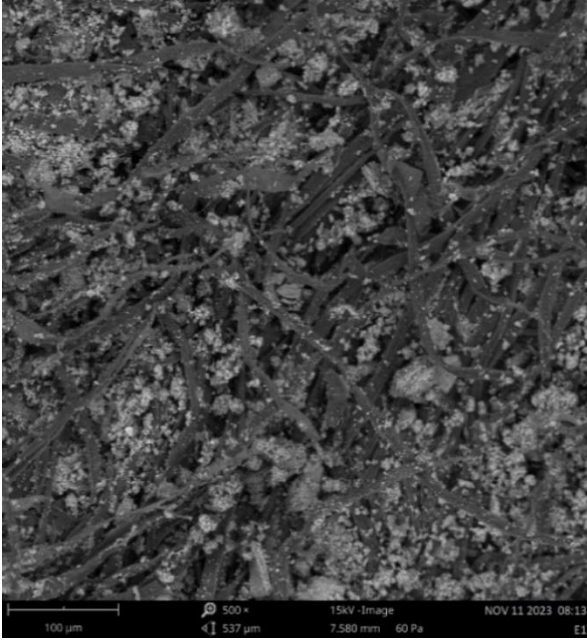


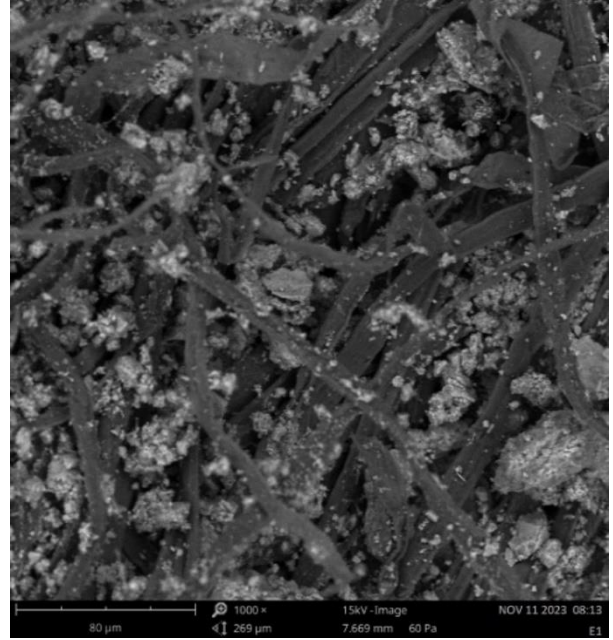
Figure 4.2: The Unused bifunctional catalyst’s TGA/DTGA plots.

4.2.1.4 SURFACE MORPHOLOGY OF THE UNBC

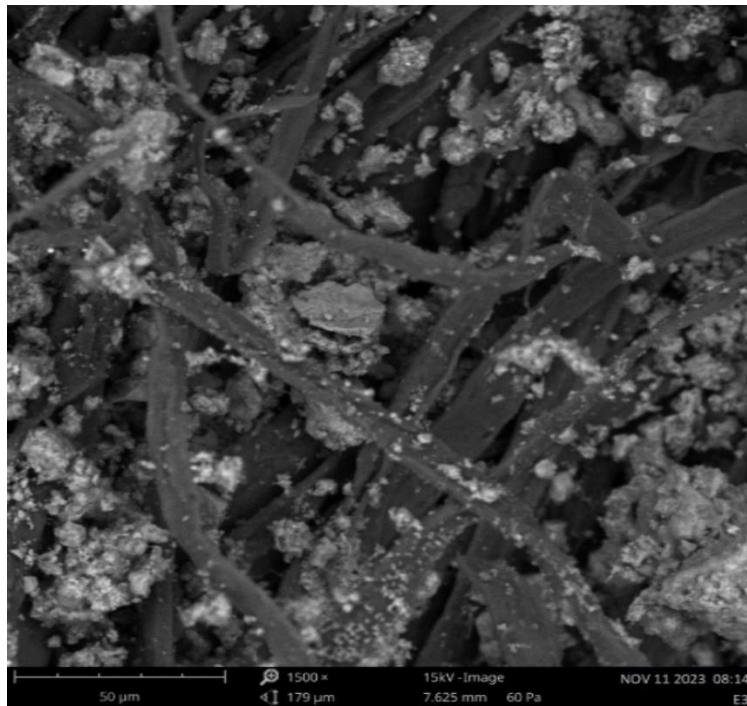
The structure of UNBC, produced from pig bones and pumpkin stalks, was analyzed through scanning electron microscopy (SEM) at various magnifications, as illustrated in Figure 4.3. As observed in the images of Figure 4.3, the catalyst appears to form strips with holes of various sizes. These strips exhibit clumps of aggregated mass not only attached to them but also to the pores.



(a) 500x



(b) 1000x



(c) 1500x

Figure 4.3: Scanning electron microscope (SEM) images of UNBC at magnifications of (a) 500x (b) 1000x and (c) 1500x

4.2.1.5 ANALYSIS OF THE CRYSTALLINE COMPOUNDS IN THE UNBC USING XRD

The X-ray diffraction (XRD) pattern displayed in Figure 4.4 was utilized to discern the crystalline compounds within the Unused Bifunctional Catalyst (UNBC) derived from pig bones and pumpkin stalks. The peaks were identified at 2θ angles in degrees Celsius. The identified peaks at 29.91° , 32.01° , 33.16° , and 40.01° signify the presence of Carbonatehydroxylapatite [$\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2$]. Additionally, Wollastonite (CaSiO_3) was detected at 42.17° and 51.49° , Quartz (SiO_2) at 49.68° , and Osumilite.

