MICROWAVE-AIDED BIODIESEL PRODUCTION FROM WASTE COOKING OIL USING A BIO-WASTE CATALYST DERIVED FROM CLAM SHELLS AND COCOA PODS: TAGUCHI OPTIMIZATION APPROACH.

BY

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CERTIFICATION

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

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DEDICATION

I dedicate this research project to the Lord, God Almighty, for giving me the life, the opportunity, and the grace to successfully accomplish this study.

This study is also dedicated to late Mr. Charles Tobrise for his love and confidence in me.

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For guiding me through the course of this study peacefully and successfully, I want to offer my sincere gratitude to God Almighty.

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ABSTRACT

This study explored the optimization of the microwave aided biodiesel production from waste cooking oil using a bio-waste catalyst derived from clamshell and cocoa pods via the Taguchi Optimization Approach.

The bio-waste catalyst was synthesized by the carbonization and sulphuration of cocoa pods to produce an acid precursor, while clam shells was calcined and treated with KOH to create the basic precursor. Both precursors were then impregnated using the wet-impregnation method. The bi-functional catalyst produced was characterized using standard techniques to establish its catalytic potency. Characterization involved SEM, EDXRF, XRD, FTIR, BET/BJH techniques and GCMS for the oil and biodiesel. Also, a model was developed to simulate the process and examine the interactive effect of process input variables on Waste cooking oil (WCB) yield using the Taguchi L16 approach. A reusability test was used to evaluate the catalyst's commercial viability by analyzing its effects on WCB yield and Acid Value. This test was carried out over five consecutive runs with the catalyst cleaned using methanol and reused, based on the optimal circumstances.

The BET analysis showed the catalyst to have a BET surface area of 393.3 m^2/g, Pore volume and diameter 0.02349 cm^3/g and 2.421 nm, respectively and the average micropore size calculated to be 5.520 nm in width and 0.1785 cc/g in volume, while the micropore surface area found to be 502.1 m^2/g. From the XRF result it is seen that calcium oxide has 68.431% followed by phosphorous pentoxide which contains 13.527% .The best combination of the input variables determined for the process is a heating power of 600W, methanol:WCO of 15:1, time of 5 min, reaction speed of 1000rpm and Catalyst loading of 2 wt% with an optimum WCB yield of 92.737 wt.% and AV of 0.408 mg KOH/g. It was shown that the WCB yield was significantly influenced by the reaction time, reaction speed, power of the reaction and the methanol to oil molar ratio but the catalyst loading, reaction speed, power of reaction and reaction time were the factors that had the biggest influence on the AV of the WCB. The WCB produced met standard specifications for biodiesel according to ASTM D6751 and EN 14214 requirements. Applying a microwave to the WCO transesterification helped to speed up the reaction's completion. The study found that clam shells and cocoa pods are viable feedstock for low-cost, environmentally friendly biodiesel manufacturing.

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NOMENCLATURE

WCB- Waste Cooking Oil Biodiesel

AV- Acid Value

FFA- Free Fatty Acid

FAME- Fatty Acid Methyl Ester

$CaCO_3$- Calcium Carbonate

WCO- Waste cooking oil

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

1.0 INTRODUCTION

1.1 Background Of Study

Based on the vital responsibilities that energy plays in human daily life, the global economy continues to give it the attention that it deserves, especially in the areas of industry, transportation, and power generation. Conventional fuels derived from fossil fuels are the main source of the amount of energy used worldwide. Fossil energy, the foundation for the global economy and pivot for other sectors to flourish, is the primary fuel used worldwide in energy consumption, having drawbacks that its prolonged use is harmful to the environment. The search for green and profitable alternative energy sources also environmentally friendly has become essential everywhere. Renewable Bio-fuels and other energy sources have the ability to meet the world's energy needs and demand lessening the harmful consequences of fossil fuels on the environment.(Falowo et al., 2019)

Due to the environmental concerns associated with the consumption and finite nature of fossil fuels, the discovery of a clean and sustainable fuel capable of reducing reliance on them will surely impact current and future energy utilization. Biodiesel and other renewable and environmentally friendly fuels are becoming more and more appealing due to the need for energy security as well as awareness of the harm that fossil fuels cause to the environment and global warming.(Abiodun et al., 2021).The price of feed-stocks has a significant impact on the biodiesel production's profitability. Up to 88% of the overall cost of producing biodiesel is spent on feed stocks. Therefore, using non-edible oils or leftover cooking oil can significantly reduce the cost of producing biodiesel. Unfortunately, the high levels of free fatty acids (FFA) in waste cooking oils and some inedible oils cause the alkali catalyst to saponify, which lowers the biodiesel output due to the challenge of product separation. Furthermore, the wastewater produced during the purification of products pollutes the environment, thus it must be treated either before it is released into the environment or before it can be reused again.(Akhabue et al., 2020). This also leads to additional cost in biodiesel production.

Selecting the right catalyst is another crucial step in the transesterification process. It depends on the oil's free fatty acid (FFA) content. High FFA oil is preferred in acid-catalyzed reactions, whereas the opposite is true with reaction catalyzed by alkali. Catalysts that are homogeneous or heterogeneous have been used to produce biodiesel. For industrial applications, homogeneous catalysis is often favored; nevertheless, it has some disadvantages, such as high cost, sensitivity to FFA and wet feedstock that causes soap formation, and excessive washing, which raises production costs. Nonetheless, there is still growing interest in alternative bio-based waste heterogeneous catalysts for the manufacture of biodiesel. The quantity and biogenic nature of the catalysts set them apart. They retain active sites with few unit operations during the manufacture of biodiesel, making them extremely efficient, economically viable, ecologically friendly, and easily recyclable while lowering the overall cost of production. There have been several published research on heterogeneous catalysts based on bio-waste that exhibit intriguing catalytic properties. It has been demonstrated that these catalysts have significant concentrations of potassium and calcium following high-temperature calcinations. The catalysts may be made from easily accessible bio-wastes at little or no cost, and they are a type of waste-to-wealth management. They are also recoverable, recyclable, and use less water during the washing process. The investigated bio-waste based catalysts fall into two categories: shell-based: Capiz shell, chicken eggshell, ostrich eggshell, crab shell, oyster shell, mussel shell, coconut shell, rubber seed shell, palm kernel shell, cockle shell, obtuse horn shell, trunk-based; oil palm trunk, pawpaw trunk, peel-based: unripe and ripe banana peel, sulfonated banana peel, banana stem, unripe and ripe plantain peel, tucuma peels, husk-based; cocoa pod husk, kola nut pod husk, elephant tree, and rice husk. Fly ash and bones are two more naturally occurring waste-based catalysts.(Betiku et al., 2024)

The unfavorable saponification results in high fuel viscosity, emulsification, and the formation of soap and gel byproducts, all of which complicate product separation. Increasing the FAME yield requires a two-step catalytic method(Mardhiah et al., 2017). The esterification of FFA in CJCO, an acid pre-treatment procedure, is the first step in the process. Its goal is to lower the FFA concentration to a safety level of less than 1%. The esterification of FFA into esters was usually accomplished in this technique using an acid catalyst. The second stage of the process, known as transesterification, will be carried out by using an alkali catalyst to change the current triglyceride into FAME product when the feedstock's FFA level has been lowered to an appropriate level. Alcohol is used in the transesterification reaction to break down triglyceride into the desired biodiesel form, fatty acid methyl ester (FAME), and glycerol as a byproduct. The three successive reversible reactions that comprise the transesterification process are as follows: first, triglyceride is converted into diglyceride; next, diglyceride is converted into monoglyceride; and last, monoglyceride is converted into ester and glycerol. This technique boosts the output of biodiesel from oils with high FFA, but it is not cost-effective due to the number of purification stages required to remove corrosive acids and the fact that the catalyst cannot be recovered. As an alternative to homogeneous catalysts in the synthesis of biodiesel, a single step process of simultaneous esterification and transesterification catalyzed by heterogeneous catalysts has recently been devised to eliminate the aforementioned shortcomings(Mansir et al., 2018). The quantity of wastewater produced during the biodiesel purification process is decreased by the use of heterogeneous catalysts in the production process. The catalyst can be recovered and reused, which has an additional benefit. The utilization of heterogeneous catalysts in the biodiesel manufacturing process has the potential to reduce the cost of production(Akhabue et al., 2020). While many researchers have employed heterogeneous catalysts to produce biodiesel through transesterification, catalysts utilized in the simultaneous processes of esterification and transesterification are unique in nature. They have both basic and acidic characteristics, making them bi-functional(Ali et al., 2018).

Microwave-assisted transesterification is a creative and efficient method for turning vegetable oils into biodiesel. Transesterification is the most widely used technique for producing biodiesel in commercial and research settings using inexpensive and ecologically friendly catalysts. By heating the reaction mixture using microwaves, this approach shortens the reaction time, speeds up the reaction rate, and produces more biodiesel. Microwaves offer several benefits over traditional techniques for transesterification, such as increased yields, lower energy use, and reduced waste production(Akhtar et al., 2023). Since microwaves transfer heat much more efficiently than traditional heating methods, this makes the reaction to occur swiftly. The microwave-irradiated method is an economical, eco-friendly, and energy-efficient way to produce biodiesel. Chemical processes can be enhanced and accelerated by direct energy delivery to the reactants during microwave irradiation(Ruatpuia et al., 2023).

1.2 Problem Statement

Biodiesel may not be fully adopted unless the problem of its high price is sufficiently resolved. The cost of feedstock accounts for 80–85% of the entire cost of producing biodiesel(Gülşen et al., 2014). The use of edible oils as feedstock would put the food supply in competition, and the switch to non-edible oils presents significant challenges due to their high FFA level, which would necessitate extra procedures (pretreatment of feedstock) and raise overall costs.

One of the most important aspects to biodiesel synthesis is the catalyst industrial production cost. For the purpose of producing biodiesel from non-edible oils, heterogeneous catalysis has surpassed traditional homogeneous catalysis in the last ten years. Numerous issues, including challenges with product separation, purification, and environmental cost concerns, as well as the former's incapacity to handle high feedstock, saponification, and catalyst consumption, are to blame for this(Betiku et al., 2019a)(Semwal et al., 2011). However, heterogeneous catalysts continue to have leaching issues in harsh environments(Thangaraj et al., 2019). Enzymes, which are thought to be more environmentally friendly for biodiesel synthesis, have issues with high cost and long reaction times, making them unfeasible for a cost-effective biodiesel synthesis process(Brahma et al., 2022).The bio-based bi-functional is a novel catalytic system that has demonstrated some encouraging trends. However, the synthesis of these catalysts is a complicated process, and the reaction kinetics need to be completely understood for the required process optimization. Therefore, the main driving forces behind this work are the difficulties associated with feedstock and the need for additional research on the reusability of this bio-based catalyst.

1.3 Relevance of The Study

The purpose of this study is to determine the critical factors and provide an appropriate strategy for increasing the production of biodiesel from waste cooking oil (WCO) by utilizing the simultaneous esterification and transesterification processes. By adjusting key variables including catalyst concentration, reaction duration, temperature, and methanol to oil ratio, it is possible to generate biodiesel with superior quality, high yield, and high methyl ester content purity.

Due to the extensive use of fossil fuels, the high energy demand in both the industrialized and domestic sectors has resulted in pollution issues. As a result, it is becoming more and more important to develop renewable energy sources that have less of an impact on the environment than fossil fuels like diesel fuels. Technically practical, economically competitive, environmentally acceptable, and widely accessible alternative fuel with knowledge of biodiesel's qualities is required. In addition to being non-toxic and biodegradable, biodiesel offers lower emission profiles than diesel fuel.

1.4 Aim and Objectives of Study

The aim of this study is the optimization of the microwave aided biodiesel production from waste cooking oil using a bio-waste catalyst derived from clamshell and cocoa pods via the Taguchi Optimization Approach.

The objectives of the research work are;

1. Preparation and characterization of bio-waste catalyst from cocoa-pods and clam shells.
2. Characterization of waste cooking oil.

3. Taguchi optimization of microwave-aided biodiesel production from WCO catalyzed by bio-waste catalyst.
4. Characterization of biodiesel produced using Taguchi optimum conditions.
5. Studying the effect of process variables on the biodiesel production process.
6. Reusability study of the bio-waste catalyst.

1.5 Scope of Study

The scope of the work is itemized below

a) Collection, washing, pulverization and preparation of the Biomass materials which are cocoa pods and clam shells into bi-functional catalyst.
b) Characterization of the waste cooking oil
c) Characterization of the used and unused Bi-waste catalyst
d) Simultaneous esterification and transesterification of waste cooking oil to yield biodiesel.
e) Efficient time management using microwave assisted technique.
f) Reusability studies on the Bi-waste catalyst.
g) Optimization of the biodiesel production.
h) Characterization of the biodiesel produced.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 ENERGY AND SOCIETY

Energy is a universal currency that has to be transformed into another form in order to accomplish anything. Stars that undergo thermonuclear explosions and huge galaxies that undergo galactic revolutions are two instances of how these processes are universally expressed. These processes can happen on Earth and include plate tectonic pressures, which split ocean floors and form new mountain ranges, as well as the gradual erosion caused by tiny raindrops. Human civilizations have produced larger populations, more intricate social and economic institutions, and an ever-improving standard of living for their citizens. The evolution of prehistoric humans and the course of human history can be interpreted as attempts to control bigger stocks and flows of more concentrated and diverse forms of energy and transform it into more efficient and useful forms such as heat, light, and motion.

For millions of years, life on Earth had an energy-neutral effect: plants and animals coexisted in a never-ending cycle. When early people learned to make fire, the natural order started to irreversibly change. Fire made it possible to prepare food, ward off predators, and shape metal into useful tools and deadly weapons. In the last 200 years, humans have discovered a way to convert heat into electricity, the most versatile and practical form of energy. Electricity has changed society and made living far more comfortable than it was for our forebears, speeding up scientific and engineering advancement. But it has created a consumer society where energy, including electricity, is viewed as a good that should be available whenever needed.

In fireplaces, stoves, and furnaces, the chemical energy of plants was burned under supervision to produce thermal energy. This heat is used for processing and finishing a wide range of items, melting metal, and burning bricks. The utilisation of fossil fuels has led to the increased prevalence and efficacy of these antiquated direct heat methods. The conversion of thermal energy from burning fossil fuels to mechanical energy was made possible by a number of important breakthroughs. Internal combustion engines and steam engines were the first to achieve this, then gas turbines and rockets. Since 1882, we have been producing electricity using water kinetic energy and fossil fuels (Smil, 2017).

A new kind of high-energy civilization emerged as a result of the use of fossil fuels and the production of electricity. This civilization has already spread over the entire planet and now relies mostly on small but rapidly expanding amounts of new renewable energy sources, mainly solar and wind. In turn, these developments have depended on a number of other things happening. Applying a flow-model analogy, human invention required a sequence of gates to be installed and opened in order for it to flow.

One of the things that makes living in the contemporary world so convenient is how much energy we use. Energy is used in everything we do. The most popular method for classifying energy use is by the final result, which can be transportation, thermal energy (such as hot water), or electricity. Energy can also be divided among the many end consumers, which are listed below.

1. **Residential energy usage**: These are the most important energy needs for homes. Using appliances, cooking, taking a shower, heating and lighting the house, doing laundry, watching TV, and using a laptop or computer at home are a few of them. Over 20% of the

world's energy is consumed for residential purposes, according to (United Nations, 2021). This kind of use produces the most rubbish globally. This can be explained by two factors: either there aren't enough energy-saving items on the market, or people don't know how to use them. The majority of consumers are unaware of the companies and goods that could assist them in monitoring and reducing their energy use.

2. **Commercial energy usage**: Energy consumption is also known as commercial utilisation in the corporate world. This comprises the electricity needed by companies and sectors of the economy in all of our cities for a variety of devices, such as copiers, workstations, fax machines, and computers. It also includes the electricity needed for lighting, heating, and cooling commercial buildings. Except for personal applications, energy use is the same in the commercial and industrial sectors. Companies, as opposed to people, are the primary focus of energy conservation efforts. Participants in the energy conservation sector should launch energy-saving projects to combat the waste culture that permeates our workplaces.
3. **Transportation:** The use of energy is essential to transportation. All forms of vehicles, including personal cars, lorries, buses, and motorcyclists, are included in the transportation industry. Aerial vehicles, railroads, ships, and pipelines are also present. In the broader battle for energy saving, the transportation sector might be quite important. Innovations in our transportation system, such as the development of alternative energy sources and more fuel-efficient automobiles, may greatly contribute to energy conservation. Global energy conservation projects could be achieved if we consider all of the uses and address each one individually. We will achieve far more in the way of

conservation if we focus on them as individual uses instead of trying to arrive at a comprehensive answer.

