MICROWAVE AIDED PRODUCTION OF BIODIESEL FROM NEEM OILUSING A BIFUNCTIONAL CATALYST DERIVED FROM COW BONES AN RICE BRAN

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FACULTY OF ENGINEERING

UNIVERSITY OF BENIN

BENIN CITY

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A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMIXAL ENGINEERING, FACULTY OF ENGINEERING, UNIVERSITY OF BENIN, BENIN SITTY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR DEGREE IN CHEMICAL ENGINEERING (B.ENG)

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CERTIFICATION

This is to certify that this project research work was performed and completed by **MAUREEN OMOKHEKPE ESIEMOKHAI** of the Department of Chemical Engineering at the University of Benin, Benin City, Edo State. Nigeria, under the supervision of PROF. C.E. AKHABUE.

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DEDICATION

This research is dedicated to the Almighty God for his unending mercies, grace and strength bestowed upon me.

To my parents – Mr and Mrs Sylvester Emobotsemhe Esiemokhai for their care, love and unwavering support that has been my bedrock through my journey in the University.

This work is also dedicated to my late brother, Ambrose Esiemokhai, your absence has impacted me in ways beyond imagination, and you've created a fighter.

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ABSTRACT

This study explored the optimization of the microwave aided biodiesel production from neem oil with a bio-waste catalyst derived from cow bones and rice bran using central composite design, an experiment analysis on response surface model.

The bio-waste catalyst was synthesized by the carbonization and sulphonation of rice bran to produce an acid precursor, while cow bones was calcined and treated with KOH to create the basic precursor. Both precursors were then impregnated using the wet-impregnation method. Also, a model was developed to simulate the process and examine the interactive effect of process input variables on neem oil biodiesel yield using the central composite approach. These inputs generated about 50 runs to be carried out with the catalyst using methanol under optimal conditions.

In this study, we aimed to optimize biodiesel production from neem oil using a microwave-assisted process with a bifunctional heterogeneous catalyst synthesized from cow bones and rice bran. Oil characterization was carried out according to the ASTM standards, the catalyst failed to facilitate the transesterification reaction resulting in no biodiesel formation. Biodiesel production was carried out using sodium hydroxide which proved the viability of the oil and this outcome underscores the critical importance of proper catalyst synthesis and activation in biodiesel production. Additionally, the presence of impurities or moisture during catalyst preparation could have led to deactivation, further inhibiting the reaction. Fresh catalyst samples have been impregnated and are awaiting analysis results.

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NOMENCLATURE

AV- Acid Value

FFA- Free Fatty Acid

FAME- Fatty Acid Methyl Ester

NaOH- Sodium Hydroxide

KOH-Potassium Hydroxide

HCL-Hydrogen Chloride

H_2SO_4- Sulphuric Acid

FTIR- Fourier Transform Infrared Spectroscopy

SEM- Scanning Electron Microscopy

BET- Brunauer-Emmett-Teller

XRD- X-ray Diffraction

XRF- X-ray Fluorescence

GC/MS- Gas Chromatography- Mass Spectrometry

MC- Moisture Content

MW- Molecular Weight

S.G- Specific Gravity

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Fossil fuels have led to significant adverse effects in ecological degradation, environmental pollution and global warming due to prolonged utilization in energy generation, combustion processes and transportation (O. E. Samuel, 2021). Fuel scarcity, especially gasoline, remains a persistent issue in Nigeria, a nation characterized by frequent shortages in recent decades. Currently, fossil fuels are the nation's predominant energy source and various factors contribute to the depletion of crude oil reserves which has led to escalating costs for its products (U. E. Samuel et al., 2023). This problem can easily be solved by expanding the research on the use of biomass in solving energy consumption.

Biomass refers to materials produced from plants and animals which can easily be converted to Biofuels which provides us with biodiesel and bioethanol. Biodiesel is a renewable and biodegradable fuel derived from natural sources such as vegetable oils, animal fats, or recycled cooking oils (Pahl et al., 2005). It serves as a viable substitute for conventional diesel, applicable in both engines and heating systems. Biodiesel is synthesized through the chemical process of transesterification, whereby oils or fats react with alcohol to form esters; the primary constituents of biodiesel. This biofuel possesses properties similar to traditional diesel, including comparable energy content, viscosity, and flash point. However, biodiesel has the added advantage of cleaner combustion, producing fewer emissions than petroleum-based diesel (Gerhard, 2016). Consequently, biodiesel is an appealing alternative, particularly in contexts where reducing emissions is a priority. While numerous studies examine esterification reactions in biodiesel production, this research specifically investigates

transesterification using bio-waste catalyst in converting the Neem oil to fatty acid methyl esters (FAME).

High free fatty acid (FFA) content in feedstock can lead to undesirable saponification, increasing fuel viscosity, emulsification, and byproduct formation, which complicates separation. To enhance biodiesel yield, a two-step catalytic process is often employed. The first step, esterification, involves acid-catalysed FFA conversion to esters, reducing FFA content below 1%. The second step, transesterification, uses an alkali catalyst to convert triglycerides into fatty acid methyl esters (FAME) and glycerol. This method improves biodiesel production from high-FFA oils but requires extensive purification and is cost-intensive due to catalyst loss and acid removal (Otera, 1993).

Transesterification plays an important role in making biodiesel and other chemical products, as it helps to create new esters and alcohols. A key aspect of this study is the use of solid (heterogeneous) catalysts, which offer practical benefits over liquid (homogeneous) catalysts like easier separation from the reaction mix, greater stability, and better control over product formation. This research uses two types of solid catalysts: cow bones (calcium) and rice bran (cellulose).

Heterogeneous catalysts offer a more efficient alternative, enabling simultaneous esterification and transesterification in a single step. These bi-functional catalysts, possessing both acidic and basic sites, enhance process efficiency while reducing wastewater and allowing catalyst recovery and reuse, lowering production costs.

Microwave-assisted transesterification further optimizes biodiesel synthesis by accelerating reaction rates, reducing energy consumption, and increasing yields. Microwaves provide rapid, uniform heating, making the process faster and more efficient than conventional

methods. This technique enhances biodiesel production in a cost-effective and environmentally friendly manner.

1.2 PROBLEM STATEMENT

Nigeria faces significant challenges in energy security, environmental sustainability, and economic development due to its heavy reliance on imported fossil fuels. Biodiesel production from locally available feedstock, such as *neem oil*, offers a viable solution to these issues. This study explores the transesterification of neem oil with methanol using calcined cow bones as a sustainable, low-cost catalyst to improve biodiesel production efficiency. By investigating the kinetics of this process, I aim to improve the efficiency and viability of biodiesel production promoting Neem oil as a sustainable and locally available feedstock, a cost effective solution that can create economic opportunities for local farmers and entrepreneurs.

The cost of catalysts significantly impacts the industrial production of biodiesel. Heterogeneous catalysis has replaced homogeneous catalysts in recent years due to easier separation, reduced purification steps, and lower environmental impact. However, issues like catalyst leaching in harsh conditions persist, while enzymatic catalysts, though eco-friendly, remain costly and slow. Bio-based bi-functional catalysts show promise but require further study to optimize synthesis and reaction kinetics. This research focuses on addressing feedstock challenges and improving catalyst reusability for efficient biodiesel production.

Successful implementation of this process can contribute to energy security by reducing reliance on imported petroleum products, enhancing environmental sustainability through reduced greenhouse gas emissions, and stimulating economic development by creating opportunities for local farmers and entrepreneurs. Additionally, utilizing neem oil as a

biodiesel feedstock can address energy access challenges in remote areas through decentralized biodiesel production facilities.

1.3 AIMS & OBJECTIVES

The aim of this study is to optimize the the process of biodiesel production using microwave aided transesterification process from Neem oil and compare the properties of biodiesel produced from the esterified oil using cow bones and rice bran as catalyst. The specific objectives of the research work are;

I. Preparation and characterization of bio-waste catalysts from cow bones and rice bran.
II. Characterization of Neem Oil.
III. Production and Characterization of biodiesel from neem oil using bio-waste catalysts at optimum conditions.
IV. To optimize microwave-assisted biodiesel production from neem oil using a bio-waste catalyst through the response surface methodology.
V. Evaluation on the effectiveness of using cow bones as a catalyst and its reusability for the transesterification process in large scale production.
VI. This study also gives a comparative evaluation of the catalysed esterified FAME product of neem oil and methanol, using cow bones and rice bran, comparing the effects of the process variables.

1.4 SCOPE OF STUDY

The scope of this research are as follows;

a) Collection of cow bones from a local abattoir.
b) Collection of rice bran from a local farm mill.
c) Pretreatment of materials.

d) Characterization of neem oil.

e) Characterization of used and unused bi-waste catalyst.

f) Optimization of the transesterification process to yield biodiesel.

g) Efficient time management using a microwave-assisted technique.

h) Characterization of biodiesel production.

1.5 RELEVANCE OF STUDY

This study aims to identify key factors and optimize strategies for enhancing biodiesel production using neem oil through simultaneous esterification and transesterification. By fine-tuning variables such as catalyst concentration, reaction time, temperature, methanol-to-oil ratio, high-yield biodiesel with superior purity and methyl ester content can be achieved.

The rising demand is increasingly crucial hence biodiesel presents a viable alternative fuel that is technically feasible, economically competitive, and environmentally sustainable. Developing efficient production methods for biodiesel can contribute to cleaner energy solutions and reduce reliance on fossil fuels.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Human advancement is deeply intertwined with energy. Early civilizations relied on manual labour and biomass, such as wood and animal waste, for heat and light. The discovery of fire marked a turning point, allowing humans to harness energy more efficiently and develop technologies. Years in the future, industrial revolution in the energy landscape has transformed as fossil fuels (coal, oil, and natural gas) became the cornerstone of economic growth. These energy sources powered industries, transportation, and modern societies, leading to unprecedented technological progress.

However, the rapid consumption of fossil fuels brought severe environmental consequences - greenhouse gas emissions, pollution from energy production clearly degrading various ecosystems. Recognizing the unsustainable trajectory of fossil fuel dependence, scientists and environmental institutions began advocating for renewable energy sources in the 20th century exploring wind, solar, hydro, and biomass viable alternatives, promising to meet energy demands while mitigating harm.

Among these, biomass-based fuel (biofuels) gained prominence as a renewable energy source capable of replacing petroleum-based fuels in transportation. The first generation of biofuels, derived from edible crops such as corn and sugarcane, sparked interest due to their potential to reduce carbon emissions. However, concerns about food security and land use prompted the development of second-generation biofuels, which utilize non-edible feedstocks like agricultural residues, waste oils, and lignocellulosic materials.

Biofuels, a renewable substitute for fossil fuel, emerged as a leading candidate due to its compatibility with existing engines and reduced environmental impact. While early processes relied on homogeneous catalysts, challenges such as catalyst recovery, wastewater generation, and feedstock limitations spurred innovation. The quest for sustainability and cost-effectiveness led to the development of heterogeneous catalysts, which can be easily separated and reused, the use of bifunctional catalysts gained attention for their ability to simultaneously catalyse esterification and transesterification reactions. These catalysts feature both acidic and basic sites and are particularly suited for low-cost feedstock with high free fatty acid content.

This possibility gives rise to my research, centering on the use of agricultural waste; **Rice bran** and **Cow bones** as bifunctional catalysts focuses on optimizing their structure and activity to enhance biodiesel yields under mild reaction conditions improving production efficiency and economic viability hence offering a pathway to more sustainable and economically feasible biodiesel production.

2.2 ENERGY

Energy is the ability to do labor (Balasubramanian, 2016). Energy acts as the essential foundation of contemporary society, fueling advancements and facilitating the smooth operation of our everyday activities. It provides the necessary power for our households, drives industrial processes, and propels transportation networks, among a myriad of other vital uses. Nevertheless, as the world confronts the pressing issues of climate change and depleting fossil fuel reservoirs, examining and embracing sustainable energy alternatives becomes crucial. (Ashnani et al., 2014; Darmawi et al., 2013; Li et al., 2022). According to (Balasubramanian, 2016), there are two types of energy sources: renewable and non-renewable.

2.2.1 NONRENEWABLE ENERGY

Non-renewable energy sources are finite, they deplete over time, and require extensive periods to regenerate. Once consumed, they are effectively exhausted due to the exceptionally long timescales needed for their formation. Fossil fuels including coal, petroleum, and natural gas, are the primary examples of non-renewable energy resources.

Despite their significant contributions to global energy production, non-renewable energy resources pose a range of environmental problems. One of the foremost concerns is the emission of greenhouse gases, such as carbon dioxide, during the combustion of fossil fuels like coal, oil, and natural gas. Carbon dioxide accounts for 55% of global warming, with its primary sources being the combustion of fossil fuels (77%) and deforestation (23%). The global atmospheric concentration of carbon dioxide has increased by approximately 30%, which could lead to a rise in global temperatures by 1°-5°C if emissions remain unchecked. Annually, the average global surface temperature increases by 0.3°-0.6°C, exacerbating climate change. Methane, responsible for about 20% of the greenhouse effect, is emitted from coal combustion, natural gas leaks, oil production, and petrol spills. Nitrogen oxides contribute significantly to acid rain formation, accounting for approximately 35% of its occurrence (Alrikabi, 2014). These emissions drive climate change impacts such as rising sea levels, global temperature increases, and extreme weather events. Additionally, the extraction and mining of non-renewable resources cause habitat destruction, soil erosion, and water pollution. The processes involved in resource extraction and refining release harmful pollutants into the environment, threatening ecosystems and human health. Such activities not only degrade natural habitats but also contribute to long-term ecological imbalances. Addressing these issues requires reducing fossil fuel reliance and transitioning to cleaner, sustainable energy alternatives (Alrikabi, 2014).