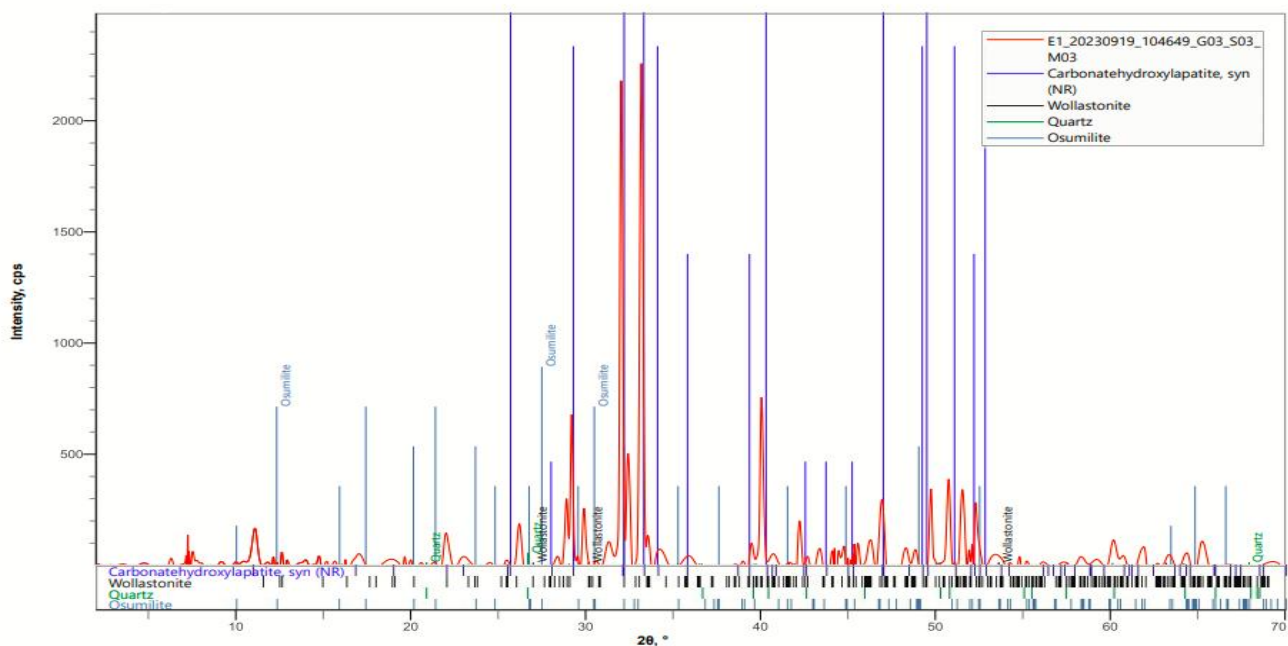


Figure 4.4: X-ray diffraction analysis for the UNBC

4.3 VARIATION ANALYSIS OF THE ONE-POT CONVERSION PROCESS

4.3.1 VARIANCE STATISTICAL ANALYSIS FOR THE ONE-POT CONVERSION PROCESS

The Taguchi L9 experimental design was utilized to introduce variations in the parameter sets necessary for the one-pot conversion of biodiesel from high free fatty acid WCO catalyzed by UNBC. Employing the experimental parameters outlined by Taguchi, as detailed in Table 4.3, the esterification and transesterification processes were conducted in triplicate. The outcomes of these

processes are presented in the table. Statistical analysis was applied to the biodiesel output and FFA conversion for the selected model. ANOVA was employed to construct a robust mathematical model. High sum of squares parameters was chosen for the model, and low sum of squares parameters were disregarded.

Table 4.3: Taguchi L9 orthogonal array-developed experimental design matrix.

| Run No. | FACTORS | | | | RESPONSES | |
|---------|------------------------------|---------------------------------|---------------------------|---------------------|-------------------------|--------------------------|
| | A: MeOH: Oil (mol/mol) | B: Cat. Loading (wt.%) | C: Temperature (°C) | D: Time (min) | WOME Yield (wt.%) | Acid Value (mg KOH/g) |
| 1 | 24:1 | 3 | 55 | 120 | 83.67 | 0.573 |
| 2 | 6:1 | 5 | 65 | 120 | 79.94 | 0.793 |
| 3 | 15:1 | 5 | 55 | 90 | 84.72 | 0.514 |
| 4 | 24:1 | 1 | 65 | 90 | 86.83 | 0.493 |
| 5 | 15:1 | 1 | 60 | 120 | 87.73 | 0.647 |
| 6 | 24:1 | 5 | 60 | 60 | 86.41 | 0.396 |
| 7 | 6:1 | 1 | 55 | 60 | 76.41 | 0.621 |
| 8 | 6:1 | 3 | 60 | 90 | 80.23 | 0.676 |
| 9 | 15:1 | 3 | 65 | 60 | 88.63 | 0.483 |

Table 4.4 displays the ANOVA results. Table 4.4a displays the results of the ANOVA conducted for biodiesel yield, while Table 4.4b exhibits the outcomes for acid value. The biodiesel yield model yielded an F-value of 252.76, with a corresponding p-value of <0.0001. For a model to be deemed significant, its p-value should be less than 0.05. To assess the relevance of each parameter, the p-value was used. The variance analysis in the table reveals that only two factors significantly affected biodiesel production yield. The most impactful factor on biodiesel yield was the methanol-to-oil molar ratio, evidenced by its sum of squares value of 114.55 and an F-value of 421.67, followed by reaction temperature with an F-value of 83.85. Examining the ANOVA results for

acid value in Table 4.4b, the model exhibited an F-value of 90.62 and a p-value <0.0004, emphasizing its significance. Similarly, only two parameters exerted a noteworthy influence on acid value, with the methanol-to-oil molar ratio emerging as the most influential.