A society needs energy to function. However, energy use is linked to a multitude of environmental and socioeconomic problems, including mining, pipelines, fracking, greenhouse gas emissions, and "embedded energy" in energy infrastructure. Even while every form of energy has disadvantages, there is no doubting that some are better than others. Reducing energy use and increasing efficiency are easy ways to lessen the impact on the environment. Energy affects society in both positive and negative ways. Humans benefit from inexpensive, dependable, safe, clean, and plentiful energy. The production, transportation, and consumption of energy can have adverse effects on a society's economy, ecology, and health.

2.2 ENERGY, FORMS OF ENERGY AND SOURCES OF ENERGY.

The Earth has an abundance of energy. Energy has been used by humans for generations. The definition of energy is the ability to do labor(Balasubramanian, 2016). The term "energy supply" refers to the total amount of useful energy available to humankind. There are various types of energy, such as mechanical, electrical, kinetic, and chemical energy. Industrial equipment including pump sets, fans, grinders, vacuum cleaners, and washing machines all require electricity. Heat energy is used in stovetop cooking, metal forging, brickmaking, and many other industrial processes that rely on heat as a catalyst or essential component. Among the various tasks that require mechanical energy are moving automobiles and lifting goods.

According to (Balasubramanian, 2016), there are two types of energy sources: renewable and non-renewable. Nonrenewable resources, such as radioactive materials and fossil fuels, are extracted from the ground and have a finite supply. In the contemporary age, these resources have been the most often used form of energy.

Renewable resources are those that come from easily accessible, replenishable sources. Examples of these include wind, water, sun, and geothermal energy. Certain resources are regenerated annually, such biofuel derived from plants and food crops.

2.3 NON-RENEWABLE ENERGY: FOSSIL FUEL AS A SOURCE OF ENERGY.

Petroleum, bitumen, coal, natural gas, and oil are examples of fossil fuels. All of them are carbon-based, having formed from the leftovers of organic material that had been generated hundreds of millions of years earlier through photosynthesis through geological processes.

Coal has been utilized by humans for energy production since ancient times, initially as a fuel for heating and later as a source of power. Three of its forms—lignite, bituminous coal, and peat—are utilized to provide energy and heat. The process of producing coal starts with the repositioning of peat. Dried peat burns easily and gives out a distinct smell and Smokey flame. Large peat reserves can be found throughout Europe, North America, and Northern Asia, but they are only harvested during periods of low coal availability. Every year, millions of tonnes of peat are used in Ireland. Russia, Sweden, Denmark, Germany, and Finland all manufacture and consume significant amounts. Peat is widely used in both England and Scotland(Chmielewski, 2014).

Lignite is used to extract bituminous coal from peat. The globe produced 308 million tonnes of lignite in 1992, with Russia producing 130 million tonnes and Germany (particularly the eastern half) producing 135 million tonnes. 38 million tonnes from Romania, 67 million tonnes from Poland, 51 million tonnes from Greece, 60 million tonnes from the Czech Republic and

Slovakia, 135 million tonnes from the CIS, and 45 million tonnes from Bulgaria (28 million tonnes). Spain, Hungary, India, Thailand, and North Korea generate 1% to 2% of the world's lignite. Typically, lignite is collected in open pits close to thermal-electric producing plants. Underground mining produces bituminous coal in countries without access to this type of coal. Lignite is easily identified by its high sulfur, moisture, and ash content. Bituminous coal is a far more efficient fuel source.

Generally, deposits of bituminous coal and anthracite are found in the Carboniferous and Permian strata. The greatest concentrations of Carboniferous coal are found in the Euro-American area, which spans from eastern South America to Europe and West Asia. This region contains more than 22 percent of the world's supply of bituminous coal. Permian carbons are unique to the Gondwanan region, which includes South America, Australia, South Africa, and Central and Eastern Asia. This region contains about 17% of the world's supply of lignite and bituminous coal. Bituminous coal from the Lower and Upper Cretaceous, Middle Jurassic, Upper and Lower Triassic, and Tertiary epochs is not very important commercially.

The combined geological resources of bituminous coal and anthracite amount to 772.5×109 t, while the remaining resources comprise 492.5×109 t. Asia has the most geological supplies (71%), whereas Asia has the highest balance resources (44%), with America coming in second (26%)(Prajapati et al., 2022). About 20,000 underground mines in 40–45 different nations are used to extract bituminous coal and anthracite, with varying degrees of gas risk. In mines that produce bituminous coal as well as other forms of coal, this danger is highest. The tendency of coals to self-ignite in underground excavations is the source of the risk. In China's small mines, cooperatives are formed up to carry out excavation.

Petroleum, commonly known as crude oil, is a fossil fuel that is used as a source of energy and is not replenishable. Shallow waters were home to plants and algae millions of years ago. After breaking down and collapsing onto the ocean floor, the organic material buried itself together with other deposits. The bones of these animals underwent a transformation into what we now refer to as fossil fuels over millions of years under extreme heat and pressure.

Petroleum may currently be found in large underground reserves that once held ancient oceans. Both the planet's and the ocean's surface contain petroleum reserves. Large amounts of petroleum can be discovered in tar pits that bubble to the surface as well as beneath the surface of the Earth. Even far down in wells used for oil extraction, petroleum is still present. Large drilling equipment is needed to extract crude oil. Crude oil can have a yellowish, reddish, tan, or even greenish color, while it can also occasionally have a black or dark brown color. Color variations reflect the chemical differences between various crude oil suppliers. For example, petroleum that has less metals or sulphides tends to be lighter (sometimes nearly clear).Petrol is the raw material used to manufacture gasoline, a need for everyday living. It is also processed and utilized in a wide range of other products, such as tires, freezers, life jackets, and anesthetics.

While plants, algae, and plankton roamed the oceans and shallow seas millions of years ago, the geological conditions that would eventually give rise to petroleum were set. When their life cycle completed, these invertebrates dropped to the ocean floor. Ultimately, millions of tonnes of sediment and further layers of plant debris crushed and suffocated them. Arid basins left over after the ultimate collapse of the ancient oceans are known as sedimentary basins. Packed into the bottom of the basin between the millions of tonnes of silt and rock above and the extremely hot Earth's mantle, was biological materials. In this nearly oxygen-free environment, organic matter started to change into kerogen, a waxy material. Through a process called catagenesis, further heat, time, and pressure caused the kerogen to change into hydrocarbons. Organic molecules consisting of carbon and hydrogen are called hydrocarbons. Different ratios of heat to pressure can be used to create a variety of hydrocarbon forms. Natural gas, coal, and peat are further examples. Petroleum is generally found in sedimentary basins, which were formerly home to ancient sea beds. The Niger Delta sedimentary basin spans parts of Equatorial Guinea, Cameroon, and Nigeria in Africa. The enormous Niger Delta basin is one of Africa's most productive oil basins, with over 500 oil deposits.

Hydrocarbons make up the majority of crude oil's composition, with carbon accounting for 85% of its weight and hydrogen for 13%. Furthermore, extremely little amounts of nitrogen (about 0.5%), sulfur (0.5%), oxygen (1%), and metals like iron, nickel, and copper (less than 0.1%) can be combined with the hydrocarbons. The molecular arrangement of a hydrocarbon is determined by the material that made up the algae, plants, or plankton millions of years ago. Changes in hydrocarbons and crude oil can also be explained by the facilities' experiences with heat and pressure.

Crude oil extracted from the earth contains hundreds of distinct petroleum compounds as a result of this diversity. Heavy oils and bitumen may only comprise 50% hydrocarbons and a sizable amount of other ingredients, in contrast to light oils, which may contain up to 97% hydrocarbons. Almost often, refinement is required to convert crude oil into products that are usable.

2.3.1 PETROLEUM REFINING

Refined petroleum is created when bitumen or crude oil is transformed into items that are more useful, such asphalt or fuel. Sand and sulfur are common contaminants found in crude oil extracted from the earth. These elements need to be disassembled. This is accomplished by heating the crude oil in a distillation tower with trays and adjustable temperatures. When oil is heated, vapors from various elements rise to different levels of the tower before condensing back into liquid on the tier-like trays because metals and hydrocarbons have varying boiling temperatures.

Other compounds, such as kerosene and propane, condense on different tower levels and can be collected separately. They are moved to other places by means of vehicles, ships at sea, and pipelines. There, they are either immediately processed further or used as fuel. When chemicals known as fuels are burned, energy is produced.(Schobert, 2010)

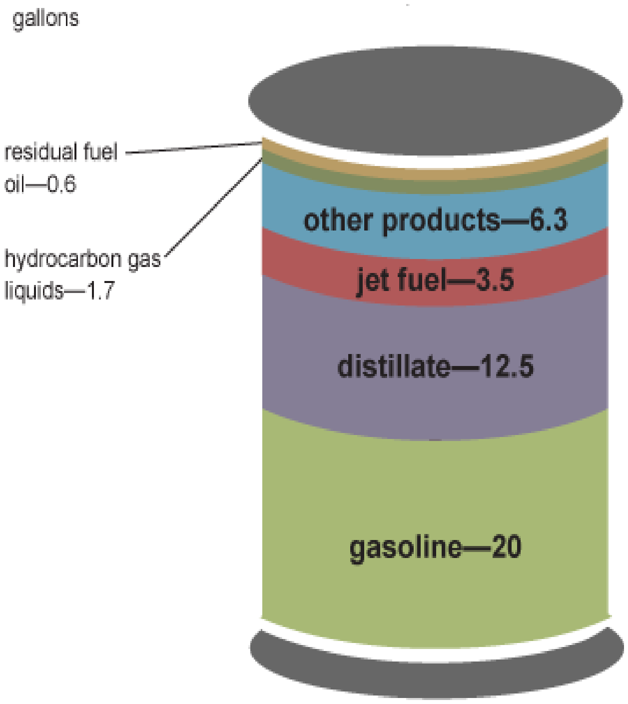


Figure 2. 1 crude oil barrels used to produce petroleum products 2021. *(Oil and petroleum products explained, 2022)*

Jet fuel, diesel, heating oil, gasoline, waxes, lubricating oils, asphalt, and distillates such as diesel and heating oil are some of the petroleum products that fall under this category.

Because most of the products that refineries manufacture have a lower density than the crude oil that they process (input), the overall amount of items that refineries generate (output) surpasses the total volume of crude oil that refineries process. We call this increase in volume "processing gain." Popped popcorn expansion is similar to this increase in volume. Compared to a popped kernel, a maize kernel is denser and smaller. In 2020, the average amount of material processed by US refineries increased by 6.3%. The average amount of refined products produced by U.S. refineries per barrel of crude oil they processed in 2020 was about 45 gallons, and this is presented in Figure 2.2.

Product	Gallons
Finished motor gasoline	19.40
Distillate fuel oil	13.44
Kerosene-type jet fuel	2.90
Petroleum coke	2.18
Still gas	1.76
Hydrocarbon gas liquids	1.55
Asphalt and road oil	0.92
Residual fuel oil	0.55
Naptha for feedstocks	0.50
Lubricants	0.42
Other oils for feedstocks	0.29
Miscellaneous products	0.25
Special napthas	0.08
Finished aviation gasoline	0.04
Kerosene	0.04
Waxes	< 0.01
Total	**44.65**
Processing gain	**2.65**

Figure 2. 2 Petroleum products produced from one 42-gallon barrel of oil input at U.S. refineries, 2020.(Petroleum Supply Annual, 2021)

2.3.2 PETROLEUM CONSUMPTION

From 3.57 billion metric tonnes at the turn of the century to 4.25 billion metric tonnes in 2021, the world's oil consumption has risen gradually over the last three decades. The months leading up to the 2020 coronavirus pandemic and the 2008–2009 financial crisis saw the only decrease throughout this time. Crude oil prices have been rising annually for the past few years. Figure 2.3 shows the constant increase in crude oil price.

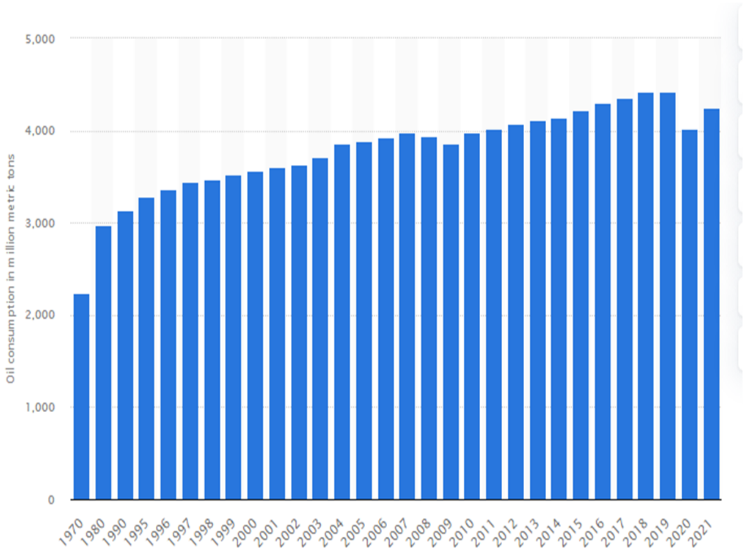


Figure 2. 3 Oil consumption worldwide from 1970 to 2021(in million metric tons) (Sönnichsen, Oil consumption worldwide from 1970 to 2021, 2022)

Based on projections, the demand for crude oil (including biofuels) is expected to rise from 91 million barrels per day in 2020 to 96.5 million barrels per day in 2021. The coronavirus pandemic's detrimental impacts on the world economy and transportation, including significant closures, are to blame for the decline in 2020. However, the rising demand pattern over the last ten years is apparent when compared to the daily oil consumption of 86.4 million barrels in 2010.

Oil is a valuable and adaptable resource that may be used in a wide range of contexts and methods. The world's largest user of oil is the transportation industry. It makes for almost one-third of the world's oil consumption, mostly from the use of petroleum-based motor spirits. According to OPEC projections, the global oil consumption by 2045 is projected to reach 109 million barrels per day, with the largest demand anticipated for transportation fuels such as diesel and gasoline. The demand for gasoline and diesel is predicted to increase, rising from 26.4 million barrels per day in 2019 to 30 million barrels per day in 2045. By 2045, there will be a 27.4 million barrel increase in the demand for gasoline.

Within the member countries of the Organization for Economic Co-operation and Development (OECD), the road transportation sector accounts for the majority of oil consumption. In 2020, the total oil consumption of motor vehicles in the OECD was 48.6%. Nonetheless, 16.2% of the GDP was derived from the petrochemical industry, which uses petroleum to produce polymers, resins, and other goods. This is clearly seen in Figure 2.4.