2.2.2 RENEWABLE ENERGY

Renewable energy comes from natural sources that replenish themselves more quickly than they are used up. There are many different types of renewable energy available to us. Examples of such sources that are continuously replaced are solar, wind, hydropower, geothermal and biomass. Renewable energy can solve the problem that is caused by the increasing energy demand as we can forge a path toward sustainable energy generation that is both environmentally friendly and in harmony with our planet's needs. (Rizwanul Fattah et al., 2020)

2.2.2.1 Types of renewable energy

Renewable energy sources provide a sustainable and eco-friendly substitute for non-renewable resources. These sources harness natural elements that can replenish themselves over time. Some types of renewable energy are:

1. **Solar Energy**: Solar power, harnessed from the sun's radiation, is widely acknowledged as a key renewable energy source. Solar energy holds immense potential as a source of clean, secure, and dependable power. The amount of solar energy reaching the Earth's continents exceeds 200 times the total annual commercial energy consumption by humans. (Alrikabi, 2014).
2. **Wind Energy**: Another prominent renewable energy source is wind power, which converts wind energy into electricity. Wind energy stands out as a highly advantageous and effective renewable energy source due to its low operating costs and wide availability (Y. Kumar et al., 2016).
3. **Hydropower**: By utilizing the energy of flowing or falling water, hydropower has been a reliable renewable energy source for centuries. The operation of hydropower

reservoirs often demonstrates their versatility by serving multiple purposes, including flood control and drought mitigation. (Owusu & Asumadu-Sarkodie, 2016).

4. **Geothermal Energy**: Geothermal energy taps into the Earth's natural heat to generate power.
5. **Bio-Energy:** Biomass, derived from organic materials, can be converted into energy through various processes.

2.2.2.2 Advantages of renewable energy over fossil fuels

Renewable energy sources offer numerous advantages compared to fossil fuels, which include:

1. **Renewable Nature**: Renewable energy sources like solar, wind, hydropower, biomass, and geothermal are sustainable and will not deplete over time, unlike finite fossil fuels.

2. **Environmental Friendliness**: Unlike fossil fuels, renewable energy sources produce minimal greenhouse gas emissions and pollutants that contribute to climate change and air pollution.
3. **Energy Security**: Developing alternative renewable fuels enhances energy security by reducing dependence on volatile fuel supplies and increasing resilience to disruptions.
4. **Cost Competitiveness**: While there may be initial infrastructure investment costs, the cost of renewable energy has been consistently decreasing and is increasingly competitive with fossil fuels.
5. **Health Benefits**: The utilization of renewable energy sources leads to significant health benefits by reducing air pollution and its associated negative impacts on human health.

6. **Job Creation**: The renewable energy sector has the potential to create more job opportunities compared to the fossil fuel industry, as it requires more labor-intensive work.

2.2.2.3 Disadvantages of fossil fuels

In contrast, fossil fuels come with several disadvantages, including:

1. **Environmental Harm:** Fossil fuels contribute to climate change through greenhouse gas emissions, and their extraction, transportation, and use can cause significant environmental damage, such as oil spills and habitat destruction.
2. **Finite Resource**: Fossil fuels are non-renewable resources, and at the current consumption rate, existing reserves will be depleted within a few hundred years.
3. **Health Impacts**: The use of fossil fuels is associated with adverse health effects, including respiratory illnesses and premature deaths due to air pollution.
4. **Energy Insecurity**: Fossil fuels are susceptible to price volatility and supply disruptions, leading to energy insecurity and potential economic repercussions.

Renewable energy offers substantial benefits while addressing several drawbacks associated with fossil fuels. (Alcheikh, 2015; Holechek et al., 2022)

2.3 BIOENERGY

On a worldwide level, about half of the overall utilization of renewable energy in 2017 came from modern bioenergy. This dominant role in contributing to renewable energy is expected to persist shortly and remain the primary source of renewable energy until 2023. It is estimated to account for 30% of the growth in renewable energy over the next five years. (Mandley et al., 2020). Bioenergy refers to the energy obtained from organic matter, known as biomass, which can include various sources such as plants, animals, and other organic

materials. Biomass is one of the renewable energy resources with the potential to be converted into an energy carrier and used as a sustainable energy source.

A recent study conducted by (Bauer et al., 2020; Hamzeh et al., 2011) presented a global energy consumption overview, revealing that only 10% of the total global energy is sourced from biomass, whereas 90% is primarily supplied by fossil fuels and other conventional energy resources. The utilization of biomass for meeting the world's energy demand is relatively insignificant when compared to the vast potential offered by diverse bioenergy resources available globally. However, it should be noted that the current contribution of biomass is largely limited to traditional applications such as cooking and heating. (Mohammed et al., 2014).

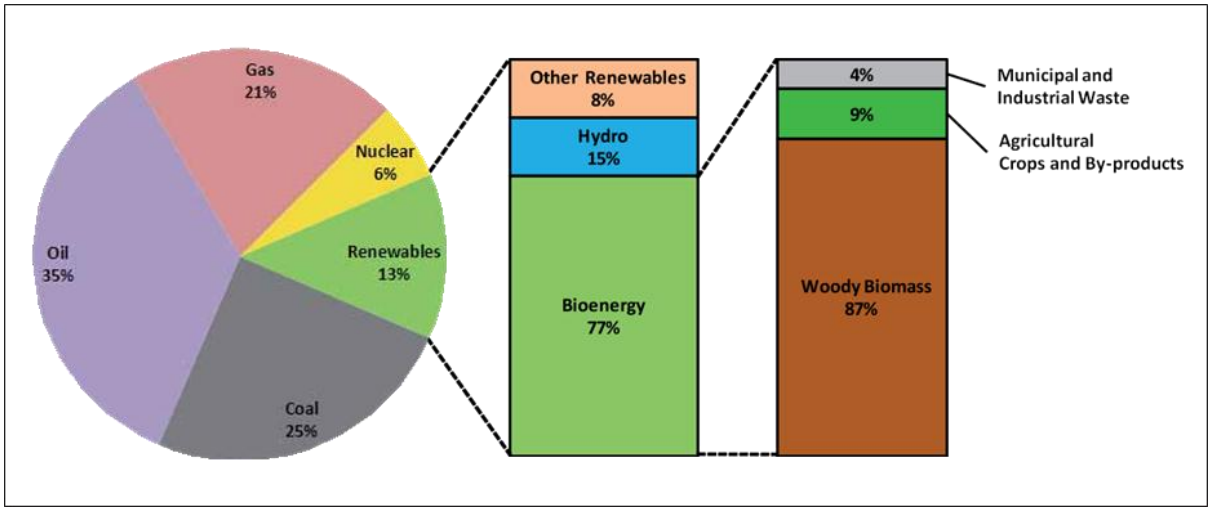

Figure 2. 1: Shows the share of bioenergy in the world's primary energy mix (Bauen et al, 2009)

In many developing countries across Africa and South Asia, biomass has long been a primary energy source, with sub-Saharan Africa alone possessing an untapped potential of approximately 15,000 MW from just 30% of crop and forest logging residues. Globally, biomass utilization for electricity generation has grown steadily, with an average annual

increase of 13 TWh between 2000 and 2008, reflecting a global shift toward renewable energy expansion. In Nigeria, despite a well-established power generation infrastructure reliant on natural gas, which accounts for 80% of electricity production, power output has consistently failed to meet growing demand driven by population growth and socio-economic changes. This mismatch between energy demand and supply highlights the need to explore alternative energy sources like biomass to address the country's energy challenges (Alrikabi, 2014). Expanding biomass utilization offers a promising solution to improve energy access while aligning with global renewable energy trends.

The use of biomass residues for energy has gained more attention in developing countries, where biomass is frequently used for heating and cooking, compared to the developed world. This approach generally has minimal impact on food security, although agricultural practices can influence this outcome. Large-scale mechanized energy crop production is often unsuitable for developing nations due to food security concerns. Traditional combustion of biomass residues is inefficient, making modern bioelectric power generation a viable alternative to reduce energy losses. Utilizing biomass residues for electricity generation provides economic, social, and environmental benefits, especially in countries like Nigeria. (Balogun, 2015) recommended establishing a national biofuels policy and incentives, supported by strong political will, to distinguish between crops for biofuel production and food crops, addressing concerns over the "food for fuel" debate.

2.4 BIOFUELS

Biofuels encompass a range of renewable fuels derived from organic matter, known as biomass. It substitutes conventional fossil fuels, such as gasoline and diesel, and finds applications in transportation, heating, and power generation. Bioethanol, biodiesel, and biogas are prominent examples of biofuels (Reid et al., 2020),

Biofuels can be distinguished based on several key attributes, such as the type of feedstock used, the conversion method employed, the technical specifications of the fuel, and its intended application. (Jeswani et al., 2020). A diverse range of raw materials, such as agricultural crop residues, forestry biomass, energy crops, livestock manure, municipal solid waste, sewage sludge, industrial effluents, and other organic waste streams, can serve as feedstock for the production of biofuels. These waste materials possess a high content of organic matter that can be extracted and utilized for conversion into biofuels using various thermochemical and biochemical technologies. (Nanda et al., 2018).

2.4.1 CLASSIFICATION OF BIOFUELS

2.4.1.1 Based on the biomass used in their production

1. **Solid Biofuels**: Biofuels are produced from solid organic, non-fossil biomass of biological origin. These materials are commonly used for heat production, energy generation, and electricity production. Examples include charcoal, biochar, wood residues, wood pellets, fuel wood, animal manure, and other renewable industrial waste (Mahapatra et al., 2022).
2. **Liquid Biofuels**: Liquid biofuels are derived from natural biomass or biodegradable materials and offer significant advantages over solid and gaseous biofuels due to their high energy density. This makes them ideal for storage, transportation, and retrofitting (Mahapatra et al., 2022). Common examples include biodiesel, bioethanol, and bio-oil. Liquid biofuels can be categorized into two main types:

- **Triglyceride-based biofuels:** These include biomass-derived products such as vegetable oil, biodiesel, hydrogenated oil, pyrolytic oil, and bio-gasoline.
- **Lignocellulose-based biofuels:** These encompass drop-in biofuels, BTL (biomass-to-liquid) diesel, and biofuel feedstock like bio-oils.

3. **Gaseous Biofuels**: Gaseous biofuels are low-density fuels in a gaseous state, with examples including biogas, bio-syngas, and biohydrogen. They are produced through processes like pyrolysis or gasification of bio-waste. These biofuels are often used in Otto engines connected to electricity generators for power or heat production (Mahapatra et al., 2022).

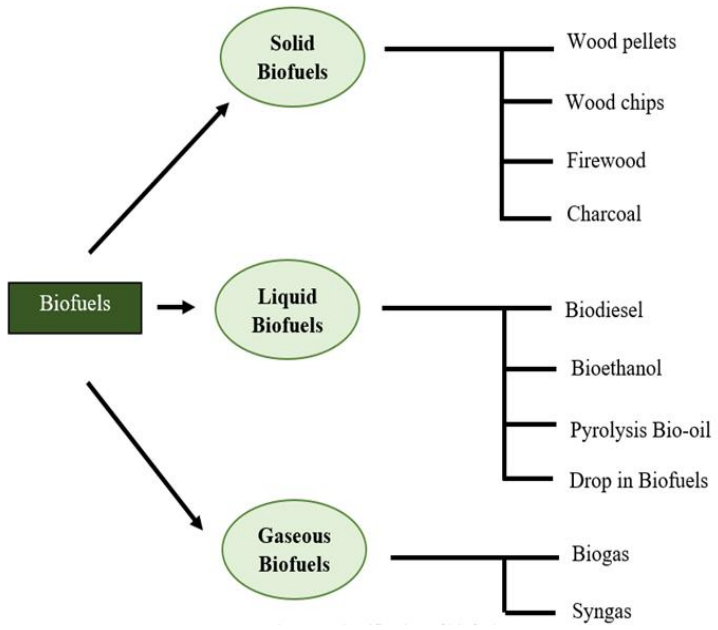

Figure 2. 2: Classification of Biofuels (Salehi Jouzani et al., 2020)

2.4.1.2 Based on the type of feedstock utilized for their manufacturing

Biofuels are classified into four generations based on the type of feedstock utilized to manufacture them: first generation, second generation, third generation and fourth generation. (Khan et al., 2021)

First generation biofuels are produced from food or animal feed crops and are often referred to as 'conventional biofuels' since they employ well-established technologies like fermentation, distillation, and transesterification.

Second generation biofuels, on the other hand, are derived from non-food sources such as dedicated energy crops (e.g., Miscanthus, switchgrass, short rotation coppice, and other lignocellulosic plants), agricultural residues, forest residues, and various waste materials (e.g., WCO and municipal solid waste).

Third generation biofuel, commonly known as biodiesel, is produced from microalgae such as algae and cyanobacteria, through conventional transesterification or hydro-treatment of algal oil. They include biomethane, biodiesel, bioethanol, biobutanol, vegetable oil gasoline, jet fuels, and aviation fuels.

Second and third generation biofuels are often referred to as 'advanced biofuels' since their production techniques or pathways are still undergoing research, development, pilot testing, or demonstration. (Jeswani et al., 2020). Throughout this paper, the terminology of 'first, second, and third generation' has been selected and consistently employed and Table 2.1 shows the examples of the feedstock used in each type.

Table 2 1: Examples of biofuels and their feedstock

Biofuels	**Examples**	**Feedstock**
First generation	Biodiesel, Bio-alcohols, Vegetable oil, bio syngas, biogas.	Cassava, sugar, sugar beet, starch, rapeseed, soya, soybean, animal fats, sunflower, maize, palm oil, sugar cane, sewage waste, jatropha, castor, canola plant, sorghum, mustard.
Second generation	Bio-alcohols, bio-oil, biodiesel, Bio-DMF, Bio Fischer Tropsch diesel, bio hydrogen.	Municipal solid wastes, non-food crops, cereal straw, corn wood, wheat straw, forest residues, energy crops, reed canary grass, alfalfa, sugarcane bagasse, agave, jatropha,

		switchgrass, and miscanthus.
Third generation	Bio-methanol, Bio-ethanol, Biodiesel, vegetable oil, jet fuels.	Algae, Cyanobacteria, microbial species, yeast, fungi.
Fourth generation	Green diesel, Bio-gasoline, Green aviation fuel.	Vegetable oil, Biodiesel.