Table 4.4a: The analysis of variance (ANOVA) results for the biodiesel yield model.

| Source | Sum of Squares | Df | Mean Square | F-value | p-value | |
|---------------------------|----------------|----|-------------|---------|----------|-------------|
| Model | 137.33 | 4 | 34.33 | 252.76 | < 0.0001 | Significant |
| A-MeOH: Oil Ratio | 114.55 | 2 | 57.27 | 421.67 | < 0.0001 | |
| C-Reaction Temperature | 22.78 | 2 | 11.39 | 83.85 | 0.0005 | |
| Residual | 0.5433 | 4 | 0.1358 | | | |
| Cor. Total | 137.87 | 8 | | | | |

Table 4.4b: The analysis of variance (ANOVA) results for the acid value model.

| Source | Sum of Squares | Df | Mean Square | F-value | p-value | |
|----------------------|----------------|----|-------------|---------|---------|-------------|
| Model | 0.1147 | 4 | 0.0287 | 90.62 | 0.0004 | Significant |
| A-MeOH: Oil Ratio | 0.0696 | 2 | 0.0348 | 110.01 | 0.0003 | |
| D-Reaction Time | 0.0451 | 2 | 0.0225 | 71.23 | 0.0007 | |
| Residual | 0.0013 | 4 | 0.0003 | | | |
| Cor. Total | 0.1159 | 8 | | | | |

4.3.2 FIT STATISTICS

The "goodness of fit" of a statistical model pertains to its ability to accurately predict a given set of observations. Typically, the disparity between the actual values and those predicted by the model in question is assessed using metrics that measure the goodness of fit. Fit statistics on the responses were run in order to further support the model's fitness. Table 4.5 displays the outcomes of both models' fit statistics. For the two variables, biodiesel yield and acid value, the coefficients of determination (R^2) were, respectively, 0.9961 and 0.9891. The ideal value is a number that is very close to unity. Both models predicted R^2 and adjusted R^2 values were reasonably consistent, with discrepancies of less than 0.2 between both. The models had adequate precisions of 42.5920 and 28.6898, both of which were higher than 4. It is possible to navigate the design space using the values acquired for both models, which provide a sufficient signal.

Table 4.5: Statistics of model fit for the one-pot high free fatty acid WCO conversion.

| Source | Value | |
|--------------------|-----------------|------------|
| | Biodiesel Yield | Acid Value |
| R^2 | 0.9961 | 0.9891 |
| Adjusted R^2 | 0.9921 | 0.9782 |
| Predicted R^2 | 0.9801 | 0.9447 |
| Adequate Precision | 42.5920 | 28.6898 |
| Std. Dev. | 0.3685 | 0.0178 |
| Mean | 83.84 | 0.5773 |
| C.V. % | 0.4396 | 3.08 |

4.3.3 COMPARISON BETWEEN PREDICTED AND ACTUAL VALUES OF WCO PRODUCED BIODIESEL YIELD AND ACID VALUE

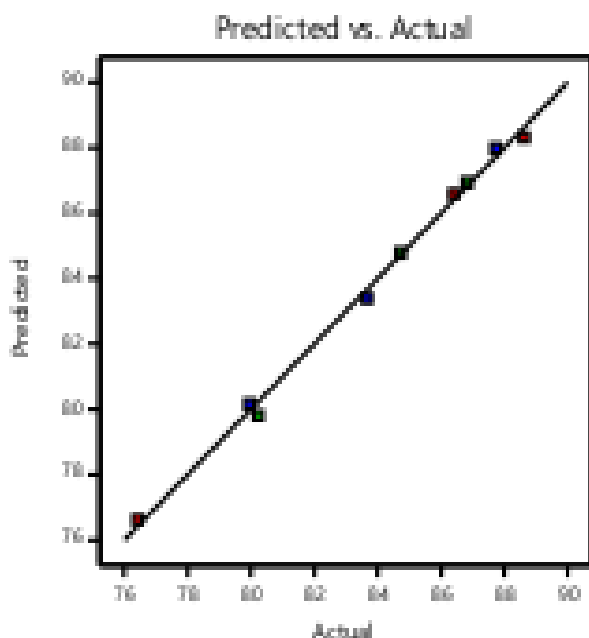
Responses with a 95% confidence level were exclusively considered in formulating the mathematical model for the response. The model for the responses was then expressed in terms of coded factors, as outlined in Equation (4.1). Equation (4.1a) illustrates the model for biodiesel yield, whereas Equation (4.1b) depicts the model for acid value.

$$\text{Biodiesel Yield (wt.\%)} = 83.84 - 4.98A[1] + 3.19A[2] - 2.24C[1] + 0.9489C[2] \quad (4.1a)$$

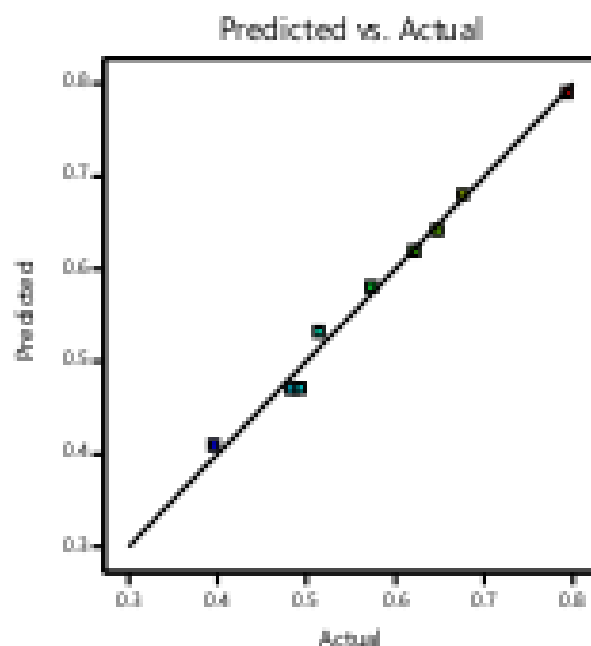
$$\text{Acid Value} = 0.5773 + 0.1193A[1] - 0.0293A[2] - 0.0773D[1] - 0.0163D[2] \quad (4.1b)$$