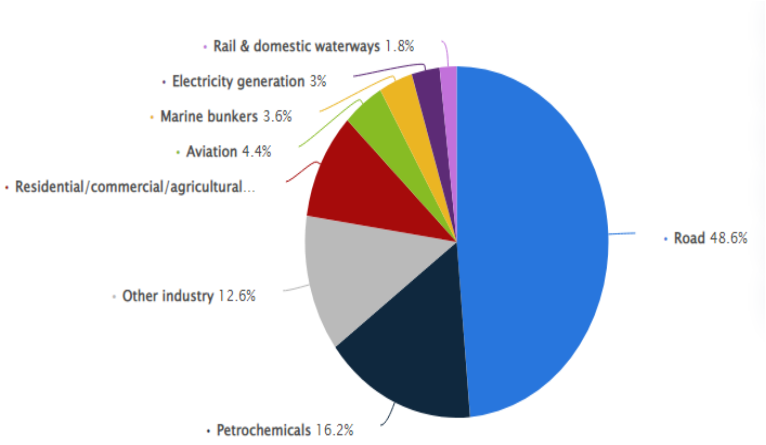


Figure 2. 4 Distribution of oil demand in the OECD in 2020, by sector(Sönnichsen, Distribution of oil demand in the OECD in 2020, by sector, 2022)

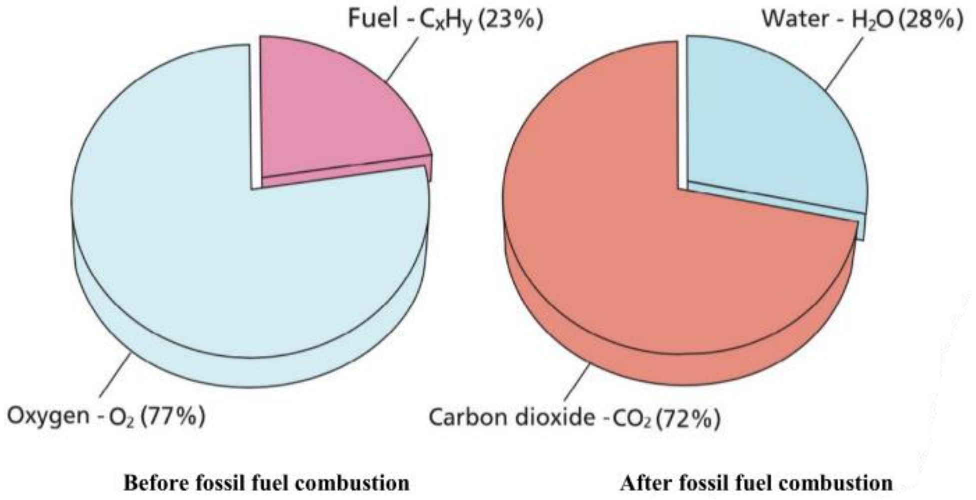
The two regions with the greatest worldwide oil demand are the Americas and the Asia-Pacific area, respectively. The Americas have the highest regional petroleum consumption in the world, and the United States alone contributes significantly to this high demand. Oil is mostly utilized as a feedstock in the chemical industry to make goods like adhesives and plastics, or as a raw material for motor fuels. Though not as much as other fossil fuels like coal and natural gas, it has historically been utilized to provide power and heat.

The two countries that use the most oil worldwide are China and the US. These two nations consumed 17.2 million and 14.2 million barrels of oil per day, respectively, in 2020. After years of steady rise, the daily demand for crude oil, including that for biofuels, reached 100.1 million barrels in 2019. But in 2020, the effects of the coronavirus pandemic on the economy and transportation will result in a daily decrease in oil consumption of about 10 million barrels. Additionally, it is anticipated that these adjustments would last until the end of 2021 because it is unlikely that travel and tourism will bounce back right away.

2.3.3 COMBUSTION OF FOSSIL FUEL AND ITS EFFECT ON THE ENVIRONMENT

The main components of fossil fuels, which are the main sources of energy for both heat and electricity, are carbon, hydrogen, and oxygen. When these three components burn in the atmosphere, carbondioxide($CO2$) and water are produced. Other byproducts produced during the burning of fossil fuels include fly ash, volatile organic compounds, sulphur oxides, and nitrogen oxides. It is believed that these byproducts harm the ozone layer, the atmosphere, and the environment. Because they are produced when fossil fuels burn, these substances are also referred to as "greenhouse gases" (GHGs).

Different classifications exist for the constituents of fossil fuels, including solids like asphalt or tar, liquids like gasoline and diesel, and gaseous chemicals. As seen in Figure 2.5, the fuel requires some oxygen to burn and cause a burn, so the majority of the exhaust is composed of carbon dioxide and water.



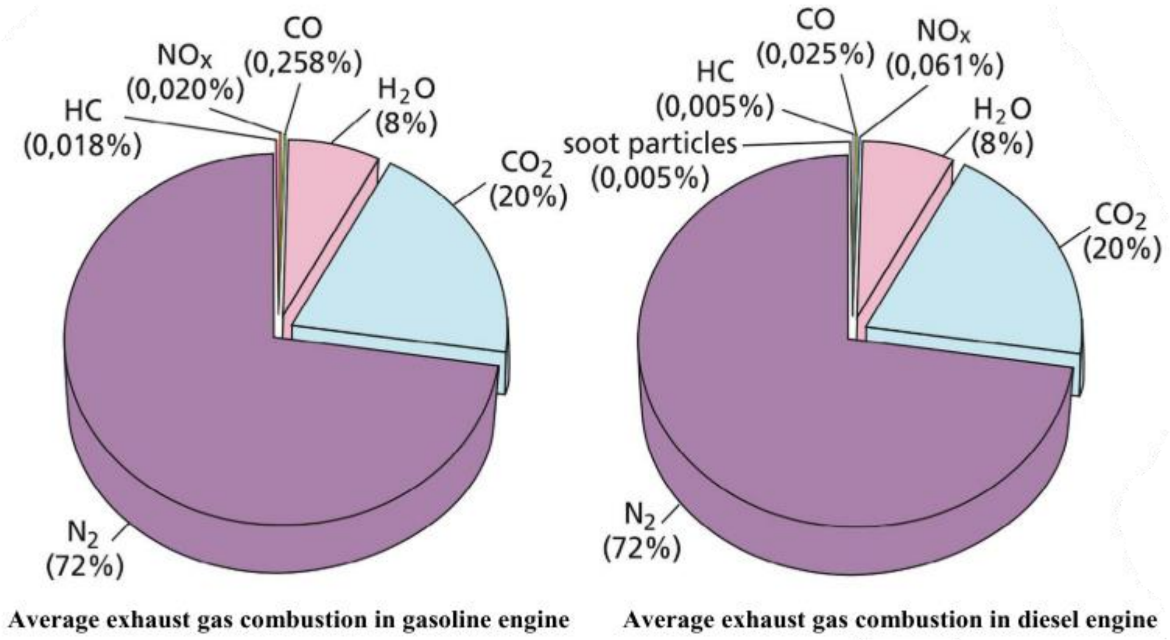
Before fossil fuel combustion **After fossil fuel combustion**

Figure 2. 5 Combustion of Fossil Fuels (Liu, 2010

Diesel engine exhaust is influenced by the engine's design and mechanics, as well as by the way the fuel burns inside the engine. Combustion by-products in a diesel engine's combustion chamber include water vapor (H2O), carbon dioxide (CO2), carbon monoxide (CO), and sulphur dioxide (SO2). Carbon dioxide makes up the majority of the products, while its percentage increases when the engine is subjected to excessively high loads and when combustion efficiency declines. Burning heavy fuel oil, which has a high sulfur content, as well as other elements obtained during the oil refining process, such vanadium, might result in the production of SO3.It can form sulfuric acid (H2SO4), which can harm engine parts, when combined with water vapor.

In diesel and gasoline engines, the combustion of fuel is rarely finished. The majority of the exhaust's constituent constituents are N2, CO2, and water (H2O). Even though they are created in very little amounts, polluting trace elements including carbon monoxide (CO), sulfur dioxide

(SO2), and particulate matter are harmful to the environment, human health, and other creatures' health. Together, these substances account for most of the emissions produced during the burning of fossil fuels. Nitrogen oxides (NOx) and soot production declines with engine load while the production of other exhaust elements remains unchanged. Gasoline combustion product are shown in Figure 2.6



Average exhaust gas combustion in gasoline engine **Average exhaust gas combustion in diesel engine**

Figure 2. 6: Combustion products in Gasoline and Diesel engines

A phenomenon known as the "greenhouse effect" occurs when heat is trapped near the Earth's surface by "greenhouse gases." The earth is maintained warmer than it would be otherwise by these heat-trapping gases acting as a blanket around it. Carbon dioxide, methane, nitrous oxide, and water vapor are examples of greenhouse gases. Scientists think that carbon dioxide's warming effect is what has stabilized the Earth's atmosphere. The greenhouse effect on land would vanish if carbon dioxide were removed. The Earth's surface temperature would be about 33°C (59°F) lower in the absence of carbon dioxide.

Any gaseous component of the atmosphere that can trap heat by absorbing infrared radiation is considered a greenhouse gas. The greenhouse effect, which is ultimately responsible for global warming, is brought on by greenhouse gases increasing the amount of heat in the atmosphere. Global warming affects every place on Earth. The following gases are the most important ones that have a greenhouse effect and hence contribute to global warming:

- **Carbon dioxide:** The primary greenhouse gas is carbon dioxide (CO2). Volcanic emissions, the burning of organic matter, the organic matter's natural decomposition, and the respiration of aerobic (oxygen-using) organisms are among the natural sources of atmospheric CO2. A range of physical, chemical, or biological processes commonly referred to as "sinks," which have a tendency to remove CO2 from the atmosphere, frequently balance out these sources. Terrestrial vegetation, which absorbs carbon dioxide during photosynthesis, is one of the main natural sinks for the gas.

  In addition, many oceanic processes serve as carbon sinks. One of these methods, called the "solubility pump," is the fall of dissolved carbon dioxide-filled surface saltwater. An alternative process known as the "biological pump" involves the uptake of dissolved CO2 by marine vegetation, other marine animals, or phytoplankton—small, free-floating photosynthetic organisms that absorb CO2 to produce structures like calcium carbonate skeletons (CaCO3). Carbon from these animals is moved downward and eventually deposited beneath the ocean floor as they die. The long-term equilibrium between these natural sources and sinks controls the background concentration of CO2 in the atmosphere.

  On the other hand, the principal method that human activities raise atmospheric CO2 levels is through the burning of fossil fuels (mostly coal and oil, and secondarily natural gas) for transportation, heating, and electricity production. And cement manufacture. A few other examples of anthropogenic factors are land removal and forest fires. As a result of human activity, an estimated 7 gigatonnes (7 billion tons) of carbon dioxide are released into the atmosphere each year. Natural sources account for about 3% of total CO2 emissions, which is substantially more than what can be offset by natural sinks (Mann, 2022).

- **Water vapor:** Despite functioning very differently from other gases in the Earth's atmosphere, water vapor is the most powerful greenhouse gas present. Rather than being a direct source of radiative forcing, water vapor is a primary climatic feedback or reaction that influences the continuous activity of the climate system. This discrepancy results from the fact that, in contrast to human behavior, air temperatures frequently have no direct impact on the amount of water vapor in the atmosphere. The rate at which water evaporates increases with surface temperature. Because of rapid evaporation, there is more water vapor in the lower atmosphere, and this vapor has the ability to absorb infrared light and reemit it back to the surface.
- **Methane**: Methane (CH4) is the second most important contributor to climate change. Because CH4 produces more radiative force per molecule than CO2, it is more effective than the latter. Furthermore, since the infrared window is less saturated in the wavelength range where CH4 absorbs light, there might be more molecules in the region. Though it is far less common in the atmosphere than CO2, CH4 is sometimes measured by volume in parts per billion (ppb) rather than parts per million (ppm). The half-life of CH4 in the atmosphere is significantly lower than that of CO2.

Methane hydrates are stored in polar permafrost and along oceanic continental shelves. Other natural sources of methane include volcanoes, seepage vents in sediment-rich seafloor areas, methane-oxidizing bacteria, wetlands in the tropics and arctic, and termites. Since methane easily combines with the hydroxyl radical (-OH) in the troposphere to form CO2 and water vapor (H2O), the atmosphere is the primary natural sink for methane. When CH4 reaches the stratosphere, it is destroyed. Methane can also be eliminated from the atmosphere naturally by soil-dwelling microorganisms that oxidize methane.

Similar to CO2, human activity is causing CH4 concentrations to rise faster than they can be lowered by natural sinks. Over 70% of annual emissions are currently attributed to anthropogenic sources, which has led to a large increase in concentrations over time. The main human activities that contribute to atmospheric CH4 emissions are burning biomass, coal, and natural gas, as well as the breakdown of organic waste in landfills and agriculture, particularly the production of rice and cows. Foreseeing future trends is quite challenging. This is partly because we still don't fully understand how the climate is impacted by CH4 emissions. Furthermore, it is challenging to forecast how future adjustments to energy consumption, animal husbandry, and rice production may affect CH4 emissions due to the growing human population.

- **Ozone:** Surface ozone (O3) is the next significant greenhouse gas. It is important to distinguish naturally occurring stratospheric O3, which plays a very different role in the planetary radiation balance, from surface-level O3, a byproduct of air pollution. Naturally occurring stratospheric O3 sinking from the upper atmosphere is the primary source of surface O3. In contrast, photochemical reactions involving the air pollutant carbon monoxide (CO) are the main human-caused source of surface O3. At present, surface O3 concentrations in the atmosphere are estimated to be 10 parts per billion, and the net radiative forcing resulting from surface O3 emissions generated by humans is around 0.35 watts per square meter.

- **Fluorinated gases and nitrous oxides**: Furthermore, nitrous oxide (N2O) and fluorinated gases (halocarbons), such as CFCs, sulfur hexafluoride, hydro fluorocarbons (HFCs), and per fluorocarbons (PFCs), are produced by industrial activities and have the potential to cause greenhouse impacts. The radiation emitted by nitrous oxide is 0.16 watts per square meter, while the radiation from all fluorinated gases is 0.34 watts. Because of normal biological activity in soil and water, nitrous oxides have low background levels, whereas fluorinated gases are largely derived from industrial sources.

2.4 RENEWABLE ENERGY

A commonly accepted definition of sustainable development is the creation, consumption, and manner of life that meets present needs without endangering the ability of future generations to meet their own needs. Finding any sustainable energy sources must be the main objective of energy production. Renewable energy is defined as any energy produced by ongoing, natural energy flows that already exist in the nearby environment.The most popular renewable energy sources at the time are biomass, solar, wind, hydro, tidal, and hydro energy. This type of energy is also known as sustainable or green energy.

2.4.1 BIOMASS ENERGY

Due to many environmental issues and the rise in carbon dioxide concentration in the atmosphere, the fossil resource industry has a substantial detrimental effect on the environment globally. Agricultural waste, also known as non-wood biomass, is the most abundant and renewable resource. It does, however, also provide financial and technological advantages. Since the paradigm of a civilization dependent on fossil fuels has guided the use of non-wood biomass, it is crucial to build sustainable methods for both production and consumption, especially in tropical places with enormous resources and biodiversity. Biomass fuel, derived from organic materials, is a renewable and sustainable energy source that may be utilized to generate multiple power sources. There is such bioenergy. Using biobased feedstock can reduce carbon emissions, replace fossil fuels, and generate revenue from waste streams, all of which help to increase the resilience of rural enterprises. The majority of biomass that is directly harvested for energy is composed of wood, some food crops, and all perennial energy crops.

Future prospects for coppices or perennial energy crops, agricultural waste, and biological waste as raw material feed stocks for lignocellulosic (non-edible) biomasses are promising. The quickest time to climate benefits is likewise associated with these feedstocks. Since the conversion of chemical energy to thermal energy is more efficient than the conversion of chemical energy to electrical energy, creating heat is frequently more "climate-friendly" than producing electricity. Because these alternative heat sources are either more expensive or have a maximum temperature at which they can produce steam, they are less able to replace the heat produced by the combustion of biomass.

2.5 HISTORICAL BACKGROUND OF BIODIESEL

Even while biodiesel has been around for a while, it wasn't until recently that it was considered a potential fuel. In 1853, E. Duffy and J. Patrick discovered the transesterification of triglycerides, which was discovered prior to the development of the first functional diesel engine. Rudolf Diesel created the first diesel engine in 1893, using peanut oil as the fuel source. The diesel engine was modified later in the 1920s to run on petroleum-diesel, a fossil fuel made from petroleum crude. Petro-diesel is the least expensive biofuel to generate; hence not many upgrades to the infrastructure supporting biodiesel have been done recently. The first method of producing industrial biodiesel based on ethanol was not patented until 1977. South Africa began investigating sunflower oil transesterification in 1979. Four years later, biodiesel of fuel quality and engine evaluated by South African agricultural engineers were revealed. Using this method, Australian businessman Gaskoks constructed the first biodiesel pilot plant, which was followed by an industrial-scale facility in 1989. Perhaps 30,000 tonnes of rapeseed would pass through the large-scale operation each year. Projections for 2006 indicated that Europe's main fuel source was biodiesel, which is produced from more than 4 million tons of rapeseed oil. Many European nations, such as Germany and Sweden, began constructing their biodiesel plants in the 1990s. By 1998, roughly 21 different countries were producing biodiesel on a commercial scale. Minnesota was the first state in the US to require that all diesel fuel supplied to its citizens contain a minimum of 2% biodiesel content (B2 and above) in September of 2005. This proved that fuel containing a blend of biodiesel is now required and cannot be avoided. A 10% objective for the use of renewable energy in road transport fuels by 2020 was included in the Renewable Energy Directive (RED), which was approved by the European Union (E. U.) on April 23, 2009. The requirements for biofuels used in the European Union also included limitations on the sorts of land that may be used to grow crops for biofuel feedstocks and a minimum rate of reduction in direct greenhouse gas emissions.