The advantages and disadvantages of each type of these four generations of biodiesel are outlined in Table 2.2

Table 2 2: Advantages and disadvantages of each of these four generations of biofuels.

Biofuels	**Advantages**	**Disadvantages**
First generation	1) Biodegradable 2) Energy security 3) Renewable and Reduced Carbon Emissions. 4) Market Availability. 5) Agricultural and Rural Development.	1) Competition with Food Production. 2) Land Use Change and Environmental Impact. 3) Limited Feedstock Options. 4) Energy Intensive Production.
Second generation	1) Reduced greenhouse gas emission. 2) Energy and security and diversification.	1) Second-generation biofuels reduce food competition but may still compete for land and resources with food production.

	3) Potential for rural development. 4) No competition with food. 5) Low cost of feedstock. 6) Higher yield and lower land. 7) Available feedstock in larger quantities. 8) Marginal lands can be used for planting advanced feedstock such as neem sp. 9) Production of high value added products.	2) Potential indirect land-use change. 3) The economic viability of second generation biofuels is uncertain due to low oil prices, making them less competitive in the market compared to conventional fuels. 4) Technical and scale up challenges due to underdevelopment in conversion technologies and research breakthroughs.
Third generation	1) There is no competition for food or land. 2) Algae cultivation can take place on land and water which is not suitable for sustainable food production. 3) Feedstock is available at low or sometimes no cost. 4) Algae-based energy production yields more	1) The processing cost is high. 2) Harvesting and processing pose significant challenges. 3) Commercial feasibility has not been achieved yet. 4) The absence of technological and research breakthroughs is evident. 5) The production of biofuels necessitates new technologies

	energy per acre compared to conventional crops. 5) It boasts a high oil yield. 6) Algae contribute to energy security. 7) There is no presence of toxic content in algae-based biofuels. 8) Bioengineered algae is a renewable resource of energy. 9) When integrated into biofuels, algae improves the performance of first and second generation biofuel technologies.	throughout the feedstock processing to the final product stage. 6) The production technology is currently in development.
Fourth generation	1) The concept of fourth generation biofuel centres on its carbon-negative attributes, surpassing mere carbon neutrality, as it effectively sequesters more	1) The first concern pertains to the high cost involved. 2) The technology is currently undergoing research and development. 3) There is a death of studies

	carbon than it emits. 2) Energy security. 3) There is a potential to utilize materials synthetic for production.	assessing its practical performance from both technical and economic perspectives. 4) It necessitates the utilization of new Technologies spanning from feedstock production to the final biofuel product.

2.5 BIODIESEL

Biodiesel is a liquid biofuel produced through chemical processes involving vegetable oils or animal fats, typically combined with alcohol (Mathew et al., 2021a). It serves as a viable alternative to conventional diesel fuel and can be used in diesel engines without any modifications. Biodiesel can be utilized in its pure form (B100) or blended with traditional diesel oil, creating various blends such as B20 (20% biodiesel, 80% diesel) or B5 (5% biodiesel, 95% diesel).

One of the significant advantages of biodiesel is its ability to be derived from renewable and sustainable feedstock. Vegetable oils obtained from oilseed crops like soybeans, canola, sunflower, and animal fats from livestock processing are commonly used. These feedstock can be cultivated or obtained from waste and byproducts, making biodiesel production environmentally friendly and reducing reliance on finite fossil fuel resources. Another characteristic of biodiesel is its biodegradability. When released into the environment, biodiesel breaks down naturally over time, minimizing any long-term adverse effects. Biodiesel is non-toxic, posing no significant harm to ecosystems or aquatic life especially

when considering the potential for fuel spills or leaks. Furthermore, biodiesel exhibits favourable properties as a fuel, it has a higher flash point compared to traditional diesel, making it safer to handle and store. Biodiesel's lubricity helps protect engine components, enhancing their longevity and reducing wear and tear as it boasts excellent combustion properties, resulting in reduced emissions of pollutants such as sulphur, particulate matter, and carbon monoxide. (Amenaghawon et al., 2022)

2.5.1 QUALITY AND CHARACTERISTICS OF BIODIESEL

The qualities and properties of biodiesel can vary slightly depending on the source from which it is derived. To ensure smooth engine operation, consistent quality is essential. (Maheshwari et al., 2022). Austria was among the first countries to regulate esters as diesel fuel made from rapeseed oil. Several countries, including the United States, Italy, France, the Czech Republic, and Germany, have established their biodiesel standards for their respective markets. (Atabani et al., 2012). All aspects of biodiesel production and usage must adhere to international biodiesel standards. Both the European Biodiesel Fuel standards and the American Society for Testing and Materials specification 6751-3 (EN 14 214) are followed to meet these requirements. (Atadashi et al., 2010). Additionally, specific standards in Czech (CSN), Germany (DIN 51 606), and Austria (ON) are available.

Biodiesel's properties, such as acid value, cetane number, calorific value, density, ash content, viscosity, cloud and pour points can vary based on the fatty acid composition it contains. To ensure optimal performance, understanding and maintaining these properties are essential aspects of biodiesel production and utilization. (Ali et al., 2013).

2.5.1.1 Flashpoint

The flashpoint of biodiesel refers to the lowest temperature at which the fuel's vapours ignite when exposed to an open flame or spark. It is a critical safety parameter that determines the risk of fire or explosion during fuel handling. Biodiesel's flashpoint is influenced by various factors, including the feedstock used for production, the percentage of biodiesel in the blend, and the presence of other additives. The average flashpoint of biodiesel is about **150ºC**, whereas the flashpoint for standard diesel is **55-66ºC**. (Rahimi et al., 2022)

The flashpoint is crucial in ensuring the safe storage, handling, and usage of biodiesel. A higher flashpoint enhances safety by reducing the likelihood of accidental ignition during routine operations. This is especially relevant in industries where biodiesel is stored in large quantities or transported over long distances. Additionally, the higher flashpoint allows biodiesel to be used in environments with higher temperatures without concerns about evaporation and ignition hazards. The flash point of biodiesel is set at 120°C according to the European norm, while the ASTM norm establishes it at 130°C. (Mabrouki et al., 2015).

Factors Influencing Flashpoint:

1. Feedstock Composition: Different feedstock used for biodiesel production can lead to variations in the flashpoint. For example, biodiesel produced from animal fats generally has a higher flashpoint compared to biodiesel from vegetable oils.
2. Blend Ratio: The flashpoint of biodiesel can be affected by the percentage of biodiesel in the blend. Higher concentrations of biodiesel in the mixture tend to increase the flashpoint.
3. Additives: Some additives, such as antioxidants and stabilizers, can impact the flashpoint of biodiesel. These additives may be used to improve the fuel's stability and prevent oxidation, but they can also influence the flashpoint.

2.5.1.2 Density

The density of biodiesel is an important physical characteristic that determines its mass per unit volume. It is worth noting that the density of biodiesel varies depending on the specific feedstock and production process. The density of biodiesel plays a significant role in its performance and combustion characteristics. It affects how efficiently the fuel is atomized and sprayed in the engine, influencing the overall combustion process. The density of biodiesel also influences its energy content, which is a critical factor in determining its calorific value and, consequently, its energy efficiency as a fuel. For blending biodiesel with petroleum diesel or other alternative fuels, knowledge of their respective densities is crucial to formulate fuel blends that meet specific performance requirements while adhering to quality standards. It is important to note that the density of biodiesel may change with temperature variations, and fuel blenders should consider temperature effects when designing biodiesel blends (Alptekin & Canakci, 2008).

2.5.1.3 Viscosity

The kinematic viscosity of biodiesel is a crucial parameter that characterises its flow behaviour and determines how it spreads and atomizes in a diesel engine. Biodiesel, being a renewable and environmentally friendly fuel, has different viscosity properties compared to conventional diesel fuel. Biodiesel has a kinematic viscosity that is approximately 1.8 times higher than that of diesel fuel. (Yahya & Aghel, 2021). The increase in viscosity can influence the atomization and spray characteristics of the fuel during injection into the combustion chamber of the engine. High viscosity can result in larger droplets, affecting combustion efficiency and potentially leading to increased engine deposits and higher smoke opacity in the exhaust. The viscosity of biodiesel, as well as its blends with diesel and other components, is affected by temperature changes. The kinematic viscosity of test fuels and

their blends at different temperatures shows that the viscosity of biodiesel, diesel, and their blends decreases as the temperature increases. This temperature-dependent behaviour is essential to consider when designing fuel formulations and understanding the fuel's performance in varying weather conditions. Blending biodiesel with diesel is a common practice, the viscosity of the resulting blends can be adjusted to achieve desired characteristics and performance. Blends of biodiesel and diesel are completely miscible, allowing flexibility in their formulation for various applications (Yahya & Aghel, 2021).

2.5.1.4 Cetane Number

The cetane number is a key metric for assessing biodiesel quality, particularly its ignition properties and cold-flow behaviour. This dimensionless value indicates the fuel's tendency to auto-ignite upon injection into a diesel engine, directly affecting ignition delay, combustion efficiency, emission levels, and engine noise. Variations in biodiesel feedstocks, derived from different vegetable oils or animal fats, lead to diverse fatty acid profiles, which in turn influence the cetane number. Even biodiesel from the same source can exhibit cetane number fluctuations due to experimental uncertainties. Given the practical challenges and costs associated with experimental cetane number determination, predictive models have been developed. These models estimate the cetane number by correlating it with metrics such as fatty acid composition, offering a cost-effective means to evaluate biodiesel quality.

2.5.1.5 Ash Content

The ash content of biodiesel pertains to the presence of inorganic minerals within the fuel. This content is typically measured as a percentage of the fuel's weight. As per standard specifications, biodiesel should not exceed 0.02% (m/m) in ash content (Woodyard, 2009). The type of feedstock used in biodiesel production can influence the ash content; biodiesel

from animal fats tends to have higher ash content compared to that from vegetable oils. Having ash in biodiesel can lead to adverse effects on engine performance and emissions. Accumulation of ash in the engine and exhaust system can result in increased wear and reduced efficiency. Hence, minimizing the ash content in biodiesel is crucial to ensure optimal engine performance and emissions (Sappok & Wong, 2007). Researchers have conducted semi-quantitative determinations of ash element content in freeze dried, defatted, sulphated, and pyrolyzed biomass of Scenedesmus sp. The sulphated ash content obtained was found to be 17.81 ± 0.15% (De Souza et al., 2020) The use of the SEM-EDS technique enabled the identification of different mineral compounds in the ashes, revealing the presence of elements such as Si, Ca, Mg, K, Na, Fe, Al, and P.

2.5.1.6 Cloud Point, Pour Point and Cold filter plugging point

The low-temperature characteristics of biodiesel play a crucial role in its performance, as fuel can undergo partial or complete freezing in cold conditions, leading to flow restrictions and engine issues. The consequences of inadequate low-temperature properties can range from fuel starvation and difficulties in engine starting to potential engine damage due to insufficient lubrication (Echim et al., 2012). The phenomenon of cloudy gasoline is attributed to the formation of wax crystals during cooling, which is defined by the temperature known as the **cloud point** (Yuan et al., 2017). As the temperature decreases further, the fuel reaches the **pour point** where all the wax is no longer dissolved, causing the fuel to become excessively thick and impeding its pourability. To assess the pour point and cloud point of biodiesel, standard formulas from ASTM D2500, EN ISO 230015, and D97 are applied. Notably, both the cloud point and pour point of biodiesel are higher compared to those of conventional diesel (Maheshwari et al., 2022). An important parameter related to low-temperature operability is the **cool filter plugging point (CFPP)**, which indicates the

temperature at which the test filter begins to clog due to the crystallization of fuel components (Giakoumis & Sarakatsanis, 2019). The CFPP serves as a measure of the effectiveness of fuels during colder months and their ability to maintain proper flow in the fuel delivery system at low temperatures. In this regard, biodiesel and diesel are associated with the filterability limit for fuels as defined by the Clean Fuels Performance Parameters (CFPP), with ASTM D6371 being the standard method used for determining CFPP (Sarin et al., 2010). Understanding and optimising these low-temperature properties are essential for ensuring the reliable and efficient performance of biodiesel in a variety of weather conditions.

2.5.1.7 Oxidation stability of fuel

The oxidation stability of biodiesel refers to its ability to resist oxidation, a chemical reaction involving the combination of a substance with oxygen (Masudi et al., 2022). Biodiesel is prone to oxidation and over time, it can degrade. This leads to the formation of sediment, gum, and heavy organic compounds. The oxidation process in biodiesel can negatively affect its properties, performance, and storage characteristics, making it essential to ensure proper stability for its long term use and storage. Standards that need to be met for the oxidation stability of biodiesel are usually outlined by recognized organizations and regulatory bodies. Some key standards include:

1. **ASTM D6751-12 (USA):** This standard specifies biodiesel requirements and test methods as a blend component in middle distillate fuels. It includes parameters for the oxidation stability of biodiesel to ensure its quality and performance.
2. **EN 14214:2012 (EU):** The European standard EN 14214 specifies the requirements and test methods for fatty acid methyl ester (FAME) biodiesel as a blend component

in diesel fuels. It sets specific criteria for oxidation stability to ensure the fuel's stability and compatibility.

3. **EN 590:2009+A1:2010 (EU):** This standard specifies requirements and test methods for automotive fuels, including diesel fuel containing up to 7% volume of FAME biodiesel.