(mg KOH/g)

The letters A, B, C, and D correspond to the methanol-to-oil molar ratio, catalyst loading, reaction temperature, and reaction time, respectively. [1] and [2] stand for the level of each parameter in the model. The model can be used to forecast the responses within a set of parameters. In the one-pot conversion of biodiesel from high free fatty acid WCO, the expected biodiesel yield and acid values are graphed in comparison to the actual values, as depicted in Figure 4.5. The proximity of the data points to the diagonal line in both plots suggests a high degree of similarity between the projected and actual responses, affirming the model's capability to make precise predictions for biodiesel yield and acid value.



(a) WCO produced biodiesel yield



(b) Acid value of WCO produced biodiesel

Figure 4.5: Predicted vs. Actual values for WCO biodiesel yield (a) and Acid value (b).

4.4 THE EFFECT OF PROCESS PARAMETERS ON BIODIESEL YIELD AND FFA CONVERSION

Investigations were also conducted to determine how the significant parameters affected the responses. The FFA conversion in the oil is notably influenced by the methanol-to-oil molar ratio and reaction time, as observed earlier. Additionally, biodiesel production is significantly impacted by both the methanol-to-oil molar ratio and the reaction temperature.

4.4.1 EFFECT OF METHANOL-TO-OIL MOLAR RATIO

The crucial process parameter determining the one-pot conversion of high free fatty acid waste cooking oil (WCO) is the methanol-to-oil molar ratio. Typically, 3 moles of methanol are needed to convert 1 mole of triglyceride into 1 mole of WCO biodiesel yield. However, due to the

reversibility of the reaction, additional methanol is required to favor the forward process. The methanol-to-oil molar ratio significantly influences the resulting biodiesel yield, as illustrated in Figure 4.6. To assess its impact, other parameters were kept constant: catalyst loading at 1 weight percent, reaction temperature at 55 °C, and time at 60 minutes. Figure 4.6 depicts the changes in biodiesel yield across various methanol-to-oil molar ratios. Elevating the ratio from 6:1 to 15:1 corresponds to an increased biodiesel yield. Nevertheless, exceeding a ratio of 15:1 results in a subsequent decline in biodiesel yield. Thus, the figure suggests that a methanol-to-oil ratio below 15:1 enhances biodiesel yield, while a ratio beyond that threshold diminishes it. As suggested by Yan et al. (2016) and Essamlali et al. (2019), the decrease in biodiesel yield beyond a methanol-to-oil ratio of 15:1 could be attributed to an excessive amount of methanol, potentially leading to catalyst weakening or deactivation. It's crucial to highlight that an overabundance of methanol usage has the potential to decrease conversion, consequently causing the equilibrium to shift in the opposite direction (Corro et al. 2016).

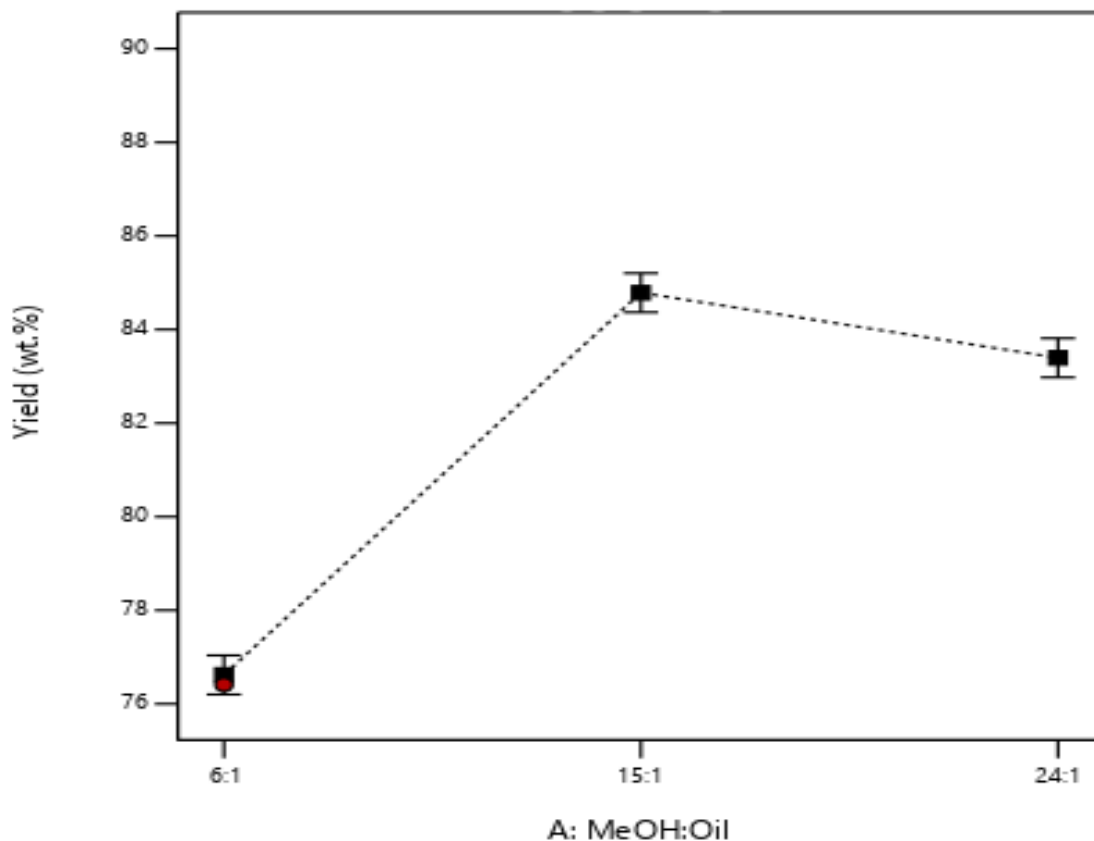


Figure 4.6: Effect of methanol-to-oil molar ratio on WCO produced biodiesel yield.