2.5 BIODIESEL

It has been determined that biodiesel is an appropriate fuel that can replace the finite and non-renewable oil supplies. It is cleaner, greener, eco-friendly, and renewable. It is a mixture of mono-alkyl ester fatty acids made from possible feedstocks such as tri-glycerides of non-edible vegetable oils that are subjected to the transesterification reaction using the right alcohol and a basic catalyst, which produces glycerol ($C_3H_8O_3$) as a reaction byproduct. D6751, American Society for Testing Materials(Demisu, 2024)

Biomass and other renewable resources are the primary raw materials used in the generation of energy. Fats derived from plants and animals are recognized as sources of renewable energy. Lipids are in great demand for use in industrial applications such fuels, bio-lubricants, and detergents as well as for use in food, feed, and personal hygiene products. These products are now more expensive and in shorter supply as a result. Does the process of turning edible lipids into biodiesel have anything to do with the recent surge in food prices?

Biodiesel was initially made from fully refined edible oils and fats, such as rapeseed oil in Europe, soybean oil in North and South America, and palm oil in Southeast Asia. Feedstock expenses make up about 80% of overall production costs(Drivers & Implications, n.d.), so it's important to investigate new starting materials that don't compete with availability locally.

The fuel was originally intended to be used in diesel engines and is known as "biodiesel" because it is made from biological ingredients. Because it is made from both plant and animal fats, biodiesel is regarded as a renewable fuel. To be clear, the term "biodiesel" may refer to and include substances other than those that fall under the official definition. Put differently, biodiesel is much more than just a biological fuel that can be utilized in diesel engines.

According to (Motasemi & Ani, 2012)Diesel fuel can be replaced with biodiesel as a fresh and environmentally friendly option. Both benefits and drawbacks come with using biodiesel as fuel. Using biodiesel has the following benefits:

• It can lower greenhouse gas emissions and emits less CO2, SO2, CO, HC, and PM than conventional diesel. • It is a renewable, biodegradable, non-toxic, and environmentally beneficial resource.

• Producing biodiesel is less complicated than producing diesel fuel, and it boosts local economies by generating a whole new infrastructure of jobs.

• It reduces noise, vibrations, and smoke emissions.

- There may be a decrease in the usage of fossil fuels and an improvement in the nation's energy security.
- Because biodiesel is generated locally, it is more economical.
- Biodiesel doesn't require engine modification up to B20 and has a high flash point, making it a safer fuel.

However, there are a number of issues with biodiesel:

- Compared to regular diesel, it releases more NOx emissions.
- In colder temperatures, its increased pour and cloud points cause issues.
- It is highly corrosive to brass and copper.
- Its volatility is low and its viscosity is higher than that of diesel fuel.

2.6.1 FOSSIL FUELS AND BIODIESEL

Natural fuels discovered in the crust of Earth are called fossil fuels. They are made of preserved plants and animals from millions of years ago. Because it takes millions of years for fossil fuels to refill, they are regarded as nonrenewable resources. Carbon and hydrogen are components of all biological things. Fossil fuels also contain carbon and hydrogen because they are derived from once-living things. Burning is the process by which fossil fuels are consumed. In order to heat homes and generate electricity, the heat emitted during this process is captured and utilized as energy. Fossil fuel combustion has several negative effects, notable among them being increased air pollution. (*Biofuels vs. Fossil Fuels | Types & Comparison | Study.Com*, n.d.)

Since they are produced from plant material and are renewable resources, biofuels vary from fossil fuels. A renewable organic substance created by living or formerly living things is called biomass. Plants use photosynthesis to transform solar energy into chemical energy. This stored energy is released when plants burn. Since biofuels naturally regenerate themselves over time, they are regarded as renewable resources.

Some of the differences between fossil fuels and biodiesel

- The major sources of biofuels are from plants and organic residues while fossil fuels are gotten from organisms that have died for millions of years.
- Biofuels have no hazardous effect on human health; fossil fuels on the other hand contain toxic substances and byproducts such as carbondioxide which is one of the major causes of respiratory problems in the human body.
- Biofuels can be produced from safer processes which are environmentally friendly while fossil fuels are obtained from unsafe processes like drilling and milling.

Table 2. 1 differences in properties of biodiesel and petroleum diesel

S/N	Property	Biodiesel	Petroleum Diesel
1	Cetane No	51-62	44-49
2	Lubricity	Greater than diesel	Lower
3	Biodegradability	Good	Poor
4	Toxicity	Non-toxic	Highly toxic
5	Oxygen	11% free oxygen	Very low
6	Aromatics	No aromatics	18-22%
7	Sulphur	None	0.05
8	Cloud point	Slightly more	------
9	Flash point	300-4000F	125
10	Spoil point	None	High
11	Heating value	2-3% higher than diesel	-------
12	Renewable supply	Renewable	Non-renewable
13	Alternative fuel	Yes	No
14	Production process	Chemical reaction	Reaction

2.6.2 PROPERTIES OF BIODIESEL

Depending on the process and feedstock used to manufacture the fuel, biodiesel might have a clear, golden, or dark brown hue. Additionally, this modifies the fuel's final qualities. Biodiesel generally has a low vapor pressure, a high boiling point, and is mildly miscible with water. Biodiesel has a flash point that can reach above 130 °C (266 °F), which is far higher than petroleum diesel, which can only reach 52 °C (126 °F). Petro diesel has a density of around 0.85 g/cm3, whereas biodiesel has a density of about 0.88 g/cm3.

Biodiesel has a calorific value of approximately 37.27 MJ/kg. Compared to standard Number 2 petro diesel, this is 9% less. The feedstock utilized determines variations in biodiesel energy density more so than the method of production. These differences are still smaller than those for petro diesel. It has been asserted that biodiesel improves lubricity and accelerates combustion, boosting engine performance and somewhat offsetting petro diesel's higher energy density.

In addition to having almost no sulfur, biodiesel also has promising lubricating qualities and cetane ratings when compared to low sulfur diesel fuels. It is frequently added to ultra-low-sulfur diesel (ULSD) fuel to help with lubrication. Petro diesel's sulfur compounds are what give the fuel most of its lubricity. Biodiesel Higher lubricity fuels have the potential to extend the useable life of high-pressure fuel injection machinery that depends on the fuel for lubrication. This could contain fuel injectors, pump injectors (also known as unit injectors), and high pressure injection pumps, depending on the engine. The characteristics of the engine are stated as follows:

2.6.2.1 CLOUD POINT

The fuel's CP indicates its operating condition in colder climates. The temperature at which reducing the fuel temperature permits the formation of crystals is known as the cloud point. The fuel gets thicker and appears hazy due to crystal formation. Fuel injectors and fuel filters are hampered by this. Additionally, this impedes the fuel's ability to operate and complicates the diesel engine's operation. Hydro processing and transesterification procedures can further lower the CP of vegetable oils used to produce biodiesel. Even at -5°C, biodiesel can function effectively. In such instances, the renewable diesel has a temperature range of -30°C to -5°C. Through isomerization, the CP of renewable diesel can be further decreased to -55°C.(Jaiswal et al., 2024)

Nevertheless, it has also been noted that the biodiesel's CN is decreased by the same technique. Compared to large hydrocarbon chains, short hydrocarbon chains enable superior biodiesel flow characteristics. Saturated bonds found in renewable diesel provide greater operating capacity. When it comes to biodiesel, the presence of saturated fatty esters lowers the CP.(Bezergianni & Dimitriadis, 2013)

2.6.2.2 VISCOSITY

The degree of a material's resistance to flow is measured by its viscosity; less viscous materials flow more easily, whereas highly viscous materials flow very difficultly. Because it influences how a fuel atomizes when injected into the combustion chamber, it results in the creation of engine deposits. The more viscosity a fuel has, the more likely it is to cause these issues. As the temperature rises, the biodiesel's kinematic viscosity value drops. There are two ways to describe a fluid's viscosity: kinematic and dynamic. Centipoises is the unit of measurement for dynamic viscosity. Measured in centistokes, kinematic viscosity takes the fluid density into consideration.(Isioma et al., 2013)

The acceptable viscosity range for biodiesel according to ASTM D6751 is between 1.9 and 6.0 mm2 /s. The upper limit for biodiesel is higher than the upper limit for normal diesel fuel (4.1mm2 /s) and should be taken into account when looking at blends. Since both low and high viscosities can negatively impact an engine's performance, the viscosity of biodiesel is a crucial factor in how well the fuel performs in an engine. High viscosities cause big droplets to develop during injection, which impairs combustion and increases emissions and exhaust smoke, whereas low viscosities may not provide enough lubrication for the precision fit of fuel injection pumps, increasing wear or causing leaks.(*Cennatek Bioanalytical Services, (2013). Kinematic Viscosity According to Astm D445. Retrieved June 13, 2013 - Google Search*, n.d.)

Due to the high viscosity of biodiesel and its blends, the engine's injector spray pattern is altered, which causes carbon deposits to build up and eventually causes issues like stuck piston rings in the cylinder and subsequent engine failures. Fuel impingement on the piston and other combustion chamber surfaces is the cause of this, albeit it would be unusual if petro-diesel were utilized.(Freitas et al., 2011) & (Yoon et al., 2008)

Fuel viscosity determines how much power the engine will lose from the outflow; if it is high, the injection pump cannot supply enough fuel to fill the pumping chamber. Once more, power loss will be the result. Typical biodiesel fuels fall into a viscosity range that overlaps with diesel fuel. Black smoke will be produced, the lubricating oil will become contaminated, and the spray in the cylinder will degrade due to too high fuel viscosity, which is the situation with vegetable oils.(Yoon et al., 2008)

High viscosity impairs fuel atomization in the engine's combustion chambers, which leads to operational issues. The design of raw material and refined product mixing as well as the optimization of biodiesel manufacturing processes would benefit from the ability to predict a biodiesel's viscosity value based on its composition.(“Biodiesel Handb.,” 2010)

2.6.2.3 FLASH POINT

The lowest temperature at which fuel generates enough vapor to ignite and produce a flame is known as the flash point. The flash point of biodiesel is higher than that of regular diesel. Additionally, biodiesel has a higher flash point specification than diesel regulations.(Gouveia et al., 2017)

It is an essential feature for assessing risks during storage and transportation. Since biodiesel often has a higher flash point than petro diesel, it is safer to carry and store in enclosed spaces like underground mines since it is less volatile. In diesel engines, incomplete combustion due to a greater flash point than in petro diesel can lead to carbon deposits in the combustion chamber. The purpose of the flash point specification is to comply with fire and insurance laws. It shields the engine from residual methanol, which the European Biodiesel Standard states shouldn't be more than 0.20% (m/m). Certain metals and elastomers in fuel systems are incompatible with methanol concentrations higher than 0.2 weight percent. B100's flash point needs to be at least 93°C in order to ensure that all alcohol is completely removed during manufacture. (Etim et al., 2022)

2.6.2.4 CETANE NUMBER

CN (cetane number) is a property of various diesel fuel types that is dependent on the fuel's chemical and physical makeup. Vaporization time, a result of the physical characteristics of the fuel, is a factor that can significantly impact the fuel's combustion and combination with the system's compressed hot air. Another factor impacting CN is the molecule structure.(Gouveia et al., 2017)

According to (Prakash et al., 2011) The cetane numbers of biodiesel derived from vegetable oil sources range from 46 to 52, whereas those derived from animal fat range from 56 to 60.Due to its high cetane rating (55–60) and ability to be made into biofuel, dimethyl ether has the potential to be used as a diesel fuel. Although the lubricity may be an issue, the majority of simple ethers, especially liquid ones like diethyl ether, can be utilized as diesel fuels.

2.6.2.5 POUR POINT

The temperature at which a biodiesel fuel ceases to flow when it is further cooled under ASTM D 97-specified conditions is known as the pour point, to put it simply. Similar to cloud point, the pour point of biodiesel fuel, when made from any kind of feedstock, is often greater than that of fossil diesel. Furthermore, compared to conventional diesel fuel, the temperature range between the cloud point and the pour point for biodiesel fuel is far smaller.(Bazooyar et al., 2015)

2.6.2.6 COLD FLOW PROPERTIES

The characteristics of fuel at low temperatures are indicated by cold flow qualities. The temperature at which biodiesel begins to aggregate and form crystals, giving the fuel a cloudy appearance when cooled, is known as the cloud point (CP). Using oil feedstocks with appropriate cold flow characteristics, such rapeseed, is often the best way to produce biodiesel with desired cold flow parameters (ultra-cold weather biodiesel). Note that saturated long-chain methyl esters tend to have greater cetane values and other beneficial fuel ignition qualities, but their molecules crystallize first in cold conditions.(Mohammadi et al., 2023)

The temperature at which gasoline components start to gel and cause the test filter to plug is known as the cold filter plugging point (CFPP). Significant operability issues result from this. Although the restrictions are not stated, the Australian, European, and US standards should be followed for reporting the cold-temperature qualities of biodiesel.(Mofijur et al., 2017)

Engine operating at low temperatures causes the fuel particles to condense and gel, which causes the molecules in the liquid to crystallize and form a continuous crystal formation inside the liquid. The liquid's molecules must produce enough thermodynamic force through robust intermolecular forces of contact for crystallization to take place. When the liquid's temperature is lowered below its melting point, this thermodynamic force is produced.(Dwivedi & Sharma, 2014)

2.6.2.7 HEATING VALUE

The thermal energy released per unit quantity of fuel that is burned and the combustion products cool to the original temperature of the combustible mixes is known as the fuel's heating value. It calculates a fuel's energy content.(Sivaramakrishnan & Ravikumar, 2011)

One of the most important characteristics of a fuel is its higher heating value (HHV) which is the amount of heat released during the combustion of one gram of fuel to produce CO2 and H2O at its initial temperature and pressure. It characterizes the energy content of the fuel. This property is also important for vegetable oils, animal fats and their derivatives studied as potential fuels.(Fassinou, 2012)

The quantity might be expressed in mol, kilograms, or standard square meters. As a result, the heating value is measured in kJ/kmol and kJ/kg units. By multiplying the mass heat of combustion by the fuel's density (mass per unit volume), one can compute the volumetric heat of combustion, or the heat of combustion per unit volume of fuel. For volume-dosed fueling systems, like diesel engines, the important combustion heat is the volumetric heat, not the mass heat.

When the water vapor created during combustion condenses and all combustion products have cooled to their pre-combustion temperature, the gross, or high, upper, heating value (Qg) is determined. The latent heat of vaporization of the water vapor produced by burning is subtracted from the gross or higher heating value to obtain the net or lower heating value (Qn). The gross heat of combustion and the net heat of combustion are related by the formula $Qn = Qg - 0.2122H$, where H is the fuel's mass percentage of hydrogen. Since the temperature of exhaust gases from internal combustion engines is higher than the boiling point of water (water vapor is released), the lower heating value of biodiesel is more significant when determining the fuel's heating value. The degree of unsaturation (the number of double bonds, ND) and molecular chain length (the number of carbon atoms, NC) are what determine the heating value of fatty acid ester. Because unsaturated esters have a larger density than saturated esters, their volume heating value is greater even if their mass heating value is lower.(Barabas & Todoru, 2011)

2.6.2.8 DENSITY

The mass per unit volume, measured in a vacuum, is known as fuel density (ρ). Given that temperature has a significant impact on density, the quality standards specify that density should be measured at 15 °C. Fuel performance is directly impacted by fuel density, as certain engine characteristics, like heating value, and viscosity are closely related to density. The fuel's density has an impact on both the combustion and atomization quality. Changes in density have an impact on the fuel mass that enters the combustion chamber and, consequently, the energy content of the fuel dose, which changes the fuel/air ratio and engine power in diesel engines where the fuel is metered by volume via the injectors and pump.