The oxidation stability of biodiesel blends is an essential parameter in this standard. (McCormick et al., 2007) Oxidation stability testing is carried out using various methods, and two common techniques are:

a. **ASTM D2274:** This test method determines the oxidation stability of middle distillate fuels, including biodiesel. It measures the formation of insoluble materials under accelerated oxidation conditions.
b. **OSI (Oxidation Stability Index) method** (e.g., Rancimat apparatus): This method measures the induction time, which is the time it takes for the sample to reach a specified conductivity value due to oxidative changes. The longer the induction time, the better the oxidation stability of the biodiesel. (Botella et al., 2014)

Factors influencing the oxidation stability of biodiesel include the content of polyunsaturated fatty acids (e.g., linolenic acid) in the biodiesel, antioxidant content, and total glycerin content. Polyunsaturated fatty acids are more prone to oxidation, leading to reduced stability. Antioxidants can improve the oxidation stability of biodiesel by inhibiting oxidation reactions. Oxidation stability is a critical parameter for biodiesel, and meeting the standards specified by ASTM and EN ensures the fuel's quality, performance, and long-term stability during storage and use.

2.5.1.8 Lubricating properties of fuel

It was observed that biodiesel offers significant advantages in terms of its impact on the lubricity and overall longevity of diesel fuel when used as an additive (Atadashi et al., 2010). The incorporation of biodiesel into diesel fuel led to noticeable improvements in the lubricating properties, thereby positively affecting the engine's performance and extending its operational life. Despite these promising lubricating capabilities, it is important to acknowledge that biodiesel, particularly in the form of fatty acid methyl ester (FAME), does come with its share of limitations and challenges. One notable concern is its susceptibility to degradation over time, which can lead to potential issues with fuel quality and efficiency. Additionally, FAME-based biodiesel tends to contain relatively higher concentrations of glycerol, which can have implications on fuel stability and contribute to the formation of undesirable deposits in the engine (Lapuerta et al., 2008). Another aspect to consider is the behaviour of biodiesel in cold weather conditions, commonly referred to as its "cold flow" qualities. Biodiesel may experience difficulties in low-temperature environments, including issues with fuel gelling and filter plugging, which can adversely impact engine performance and reliability. To address these challenges and further optimize the use of biodiesel, researchers like (Maheshwari et al., 2022) propose the adoption of high-quality biodiesel lubricants. By employing advanced and well-formulated biodiesel lubricants, it is possible to minimize friction losses, enhance the engine's overall efficiency, and maximize braking performance. This highlights the potential of leveraging biodiesel not only as a fuel alternative but also as a means to improve the overall performance and reliability of diesel engines in a more sustainable and eco-friendly manner.

Table 2 3: Comparison of the physical and chemical properties of biodiesel (fatty acid methyl esters, FAME) and conventional diesel fuel (petroleum-based diesel) (Saad et al., 2023; Sani et al., 2018; Sohrab Hossain et al., 2021)

Property	**Biodiesel**	**Diesel Fuel**
Chemical Formula	Fatty Acid Methyl Esters (FAME)	Complex hydrocarbon mixture
Source	Vegetable oils, animal fats	Crude oil
Density (g/cm³)	~ 0.86-0.90	~ 0.82-0.85
Flash Point (°C)	>130	52-96
Pour Point (°C)	-12 to -15	-15 to -30
Cetane Number	~ 50-60	40-55
Viscosity (mm²/s at 40°C)	~ 3.5-5.0	~ 1.9-4.1
Sulfur Content (ppm)	Low (varies depending on feedstock)	Varies (can be low or high)
Cloud Point (°C)	-3 to 16	Varies
Carbon Residue (% mass)	<0.05	<0.15
Distillation Range (°C)	~150-370 (depending on feedstock)	~150-360 (typical)
Oxidation Stability (h)	>3.0	~ 2.0-5.0
Energy Content (MJ/L or MJ/kg)	~ 34.2-38.6 (LHV)	~ 32.4 (LHV)
Greenhouse Gas Emissions	Lower than diesel	Higher than biodiesel
Biodegradability	Yes	No

Lubricity	Good	Moderate to poor
Renewable Resource	Yes	No

Note: The values provided are general ranges and may vary depending on the specific feedstock and production processes used for biodiesel and diesel fuels. Additionally, biodiesel properties can be influenced by the type of alcohol used in the transesterification process (e.g., methanol, ethanol).

2.5.2 FEEDSTOCK FOR BIODIESEL PRODUCTION

The selection of feedstock is a critical factor in the process of biodiesel production. Various feedstock are utilized, each with its unique characteristics and implications. Feedstock for biodiesel production encompasses a diverse range, including both edible and non-edible oils, waste materials, and biomass-derived oils. Edible oils like soybean and canola oil have high conversion rates and produce quality biodiesel (Moser, 2011; Topare et al., 2022). However, there are concerns about competition with food resources. Non-edible oils, such as jatropha and camelina, are promising alternatives as they can be cultivated on marginal lands without impacting food crops. Additionally, waste oils like used cooking oil and rendered animal fats can be recycled into biodiesel, reducing waste and enhancing sustainability. Innovative feedstock like waste plastics, biomass pyrolysis oil, and tire pyrolysis oil are gaining attention for their potential in biodiesel production. These sources not only help manage waste but also contribute to a circular economy by converting discarded materials into valuable biofuels. Ultimately, the choice of feedstock depends on factors such as availability, sustainability, and regional considerations (Topare et al., 2022). Researchers and the biodiesel industry continue to explore new feedstock and production methods to make biodiesel production more sustainable, economically viable, and environmentally friendly. The ongoing evolution of

feedstock options is essential in the journey toward cleaner and more sustainable energy alternatives.

2.5.2.1 Edible Oils

Edible oils, such as soybean, canola, and palm oil, have gained prominence in biodiesel production due to their favourable properties. These oils are rich in triglycerides which is the key component for biodiesel synthesis, they offer high energy content, making them efficient sources for biofuel. The availability of edible oils on a large scale contributes to the feasibility of biodiesel production. The transformation of edible oils into biodiesel involves a process called transesterification, where triglycerides are converted into fatty acid methyl esters (FAMEs). This conversion process is relatively straightforward and efficient, resulting in biodiesel that can directly substitute traditional diesel fuels. Also, edible oil-based biodiesel exhibits excellent combustion characteristics, reduced emissions and lower sulfur content compared to petroleum-based diesel contributing to cleaner air and reduced greenhouse gas emissions. Researchers are actively exploring ways to mitigate these concerns through sustainable agriculture practices and the use of non-edible oil sources (Guo et al., 2015; Nanda et al., 2018).

According to (Gui et al., 2008; Suzihaque et al., 2022), the advantages and disadvantages of using edible oil feedstock are:

Advantages:

1. **Abundant and Renewable**: Edible oils, like soybean and palm oil, are readily available and can be replenished through sustainable agriculture, reducing dependence on fossil fuels.

2. **High Energy Content**: Edible oils have a high energy content, making them efficient sources for biodiesel production, which can provide a viable alternative to conventional diesel.
3. **Compatibility:** Biodiesel derived from edible oils is compatible with existing diesel engines and distribution infrastructure, requiring minimal modifications.
4. **Reduced GHG Emissions**: Biodiesel from edible oils typically results in reduced greenhouse gas (GHG) emissions compared to fossil diesel, contributing to environmental sustainability.

Disadvantages:

1. **Competition with Food Resources**: Using edible oils for biodiesel production can raise concerns about competition with food production, potentially leading to food price increases and food security issues.
2. **Land Use and Deforestation**: The cultivation of crops for edible oils can drive deforestation and land-use changes, particularly in regions like Southeast Asia, posing environmental challenges.
3. **Limited Sustainability**: While edible oils offer advantages, their sustainability depends on responsible farming practices and efforts to mitigate environmental impacts.
4. **Cost and Price Volatility**: Edible oil prices can be volatile, impacting the economic feasibility of biodiesel production.

While edible oils offer advantages like high-quality biodiesel and availability, they also come with significant drawbacks, including concerns about food competition and environmental impacts. Striking a balance between these factors and implementing sustainable practices is crucial for responsible edible oil-based biodiesel production.

2.5.2.2 Non Edible Oils

Non-edible oils have gained prominence as a promising feedstock for biodiesel production due to their ability to address concerns related to competition with food resources and offer sustainable alternatives (Silveira Junior et al., 2022). Various inedible oil sources, such as Jatropha, neem, cotton, mahua, and rubber seed oil, have emerged as viable options for biodiesel production. For instance, Neem oil is extracted from the seeds of the neem tree (*Azadirachta indica*), primarily through mechanical pressing or solvent extraction methods, which can thrive on marginal lands, minimizing the need for fertile soil and avoiding land-use conflicts with food crops. These non-edible oils offer substantial yields and can be grown on wastelands, contributing to land reclamation efforts. Furthermore, their properties are conducive to biodiesel production, making them valuable resources for the sustainable production of biofuels (Abdul Hakim Shaah et al., 2021; S. Kumar et al., 2023). One of the critical advantages of non-edible oil-based biodiesel is its potential to reduce the fuel vs. food debate. As the demand for biodiesel increases, concerns about diverting edible oils away from the food supply have intensified. Non-edible oils, by their inedible nature, alleviate these concerns and provide a way to meet the growing demand for biofuels sustainably. However, challenges such as low oil yield in some non-edible crops and variations in oil quality must be addressed through ongoing research and development to unlock the full potential of these alternative feedstock.

Advantages and disadvantages of using non-edible oils for biodiesel production are: (S. Kumar et al., 2023; Silveira Junior et al., 2022)

Advantages of Non-Edible Oil as Biodiesel Feedstock:

1. **Abundant Resources**: Non-edible oil sources, including various plants and seeds, provide a vast and sustainable resource pool for biodiesel production.

2. **No Competition with Food**: Unlike edible oils, using non-edible oils does not raise concerns about diverting resources from the food supply, ensuring food security.
3. **Lower Environmental Impact**: Non-edible oil crops can thrive on marginal lands, reducing the pressure on fertile soil and minimizing land-use change and deforestation.
4. **Diverse Sources**: Non-edible oil sources encompass a wide range of plants and seeds, offering flexibility and resilience in the face of changing market conditions.

Challenges and Disadvantages:

1. **Research and Development**: Further research is needed to optimize the extraction and conversion processes for non-edible oils, making them economically viable.
2. **Cultivation Challenges**: Some non-edible oil crops may require specific conditions for growth, and their cultivation may face local challenges.
3. **Technology Adaptation**: Adapting existing biodiesel production infrastructure and engines to efficiently use non-edible oil-based biodiesel may require investments.
4. **Market Development**: Creating a market for non-edible oil-based biodiesel and scaling up production can be a complex process.

Non-edible oils hold promise as a sustainable and ethically responsible feedstock for biodiesel production. While challenges exist, ongoing research and development efforts aim to unlock the full potential of non-edible oils in the transition to cleaner, greener fuels.

2.5.3 METHODS OF SYNTHESIZING BIODIESEL

The choice of biodiesel synthesis method depends on factors such as feedstock composition, availability, and the desired properties of the biodiesel. Transesterification remains the dominant method due to its versatility and efficiency, but researchers continue to explore

alternative approaches like pyrolysis and enzymatic processes to enhance sustainability and reduce waste in biodiesel production (Amenaghawon et al., 2022; Mathew et al., 2021; Okpo et al., 2012).

2.5.3.1 Direct Blending

Direct blending is a method for biodiesel production that involves the mixing of biodiesel (fatty acid methyl or ethyl esters) with conventional petrodiesel. This approach is often referred to as a biodiesel blend and is represented as a ratio, such as B5 (5% biodiesel, 95% petrodiesel) or B20 (20% biodiesel, 80% petrodiesel). (Abbaszaadeh et al., 2012; Huang et al., 2012).

Key points regarding direct blending as a biodiesel production method:

1. **Compatibility**: Biodiesel blends are compatible with existing diesel engines and infrastructure. They can be used as drop-in replacements for petrodiesel without requiring engine modifications.
2. **Emissions Reduction**: Biodiesel blends have the advantage of reducing greenhouse gas emissions and air pollutants compared to pure petrodiesel, contributing to improved air quality and reduced environmental impact.
3. **Renewable Energy Source**: Biodiesel is derived from renewable resources such as vegetable oils or animal fats, making it a sustainable alternative to fossil fuels.
4. **Blending Ratios**: Blending ratios vary depending on regulatory requirements and desired properties. Common blends include B5, B10, and B20, with higher percentages of biodiesel offering greater environmental benefits but potentially requiring engine modifications.

5. **Cold Weather Performance**: Biodiesel blends may have different cold flow properties than pure petrodiesel. Adjustments or additives may be needed in colder climates to prevent gelling.
6. **Feedstock Diversity**: Biodiesel can be produced from a variety of feedstocks, including soybean oil, canola oil, and waste cooking oil, allowing flexibility in the choice of raw materials.

Direct blending offers a practical way to introduce biodiesel into the transportation sector while capitalizing on its environmental benefits. It is commonly used in regions where biodiesel mandates or incentives promote its integration into the fuel supply.

2.5.3.2 Micro-Emulsion

Microemulsion is an innovative approach to biodiesel production that offers several advantages. In this process, a stable colloidal system is created, typically comprising water, oil, surfactants, and co-surfactants. This system allows for the efficient mixing of feedstock, such as vegetable oils or animal fats, with alcohol for transesterification, the key reaction in biodiesel production (Leng et al., 2018).

The primary advantage of using micro-emulsion in biodiesel production is its ability to significantly enhance reaction kinetics. Micro-emulsions provide a vast interfacial area between the oil and alcohol, promoting rapid mass transfer and reaction. This results in faster conversion of triglycerides into biodiesel, reducing processing time. Also, micro-emulsion systems achieve homogeneous mixing without the need for intense mechanical agitation, which is common in traditional methods. This reduces energy consumption and simplifies the production process. Micro-emulsions often produce biodiesel with fewer impurities, leading to a higher-quality end product. This can reduce the need for additional purification steps, making the overall process more efficient (Leng et al., 2018; Pikula et al., 2020).