4.4.2 THE EFFECT OF REACTION TEMPERATURE

The temperature of heterogeneous catalyzed processes plays a pivotal role in biodiesel production. Elevated temperatures are frequently essential for ensuring the completion of most heterogeneous catalyzed reactions (Mardhiah et al. 2017; Dantas et al. 2017). However, high temperatures can lead to reactant loss and product deterioration. Figure 4.7 demonstrates the impact of temperature on biodiesel production yield. The plot suggests that an increase in temperature from 55 °C to 60 °C corresponds to an increase in biodiesel yields. Moreover, as the temperature rises from 60 °C to 65 °C, the biodiesel yield remains constant, maintaining the optimal yield achieved between 60 °C and 65 °C. In essence, a rise in the initial reaction temperature leads to an increased biodiesel yield, but beyond a certain threshold, further temperature increases do not affect the yield.

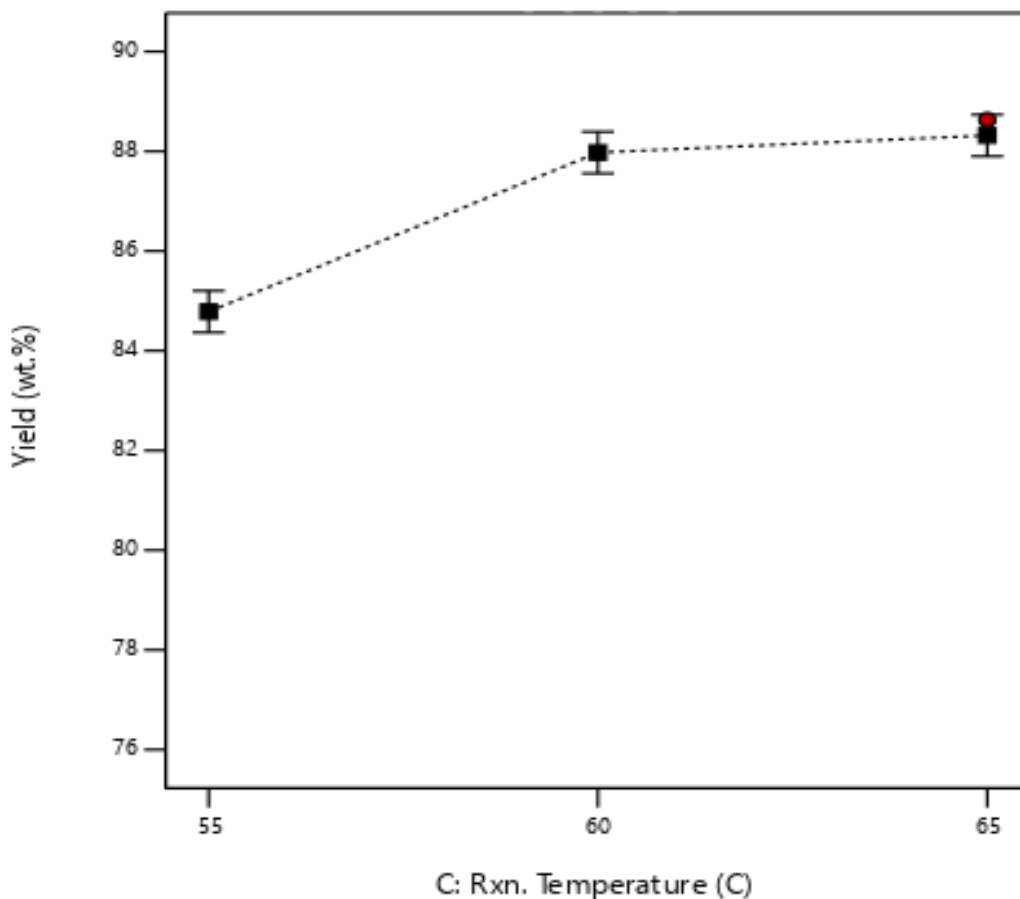


Figure 4.7: Effect of reaction temperature on the yield of WCO produced biodiesel.

4.4.3 EFFECT OF REACTION TIME

The reactants must be given sufficient time to interact for maximal biodiesel production to be achieved. In Figure 4.8, the influence of reaction time on the acid value of the produced biodiesel is depicted. Under constant conditions of a 15:1 methanol-to-oil ratio, 1% catalyst loading, and a temperature of 55 °C, the plot reveals a reciprocal correlation between time and the acid value of biodiesel. The data indicates that with an increase in reaction time, the acid value decreases, and conversely, the acid value started declining as the reaction time extended from 60 to 120 minutes.