Since density is a crucial factor to consider in the design of these processes, it is also required to know when making, storing, transporting, and distributing biodiesel. Esters' density is influenced by temperature, water concentration, free fatty acid content, and molar mass. Biodiesel's density is usually higher than diesel fuel's and is influenced by the purity and makeup of the fatty acids. The density of biodiesel varies within narrow ranges since it is composed of a small number of methyl or ethyl esters with extremely similar densities. Density can serve as an indicator of contamination in biodiesel since contamination has a major impact on it.(Barabas & Todoru, 2011)

2.6.2.9 LUBRICITY

The capacity of a fuel to lessen friction between surfaces under stress is referred to as lubricity. This feature lessens the potential harm that friction in gasoline injectors and pumps can cause. Biodiesel does not require sulfur for lubrication, in contrast to diesel fuel. Rather, the lubricating properties of biodiesel are derived from the oxygen present in the fuel. (In addition, it helps biodiesel burn more thoroughly than petroleum-based fuel by raising its Cetane number.) Furthermore, biodiesel performs better than average in lubricating engines. According to a 2007 study, a B2 mix performed better in terms of lubricity than eighteen other brands available on the market.

2.6.2.10 WATER AND SEDIMENTS

The biodiesel's water content serves as a purity indication. To get the water standard below 500 ppm (0.050%), biodiesel needs to be dried after being washed with water. Water can build up in biodiesel during storage and transit, even if the producer has dried the fuel appropriately. The concentration of free fatty acids rises as a result of the moisture that builds up in biodiesel, which can erode metal components of the engine's fuel system. Compared to diesel oil, biodiesel is far more hygroscopic (it collects water). During storage, the biodiesel absorbs water at higher temperatures, and the absorbed water precipitates at lower temperatures. The water that has accumulated as a result of these repeated procedures ends up at the bottom of the tank. Water in biodiesel promotes sediment formation and microbiological growth.

2.6.3 STANDARDS FOR BIODIESEL

The long-term viability of a biofuel—that is, its successful use without technical issues requires quality. The quality of biodiesel is determined by a number of variables that mirror its physical and chemical properties. A multitude of factors can impact the quality of biodiesel. variables include the feedstock's quality, the parent vegetable oil or animal fat's fatty acid composition, the production method and its associated components, the postproduction parameters, handling, and storage. The physicochemical characteristics of biodiesel ought to be comparable to those of diesel oil because the majority of modern diesel engines are built to run on biodiesel fuel. A key strategy for guaranteeing acceptability in using biodiesel fuel quality is the development of strict fuel requirements, including ASTM D6751 (for the United States) and EN 14214 (for the European Union). Many other nations have established their own standards, many of which are based on ASTM D6751 or EN 14214. Additionally, a few nations have collaborated to establish criteria for regional biodiesel standards. It is only permitted to use and sell biodiesel for commercial purposes if it satisfies the biodiesel standards EN14214:2009 (EN) or ASTM D6751 (USA) as presented in Table 2.2

Table 2. 2 Standards for biodiesel fuels include ASTM D6751 and EN 14214(Sakthivel et al., 2018)

BIODIESELPROPERTY SPECIFICATION					
Property	Units	ASTM D6751		EN 14214	
		Tests	Limits	Tests	Limits
Flash point	°C	ASTM D93	130 minimum	EN ISO 3679	101 minimum
Cloud point	°C	ASTM D2500	−3 to −12	–	–
Pour Point	°C	ASTM D97	−15 to −16	–	–
Cetane number		ASTM D613	47 minimum	EN ISO 5165	51 minimum
Density at 15 °C	Kg/m^3	ASTM D 1298	880	EN ISO 3675/ 12185	860–900
Kinematic viscosity at 40 °C	mm^2/s	ASTM D445	1.9–6.0	EN ISO 3104	3.5–5.0
Iodine number	g I_2/100 g	–	–	EN 14111	–
Acid number	mg KOH/g	ASTM D664	0.5 maximum	EN 14104	0.5 maximum
Saponification value	mgKOH/g	ASTM D5558	370 maximum	–	–
Boiling point	°C	ASTMD7398	100–615	–	–

Ash content	%Mass	–	–	–	–
Water and sediment	%Mass	ASTM D 2709	0.005 vol% Maximum	EN ISO 12937	500 mg/kg

2.6.4 BIODIESEL STORAGE

When distributed improperly, biodiesel that is in good condition when it leaves the producing plant may lose its acceptability. Oxidation, contact with water, and/or microbiological activity can cause biodiesel to break down. Petro-diesel generally degrades more slowly than biodiesel. This is advantageous in that a biodiesel spill will decompose more quickly than a petro-diesel spill and won't harm the environment as much. Even still, both fuels will ultimately deteriorate, and maintaining biodiesel will only be made easier by following the same cleaning procedures that apply to petro-diesel. An additional issue is that, in comparison to petroleum-diesel, biodiesel tends to gel, or freeze, at greater temperatures. Tanks used for storage and transportation must therefore be built to withstand this inclination. Furthermore, some materials used in gaskets, hoses, and seals may degrade due to the incompatibility of biodiesel with specific elastomers commonly used with petro-diesel.

Biodiesel oxidizes and sediments start to accumulate in the fuel. Fuel filters may then get clogged by these sediments. Fuel derived from saturated fats, like animal fats, has a slower rate of oxidation and degradation than biodiesel made from unsaturated fats, like vegetable oils. Furthermore, oxidation will be accelerated by any procedure (such as bleaching, deodorizing, or distilling) that eliminates the oil's natural antioxidants. The conditions of storage are crucial. For instance, because these metals will speed up degradation, biodiesel shouldn't be transported or kept in copper, brass, bronze, lead, tin, or zinc. Select containers instead that are constructed of fiberglass, Teflon®, aluminum, steel, and fluorinated polyethylene and polypropylene. Biodiesel may be easily stored in tanks intended for the transportation and storage of petro-diesel. Additionally, oxygen, heat, and sunshine will speed up the breakdown of biodiesel, therefore storage should limit exposure to these elements. A stability ingredient should be applied if biodiesel is going to be stored for more than four to five months, particularly in more southern climates where temperatures and humidity are higher. When biodiesel comes into touch with water, it might break down. Fuel can become contaminated during storage and delivery by airborne moisture or water found in the distribution system's tanks and pipes. In biodiesel, up to 1,500 parts per million of water can dissolve. The extra water left over after this point is achieved is referred to as "free water." In addition to causing rust in engines and storage tanks, this free water encourages the growth of bacteria in the biodiesel. Make sure storage tanks are cleaned and dried before adding biodiesel to avoid the buildup of free water. Reduce the amount of air space above the fuel as much as you can; 2% of air space is advised to allow for thermal expansion. More room to breathe could help the plant absorb more water from the atmosphere. Drain any free water from the bottom of storage tanks as often as you can.

If biodiesel is kept in storage for longer than a few months, the dissolved water in the fuel may also become an issue. Acids from this water may build up in the gasoline and eventually chew a hole in the storage tank. Due to the fact that water is commonly found in diesel storage tanks and since biodiesel may absorb water from the air, it is practically difficult to keep water out of it. The best defense against water deteriorating biodiesel is to use it up within a few months. Biodiesel might not be the ideal choice if you need to stockpile fuel for months or years (for example, to run an emergency generator). It could be preferable to use petro-diesel or another more stable fuel in those circumstances. Biodiesel is vulnerable to microbial deterioration, just as petroleum-diesel. If given the right circumstances, microbes will proliferate; typically, they require nitrogen and water. To solve this issue, make sure the biodiesel is kept out of touch with water by keeping an eye on the storage tanks. Chemicals known as biocides, which stop microorganisms from growing, are also added to fuel and are frequently combined with petro-diesel. Diesel fuel companies offer biocides for sale.

The oil or fat that was used to make the biodiesel determines its gel point. Compared to biodiesel derived from unsaturated fats, biodiesel made from saturated fats often gels at higher temperatures.

Pure biodiesel produced from vegetable oil may generally be stored securely between 45° and 50°F. Underground tanks can keep gelling in cold areas. Depending on where they are located, above-ground tanks could require insulation or heating. Depending on the ratios of biodiesel to petro-diesel, blended biodiesel has a lower gel point than pure biodiesel.(*Transportation and Storage of Biodiesel – Farm Energy*, n.d.)

2.6.5 METHODS FOR BIODIESEL PRODUCTION

Many techniques, such as pyrolysis, transesterification, micro-emulsion, dilution, and supercritical techniques, can be used to make biodiesel The four ways for producing biodiesel are microemulsion, direct use of vegetable oil, transesterification, and thermal cracking. Of these, transesterification is a straightforward and often used process to effectively manufacture biodiesel. This process produces the chemical product known as bio-diesel, which is methyl or ethyl esters, from the reaction of animal and vegetable oils, such as edible or non-edible oils containing triglycerides, with alcohol and a catalyst [9]. Depending on the catalyst used, a significant contribution to the production of high-quality biodiesel and its yield % in varying reaction times is made by the catalyst.(Basumatary et al., 2024). Every technique has benefits and drawbacks of its own. Transesterification is a cheap process, but it needs high temperatures and a catalyst. The thermal process of pyrolysis can make biodiesel from vegetable and animal fats, but it uses a lot of energy and yields a lot of byproducts. The high purity of biodiesel produced by the micro-emulsion process is an advantage, although separation and purification steps are extra. Overall, considerations including cost, effectiveness, and environmental impact influence the choice of biodiesel production technology.

2.6.5.1 DILUTION METHOD

The dilution method is a process of thinning waste and vegetable oils by combining them in certain amounts with a solvent or diesel fuel. Combining oils with diesel fuel is the most popular of these methods. As a result, less diesel fuel is used and oil viscosity is decreased. The following are the ratios of oils to diesel fuels: B20, B30, B40, B50, and B80. To put it briefly, there are 20, 30, 40, 50%, and 80% of waste, animal, or vegetable oil. Oils used in the dilution process of making biodiesel include waste oils, peanut oil, rapeseed oil, and sunflower oil.(Aktaş et al., 2020)

2.6.5.2 MICRO-EMULSION

Micro-emulsion is a technique that employs short-chain alcohols like methanol, ethanol, or 1-butanol, is another way to lessen the high viscosity of Vegetable oils. A micro-emulsion is an equilibrium distribution of optically isotropic liquid microstructures with sizes ranging from 1 to 50 nm. Two immiscible liquids are routinely mixed with one or more active chemicals to create this. Methyl and ethyl alcohol are short-chain alcohols, which has the drawback of reducing the heat values of micro-emulsified Vegetable oil in contrast to petroleum diesel fuel.

2.6.5.3 PYROLYSIS

The thermal breakdown of oils in the presence of nitrogen gas or air is known as pyrolysis. It is possible to obtain fuel using pyrolysis at a lower cost than transesterification. This is achievable with cheaper basic materials. Pyrolysis, for instance, might be utilized as a raw material for restaurants.

Food oil wastes, oil products from industries that produce food oil, and oil wastes from the transesterification process. The process of pyrolysis begins with heat energy breaking down vegetable oils inside a closed container. Followed by distilling the prepared materials and using vegetable and waste oils, they break down into thermal energy. The resulting biodiesel has qualities that are comparable to those of diesel fuels.

This process breaks down the molecules of vegetable oil into smaller ones at a high temperature without the presence of oxygen. C-C or CH bond separations are the result of this procedure. The three steps of this process are thermal cracking, catalytic cracking, and hydro cracking. The procedure followed and the reaction conditions determine how much product is produced. For instance, at low reaction rates and low temperatures, a solid product is produced, and more liquid product is obtained through quick, high-temperature cracking operations.

The main drawback of the pyrolysis process is considerable energy consumption, even though the fuel qualities of vegetable oils are similar to those of diesel fuel. In addition to producing fuel, the pyrolysis method is a useful technique for assessing urban and industrial wastes. A simple and effective technique among others is pyrolysis.

2.6.5.4 TRANSESTERIFICATION

Transesterification is the method most commonly used to make biodiesel. Transesterification, the general term for the transfer of alkoxide groups from one ester to another, refers to a family of important chemical processes in which one ester is altered. Because transesterification is so simple for this operation, it is seen to be the best option.

The process known as transesterification is used to convert vegetable oils into biodiesel (alcoholysis). The main byproducts of the transesterification reaction, which happens when oil is esterified with monohydric alcohol (ethanol, methanol) (acidic, basic catalysts and enzymes), are fatty acid esters and glycerine. During the esterification process, free fatty acids, additional reactants, and diglycerides and monoglycerides are generated. When making biodiesel, the ideal ingredients to use are rapeseed, sunflower, soy, and used frying oils. Alkali catalysts, such as sodium or potassium hydroxide, are also recommended, along with methanol as the alcohol. Animal oils can also be used to make biodiesel. The transesterification reaction is seen in Figure 2.7.

The majority of the oil is composed of triglycerides, which are converted into mono-alkyl esters during the transesterification process. The esterification reaction leaves behind free fatty acids, surplus reactants, and di- and monoglycerides. For the production of bio motors, rapeseed, sunflower, soybean, and leftover frying oils are utilized in addition to methanol, an alcohol, and alkali catalysts (sodium or potassium hydroxide). Additionally, animal lipids can be used to generate biomotorin. As such, the refinement process becomes crucial. Making is simple. The most crucial step in the process is figuring out the biodiesel's quality. For this reason, the refining phase is crucial. A biomotor that is created must be at least 99% pure.

The production technology is not sophisticated. The quality of the biodiesel produced is the most crucial factor. As such, the refinement process becomes crucial. Water, alcohol, biodiesel, and fatty acid esters with a homogeneous or heterogeneous catalytic effect are all produced via the direct esterification of fatty acids. Since water is more vaporous than fatty acid esters, it can be removed from the reactor in any way and still achieve very high conversion rates.

In the process of making biodiesel, three primary categories of catalysts are utilized: alkalis, acids, and enzymes. Simple purification is achieved, and soap production is prevented by the use of enzyme catalysts, which have gained popularity recently. Due to their higher cost and slower reaction times, they are not as frequently utilized in business. Recently, some scientists have invented novel biocatalysts to lower costs. One example of this is the immobilized "whole-cell biocatalysts" found in biomass support particles. The fact that these biocatalysts do not require purification is helpful. Alkali and acid catalysts are more frequently utilized in the manufacture of biodiesel than enzyme catalysts.

With alkalis and acids, catalysts that are homogeneous or heterogeneous can be employed. Alkali-catalyzed transesterification is the most widely used commercial method. NaOH and KOH are commonly used as alkali homogeneous catalysts in this process due to the low cost of raw materials. These materials are the most economically advantageous because the alkali-catalyzed transesterification process is conducted in a low-temperature and pressure environment with a high conversion rate without the need for intermediate stages. Alkali homogenous catalysts are highly hygroscopic and absorb moisture from the air when in storage. When they dissolve in the alcohol reactant, they both give less and create water. Thus, it's critical to treat them with caution. Conversely, certain heterogeneous catalysts are solid and can be readily filtered out of the product, minimizing the need for washing. If solid heterogeneous catalysts are employed to initiate the transesterification and esterification reactions, a pre-esterification phase might not be required. This indicates that feed-stocks with high levels of free fatty acids will be especially advantageous for these catalysts. The three-phase system that the reaction mixture creates, which is hindered by diffusion, causes the reaction to proceed more slowly when a solid catalyst is used. Amyl alcohol, propanol, butanol, ethanol, and methanol are a few types of alcohol that can be used in the transesterification process. The two most often utilized alcohols are methanol and ethanol. Methanol is especially helpful because of its advantageous physical and chemical characteristics as well as its lower cost. Triglycerides with methanol may react quickly and the alkali catalyst is simple to dissolve in it. Despite having no color and no smell, methanol fumes can be quite explosive due to their low boiling point. Both methoxide and methanol are extremely hazardous chemicals that should be handled with extreme caution. It must be ensured that no one is exposed to these materials while making biodiesel. When compared to heating and micro emulsification, transesterification seems to be the most effective technique for lowering viscosity and minimizing engine issues out of the three main ways to produce biodiesel from oils.(Oyedoh et al., 2022)

2.6.5.5 MICROWAVE ASSSTED TECHNIQUE

Biodiesel production using traditional methods has encountered several challenges, including extended reaction times and high energy consumption. These issues can be effectively addressed by incorporating alternative techniques such as microwave (MW) or ultrasound, or by combining both methods. Microwave irradiation, in particular, offers a promising solution by providing environmentally friendly heat for the reaction process, thus mitigating these challenges. The use of Microwave heating systems presents numerous advantages, including precise control, efficiency in time and thermal energy usage, production of clean products, and reduced need for downstream treatment. Despite these benefits, a key challenge associated with MW reactors is the difficulty in accurately monitoring power and temperature, leading to lower process accuracy and repeatability. An MW reactor typically consists of an MW source equipped with a power supply and control mechanisms responsible for transmitting electromagnetic energy through the chemical reactor contained within an applicator(Amesho et al., 2022).