2.5.3.3 Pyrolysis

Pyrolysis is a thermochemical process used in biodiesel production that involves heating biomass, such as plant materials or agricultural waste, in the absence of oxygen. This process typically occurs at temperatures between 400 to 500 degrees Celsius. Pyrolysis is a versatile technique with several classifications based on the precursor material, the scale of the reaction, and the target products (Hsu, 2012). In the context of biodiesel production, pyrolysis primarily aims to convert biomass into bio-oil as illustrated in Fig 2.3, a substance that resembles crude oil. This bio-oil can then be further processed to obtain usable transportation fuels, including biodiesel.

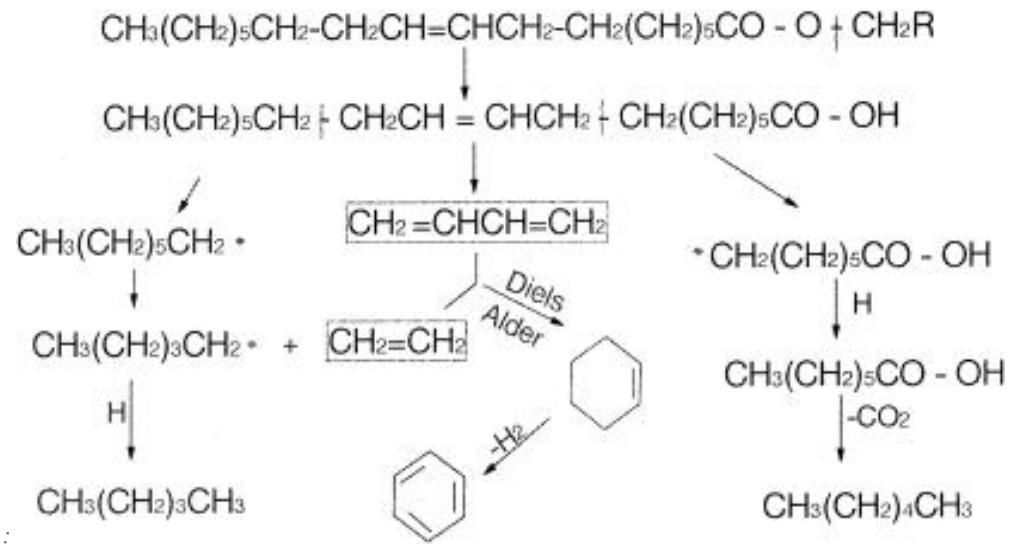

Figure 2. 3: Thermal breakdown of triglycerides (Balat & Balat, 2010)

The pyrolysis process can be summarized as follows:

1. **Feedstock Preparation**: Biomass feedstock, which can be derived from various sources like wood chips, agricultural residues, or even algae, is collected and prepared for pyrolysis.

2. **Heating in the Absence of Oxygen**: The prepared biomass is subjected to high temperatures in an oxygen-free environment. This prevents combustion and instead initiates the thermal breakdown of the biomass.
3. **Bio-Oil Production**: During pyrolysis, the biomass breaks down into various products, with bio-oil being one of the main components. This bio-oil contains a mixture of organic compounds, including those suitable for biodiesel production.
4. **Upgrading Bio-Oil**: The bio-oil obtained from pyrolysis requires further treatment and upgrading to meet the specifications for biodiesel. This may involve removing impurities and adjusting the composition of the bio-oil.
5. **Biodiesel Production**: The upgraded bio-oil is then processed through transesterification or other biodiesel production methods to yield biodiesel as the final product.

One of the advantages of pyrolysis is its ability to utilize a wide range of feedstock, making it a potentially sustainable method for biodiesel production. Additionally, the use of biomass for pyrolysis can contribute to reducing greenhouse gas emissions when compared to fossil fuel alternatives (Devi & Rawat, 2020).

2.5.3.4 TRANSESTERIFICATION

Transesterification is a crucial process in biodiesel production, serving as the method for converting triglycerides found in fats and oils into biodiesel, which is a sustainable and clean energy source (Huang et al., 2012). Transesterification is a chemical reaction that plays a pivotal role in the creation of biodiesel. It involves the conversion of triglycerides, which are the main constituents of animal fats and vegetable oils, into alkyl esters, the key components of biodiesel.

This process requires the use of alcohol, typically methanol or ethanol, and a catalyst, often sodium hydroxide or potassium hydroxide as shown in Fig 2.4. The process begins by mixing the alcohol with the oil or fat feedstock. The alcohol molecules replace the glycerol in the triglyceride structure, resulting in the formation of biodiesel (alkyl esters) and glycerol as a byproduct. This reaction lowers the viscosity of the feedstock, making it suitable for use as a diesel engine fuel (Nabgan et al., 2022a).

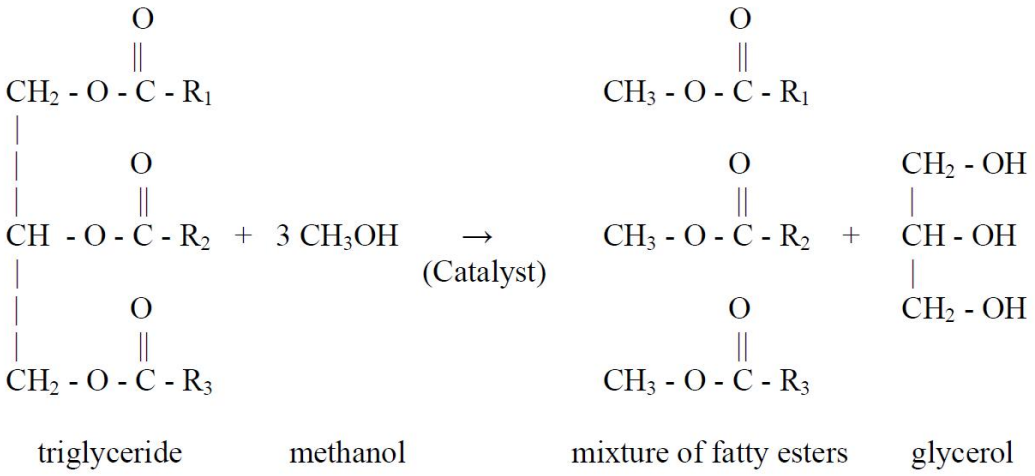

Figure 2. 4:** Transesterification reaction for biodiesel production **(EVC1: Transesterification to Biodiesel, n.d.)

Several factors significantly influence the success and efficiency of this biodiesel production process. Both methanol and ethanol find common usage in the transesterification process. Methanolysis involves the transesterification procedure where methanol reacts with free fatty acids. This process employs heat and high pressure to convert oil (80-90 percent), and methanol (10-20 percent), along with a minimal catalyst amount into fuel. Due to methanol's limited solubility in oil, achieving thorough mixing is essential. In the biodiesel production process, the residual product is fatty acid methyl ester (FAME) (Verma & Sharma, 2016). Methanol is favoured for transesterification due to its higher reactivity and cost-effectiveness compared to other alcohols. Conversely, if ethanol is used to react with free fatty acids, the

transesterification process is referred to as ethanolysis. Ethanol marginally enhances the fuel's cetane rating and thermal efficiency while offering significantly lower toxicity compared to other alcohols (Hajjari et al., 2017).

Transesterification can utilize various feedstock, including palm oil, sunflower oil, rapeseed oil, cottonseed oil, soybean oil, and even algal oil, highlighting its versatility in biodiesel production. It offers several advantages, such as reduced greenhouse gas emissions and a lower environmental impact compared to traditional fossil-based diesel fuels.

In the quest for sustainable energy sources, biodiesel produced through transesterification stands out as an eco-friendly alternative, promoting a cleaner and greener future for the transportation sector. Its compatibility with existing diesel engines and extensive feedstock options further enhance its appeal as a viable and environmentally responsible energy solution (Nabgan et al., 2022b).

Transesterification is the cornerstone of biodiesel production, facilitating the transformation of renewable resources into a sustainable energy source. This process contributes to the reduction of greenhouse gas emissions, making biodiesel a crucial player in the transition towards a more environmentally friendly transportation industry.

Factors affecting Biodiesel production from transesterification

Biodiesel production through transesterification is a complex process influenced by various factors that impact its efficiency, safety, and environmental sustainability. Biodiesel, a renewable and environmentally friendly alternative to conventional diesel fuel, is produced through the transesterification of triglycerides found in fats or oils.

1. **Reaction temperature**: The temperature during biodiesel production plays a pivotal role in determining the final yield and quality of biodiesel. When the temperature rises,

the reaction rate increases due to a reduction in the oil's viscosity. However, it's crucial to avoid excessively high temperatures as they can lead to saponification, a reaction that negatively impacts biodiesel synthesis (Mathiyazhagan & Ganapathi, 2011).

`To maintain efficient transesterification and prevent alcohol evaporation, it is recommended to keep the temperature below the boiling point of the alcohol used in the process. The optimal temperature range for biodiesel production generally falls between 50°C and 60°C. This specific temperature range can vary based on the catalyst and the type of oil being processed (Chozhavendhan et al., 2020). Therefore, controlling and optimizing the reaction temperature within this range is crucial for achieving high biodiesel yields while maintaining product quality.

2. **Reaction time:** To achieve a 99 percent conversion rate, an extended reaction time is necessary. The availability of reactants within the reaction mixture directly influences the conversion rate. Poor control of the reaction's variables can trigger a reverse reaction and result in a decrease in conversion. For processes catalyzed by lipase, a duration ranging from 7 to 48 hours might be required (Silitonga et al., 2017). Research has also demonstrated that reaction time has an impact on production costs.

   Additionally, it has been observed that the specific gravity of the final product decreases exponentially as the reaction time increases, eventually stabilizing at a constant value (Al-widyan & Al-shyoukh, 2002). For instance, biodiesel conversion reached 96.10% after 1 hour and showed minimal change at 2 or 3 hours at 96.35 percent (Refaat et al., 2007). Given that minimizing production costs is contingent upon reducing reaction time, achieving this goal becomes imperative.

3. **Free fatty acid (FFA) and water content:** The reaction rate exhibits heightened sensitivity to the concentrations of free fatty acids and water. In the case of alkali-catalyzed alcoholysis using oil samples, it is imperative that the free fatty acid (FFA) content remains below one percent, and all other components should be thoroughly dried. If the FFA concentration exceeds 1 percent, a greater quantity of base catalyst will be needed for FFA neutralization. Water plays a dual role, increasing viscosity and retarding the reaction by causing foaming and the formation of soap. Foaming and gel formation introduce complications in glycerol separation, while the formation of soap depletes the available catalyst (Ayhan Demirbas, 2009b).

   In conventional transesterification processes for biodiesel synthesis using fats and vegetable oils, the presence of free fatty acids and water leads to the formation of soap, increased catalyst consumption, and a decrease in efficiency (Kusdiana & Saka, 2004). This underscores the critical importance of controlling the water content in vegetable oils for the conventional catalytic transesterification process.

4. **Alcohol to oil ratio**: The alcohol-to-oil stoichiometric ratio typically stands at 3:1. However, when it comes to transesterification, the choice of catalyst governs the specific oil-to-methanol ratio. Acid catalysts often necessitate a higher oil-to-methanol ratio compared to their base catalyst counterparts. In the case of acid-catalyzed transesterification, the oil-to-methanol ratio can reach as high as 1:15, whereas, for base catalysts, it's typically around 1:6 (Leung et al., 2010).

   For instance, in a study focused on converting waste eggshells into soybean biodiesel using CaO as a catalyst, an optimal oil-to-methanol ratio of 1:9 was identified (Wei et al., 2009). Meanwhile, in another research effort, Syazwani et al. (2017) successfully generated palm oil biodiesel with an oil-to-methanol ratio of 1:15, utilizing a CaO catalyst derived from waste venus clam shells. In a separate investigation, CaO

obtained from calcined chicken manure was determined to be the most suitable CaO source for producing biodiesel from waste cooking oil, requiring a 1:15 oil-to methanol ratio (Maneerung et al., 2016b).

5. **Agitation speed**: This is important in the synthesis of fatty acid methyl esters because it has a direct effect on the rate at which the oil and catalyst combination reacts (Mathiyazhagan & Ganapathi. 2011). For instance, while keeping all other variables the same, we settled on 60 minutes of mixing at intensities of 200, 400, 600, and 800 rpm. The end product conversion rate increased to 400 rpm. Soap formation happens at greater agitation speeds, whereas poor product formation occurs at lower agitation speeds. This is owing to the transesterification reaction's reversal behaviour (Ayhan Demirbas, 2010).
6. **Catalyst dosage:** The effectiveness of transesterification heavily depends on both the type and quantity of catalyst employed. In broad terms, feedstocks with a high free fatty acid (FFA) content tend to perform best with acid catalysts, whereas those with lower FFA concentrations are more suited to base catalysts. Catalysts, regardless of their type, facilitate reactions by lowering their activation energy (Mansir et al., 2018). Different catalyst types require varying concentrations. Even if two catalysts are chemically identical, differences in other factors can necessitate distinct catalyst concentrations to achieve the same biodiesel yield (Gondra, 2010).

   Catalyst concentration stands out as one of the most critical variables influencing biodiesel production (B. Karmakar & Halder, 2019). Lower catalyst concentrations often result in reduced biodiesel yields. One reason for this decrease is the limited catalytic surface area available for transesterification when less catalyst is used (Korkut & Bayramoglu, 2018; Tan et al., 2015). Another factor contributing to lower yields with reduced catalyst concentrations is the solubility of methanol in the

byproduct glycerol. Inadequate catalyst concentration can lead to excessive unreacted methanol dissolving into glycerol, hindering biodiesel production efficiency (A. Reddy et al., 2016). Interestingly, as catalyst concentration increases, biodiesel yields often reach a peak and then decline. Higher catalyst concentrations can reduce biodiesel yields by causing slurry formation, increasing viscosity, and ultimately promoting soap formation (Korkut & Bayramoglu, 2018; Mata et al., 2011; A. N. R. Reddy et al., 2014). Hence, catalytic studies focused on biodiesel synthesis through transesterification frequently investigate the optimal catalyst concentration (Fayyazi et al., 2015).