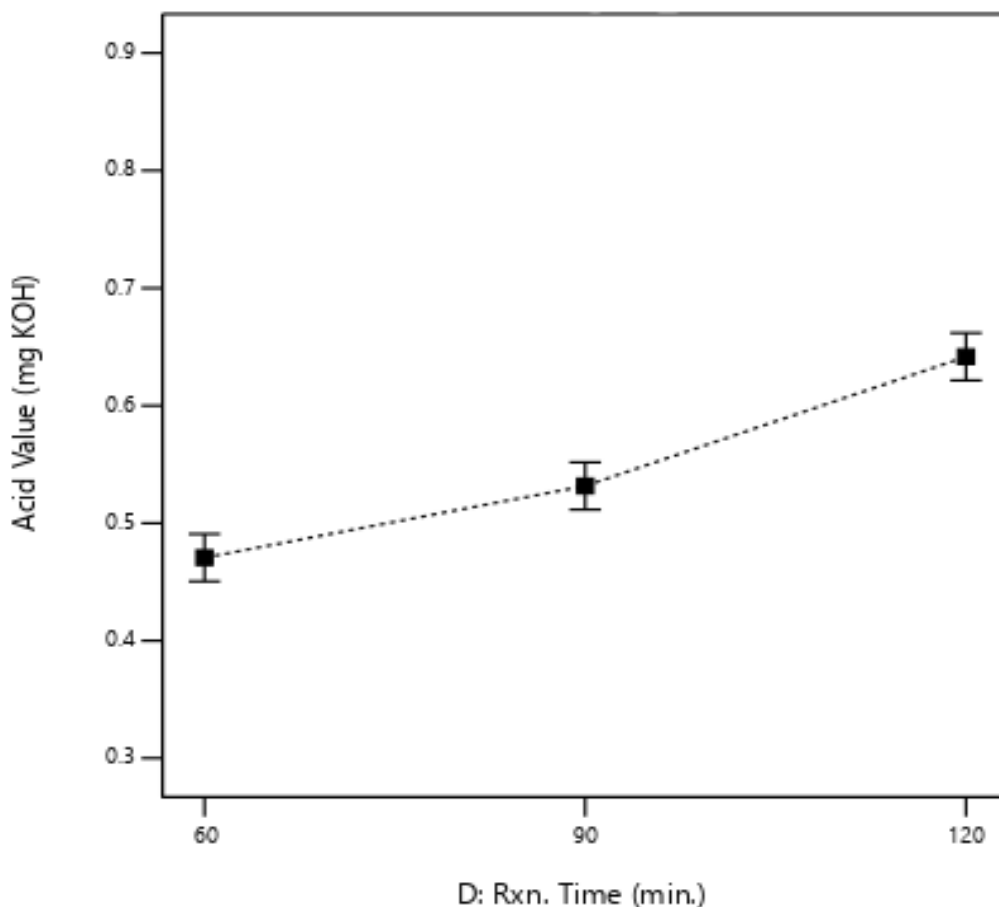


Figure 4.8: Effect of time on the acid value of biodiesel.

4.4.4 EFFECT OF METHANOL-TO-OIL RATIO ON THE ACID VALUE OF WCO PRODUCED BIODIESEL

The design also took into account the influence of the methanol-to-oil ratio on the acid value of biodiesel. In biodiesel production, the methanol-to-oil ratio significantly affects the acid value, a crucial parameter as it serves as an indicator of the concentration of free fatty acids (FFA) in biodiesel. Lower acid values signify a lower FFA concentration, contributing to enhanced stability, performance, and overall higher quality of biodiesel. Determining the appropriate ratio is crucial for efficient conversion and reduction of free fatty acids (FFA), as the methanol-to-oil ratio directly impacts the transesterification process. This chemical reaction converts triglycerides in waste cooking oil (WCO) into biodiesel. Biodiesel producers can optimize their processes by comprehending the correlation between the methanol-to-oil ratio and the acid value. By selecting the right ratio, they can diminish FFAs and improve the overall quality of the end product. In Figure 4.9, the impact of the methanol-to-oil molar ratio on the acid value of the produced biodiesel is demonstrated. The investigation was conducted under specific conditions, including a 1% catalyst loading, a reaction temperature of 55 °C, and a reaction time of 60 minutes. The plot illustrates an inverse relationship between the methanol-to-oil molar ratio and the acid value of biodiesel. The data indicates that as the methanol-to-oil ratio increases, the acid value of the biodiesel decreases. The highest acid value was observed at a methanol-to-oil ratio of 6:1, but further increments beyond 6:1 led to a decrease.