Chemical synthesis based on microwave energy offers many advantages and is significant from a scientific and engineering perspective. Microwaves have been used in many inorganic and organic chemical synthesis processes since it was found that they could function as a heat source. Recent laboratory-scale microwave uses in the manufacture of biodiesel demonstrated the technology's ability to outperform traditional methods in terms of results. The main findings that numerous studies have documented are shorter reaction times, cleaner reaction products, and shorter separation-purification periods. (Mahfud et al., 2020) and (Gladstone Kombe, 2023) investigated the transesterification process with microwave aid . They employed waste cooking oil as the raw material for the transesterification process and microwave ovens as the reactor. The study shows that compared to conventional procedures, microwave-assisted transesterification can yield up to 96% more biodiesel. It was also demonstrated that the procedure was less wasteful, faster, and more energy-efficient. The team's findings will have a big impact on developing more affordable and ecologically friendly biodiesel production processes. In a recently published study, (Razzaq et al., 2022) used microwave-assisted transesterification to create biodiesel using palm and cotton seed oil as the fuel. They discovered that, in comparison to traditional methods, their method produced more biodiesel while requiring less energy and reaction time.

(Akhtar et al., 2023) carried out a study with the goal of optimizing the production of biodiesel produced from CBO. CBO has been transformed into biodiesel using a microwave-assisted transesterification technique

A few publications on the transesterification of different oils using microwave irradiation to produce biodiesel are available in the literature. Sharma (2011) achieved a yield of 90.41 weight percent biodiesel using microwave-assisted transesterification of waste cottonseed cooking oil. The process used a methanol to WCO molar ratio of 9.6:1, a reaction duration of 9.7 minutes, and a microwave heating power of 180 W. In a different investigation on papaya oil, a yield of 99.3 weight percent was attained with a 0.95 weight percent NaOH dosage, a 3.3-minute reaction time, a 9.5-to-1 molar ratio of methanol to papaya oil, and a 700 W microwave heating power. Microwave-assisted transesterification procedures have also made use of heterogeneous catalysts derived from biomass sources. When calcined Enterolobium cyclocarpum pod husk ash dosage of 2.96 wt%, neem / rubber-seed oil blend was employed in a reaction with methanol / oil blend molar ratio of 11.44:1, reaction period of 5.88 min, and 150 W of microwave heating power, a biodiesel yield of 98.77 wt% was reported.(Fadara & Engineering, 2021).

2.6.6 BIODIESEL PURIFICATION

The extraction of impurities from biodiesel is an essential step in guaranteeing that the fuel meets all regulations, offers enhanced efficiency, and protects the engine from deterioration. Once crude biodiesel is obtained, residues such as glycerol, soap, water, a catalyst, and triglycerides must be removed. One of the most crucial steps in the manufacturing of biodiesel is purification. Adsorbents based on membranes, ion exchange, and water washing are the most widely used technology for biodiesel purification. The efficacy of engine performance is dependent on this purifying technique. High amounts of free fatty acids can cause deposit accumulation in storage tanks and even injectors, so shortening engine life. Moreover, cars' engines may deteriorate due to the excessive water content. As a result, purifying crude biodiesel might be difficult and raise operational costs for biodiesel production. This starts a conversation about potential substitutions for the traditional purification process for biodiesel.(Wan Osman et al., 2023)

Without a doubt, one of the most crucial stages in the manufacturing of biodiesel is purification. The primary objective of the production process is to produce fuel of the highest caliber with minimal impurities that could compromise its quality. Biodiesel may contain contaminants such as soap, glycerol, alcohol (specifically, methanol), free fatty acids, leftover salts, metals, and catalysts used in synthesis. It is evident that centrifugation and gravity settling are the appropriate methods for separating biodiesel and glycerol due to their different densities(Atadashi et al., 2011). Another factor that influences the quick separation of the ester and glycerol is their differing polarity. Since glycerol includes a significant amount of biodiesel contaminants, it needs to be filtered because the impurities would collect at the bottom of the fuel tank and foul the injector (Atadashi, 2015). The total removal of glycerol is indicative of the high caliber of biodiesel. Methanol is another polar material that must be eliminated because of its low flash point, which makes it difficult to use, store, and transport.

2.6.6.1 WATER WASHING

Reacted biodiesel can be cleaned by running it under warm water to get rid of soap and other impurities. This usually entails bubbling air through water with the biodiesel floating on top, or mist spraying water over the biodiesel. Water prewashing, a type of water washing done in the processor prior to the glycerol being drained off, is not the same as water washing.

There will always be some level of pollutants in biodiesel, even the highest grade. A large number of them, including soaps, glycerol, methanol, and catalysts, are soluble in water. While water washing does a good job of eliminating these pollutants, it leaves the biodiesel with traces of water that must be eliminated through further drying. Ideally, you should wash the glycerol with water about eighteen hours after it is emptied. This makes cleaning easier and faster by allowing the majority of pollutants to settle out. The biodiesel should ideally be transferred to a wash tank for the washing process after this settling has taken place in a different tank.(*Water Washing - Biopowered*, n.d.)

With the exception of distillation, every method for purifying biodiesel depends on the contaminants' molecular polarity differing from that of the methyl esters in biodiesel. Due to their polarity, methanol, soap, and glycerin are all highly attracted to one another as well as polar solvents like water. Because methyl esters are not very polar, they are not very soluble in water or other substances. Depending on the temperature, methanol dissolves in methyl esters only 4–6% of the time. Soap and free glycerin solubilities are significantly lower, despite being higher in the presence of methanol, which serves as a co-solvent. Water typically separates into its own phase when added to biodiesel, and due to their stronger attraction to water, methanol, soap, and free glycerin preferentially partition into this phase. Removing the water phase through centrifugation or gravity settling will lower the concentrations of the pollutants. Often, it takes several washing cycles to get the pollutants down to a sufficiently low level. A few manufacturers have refrained from water washing due to:

1) Their aim to reduce the amount of waste water generated;

2) Natural surfactants, such soap and monoglycerides, can create emulsions when present

3) Recycling becomes more difficult if methanol dissolves in water.

If the methanol is eliminated prior to the washing process, the issue of methanol contamination of the wash water can be resolved. But in the absence of methanol, the soap can separate from the methyl esters and condense into a thick, sticky substance that clogs pipes, screens, and filters.(Jon H, 2017)

2.6.6.2 MEMBRANE-BASED ADSORBENTS

Wet and dry washing are the conventional techniques used to separate and purify biodiesel (Torres et al., 2017). The water wash process uses a lot of water, which causes a scarcity and does not separate biodiesel well. Adsorbents including carbon, silica, and magnesol are used in dry washing to remove contaminants from biodiesel. This process results in issues with disposal and adsorbent regeneration in addition to inadequate biodiesel separation(Gomes et al., 2010)(García-Moreno et al., 2014).

The membrane yields encouraging results when it comes to biodiesel purification. The water usage of the membrane technique (0.05–0.1 g water/1 g biodiesel) is 100 times less than that of traditional methods, making it environmentally sustainable. Additionally, it has been discovered that the membrane works better for purifying and separating biodiesel. The membrane has several advantages over conventional techniques. Both water loss and pollutants to the environment are decreased. Separating the solvent and adsorbent is not necessary. It generates biodiesel in compliance with the necessary specifications. However, the membrane has a number of drawbacks. For example, the materials used to make the membrane must be resistant to organic solvents, modestly fouling, and inexpensive. Finding the right membrane material for separation is therefore crucial. Selectivity determines the membrane flux; more selective membranes result in higher permeate flow rates and greater fouling resistance(Baroutian et al., 2011).

The process of producing and separating biodiesel is fraught with issues, including low reaction rates, poor reactant conversion, the utilization of batch reactors, and the inactivation of enzymes by glycerol and methanol. These problems can be significantly resolved using membrane reactors, which combine reaction and separation into a single unit and have cheaper installation and running costs due to the elimination of intermediate processes. On the other hand, the generation and separation of biodiesel has been more successful using the modified membrane.(Bansod et al., 2021)

2.6.6.3 ION-EXCHANGE ADSORBENTS

Once biodiesel is produced, it needs to be cleaned to get rid of contaminants like glycerin and soap. If the fuel is not sufficiently dried, the conventional water wash process might result in emulsions and deteriorated biodiesel, among other issues. Additionally, it produces a lot of waste water. Waterless techniques for biodiesel purification, like ion exchange resins and synthetic magnesium silicate, have been brought to market. Ion exchange resins, which are tiny polymer beads, are produced by a number of different businesses to clean biodiesel. Despite the goods' similarities, the ways in which the corporations explain how they operate might occasionally differ greatly. Many firms claim, for instance, that the beads function by exchanging ions; on the bead surfaces, hydrogen ions are exchanged with sodium or potassium ions from the soap in the biodiesel. But according to a business that sells comparable beads, they function by interacting with soap and glycerin. The University of Idaho carried out a number of studies on ion exchange resins to ascertain their functionality, including how long they last. Three different kinds of beads were put to the test: Thermax's T45BD and T45BD Macro, Amberlite BD10Dry from Rohm and Haas, and both.

To achieve the required levels of soap and glycerin, the tests were performed with clean biodiesel that had been additized with varying concentrations of glycerin, sodium methoxide, and methanol. (Sodium methoxide and methyl esters will react to form soap).

FOUR POSSIBLE MODES OF CLEANING

Four possible mechanisms of action for the ion exchange resins were proposed by the researchers.

It is assumed that the beads function through ion exchange, whereby they swap a hydrogen ion for a sodium or potassium ion found in the soap. Since the resin is holding onto the sodium or potassium portion of the soap, the fatty acid portion is released into the effluent biodiesel, increasing the percentage of free fatty acids in the biodiesel. The acid value of the biodiesel will probably be higher than the ASTM standard of 0.5 mg KOH/g (the quantity of KOH needed to neutralize one gram of fuel) if the soap content in the fuel is more than 2500 ppm.

Filtration is an additional cleaning technique that is possible. Filtration is possible using the ion exchange bed. Filtration is an easy way to separate soap and glycerin from a solution if they have precipitated, which they usually do when the co-solvent methanol is eliminated.

A third potential cleaning mode is adsorption. Adsorption happens when polar impurities are drawn to the surface of the bead by intermolecular interactions. Actually, it is discovered that synthetic magnesium silicate, another well-liked waterless biodiesel cleaning technique, functions by adsorbing polar soap or glycerin molecules on its surfaces. Maybe this is also how the ion exchange beads function in part. This is most likely a crucial process in the elimination of glycerin.

The interaction between soap and glycerin is the fourth potential cleaning method. Adsorption or filtering is assumed to be the process by which glycerin is extracted from biodiesel. Due to its strong polarity, glycerin is attracted to other polar groups on the adsorbent's surface, which keeps it there. Since soap dissolves in glycerin, it would be taken out of the biodiesel along with the glycerin.(National & Education, 2010)

2.6.7 CATALYSED TRANSESTERIFICATION OF BIODIESEL

The next section discusses several catalytic techniques for the transesterification process of wasted cooking oil, as well as the significance of heterogeneous acid catalysts and enzymes in the production of more environmentally friendly biodiesel. Alternative oils with high FFA levels are utilized to represent waste cooking oil in order to better understand the potential of these catalysts because there is insufficient information available on the transesterification of waste cooking oil for specific types of catalysts. However, research that uses used cooking oil as a feedstock will be prioritized when talking about alternative strategies.

2.6.7.1 HOMOGENEOUS BASE CATALYSED TRANSFERICATION

Currently, homogeneous base catalysts like potassium hydroxide (KOH) or sodium hydroxide (NaOH) are frequently used in the manufacture of biodiesel. These catalysts are widely employed in industries for a number of reasons, including as their affordability and accessibility, their ability to catalyze reactions at low reaction temperatures and atmospheric pressure, and their quick creation of high conversion rates. In Fit states that the rate at which bases catalyze reactions is 4,000 times faster than the rate at which acids catalyze reactions. Refined vegetable oils with an acid value of less than 1 mg KOH/g or less than 0.5 weight percent FFA are the only ones that can use this catalyst.For the base-catalyzed transesterification process, it is clear that the FFA level in the oil feedstock should be as low as feasible (range from less than 0.5 wt% to less than 2 wt%). Therefore, the base catalyst shouldn't be utilized if the average FFA level in the used cooking oil is higher than 6 weight percent.

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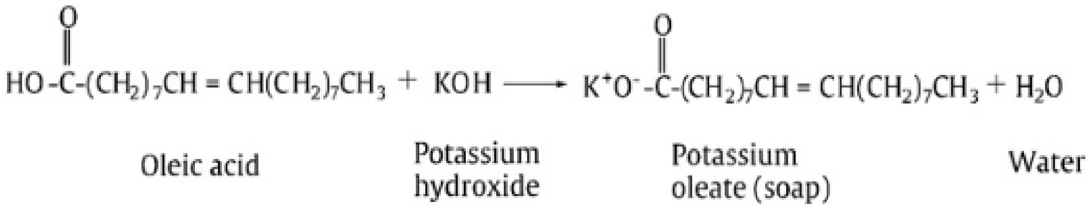
Long carbon chains that aren't attached to the glycerol backbone make up FFA. They are occasionally referred to as "carboxylic acids". When an oil or fat with a high FFA concentration is used to make biodiesel, like oleic acid, an alkali catalyst frequently reacts with it to form soap, which is highly undesired. An example of a reaction using FFA (oleic acid) and a base catalyst (KOH) is shown in Figure 2.7.



$$HO\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_7CH = CH(CH_2)_7CH_3 + KOH \longrightarrow K^+O^-\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_7CH = CH(CH_2)_7CH_3 + H_2O$$

Figure 2. 7 Saponification

Because the catalyst is dormant and unable to accelerate transesterification, this reaction is highly unfavorable. Excessive soap content can have a significant negative impact on the generation of fatty acid methyl ester (FAME) and the following purification of biodiesel, which includes glycerol separation and water washing (Lam et al., 2010).

Additionally, used cooking oil with a high water level affects the methyl ester production process. When present, especially at high temperatures, triglycerides can be hydrolyzed by water to produce diglycerides and free fatty acids. In Figure 2.8, the hydrolysis process is displayed. The FFA will next react to form soap in the presence of a base catalyst, as Figure 2.8 illustrates. As a result, excessive soap manufacturing typically occurs when the reactant contains water. In addition, too much soap added to a reaction mixture may cause it to gel up and create a difficult-to-recover semi-solid mass since saturated fatty acid soaps tend to harden at ambient temperature.