2.5.4 CATALYST

Catalysis plays a pivotal role in the transesterification step of biodiesel production, acting as a catalyst to accelerate the conversion of triglycerides into biodiesel and glycerol. This essential process is influenced by various factors, including the type of catalyst used, reaction conditions, and catalyst concentration (Rizwanul Fattah et al., 2020).

Two primary categories of catalysts are employed in transesterification: acid and base catalysts. Acid catalysts, such as hydrochloric acid or sulfuric acid, are effective for feedstock with high levels of free fatty acids (FFA). They esterify FFAs, converting them into biodiesel. Conversely, base catalysts, typically alkali metal or alkaline earth metal hydroxides like sodium hydroxide (NaOH) or potassium hydroxide (KOH), are preferred when the feedstock has a low FFA content. Base catalysts are known for their rapid reaction rates and milder operating conditions.

The choice of catalyst significantly influences reaction kinetics and efficiency. Different catalysts may require varying reaction times, temperatures, and methanol-to-oil ratios to achieve optimal biodiesel yields. Researchers often explore the influence of catalyst

concentration, temperature, and other variables to fine-tune the transesterification process (Ludwig & Schindler, 2017). Moreover, the economics of biodiesel production are impacted by the cost and reusability of catalysts. Catalyst selection is a crucial consideration for both the feasibility and sustainability of large-scale biodiesel manufacturing.

Evidently, catalysis is an indispensable step in the transesterification of biodiesel production. It not only accelerates the conversion of triglycerides into biodiesel but also influences reaction conditions, efficiency, and economics. The choice of catalyst is a critical decision, and ongoing research seeks to optimize this essential component of biodiesel production for a greener and more sustainable energy future.

2.5.4.1 Homogeneous Catalysts

Homogeneous catalysts, as the name suggests, are in the same phase as the reaction system. They are favoured for their simplicity and efficiency in promoting the esterification of triglycerides into biodiesel. These catalysts are typically chemicals, and they expedite the reaction by lowering the activation energy required.

One of the most widely used homogeneous catalysts in biodiesel production is the alkaline catalyst, including sodium hydroxide (NaOH), potassium hydroxide (KOH), and others like sodium bicarbonate (CHO_3Na) and potassium methylate (CH_3OK). These catalysts are particularly effective when dealing with feedstock that have a lower concentration of free fatty acids (FFA). The alkaline catalysts facilitate the conversion of triglycerides into biodiesel by breaking ester bonds and promoting esterification reactions.

The advantages of homogeneous catalysts include their speed in achieving a complete reaction and their ease of use. However, it's essential to consider the FFA content of the feedstock when choosing the appropriate catalyst. High FFA content may require additional steps to neutralize FFAs before the esterification process begins.

Homogeneous catalysts, especially alkaline catalysts, are pivotal in the esterification process of biodiesel production. They simplify the conversion of triglycerides into biodiesel, contributing to the efficiency and viability of this sustainable energy source. Researchers continue to explore and optimize the use of homogeneous catalysts to make biodiesel production even more environmentally friendly and economically viable (Atadashi et al., 2013; De Lima et al., 2016).

2.5.4.2 Heterogeneous Catalysts

Heterogeneous catalysts play a crucial role in the biodiesel production process, offering distinct advantages over homogeneous catalysts. These catalysts are characterized by being in a different phase from the reactants, typically as solid materials. They have become an area of significant research focus due to their potential to enhance the sustainability and efficiency of biodiesel production.

One key advantage of heterogeneous catalysts is their reusability, which significantly reduces waste and production costs. For example, recent research has explored the use of a heterogeneous solid acid catalyst derived from rice straw in biodiesel production, resulting in highly operative and sustainable processes (Mandari & Devarai, 2021). Also, heterogeneous catalysts offer high yields of biodiesel even under typical transesterification conditions, making them a cost-effective choice. Their reusability further adds to their economic appeal (Gupta & Pal Singh, 2023). Recent studies have also emphasized the use of nanoparticles as heterogeneous catalysts, highlighting their effectiveness in the production of biodiesel (Narasimhan et al., 2021).

The environmental benefits of biodiesel produced with the aid of heterogeneous catalysts are substantial. Biodiesel production from fully renewable resources aligns with green chemistry principles and contributes to closing the carbon cycle, making it an eco-friendly alternative to

fossil fuels (Radu & Kraus, 2015). Heterogeneous catalysts have emerged as a pivotal component of biodiesel production, offering reusability, cost-effectiveness, and environmental benefits. Ongoing research in this field aims to further optimize these catalysts and their applications, ensuring a sustainable and efficient future for biodiesel production. Heterogeneous acid and basic catalysts play pivotal roles in biodiesel production, each contributing to specific stages of the transesterification process. Heterogeneous acid catalysts, often in the form of solid acids, are employed to catalyze the esterification of free fatty acids (FFAs) in the feedstock, a critical step when dealing with low-grade or high-FFA feedstock. These catalysts offer advantages over their homogeneous counterparts by simplifying the separation process, promoting reusability, and reducing the need for additional processing costs. They are particularly effective in converting FFAs into biodiesel and have the potential to replace traditional homogeneous acid catalysts in biodiesel production (Melero et al., 2009; Thangaraj et al., 2019).

Conversely, heterogeneous basic catalysts are integral in the transesterification of triglycerides present in oils and fats. These catalysts, often supported by materials like silica, offer high activity and longevity. They facilitate the conversion of triglycerides into biodiesel by reacting with alcohol, breaking the ester bonds in the feedstock. Heterogeneous basic catalysts are known for their ease of recovery, reusability, and cost-effectiveness, making them valuable in biodiesel production, particularly when dealing with various feedstock and high FFA content. They contribute to a green and sustainable biodiesel production process, reducing both environmental impact and processing costs (Jayakumar et al., 2021).

2.5.4.3 Heterogeneous Bifunctional Catalysts

Heterogeneous bifunctional catalysts have garnered significant attention in biodiesel production due to their ability to simultaneously facilitate multiple crucial reactions in the transesterification process. These catalysts are designed to have **two** distinct active sites, one

for acid-catalyzed esterification of free fatty acids (FFAs) and another for base-catalysed transesterification of triglycerides. This dual functionality makes them particularly effective in converting diverse feedstock into biodiesel. Recent advancements in heterogeneous catalysis for biodiesel production have explored the potential of bifunctional catalysts, aiming to optimize the process for circular bio-economy and sustainability. These catalysts offer advantages such as improved efficiency, reduced environmental impact, and the ability to convert both FFAs and triglycerides effectively, making them promising candidates for enhancing biodiesel production processes (Orege et al., 2022; Talha & Sulaiman, 2016). Furthermore, Nano and bifunctional catalysts, with their high surface area, have emerged as powerful options, enabling the conversion of free fatty acids and triglycerides while contributing to the economic viability and eco-friendliness of biodiesel production (Talha & Sulaiman, 2016).

2.5.5 OPTIMIZATION OF BIOBIESEL PRODUCTION

The primary objective of the production unit is to achieve the highest possible yield in biodiesel production, a goal attainable through precise adjustments of the transesterification process parameters (Ong et al., 2019). Through the modelling and optimization of biofuel production processes, we can gain insights into the key factors that contribute to maximizing yield and production rate. The fundamental aim of this modelling endeavour is to bolster yields by improving the efficiency of biofuel production. In the field of biofuel manufacturing, various modelling techniques have been employed (Nath & Das, 2011; Saraphirom & Reungsang, 2010; J. Wang & Wan, 2009), and the application of modelling and optimization has consistently demonstrated its ability to enhance biofuel output (Ghosh et al., 2012; Gueguim Kana et al., 2012). For instance, Ghosh et al. (2012) and Milano et al. (2018) successfully optimized biofuel production using the response surface technique (RSM). Multiple optimization approaches are available, including One-factor-at-a-time,

Plackett-Burman design, Genetic algorithms, Factorial design, Artificial neural network, and Response surface methodology. The principles and constraints of widely-used methods such as the one-variable-at a-time approach (OVAT), factorial Design of Experiment (DOE), and response-surface methodology (RSM) are well-documented. OVAT, for instance, may overlook optimal set points because it doesn't consider the interactive effects of parameters on the process (Gueguim Kana et al., 2012; Y. X. Wang & Lu, 2005). Additionally, there's a limited number of experimental configurations available for identifying the best optimum with this method (Lotfy et al., 2007). Factorial design of experiments, while comprehensive, becomes resource-intensive with an increasing number of input variables, making it less favoured (J. Wang & Wan, 2009).

2.6 DESIGN OF EXPERIMENT

Experimental design, also known as the design of experiments (DOE), is a systematic and well-structured methodology employed for conducting controlled tests and assessing their impact on a response variable (Telford, 2007). DOE is a potent technique for optimizing the utility of data obtained from a study while minimizing the time and effort invested in data collection, primarily by reducing the total number of experimental runs (Uy & Telford, 2009). Within this approach, the experiment's design prescribes specific parameter settings and combinations for each run, allowing for the simultaneous examination of multiple factors through multivariate testing.

By independently manipulating each variable, a causal predictive model can be developed, distinguishing DOE from observational studies and other data collection techniques that can only establish correlations, not causations. The traditional experimental method, which involves altering one variable at a time, is associated with its limitations, such as inefficiency and an inability to detect outcomes resulting from the interaction of multiple variables (Telford, 2007).

The core principles of experimental design aim to enhance the efficiency of experiments by addressing the influence of two potential nuisances that can occur during testing. These guiding principles include:

1. Randomization
2. Blocking
3. Replication
4. Orthogonality
5. Factorial experimentation

Experimental designs encompass a variety of methodologies used to systematically structure experiments. Some of these designs include:

1. **Factorial Design**: This approach involves studying multiple factors and their interactions to understand their combined effects on an outcome.
2. **Randomized Complete Block Design (RCBD)**: In RCBD, experimental units are grouped into blocks to minimize variability within groups. This design helps account for potential sources of variation.
3. **Central Composite Design**: This design is used in response surface methodology (RSM) to explore the relationship between multiple factors and a response variable by examining both linear and quadratic effects.
4. **Box-Behnken Design**: This design, often used in chemical processes, allows for efficient testing of factors and their interactions to optimize processes.
5. **Saturated Design**: Saturated designs involve testing all possible combinations of factors and levels, providing comprehensive information about the system under study.
6. **Mixture Design**: Mixture designs are employed when a system involves multiple components or ingredients with varying proportions.

These different experimental designs offer researchers valuable tools for conducting experiments, each suited to specific research questions and objectives.

Design of Experiments (DOE) utilizing Response Surface Methodology (RSM) is a prevalent statistical approach for developing empirical models to optimize responses influenced by multiple independent variables. The RSM optimization process typically involves selecting an appropriate statistical model, conducting experiments in a randomized sequence, and performing analysis of variance (ANOVA) to identify optimal conditions. Among the various designs employed in RSM, Central Composite Design (CCD) and Box-Behnken Design (BBD) are particularly prominent. CCD is advantageous for its flexibility and efficiency in fitting a full quadratic model, making it suitable for sequential experimentation. BBD, on the other hand, is designed to estimate second-order (quadratic) models efficiently without involving extreme factor combinations, thereby reducing the number of required experimental runs. Both designs are instrumental in exploring the relationships between factors and responses, facilitating the identification of optimal conditions in complex processes.

CHAPTER THREE

MATERIALS AND METHODOLOGY

3.1 MATERIALS

3.1.1 MATERIALS AND REAGENTS USED

The table below is a list of materials and reagents used for the production of biodiesel:

Table 3. 1***: The raw materials and reagents used***

S/N	Materials	Source	Uses
1	Distillled water	Central Research Lab, UNIBEN	It is used for dilution, prepare standard solutions and also for washing biodiesel.
2	Rice bran	Danesi & Sons Rice Milling Factory, Auchi, Edo State.	It is a feedstock for the basic precursor of the heterogeneous bi-functional catalyst.
3	Cow bones	UBTH abattoir, Benin, Edo State.	It is a feedstock for the basic precursor of the heterogeneous bi-functional catalyst.
4	Neem oil	Local Market	It is a feedstock for biodiesel production.
5	Ethanol (CH_3OH)	Guangbang Guanghua Chemical Factory Co Ltd.	It is for the determining acid saponification value of neem oil and acid value of biodiesel production.
6	Phenolphthalein indicator	Spectrum Reagent and Chemical Pvt, Ltd.	It serves as an indicator for titration in determining the acid

			value of the oil.
7	Potassium hydroxide (KOH)	Labtech Chemicals Ltd.	It is for the pretreatment of the basic precursor and in determining the acid value of neem oil and biodiesel.
8	Sodium hydroxide (NaOH)	NIKE Chemical, India.	It is for neutralization during carbonization of the catalyst.
9	Hydrochloric acid (HCl)	Guangbang Guanghua Chemical Factory Co Ltd.	It is for biodiesel production.
10	Potassium Iodate (KI)	Labtech Chemicals Ltd.	It is for determining the iodine value.
11	Chloroform	Loba Chemie Pvt, Ltd.	It is used for determining the saponification value.
12	Benzene (C_6H_6)	Guangbang Guanghua Chemical Factory Co Ltd.	It is used for determining the free fatty acid content.
13	Sulphuric acid (H_2SO_4)	Guangbang Guanghua Chemical Factory Co Ltd.	It is for the pretreatment of the acid precuror.
14	Methanol	Guangbang Guanghua Chemical Factory Co Ltd.	It is used to stimulate the simultaneous esterification and transesterification of Neem oil to produce biodiesel.
15	Wiji Reagent	VWR International, India.	It is for determining the iodine value.
16	Acetic Acid	Guangbang Guanghua Chemical Factory Co Ltd.	It is used for peroxide value.