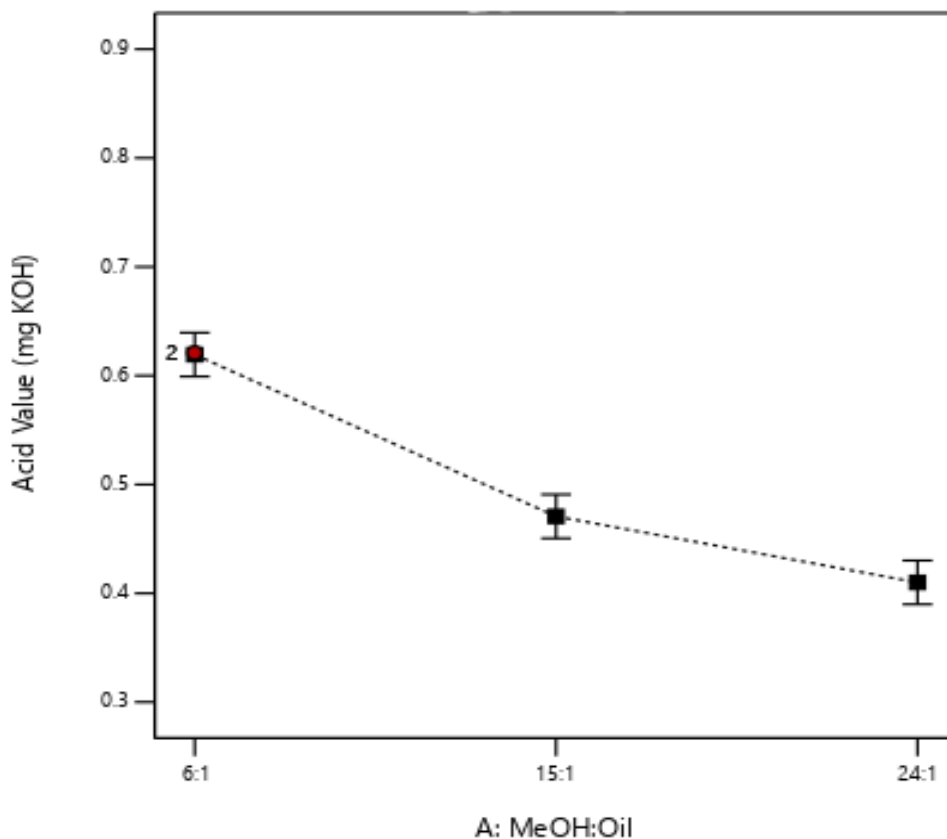


Figure 4.9: Effect of methanol to oil ratio on the acid value of biodiesel.

4.5 OPTIMIZATION AND VALIDATION OF MODEL

Optimizing the one-pot conversion of biodiesel from high free fatty acid WCO was crucial to identify the optimal parameter values for maximizing both WCO biodiesel yield and FFA conversion. Following numerical optimization, the parameters were set within their defined ranges. Biodiesel yield was influenced by the methanol-to-oil molar ratio and reaction temperature, whereas FFA conversion was impacted by the methanol-to-oil ratio and reaction time. In this study, the optimal parameters were identified as a methanol-to-oil molar ratio of 24:1, a catalyst loading of 1 weight percent, a reaction temperature of 65 °C, and a reaction time of 60 minutes. Under these conditions, the biodiesel yield was 86.929 wt.%, and the acid value was 0.410 mg KOH/g. To validate these estimations, a practical test of the one-pot conversion reaction using 50 g of WCO at the specified conditions was carried out, resulting in a biodiesel yield of 84.297 wt.%

and an acid value of 0.405 mg KOH/g. The performed test at the model's optimum conditions revealed a disparity of +2.632 wt.% in biodiesel yield and a difference of 0.005 mg KOH/g in acid value compared to the model's projections.

4.6 CATALYST REUSABILITY AND RECOVERY IMPACT ON WCO PRODUCED BIODIESEL

In order to evaluate the economic potential for commercial biodiesel production and examine the reusability of the bifunctional catalyst, a study on its reusability was conducted. The main objective of this reusability examination was to determine how it influenced the yield and acid value of biodiesel generated from high free fatty acid waste cooking oil (WCO). Six test runs were conducted, following the optimal conditions determined during the optimization process. In the first five runs, significant yields and moderate acid values were obtained. However, the sixth run resulted in an insignificant yield and a considerably higher acid value compared to the other runs. The catalyst was recovered and reused without additional treatment after each run. During the initial operation with 500 g of high free fatty acid WCO, a biodiesel yield of 88.26 wt.% and an acid value of 0.435 mg KOH/g were obtained. In the subsequent trial with 300 g of high free fatty acid WCO, the biodiesel yield was 73.58 wt.% with an acid value of 0.458 mg KOH/g. In the third iteration involving 250 g of high free fatty acid WCO, there was a 67.08 wt.% decrease in biodiesel yield, and the acid value increased by 0.684 mg KOH/g. This pattern of increasing acid value and decreasing biodiesel yield persisted in the fourth and fifth runs. This trend remained consistent throughout these runs. However, in the sixth and final run, no significant biodiesel yield was obtained, and the acid value was considerably higher compared to the acid values of the other runs. The lack of significance in the biodiesel yield during the sixth run can be attributed to the elevated acid value. In conclusion, the bifunctional catalyst demonstrates effective reusability in up to five consecutive runs, offering the potential for substantial yield and, consequently, a reduction in catalyst production costs. Table 4.6 presents the findings from the reusability study, while Figure 4.10 illustrates the impact of reusability on biodiesel yield and acid value.

Table 4.6: Obtained results from reusability study.

| RUNS | Weight of Oil (g) | Yield (wt.%) | Acid Value (mg KOH/g) |
|-------------|------------------------------|-------------------------|----------------------------------|
| 1 | 500 | 88.26 | 0.435 |
| 2 | 300 | 73.58 | 0.518 |
| 3 | 250 | 67.08 | 0.684 |
| 4 | 200 | 55.55 | 0.710 |
| 5 | 150 | 44.63 | 0.798 |
| 6 | 100 | 0 | 8.514 |