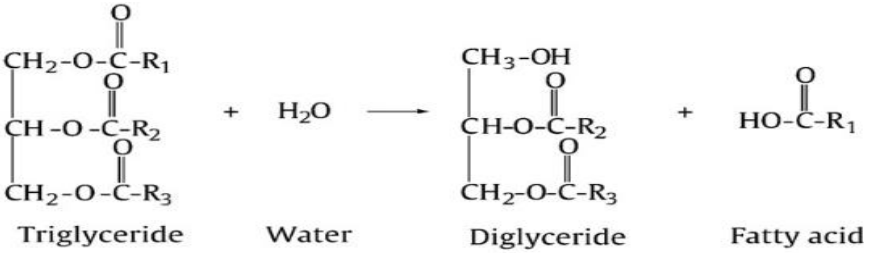


Figure 2. 8 hydrolysis reaction

2.6.7.2 TRANSESTERIFICATION WITH HOMOGENEOUS ACID CATALYST

The problems with the liquid base-catalyzed transesterification process are solved by liquid acid catalysts, especially when it comes to oil or fat with a high FFA content. Thus far, the two most studied acid-catalyzed system catalysts are sulfuric acid (H2SO4) and hydrochloric acid (HCl). Since the acid catalyst may catalyze both esterification and transesterification simultaneously and is unaffected by the presence of FFAs in the feedstock, acid-catalyzed transesterification has a substantial advantage over base-catalyzed methods. Esterification is a chemical reaction in which two reactants, usually an alcohol (like methanol) and an acid (like FFA), combine to form an ester as the final product. As two reactants, usually an acid (like FFA) and an alcohol (like methanol), contact during the chemical process of esterification, an ester is produced. Acid catalysis is considered to be more effective when the oil's FFA content is greater than 1% weight.

A recent economic analysis found that the acid-catalysed approach requires only one step to convert FFA to methyl esters, whereas the base-catalysed method requires more money. A solid acid catalyst is better suited for oils with high fatty acid content compared to conventional catalysts.(Liu et al., 2024).However, due to their slower reaction rate, high reaction temperature need, high alcohol to oil molar ratio, catalyst separation, and serious environmental and corrosion-related problems, acid-catalyzed systems are not commonly used in industrial applications. The mechanism of the acid-catalyzed reaction is depicted in Figure 2.9. One crucial stage in the catalyst-reactant interaction is the protonation of the carbonyl group, which is shown in the picture. Because of the initial chemical pathway, the neighboring carbon atom is now more electrophilic, which increases the susceptibility of the intermediate molecules to nucleophilic attack. On the other hand, the base catalysis follows a more direct path, where the alkoxide ion is first generated and acts as a strong nucleophile right away. The mechanism of the base-catalyzed reaction is shown in Figure 2.9

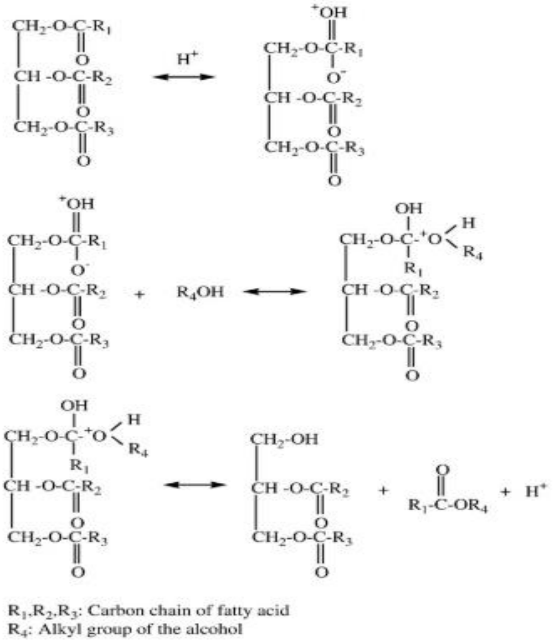
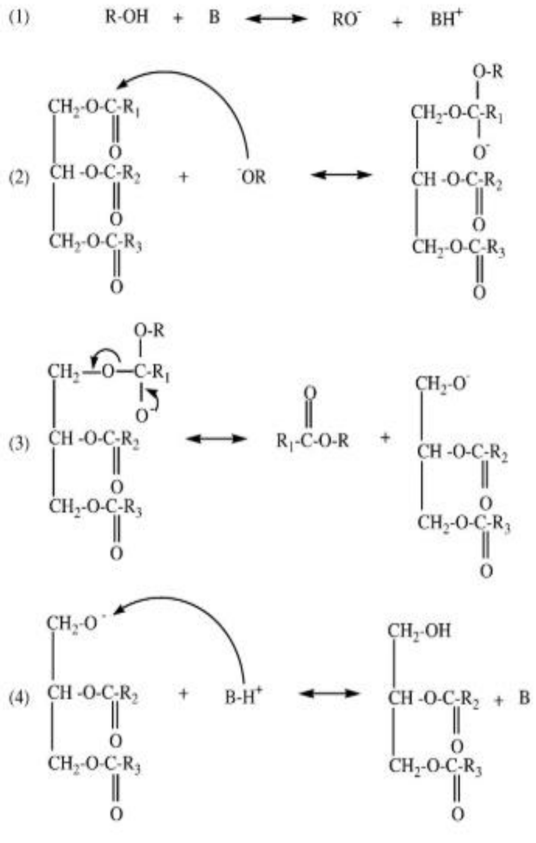


Figure 2. 9:Homogeneous acid-catalysed reaction mechanism for the transesterification of triglycerides

This fundamentally different approach is the ultimate contributor to the fluctuation in the transesterification reaction's catalytic activity (formation of electrophilic species by acid catalysis versus synthesis of greater nucleophile by base catalysis).

2.6.7.3 HOMOGENEOUS ACID AND BASE-CATALYSED TRANSESTERIFICATION

Owing to the advantages and disadvantages of homogenous acid and base catalysts, research has attempted to mix the two catalysts in order to produce biodiesel from oil with elevated quantities of free fatty acids. A catalyst that was acidic was initially used to start the esterification of FFAs. A base catalyst can trans-esterify the oil when the FFA concentration is less than 0.5–1 weight percent. Homogeneous catalytic transesterification of triglyceride is shown in Figure 2.10.



B: Base catalyst
R_1,R_2,R_3: Carbon chain of fatty acid
R_4: Alkyl group of the alcohol

Figure 2. 10 Triglyceride Transesterification via a Homogeneous Base-Catalysed Mechanism

Canakci and Van Gerpen have built a prototype plant to make biodiesel from feedstock with a high FFA level using a two-step process of esterification and transesterification(Canakci & Van Gerpen, 2003)

Homogeneous base KOH was utilized to catalyze the transesterification process after the feedstock had been treated with H2SO4 to lower the FFA level to less than 1 weight percent. Even while a large amount of FAME could be produced, the FFA esterification reaction proceeded somewhat slowly. The reaction needs additional acid catalyst to proceed more quickly. The drawback of this two-step process is further highlighted by the fact that further separation stages are required in both steps in order to eliminate the catalyst. The cost of producing biodiesel will increase if additional base catalysts are needed, even though the problem of catalyst removal from the first stage can be solved by using base catalyst from the second stage through the neutralization process.

2.6.7.4 HETEROGENEOUS BASE-CATALYSED TRANSFERICATION

Transesterification of vegetable or animal fats in the presence of a homogeneous or heterogeneous catalyst yields biodiesel. However, because of their decreased toxicity, ease of separation, reduced waste water creation, and reusability, heterogeneous catalysts are chosen over homogeneous ones (Parida et al., 2022). The key to a successful transesterification reaction is a highly efficient catalyst. At the moment, CaO is the most commonly used heterogeneous catalyst for this reaction. Many solid wastes rich in Ca element, such as egg shells, crab shells, carbide slag, etc., were used as the sources of CaO to reduce the catalyst cost from raw materials. In particular, river snail shells, the amount of which is generated annually due to the rapidly developing aquaculture industry, and which urgently need to be disposed of, recycled, and used. However, the loss of CaO active components limited its further application, so certain measures should be taken, where incorporation of support(Xia et al., 2024). Kouzu et al. (2008a) found that the CaO generated by calcining powdered limestone and CaCO3 at 900 °C for 1.5 h in the flow of helium gas exhibited astonishingly good results in the transesterification of refined soybean oil. The yield of FAME was 93% after an hour of reaction time at methanol reflux temperature and a 12:1 methanol to oil ratio. Figure 2.12 illustrates the function of CaO as a heterogeneous base catalyst in transesterification. However, the yield of FAME dropped to 66% when waste cooking oil with an FFA level of 2.6 wt% was used under the same reaction conditions. It is obvious that the basic CaO sites were contaminated by the significant adsorption of FFAs on the catalyst's surface(Kouzu et al., 2008). There was very little catalyst recovery because some of the catalysts interacted with the FFAs that were adsorbed and turned into calcium soap. The reaction result exceeded the basic biodiesel standard, which states that mineral matter concentrations should not exceed 200 ppm, with a calcium concentration of 3065 ppm.

Furthermore, a number of researchers observed that soluble CaO particles can leak out during transesterification. Gryglewicz (1999) asserts that methanol does not entirely dissolve calcium oxide. When methanol was used to transesterify sunflower oil, Lopez et al. observed that the reaction product included some dissolved calcium oxide. The soluble molecule was further identified by Kouzu et al. (2008b) as calcium Di-glyceroxide, which was created when glycerol and CaO interacted during the transesterification of soybean oil with methanol. Therefore, an additional purification process is required to eliminate the soluble component in the biodiesel, such as the use of ion-exchange resin (Kouzu et al., 2008).Heterogeneous catalytic transesterification of triglyceride is shown in Figure 2.10.

2.6.7.5 TRANSESFERICATION WITH HETEROGENEOUS ACID CATALYST

The main goal of biodiesel research is to create novel, long-lasting solid acid catalysts for the transesterification process. Furthermore solid acid catalysts may be able to easily replace liquid acid catalysts. Using a solid acid catalyst has several benefits, such as reduced corrosion issues (DaSilveira Neto et al., 2007), insensitivity to FFA concentration, simultaneous esterification and transesterification, elimination of the biodiesel washing phase (Jitputti et al., 2006), and ease of catalyst regeneration and recycling. In fact, a continuous flow reactor ought to take into account the dynamic nature of heterogeneous catalyst systems(Lotero et al., 2005).This continuous strategy needs to reduce the cost of product separation and purification in order to compete with commercial diesel fuel derived from petroleum. Over the past few decades, there have been numerous advancements in acid-catalyzed biodiesel processes. Solid catalysts require various acidic active sites to enhance their catalytic effectiveness. It is likely that Bronsted acidic sites would exhibit greater activity for FFA esterification, whereas Lewis acidic sites would demonstrate more effectiveness in oil transesterification(K. Li & Xie, 2024).

The solid acid catalyst for transesterification should have the following characteristics: a hydrophobic surface, a moderate to high concentration of strong acid sites, and an optimal broad pore network(Kulkarni & Dalai, 2006). It's possible that the slow reaction rate and potential for undesirable side reactions have prevented much study on the direct application of solid acid catalysts for the synthesis of biodiesel. There is also a knowledge deficit with regard to basic research on the reaction pathway of triglycerides on solid acids. These catalysts include zeolites, zirconium oxide (ZrO2), titanium oxide (TiO2), tin oxide (SnO2), sulfonic modified mesostructured silica, sulfonic ion-exchange resin, and heteropoly acids (HPAs).

2.6.7.6 TRANSESTERIFICATION CATALYSED BY AN ENZYME (BIOCATALYST)

Over the past ten years, interest in enzymatic transesterification—particularly those that use lipase—has increased due to the issues with downstream processing caused by chemical transesterification. The environmental impact of producing biodiesel is high, and the high cost of glycerol recovery and huge wastewater discharge contribute to this. In contrast, high FFA oil has no effect on enzyme catalysis, which continues without generating any waste products, is easy to extract the result from, and has gentle reaction conditions. Additionally, the catalyst can be reused (Kulkarni & Dalai, 2006). These benefits demonstrate the great potential of enzyme catalysis, which generates biodiesel, as an environmentally benign technology and a viable substitute for the chemical process. A few drawbacks, particularly when used on an industrial scale, are the expensive cost of the enzyme, the slow rate of reaction, and the deactivation of the enzyme (Bajaj et al., 2010).

2.7 FACTORS AFFECTING YIELD OF BIODIESEL

The yield of biodiesel in the presence of transesterification is affected by several process parameters which include; presence of moisture and free fatty acids (FFA) reaction time, reaction temperature, catalyst and molar ratio of alcohol and oil.

2.7.1 EFFECTS OF MOISTURE AND FREE FATTY ACIDS

(Wright et al., 1944) underlined that certain parameters must be met by the raw materials used in alkali-catalyzed transesterification of glycerides. The glyceride must be mostly anhydrous and have an acid value of less than 1. More NaOH was needed to neutralize the free fatty acids when the acid value surpassed 1. Water also led to the formation of soap, which used up the catalyst and diminished its efficiency. The resulting soaps increased viscosity, created gels, and made it harder to separate glycerol. (Feuge & Gros, 1949) also underlined the value of dry oils that are free of free fatty acids (0.5%). If the reactants didn't fit these specifications, according to (Freedman et al., 1984), ester yields were drastically lowered. When moisture and carbon dioxide in the air were present, sodium hydroxide or sodium methoxide reacted, diminishing their efficacy. Despite what (Feuge & Gros, 1949)and (Gauglitz et al., 1961) suggested, transesterification does not require a nitrogen atmosphere. A condenser connected the reactor to the atmosphere. As the reactant heated, oxygen that had been dissolved in the oil was released into the atmosphere. The process was additionally made easy by alcohol vape. Investigations were done into how water and free fatty acids affected the transesterification of cow tallow with methanol(Ma & Hanna, 1999). The findings suggested that for the best conversion, beef tallow's water concentration and free fatty acid level should both be kept below 0.5% w/w and 0.06% w/w, respectively. In the transesterification process, water content played a more critical impact than free fatty acids. The highest concentration of free fatty acids supported the research findings of (Feuge & Gros, 1949)

2.7.2 EFFECT OF REACTION TIME

The rate at which the transesterification process converts raw materials into desired products is influenced by various factors, with reaction time being a crucial one. This is particularly significant because the longer the reaction proceeds, the higher the conversion rate tends to be. (Freedman et al., 1984) delved into this phenomenon by investigating the transesterification of different oils—peanut, cotton-seed, sunflower, and soybean oils—utilizing specific conditions: a methanol to oil ratio of 6:1, a 0.5% sodium methoxide catalyst, and a temperature of 60°C. Their findings revealed that after just one minute, approximately 80% yield was achieved for both soybean and sunflower oils. However, as the reaction progressed over an hour, yields ranging from 93% to 98% were attained for all four oils, indicating a convergence in performance.

Moreover, the duration the reactants spend in the reactor, termed residence time, plays a crucial role in determining the extent of conversion from the initial reaction mixture to the final products. This underscores the intricate interplay between reaction kinetics, catalyst efficiency, and process parameters in optimizing transesterification reactions for enhanced product yields.

2.7.3 EFFECTS OF REACTION TEMPERATURE

The main step in the synthesis of biodiesel, known as transesterification, is converting feedstock triglycerides into fatty acid methyl esters (FAMEs) with the use of a catalyst, usually an acid or alkali. The kinetics of this reaction are significantly influenced by temperature. By supplying the required activation energy, elevated temperatures often speed up reaction rates and encourage the faster conversion of triglycerides to glycerol and biodiesel. Overly high temperatures, however, have the potential to cause thermal deterioration of the feedstock and the biodiesel that results, which will have a negative impact on product quality and production. The ideal temperature varies based on the particular catalyst and feedstock utilized. Temperatures between 50°C and 65°C are generally suitable for transesterification reactions involving vegetable oils including soybean, sunflower, and palm oil, according to empirical investigations. Diminished returns could be seen above this point because of higher energy usage and unfavorable side effects. To get the maximum biodiesel output, it is crucial to find a balance between optimizing reaction kinetics and reducing energy input.

Temperature has a substantial effect on the quality attributes of biodiesel in addition to reaction kinetics and yield. The temperature at which transesterification takes place affects a number of parameters, including viscosity, density, oxidative stability, and cold flow characteristics. Elevated temperatures often lead to reduced viscosity and enhanced fluidity in biodiesel, which is beneficial for engine combustion and fuel atomization. On the other hand, prolonged exposure to heat can quicken oxidation processes, increasing the amounts of peroxides, free fatty acids, and other unwanted byproducts that lower the quality of biodiesel.

2.8 ALCOHOLS

The manufacturing of biodiesel can be achieved by using short-chain alcohols such as methanol, ethanol, butanol, and amylic alcohol. Due to their low cost and unique qualities, methanol (CH3OH) and ethanol (C2H5OH) are the most commonly utilized alcohols. Despite its high toxicity, methanol is frequently chosen over ethanol because it may be used to produce biodiesel with less complicated equipment, recover extra alcohol at a lower cost, and achieve faster reaction rates.