17	Starch Indicator	Renew Cold Water Fabric Starch	An indicator for the iodine value.

3.1.1 EQUIPMENTS USED

The table below is a list of different apparatus and their uses.

Table 3. 2: List of apparatus used for biodiesel production

S/N	Equipment	Function
1	Sieve	For separating particle sizes.
2	Funnel	Used for safe of transfer of liquids into measuring cylinder and conical flask
3	Beaker	As a container for substances.
4	Retort stand	For holding burette and separating funnel.
5	Burette	Use for holding reagent during titration experiments.
6	Dropper	For holding liquids in very small quantities. For adding drops of indicators.
7	Conical flask	or preparation and storing of solutions.
8	Crucible	Use for holding hot materials
9	Furnace	For calcination of cow bones and carbonization of rice bran at high temperature.
10	Viscometer	Ascertaining the viscosity of both biodiesel and neem oil.
11	Weighing scale	Used for measuring the mass of substances
12	Measuring cylinder	For volumetric measurement of liquids.
13	Stirrer	Use for mixing or stirring for uniform mix,
14	Evaporating dish	Used to determine the moisture content.
15	Microwave aided reactor	This is used to produce biodiesel at very time difference.

16	Centrifuge	Used to separate the biodiesel mixture obtained after reaction.
17	Round bottom flask	Used as reactor in the production of biodiesel.
18	Magnetic stirrer	This equipment supplies heat to the reaction and ensure uniform and continuous stirring.
19	Separating funnel	For separation and washing of biodiesel. Also used to hold up the reacted mixture so at to allow phase separation by gravity.
20	Oven	Used for heating and evaporation purpose

3.2 METHODS

3.2.1 CATALYST PREPARATION

Cow bones were collected from the University of Benin Teaching Hospital (UBTH) Cooperative Abattoir. The collected cow bones were washed and scrubbed thoroughly with water to remove impurities and any little meat left attached to the bones. It was sun dried for 8 days to remove moisture content before grinding. Once the bones were dried, it was crushed and grinded using a mechanical grinder at Uselu market in Benin City, Edo state. The grinded cow bones were sieved for uniform catalytic activity before then calcined in a muffle furnace at a temperature of $900^{O}C$ for 4 hours. The calcined cow bones are then soaked in 1M KOH for 48 hours to ensure effective contacting so as to enhance the catalyst surface area and activity. After that, the excess water was evaporated by drying in a furnace at 120oC for 4 hours. The activated sample is then cooled to room temperature and washed thoroughly with distilled water to remove residual KOH and byproducts (e.g potassium salts). It is continuously washed until the pH of the wash water is neutral (~7). The washed sample

is then dried in an oven at 100^0C for 6 hours to remove any moisture content and allowed to cool before being stored in an airtight container to prevent atmospheric interaction.

Rice bran was used as the support for the bifunctionality of the catalyst. Rice bran was procured from Danesi & sons milling factory, Auchi. The rice bran was washed with water to remove dirt and impurities and is then dried in an oven at 100^0C for 24 hours. It is sieved using a 0.060mm mesh size to attain a consistent particle size distribution. The sieved rice bran is soaked in 1.5M of H2SO4 solution for 24 hours at room temperature to allow the acid fully penetrate the material and initiate part carbonization. After soaking, the excess liquid is removed by filtration/decantation and placed in an oven to dry at 110^0C. The dried bran is carbonized by heating to 220^0C for 3 hours (P. Wataniyakul et al., 2018) before it is left to cool at room temperature. This process converts the bran into biochar with high catalytic potentials. The carbonized rice bran is washed with distilled water to remove residual H2SO4 and any byproducts. It is continuously washed until the pH of the wash water is neutral (~7) and then dried in an oven at 100^0C for 10 hours to remove any moisture content. The activated rice bran is stored in an airtight container to maintain its catalytic properties and prevent contamination.

By using the wet impregnation method, the acid and basic catalysts were combined in a beaker. The calcined cow bones were dissolved in distilled water for this process, and the appropriate quantity of rice bran catalyst was measured and added to the mixture. It was mixed thoroughly on a magnetic stirrer until a thick slurry was formed and then placed in an oven for 1 hour to dry. After that, the impregnated catalyst was heated in a furnace at 400^0C for 4 hours. The sample is taken out and allowed to cool in a desiccator for 24 hours before being transferred to an airtight container.

3.2.2 OIL CHARACTERISATION

The neem oil was characterized based on its physical and chemical properties. The determination of feedstock qualities allows not only to know the state of the oil but also to make specific decisions on whether it requires further treatment or not. The determined physio-chemical attributes are as follows:

3.2.2.1 Acid Value

This test was used to determine the amount of free fatty acid content of the neem oil using the acid base titration technique. The acid value is the quantity of KOH required to neutralize one gram of oil free fatty acid content, or one gram using two drops of phenolphthalein as indicator. KOH solution with normality of 0.10 was used as a titrated solution to measure acid value and free fatty acid. (Atabani.A.E. et al., 2012). In this method, 1 g of the oil sample was weighed in a conical flask using a weighing scale. 10 mL of benzene and 10 mL of ethanol and poured into the conical flask. 3 drops of phenolphthalein indicator were added to the flask. The mixture was stirred vigorously until it turned pink. The volumes obtain from the blank and main titration were used to calculate for the acid value as follow:

$$\textbf{Acid Value (KOH/g)} = \frac{\boldsymbol{N\ of\ KOH} \times \mathbf{56.1} \times (\boldsymbol{V_s - V_b})}{\boldsymbol{weight\ \ of\ oil\ sample(g)}}$$

Molecular mass of KOH = 56.1

N = Normality of KOH

Vs = Volume of KOH used with oil

Vb = Volume of KOH used without oil (blank solution)

W = Weight of oil sample

$$\textbf{Percentage Free Fatty Acid} = \frac{\boldsymbol{Acid\ Value}}{\mathbf{2}}$$

3.2.2.2 Saponification Value

Saponification is the process of breaking down or degrading a neutral fat into glycerol and fatty acids by treating the fat with alkali. The saponification number (value) is defined as the milligrams of potassium hydroxide (KOH) required to saponify 1g of fat. It is an index of average molecular weight of the triacylglycerol's in the sample (Odoom W. & Edusei V., 2015). An oil sample weighing 1 g was placed in a conical flask, and 50 mL of 0.5 M alcoholic KOH solution was added. The mixture was refluxed for one hour using a reflux condenser. After cooling, two drops of phenolphthalein were added, producing a pale pink coloration. The mixture was then titrated against 1 M HCl until the pink color disappeared. A blank test was conducted under the same conditions without the oil sample. The saponification value was calculated using this formula:

$$\textbf{Saponification Value} = \frac{N \times 56.1 \times (V_b - V_s)}{W}$$

N = Normality of HCl

Vb = Blank titre value

Vs = Sample titre value

W = Weight of oil sample (Neem oil)

3.2.2.3 Peroxide Value

The Peroxide Value (PV) indicates the condition of unsaturated oils and fats, as oxidation causes them to become rancid by forming peroxides. PV measurement helps monitor the formation of peroxides during the early stages of oxidation (Popa et al., 2017). 2.5g of oil was weighed into a conical flask, and 30ml of a 3:2 mixture of acetic acid and chloroform was added to the oil. The previous procedure was done without the use of oil. 2 ml of KI solution

was measured into two separate beakers A and B. Beaker A contains chloroform, acetic acid, and oil, and beaker B contains simply chloroform and acetic acid. For at least 60 seconds, the beakers were shaken. Each beaker received 30ml of water, and the mixture received 1 ml of starch solution. After that, the mixture was titrated with 0.1M sodium thiosulphate. The absence of the brown blue coloring denotes the end point.

Peroxide Value = $\frac{\mathbf{0.01 \times 1000 \times (V_b - V_s)}}{\boldsymbol{W}}$

Vb = Blank titre value

Vs = Sample titre value

W = Weight of oil sample (Neem oil)

3.2.2.4 Iodine Value

This is a measure of the degree of unsaturation in any vegetable oil or animal fat. It is the weight of iodine absorbed by 100 parts by weight of the sample. It is expressed in (mg/g). To determine the iodine value of Waste Cooking Oil, 1 gram of the oil was mixed with 10 mL of chloroform (CCl_4) in a conical flask, heated gently, and then left to cool for 10 minutes. 25 mL of Wij's reagent (iodine trichloride solution) was added, and the flask was shaken vigorously before being kept in the dark for 30 minutes to prevent light interference. After this, the mixture was titrated with sodium thiosulfate until it turned yellow. Then, 20 mL of 10% potassium iodide (KI) solution and 150 mL of distilled water were added. The resulting yellow solution was titrated again with sodium thiosulfate, using starch as an indicator, until the color changed from blue-black to colorless, marking the endpoint. A blank test was also carried out under the same conditions for accuracy.

Iodine Value = $\frac{\boldsymbol{N \times 12.69 \times (V_b - V_s)}}{\boldsymbol{W}}$

N = Normality of HCl

Vb = Blank titre value

Vs = Sample titre value

W = Weight of oil sample (Neem oil)

3.2.2.5 Kinematic Viscosity

The kinematic viscosity of the waste cooking oil was measured using a calibrated capillary calorimeter. The viscosity of both the oil and the biodiesel was determined. The equipment was switched on and 200 g of oil was measured in a beaker and placed under the calorimeter for readings.

3.2.2.6 Density

The density of the waste cooking oil was determined using a 50 mL density bottle. First, the empty bottle was weighed using a balance, and its weight was recorded. Then, the bottle was filled with the oil and the combined weight of the bottle and oil was measured. The mass of the oil was obtained by subtracting the weight of the empty bottle from the total weight. The density of the oil was then calculated by dividing the mass by the 50 mL volume of the density bottle. The density, expressed in kg/m³, was determined using the equation below.

$$\textbf{Density} = \frac{\boldsymbol{Weight\ of\ Neem\ Oil}}{\boldsymbol{Volume\ of\ Neem\ Oil}}$$

3.2.2.7 Moisture Content

A known-weight beaker was used to hold 5.00 g of waste cooking oil. The combined weight of the beaker and oil was measured using a weighing balance before the sample was placed in an oven at 120°C for 1 hour to allow evaporation. After evaporation, the beaker with the

dried oil was weighed again, and the final weight was recorded. The percentage moisture content was calculated as follow;

$$\textbf{Moisture Content} = \frac{(Wi - Wf)}{Wi} \textbf{ x 100\%}$$

Wi = Initial weight of Neem Oil

Wf = Final weight of Neem Oil

3.2.3 CATALYST PREPARATION

The optimization of biodiesel production from Neem Oil will involve the use of cow bones and rice bran as basic and acidic precursor feedstock for synthesizing heterogeneous bifunctional catalysts. These catalysts will facilitate both the transesterification of triglycerides and the esterification of free fatty acids in Neem Oil. Through kinetic studies and process optimization, the catalysts will enhance biodiesel production in a more efficient, cost-effective, and environmentally friendly manner.

3.2.3.1 Preparation of Acidic Precursor

Rice bran was obtained from Danesi & Sons Rice Milling Factory in Auchi. The preparation process began with cleaning, followed by sieving and washing with distilled water to remove impurities. The washed rice bran was then dried in an oven at 120°C for 1 hour. After drying, a 0.6mm sieve was used to filter to ensure a consistent particle size distribution. The sieved bran carbonized by heating in a furnace at 250°C for 2 hours. Once carbonization was complete, the rice bran was removed from the furnace and allowed to cool to room temperature.

The next step involved sulfonation, where the carbonized rice bran was treated with a 1.5M sulphuric acid (H_2SO_4) solution in an airtight container. The sample was left for 48 hours

before being washed with distilled water to remove sulphate ions. Following this, it is filtered using distilled water and a filtering net to eliminate contaminants and free ions. Finally, the sulfonated rice bran was sun-dried, then further dried in an oven at 150°C to achieve a powdered form, and stored in an airtight container.

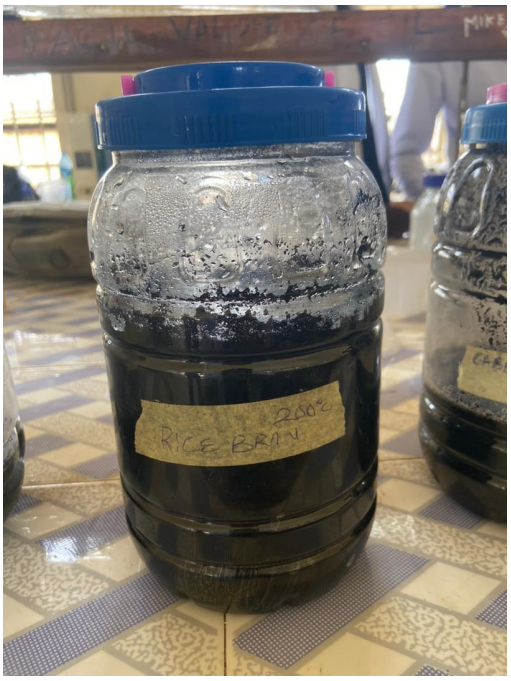

Plate 3.1: Carbonized rice bran been treated with sulphuric acid in an airtight container

3.2.3.2 Preparation of Basic Precursor

Cow bones were obtained from UBTH Cooperative and initially washed in warm water to remove any contaminants or residual meat. The cleaned bones were then left to dry under the sun for five days. Once dried, they were crushed into smaller bits and grinded. The grinded cow bones are filtered with a 0.75mm sieve and calcined at 900°C for four hours. After calcination, the bones were soaked in a 1M KOH solution for 48 hours, then filtered and thoroughly washed with distilled water. The sample was subsequently sun-dried before being placed in an oven at 150°C for three hours. After drying, it was allowed to cool to room temperature and stored in an airtight container (Akhabue & Ogogo, 2018).