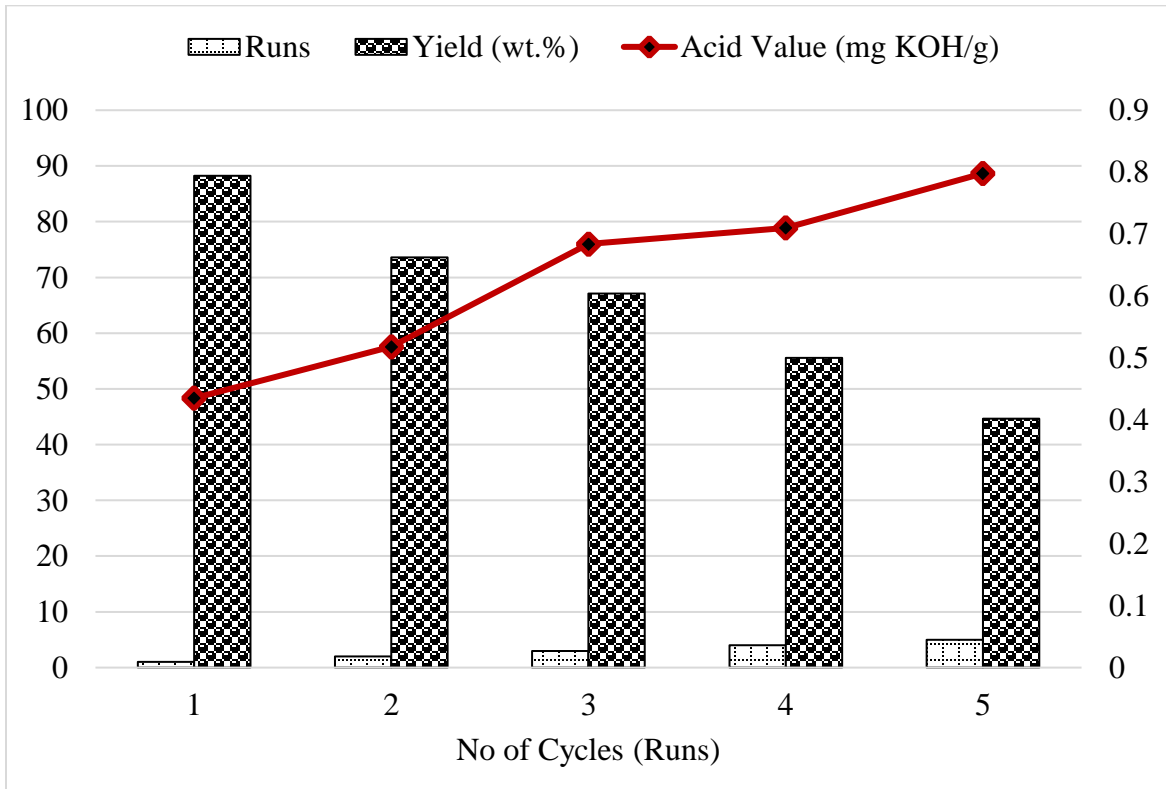


Figure 4.10: Effect of reusability study on biodiesel yield and acid value.

4.7 CHARACTERIZATION OF THE WCO PRODUCED BIODIESEL

Table 4.7 presents the physicochemical attributes of biodiesel generated from waste cooking oil (WCO) through the optimal conditions of a one-pot conversion reaction. The analysis of the biodiesel produced from high free fatty acid WCO under these optimal conditions involved the examination of various characteristics, including density, viscosity, acid value, moisture content, and specific gravity, using ASTM standard test procedures.

Table 4.7: Physiochemical properties of high free fatty acid WCO produced biodiesel at optimum conditions.

| Properties | Unit | Value |
|-------------------------------|-------------------|--------|
| Density | Kg/m ³ | 802 |
| Acid Value | mg KOH/g oil | 0.435 |
| Free Fatty Acid Content (FFA) | mg KOH/g oil | 0.2175 |
| Saponification Value | mg KOH/g oil | 197.38 |
| Viscosity at 40 °C | mPa.S | 14.2 |
| Specific Gravity | - | 0.888 |
| Iodine Value | mg KOH/g oil | 55.16 |
| Moisture Content | % | 0.062 |
| Peroxide Value | mol/kg | 4.838 |

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

In this research, a bifunctional catalyst was created by synthesizing it from heterogeneous solid wastes like pig bones and pumpkin stalks. This catalyst was then utilized in the one-pot conversion process of high free fatty acid waste cooking oil (WCO). The synthesized bifunctional catalyst comprises substantial concentrations of both basic and acidic oxides, featuring a BET surface area of 569.182 m²/g, a pore volume of 0.310 cm³/g, and a pore diameter of 2.141 nm. Utilizing the Taguchi L9 approach, the optimization of the one-pot conversion process for high free fatty acid WCO was achieved, resulting in a biodiesel yield of 84.291 wt.% and an acid value of 0.405 mg KOH/g under optimal conditions. These conditions included a methanol-to-oil molar ratio of 24:1, a catalyst loading of 1 wt.%, a reaction temperature of 65 °C, and a reaction time of 60 minutes. As per the findings from the ANOVA design, three crucial factors impacted the process: the methanol-to-oil molar ratio, reaction temperature, and reaction time. The economically favorable nature of the synthesized bifunctional catalyst stems from its efficient catalytic activity, leading to a substantial yield of biodiesel from waste cooking oil (WCO) across five consecutive runs with the same catalyst. The biodiesel's physicochemical characteristics, produced using the bifunctional catalyst, underwent analysis in accordance with ASTM D6751 and EN standards. Drawing insights from the reusability study outcomes presented in Table 4.6 and its influence on both WCO biodiesel yield and acid value, depicted in Figure 4.10, it can be deduced that the bifunctional catalyst is cost-efficient. This suggests its potential to contribute to lowering the overall expenses of biodiesel production, enhancing its affordability for commercial applications.

5.2 RECOMMENDATION

To enhance comprehension of this study, which involves the one-pot conversion of high free fatty acid waste cooking oil using a bifunctional catalyst derived from pig bones and pumpkin stalks and optimization via the Taguchi approach, it is essential to explore the following topics:

1. Further research work should be carried out on the use of pig bones and pumpkin stalks for bifunctional catalyst synthesis and comparison studies.
2. Investigate the kinetic effects of the reaction.
3. Conduct comparative studies on the use of low FFA feedstock for one-pot conversion transesterification processes using a bifunctional catalyst.
4. Examine the impact of the synthesized catalyst's exposure to the atmosphere, as well as particle size.
5. Research the effects of calcination and carbonization temperatures on the catalyst over time.

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