Plate 3.2: Calcinated cow bones been treated with Potassiun hydroxide in an airtight container

Plate3.3: Drying of acid and basic precursor in an oven

3.2.3.3 Catalyst Impregnation

This is carried out by combining the basic and acidic precursors in a 1:2 ratio in a beaker and mixed together. The mixture is washed with distilled water and then put in sunlight before

being dried at 150°C in the oven. The dried mixture was heated once more in a muffle furnace at 700°C for 3 hours before then placed in a desiccator and allowed to cool. The impregnated catalyst is transferred into an airtight container.

Plate 3.4: Combination of acid and base precursor mixed together

Plate 3.5: Catalysts loaded in a desiccator to cool

3.3 CATALYST CHARACTERIZATION

3.3.1 SURPHASE MORPHOLOGY OF PROCESSED CATALYST

Scanning Electron Microscopy (SEM) is a powerful analytical technique used to examine various materials at high magnifications, producing high-resolution images. SEM operates by detecting high-energy electrons emitted from a sample's surface when it is exposed to a focused electron beam from an electron gun. The objective lens of the SEM directs this beam onto a small region of the sample surface.

To achieve high-quality imaging, parameters such as the accelerating voltage, aperture size, and working distance (the gap between the sample and the electron gun) can be adjusted. Electrons can be detected in two ways, each providing valuable insights through different imaging and processing techniques. Backscattered electrons help create contrast in an image based on the chemical composition of the sample, while secondary electrons, emitted near the surface, reveal surface topography (Scanning Electron Microscopy (SEM) Analysis and Imaging - TWI, n.d.).

During SEM analysis, a low-energy electron beam scans the sample surface, interacting with the material and causing the emission of photons and electrons. These interactions generate signals that offer critical information about the sample's surface characteristics, chemical composition, crystalline structure, and the arrangement of its components. The extensive data obtained from these interactions enables a detailed examination of the material's properties (Omidi et al., 2017).

3.3.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR spectroscopy is highly valued for its effectiveness in analyzing the chemical properties and structures of various materials, including biological samples (Rosset & Perez-Lopez, 2019). In industrial applications, it is a widely used technique for quality control and is often the first step in material analysis. Changes in distinct absorption band patterns can indicate variations in material composition or the presence of contaminants.

FTIR microanalysis is commonly employed to identify the source of product defects detected through visual inspection. It is particularly useful for analyzing both larger surface areas and small particles, typically ranging from 10 to 50 microns, to determine their chemical composition.

During FTIR analysis, a sample is exposed to infrared radiation within the range of 10,000 to 100 cm^{-1}. Some of this radiation is absorbed, while the rest passes through the sample. The absorbed radiation causes molecular vibrations and/or rotational energy changes. The resulting signal, detected as a spectrum, serves as the sample's unique chemical fingerprint, usually spanning from 4000 cm^{-1} to 400 cm^{-1}. Since each molecule or chemical structure produces a distinct spectral pattern, FTIR analysis is an excellent tool for chemical identification (FTIR Analysis | RTI Laboratories, n.d.).

3.3.3 BET SURFACE AREA ANALYZER

The Brunauer-Emmett-Teller (BET) theory is a key analytical method used to determine the specific surface area of materials by explaining the physical adsorption of gas molecules onto solid surfaces. It applies to multilayer adsorption systems and is widely used to measure surface area using non-reactive probe gases as adsorbates. Nitrogen is the most commonly used adsorbate in BET analysis, with standard measurements typically conducted at its boiling point. Other gases, such as water, carbon dioxide, and argon, are also used at different

temperatures and measurement scales, though less frequently. The specific surface area determined through BET analysis depends on the choice of adsorbate molecule and its adsorption cross-section, as surface area is a scale-dependent property without a universal value (Nasrollahzadeh et al., 2019).

Porous materials are frequently used in chemical reactions and separation processes, and their performance is assessed using empirical gas adsorption data. The BET theory, an extension of the Langmuir monolayer adsorption model into a multilayer adsorption framework, is commonly applied to determine a material's specific surface area. This method is used for both crystalline and amorphous porous materials, making it a standard approach for surface area analysis (Pourhakkak et al., 2021).

3.3.4 ELECTRON DISPERSIVE X-RAY SPECTROSCOPY (EDX)

Energy-dispersive X-ray spectroscopy (EDS, also known as EDX or XEDS) is an analytical technique used for elemental analysis and chemical characterization of samples. It is also referred to as energy-dispersive X-ray analysis (EDXA) or energy-dispersive X-ray microanalysis (EDXMA). EDS allows for the mapping of elemental composition at specific locations or across an imaged area. Additionally, it can provide compositional data for quasi-bulk samples using high accelerating voltage and low SEM magnification, as well as for specific particles, morphologies, or isolated regions on filters and within deposits (Ismail et al., 2019).

EDS operates based on the interaction between electrons and bionanomaterials, which results in the emission of X-rays. The ability to characterize elements effectively depends on their unique atomic structures, which produce distinct peaks on the X-ray spectrum. EDS is often integrated with scanning electron microscopes (SEMs) to analyze the elemental composition of nanoparticles. The EDS detector captures the X-rays emitted from the nanoparticle sample

and quantifies the intensity of the emitted X-rays relative to their energy (Akintelu et al., 2023).

3.3.5 X-RAY DIFFRACTION (XRD)

X-ray diffraction (XRD) is a highly versatile technique used for phase and elemental analysis, offering valuable chemical insights. In addition to chemical characterization, XRD is essential for texture analysis and stress measurement. While it is primarily used for crystalline samples, it can also assess the degree of crystallinity in polymers. Traditionally applied to bulk samples, advancements in optical techniques have expanded its use to thin film analysis. XRD operates based on Bragg's law of diffraction (Nasrazadani & Hassani, 2016).

XRD is also a key method for characterizing polymeric nanocomposites, serving as a primary tool for identifying bonding types and the crystalline organization of amorphous polymeric nanocomposites. These materials exhibit strong XRD responses due to their crystalline behaviour after formation. The technique enables the detection of microstructural changes and variations in interlayer spacing within the samples (Assad et al., 2023).

3.3.6 THERMO GRAVIMETRIC ANALYSIS (TGA/DTGA)

Thermogravimetric analysis (TGA) is a thermal analysis technique used to assess changes in the mass of materials based on their chemical and physical characteristics. TGA measurements are typically conducted in two ways: by monitoring mass loss over time at a constant temperature or by observing temperature changes at a constant heating rate. This method allows for the investigation of physical processes such as second-order phase transitions, vaporization, and desorption, as well as chemical reactions like dehydration and decomposition.

TGA is particularly useful for evaluating mass variations in samples due to oxidation, thermal degradation, or the loss of volatile components. Additionally, standardized TGA testing protocols can be applied to determine a material's thermal stability and its resistance to degradation (Parameshwaran et al., 2018).

3.4 BIODIESEL PRODUCTION

Biodiesel was produced using neem oil, methanol, and a bifunctional catalyst synthesized from rice bran and cow bones. First, the neem oil was sieved to remove impurities and then weighed using an electronic balance before being transferred into a round-bottom flask. The catalyst and methanol were added according to the optimized reaction conditions. The mixture was then placed in a microwave, where both the magnetic stirrer and microwave were set to the specified conditions for the reaction.

Once the reaction was complete, the resulting biodiesel was centrifuged to separate the glycerol, biodiesel, and catalyst. The separated mixture was then transferred into a separating funnel and allowed to settle for a period of time. The biodiesel was then extracted, washed with warm water to remove residual impurities, and finally heated using a magnetic stirrer to ensure purity.


LG
Watt
Min


LG

Plate 3.6: Microwave set-up *Plate 3.7: Oil placed within the set-up*

Plate 3.8: Separation in the separating funnel

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 OIL CHARACTERIZATION

The Neem Oil was analyzed for its physical and chemical properties following ASTM standards. The results of this characterization are presented in the table below:

Table 4.1: Physiochemical properties of Neem oil.

Properties	**Values**
Acid Value (mg KOH/g)	17.67
Free Fatty Acid Content (%)	8.835
Saponification Value (mg KOH/g)	196.91
Iodine Value (mg KOH/g)	88.83

Peroxide Value (mol/kg)	5.0
Molecular Weight (g/mol)	941.91
Density (g/ml)	0.924

The physicochemical properties of neem oil are crucial in assessing its potential for biodiesel production. An acid value of 17.67 mg KOH/g corresponds to a free fatty acid (FFA) content of 8.835%, indicating a significant presence of FFAs. High FFA levels can lead to soap formation during biodiesel processing, complicating the transesterification reaction. The saponification value of 196.91 mg KOH/g suggests the oil contains medium-chain fatty acids, which can influence the biodiesel yield and quality.

The iodine value of 88.83 reflects a moderate degree of unsaturation, affecting the fuel's oxidative stability and cold flow properties. The peroxide value of 5.0 meq/kg indicates initial stages of oxidation; while relatively low, it suggests the oil should be processed promptly to maintain quality. A molecular weight of 941.91 g/mol provides insight into the size of the fatty acid molecules, essential for calculating reactant ratios in biodiesel production. Lastly, a density of 0.924 g/ml is within the typical range for vegetable oils, influencing the energy content and combustion characteristics of the resulting biodiesel. In summary, while neem oil exhibits properties favorable for biodiesel production, its high FFA content necessitates pretreatment to reduce FFAs, ensuring efficient conversion and high-quality fuel output.

In biodiesel production, feedstocks like waste vegetable oils often contain high levels of free fatty acids (FFAs), which traditionally necessitate a two-step process: acid-catalyzed esterification to reduce FFAs, followed by base-catalyzed transesterification to convert triglycerides into biodiesel. This conventional approach can be time-consuming and costly due to the need for multiple reaction steps and extensive purification.

Heterogeneous bifunctional catalysts offer a more efficient alternative by combining acidic and basic sites within a single catalyst. This dual functionality enables the simultaneous esterification of FFAs and transesterification of triglycerides in one step, streamlining the process. For instance, a study utilizing a calcium oxide on alumina (CaO/Al_2O_3) catalyst demonstrated effective concurrent esterification and transesterification of waste palm and sunflower oils, achieving high yields of fatty acid methyl esters (FAMEs) under optimized conditions.

The advantages of using heterogeneous bifunctional catalysts include reduced processing time, lower energy consumption, and simplified product separation, as these solid catalysts can be easily recovered and reused. Additionally, their ability to handle feedstocks with high FFA content without prior esterification expands the range of suitable raw materials for biodiesel production, enhancing both economic viability and environmental sustainability.

4.2 OPTIMIZATION OF BIODIESEL PRODUCTION

The biodiesel was prepared following the methodology stated in 3.4. The production was obtained along with Glycerol in the separating funnel as shown below:

Plate 4.1: Separating funnel containing product

The product was tested and discovered ***NO biodiesel was formed***, product contained only excess methanol and neem oil.

The Biodiesel to be produced was optimized by adopting the Central Composite Design (CCD). The design of experiments involving reaction parameters such as oil to methanol ratio, catalyst loading, power intensity, speed and time were coded as A, B, C, D and E respectively is shown in Table 4.2 below. A total of 50 runs was to be done but stopped after the first five failed to produce biodiesel upon separation.

Table 4.2: CCD experimental design showing intended parameter for first five runs

Run	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Actual	Predicted
	A: Oil to Methanol Ratio	B: Catalyst Loading (grams)	C: Power Intensity (Watts)	D: Stirrer Speed (rpm)	E: Time (minutes)	Yield (%)	Yield (%)
1	15.00	5.00	800.00	500.00	5.00		
2	15.00	5.00	800.00	2000.00	2.00		
3	10.50	3.50	490.00	1250.00	3.50		
4	10.50	3.50	490.00	1250.00	2.00		
5	15.00	2.00	180.00	2000.00	2.00		

4.2.1 POSSIBLE REASONS FOR NON FORMATION OF BIODIESEL

1. **Improper activation of catalyst**: Bifunctional catalyst require proper activation especially during thermal treatment and need proper integration to facilitate simultaneous esterification and transesterification reactions. Improper functionalization can hinder the catalyst performance especially for processing feedstock with high FFA.
2. **Catalyst deactivation**: Exposure to moisture, air or impurities during catalyst preparation or storage can lead to deactivation.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

a. CONCLUSION

This research focused on optimizing microwave-assisted biodiesel production from neem oil using a bifunctional catalyst derived from cow bones and rice bran. The neem oil exhibited a free fatty acid (FFA) content of 8.835% and an acid value of 17.67 mg KOH/g, necessitating simultaneous esterification and transesterification processes. The catalyst was synthesized by calcining cow bones and rice bran, aiming to provide both acidic and basic sites for the reaction. Key parameters—including catalyst loading, methanol-to-oil ratio, microwave power, stirring speed, and reaction time—were optimized using response surface methodology. The microwave-assisted approach significantly reduced reaction time and energy consumption. Characterization of the produced biodiesel indicated that its physicochemical properties met ASTM D6751 and EN 14214 standards. This study demonstrates the feasibility of utilizing high-FFA neem oil and bio-waste-derived catalysts for efficient and sustainable biodiesel production.

b. RECOMMENDATION

This study demonstrated that utilizing waste cooking oil as a feedstock, with cow bones and rice bran serving as catalysts, can yield high-quality biodiesel. The effectiveness of agricultural bio-waste as catalyst in biodiesel production has been previously. To enhance biodiesel production, it is recommended that governments promote the efficient collection and utilization of waste clam shells and cocoa pod husks. Additionally, microwave-assisted transesterification has proven to significantly reduce reaction times while maintaining high biodiesel yields. Investing in larger-scale microwave reactors equipped with magnetic stirrers could facilitate increased biodiesel output. Adopting biodiesel as an alternative to conventional diesel offers several benefits including, enhanced engine performance due to

superior lubricity and ignition quality leading to improved efficiency and longevity; environmental advantages through the reduction of greenhouse gas emissions, thereby mitigating climate change impacts; and seamless integration into existing diesel engines without the need for modifications. These findings underscore the potential of waste-derived catalysts and microwave-assisted techniques in producing sustainable and efficient biodiesel.

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