2.8.1 METHANOL

As was previously noted, methanol is the most common alcohol utilized in the transesterification process, which produces biodiesel. An alcohol's water content determines how well it works in the biodiesel synthesis process. This is due to the fact that the hydrolysis of triglycerides into free fatty acids occurs during the transesterification process when water is present, resulting in the generation of soap and a low yield. Regretfully, short-chain alcohols can readily absorb water from their surroundings due to their hygroscopic nature. On the other hand, long-chain alcohols are frequently affected by contaminated water. Many types of alcohol can be used to make biodiesel, and according to (“Biodiesel Handb.,” 2010), it doesn't matter what sort of alcohol is used throughout the production process as long as the final product satisfies ASTM D6751 because it won't have any chemical effects. However, transesterification operations often avoid employing larger chain molecular alcohols due to the steric hindrance effect.

2.8.2 OTHER ALCOHOLS

Ethanol is generally quite fascinating since it is more cost-effective than methanol and produces biodiesel that is solely derived from biomass. Moreover, biological materials can be used to synthesize butanol, which yields biodiesel that is likewise solely generated from biological sources. On the other hand, petrochemical resources are frequently used in the production of alcohols such as methanol, propanol, and iso-propanol. In the case of methanol, this resource is methane from natural gas. Ethanol is the most ideal methanol replacement due to its renewable nature, carbon dioxide neutrality, reduced toxicity, and environmental friendliness. Compared to ethanol, methanol is more reactive and less expensive. Van Gerpen noted that the alcohols, like ethanol or isopropanol, that are utilized in the production of biodiesel are difficult to remove because they react with water to form an azeotrope. Nevertheless, the water can be eliminated using a molecular sieve.

2.9 WASTE COOKING OIL

The term "waste cooking oil" describes edible oil that was once used for frying in homes, hotels and restaurants but is no longer in use for that purpose. Most developing-nation municipalities, like Ethiopia's, just dispose of used cooking oil in the open. Serious issues with the environment, society, economy, and health result from this. The amount of organic contaminants in water is increased when cooking oil waste is improperly or poorly disposed of in water bodies. This drastically reduces the quality of the water, which has an impact on fisheries, other aquatic life, and the local community.(Degfie et al., 2019). In accordance with the World Health Organization, one liter of waste cooking oil can pollute one million liters of water, and waste cooking oil accounts for 25% of wastewater contamination. Cooking oil waste covers the water's surface, stops oxygen from entering the water from the air, speeds up the oxygen in the water's depletion, and harms fish and birds as well as the aquatic ecosystem as a whole. This results in sewage blockage, long-term pollution of water and soil, and degradation of the marine ecology.(Ulukardesler, 2023)

According to (Demirbas, 2009)&(M. Li et al., 2014)WCO produces biodiesel in an environmentally responsible manner by recycling waste cooking oil and producing renewable energy with less pollution. It reduces the cost of waste disposal and partially replaces imports of petrochemical oil. There are three ways to produce biodiesel from leftover cooking oil: economically, environmentally, and through waste management.

2.10 COCOA PODS

Cocoa pod husk, serving as a primary source of potash, represents a significant agricultural waste in countries like Ghana, Nigeria, and most cocoa-producing regions globally(Alagumalai et al., 2021).Theobroma cacao, often known as the cocoa tree or cacao tree is a tiny, evergreen tree in the Malvaceae family that grows to a height of 6–12 m (20–39 ft).Chocolate liquor, cocoa solids, cocoa butter, and chocolate are all made from its seeds, or cocoa beans. Originating in the Americas' tropical regions, Ivory Coast produced 2.2 million tons of cocoa beans in 2018, making it the world's top producer. The Greek term "food of the gods," θεός (theos), which means "god" or "divine," and βρῶμα (broma), which means "food," are the sources of the generic name Theobroma. The term "cacahuatl," which means "bean of the cocoa-tree," is the Hispanization of the plant's native Mesoamerican names, which include "kakaw" in Tzeltal, K’icheʁ, and Classic Maya, "kagaw" in Sayula Popoluca, and "cacahuatl" in Nahuatl.

Its alternating, whole, unlobed leaves are 10–50 cm (4–20 in) in length and 5–10 cm (2–4 in) in width. When fully ripe, the ovoid fruit, known as a cacao pod, measures 15–30 cm (6–12 in) long and 8–10 cm (3–4 in) wide. It ripens from yellow to orange and weighs roughly 500 g (1 lb). The pod holds 20–60 seeds, which are commonly referred to as "beans" and are embedded in a white pulp. While the pulp is utilized in some places to make refreshing juices, smoothies, jellies, and creams, the seeds are the primary ingredient in chocolate. Traditionally thrown out until 21st-century traditions altered, the fermenting pulp can be distilled to produce an alcoholic drink. Forty to fifty percent of the fat in each seed is in the form of cocoa butter. Theobromine, a stimulant that resembles caffeine, is the fruit's active ingredient. Large amounts of waste are produced during the manufacture of cocoa. In fact, only 10% of the weight of the cocoa fruit is utilized for commercial purposes; the other 90% is thrown away as waste or byproduct. The outer tegument that covers the cocoa beans—also referred to as cocoa bean shells—is one of these byproducts that are produced during the previously stated roasting process. According to certain research, the percentages of CBS, which make about 10%–17% of the total weight of cocoa beans, may differ according on the type of fermentation process used to produce the beans.. Husk from cocoa beans is a suitable biomass source for generating power. Potassium is abundant in waste ash and can be used to make a variety of chemical products, most notably high-purity potassium carbonate(Rojo-Poveda et al., 2020)

2.11 CLAM SHELLS

A frequent term for a variety of bivalve mollusks is "clam." The term is frequently limited to species that are edible, classified as infauna, and spends the most of their life partially submerged in the sand of riverbeds or the seafloor. Clams have a strong digging foot and two equal-sized shells joined by two adductor muscles. Both freshwater and marine habitats are home to them; in the latter, they like to burrow into the mud. The turbidity of the water needed varies according on the species and the area; North America has the highest diversity of these. In the culinary sense, clams do not live close to the bottom like scallops do, nor do they attach themselves to a substrate like oysters and mussels do. Clams are often used as marine bivalves in cooking, such as in clam chowder and clam digging. A lot of clams that are edible, including palourde clams, are ovoid or triangular in shape. On the other hand, razor clams have an extended shell with parallel sides that resembles an old-fashioned straight razor.While some clams have a one-year life span, at least one has reached an age of almost 500 years. Every clam is a filter feeder and consists of two calcareous shells or valves connected at a hinge by a flexible ligament.

The two (often equal) valves that make up a clam's shell are joined by an internal or exterior ligament and a hinge joint. One or two adductor muscles can contract to close the valves, while the ligament applies stress to open them. In addition, clams have nerve systems, mouths, stomachs, hearts, and kidneys. Many own a siphon.

The process of bio-mineralization is how the shell forms, just like it does for all other hard structures in animals. In this instance, the organism creates hard minerals that are subsequently mixed into a soft tissue matrix. The bulk of the clam shell is composed primarily of calcium carbonate, with traces of other tissues. Material scientists are studying these shells because they have some extremely intriguing mechanical features. A clam shell's fracture toughness, for instance, is significantly higher than the fracture toughness of the individual crystals that make up the shell, indicating that the composite's formation process plays a key role in determining the shell's toughness.(*Clam Shell - Materials - Materials Library - Institute of Making*, n.d.)

2.12 CATALYST

Catalysis plays a crucial role in numerous chemical procedures and is widely employed in both academic and industry research, as well as laboratory environments. Catalysis is indispensable for facilitating chemical reactions. By employing catalytic reagents, it is possible to potentially minimize undesired side reactions, decrease the temperature required for a chemical change, diminish the amount of waste generated by the reagents, and enhance the specificity of a reaction. These factors all contribute to the development of environmentally friendly technologies.

A catalyst is any substance that speeds up a chemical process without undergoing any chemical changes itself. There are three distinct categories of catalysts: homogeneous, heterogeneous, and enzymatic catalysts. Enzymatic catalysis is the most effective and sustainable kind of catalysis observed in nature. It is one of the three recognized types of catalysis, along with homogeneous and heterogeneous catalysis. There is a pressing need for a novel catalytic system that combines the activity of homogeneous catalysis with the ease of recovery of heterogeneous catalysts. Both homogeneous and heterogeneous catalysis have distinct advantages and disadvantages. Nano-catalysts can combine the advantages of both homogeneous and heterogeneous catalytic systems. With its capacity to isolate and recover the catalyst with ease, nano-catalytic systems deliver rapid, selective chemical transformations with significant product yield. An essential requirement for any catalyst to be utilized in industrial processes for the synthesis of environmentally friendly compounds is its capacity for system recovery. The surface area of nanoscale objects indicates that they have a high rate of contact with reactants and catalysts. The catalyst is heterogeneous as a result of its insolubility on the reaction solvent and may thus be readily isolated from the reaction mixture.

Catalysis was one of the early applications for nanoparticles. Numerous materials and components, including aluminum, iron, titanium dioxide, clays, and silica, have all been utilized as nanoscale catalysts for a very long time. But there is currently no good explanation for the peculiar catalytic behavior that NPs have displayed. A likely explanation for nanoparticles' catalytic activity is their high surface areas, which have an obvious favorable effect on reaction rates. Any material's catalytic activity can be altered by its shape- and structure-based nanoscale features. By fine-tuning the composition of nano-catalysts, higher selectivity has been reached (bimetallic, core-shell type, or employment of supports).Consequently, the subject at hand is how the physical qualities of nanoparticles affect their catalytic properties, and how fabrication parameters may affect those physical attributes in turn. By having a deeper grasp of them, a scientist can build nano-catalysts that are extraordinarily active, highly selective, and highly resilient. All these advantages will make industrial chemical reactions more resource-efficient, waste-free, and energy-efficient, which will help minimize the environmental effect of our reliance on chemical processes. Nanoparticles are considered as the most essential industrial catalyst because they have a larger range of functions, such as energy storage and energy conversion. The variable and particle-specific catalytic activity of nanoparticles is related to their heterogeneity and characteristic size and shape changes. In a homogeneous system, a nano-catalyst is commonly a suspension or solution of nanoparticles in a solvent. However, while developing a nano-catalyst for utilization in a solution for homogeneous Nano-catalysis (the catalyst is in the same phase as the reactants), it is vital to take into account how to stop the catalyst from aggregating. If this tendency to aggregate and clump together into larger particles is not properly avoided, nanoparticles will lose their tremendous surface area and other advantages. The most efficient way to stabilize nanoparticles in solution is by polymer-based stabilization, which keeps them from aggregating. It is impossible for the nanoparticles to collide and aggregate or clump together to generate larger particles when long chain molecules are present. However, by restricting the amount of nanoparticle surface available to the interacting molecules, such stabilization decreases the total catalytic activity of the nano-catalyst. Heterogeneous catalysis, which uses a catalyst in a separate phase from the reactants, is generally seen as being more environmentally benign due to its high rate of recoverability. The heterogeneous catalyst might be a solid unto itself or is usually immobilized on a solid inert matrix. The catalytic potential of various nanoparticle-support systems is a topic that the scientific community is getting more and more interested in exploring. Nanoparticles composed of copper, ruthenium, rhodium, silver, palladium, iron, gold, nickel, and platinum are a few recent examples. The supports used range from carbon fibres and biowaste materials through silica, clays, zeolite, and alumina. In nanostructured materials, heterogeneous nano-catalysts have also been explored. By molding a solid substance around a molecular template, you can make nano-porous materials. As a strategy to increase surface area and exert some control over reactant flow on the catalyst surface, nanoscale patterns can also be etched into the surface of a catalyst using traditional lithography techniques. One of the most exciting scientific and practical difficulties involved with the use of nanoparticles as catalysts is figuring out how their atomic-scale structure and composition give the optimal catalytic activity. The generation of these particles while exercising the most control over their shape and makeup is the second issue. Modern nanotechnology approaches offer a very high potential for increasing the characterization and manufacture of heterogeneous catalysts based on supported nanoparticles. The advantages of both homogeneous and heterogeneous catalysis may be observed in nano-catalysis, which is more akin to heterogeneous catalysis due to its high catalytic activity (turn over frequency TOF), selectivity, and recyclization like homogeneous catalysis. Traditional heterogeneous catalyst systems differ from their homogeneous counterparts in two fundamental ways: (i) the reduced surface area that reactant molecules can reach, which restricts their catalytic activity; and (ii) the resulting overly high consumption of expensive catalyst materials. Nano sized catalytic materials can alleviate these challenges by improving the surface to volume ratio (S/V). These features constitute the basis of the current state of nano catalysis(Tandon, 2015).

2.12.1 DEVELOPMENT OF HETEROGENEOUS CATALYSTS FROM AGRICULTURAL WASTE

Over the past few decades, a number of feedstocks have been employed to create biodiesel, and the usage of commercial heterogeneous catalysts has been fully explored and described in the literature. Metal oxides and mixed metal oxides can be bought from commercial sources in various forms. Calcium Di-glyceroxide, magnesium oxide, calcium oxide (CaO), calcium methoxide, magnesium zirconate (Mg2Zr5O12), aluminium oxide supported calcium oxide, sodium molybdate, magnesium pyrophosphate, sulphated zirconia, and others are a few examples(Awogbemi et al., 2021). Despite claims that some of these catalysts have great conversion efficiency, their labour-intensive and challenging preparation processes prevent them from being used as catalysts in the synthesis of biodiesel. Commercial catalysts are created from non-renewable resources, and their use has an impact on the environment and disposal problems. Catalysts made from agricultural waste are abundantly available, affordable, non-toxic, and non-corrosive. They also produce no wastewater. They are highly convertible, biodegradable, and provide biodiesel producers with a viable means of getting rid of agricultural waste. Various agricultural wastes have been manufactured, transformed, and employed as affordable and environmentally acceptable catalysts for the synthesis of biodiesel using a variety of low-grade feedstocks in recent years. kola nut pod husks (Betiku et al., 2019b), cocoa pod husks(Ofori-boateng & Lee, 2013), waste shells of Turbonillastriatula (Boro et al., 2014), waste oyster shells

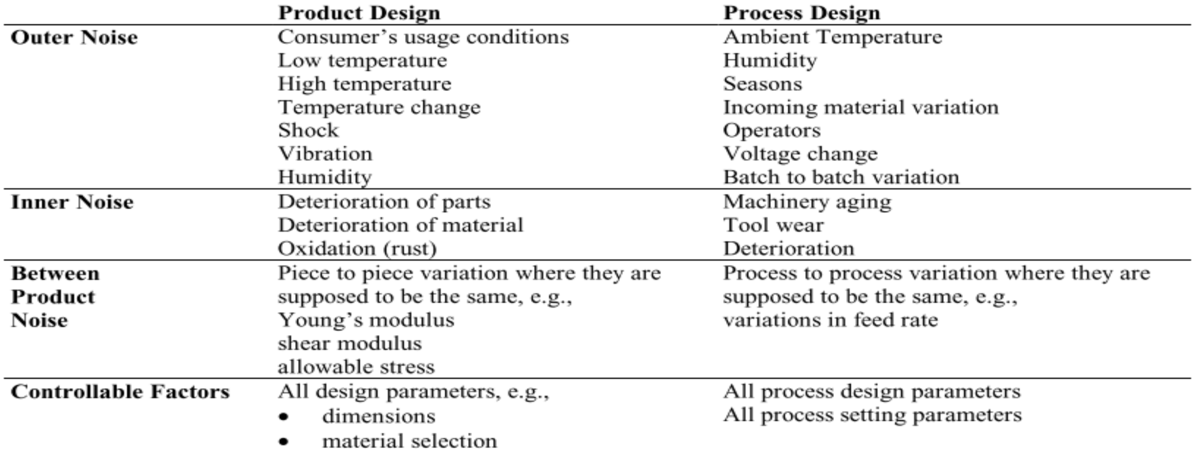
(Lin et al., 2020), corncobs and Chicken Eggshell(Akhabue et al., 2020), coconut husk ash(Vadery et al., 2014) waste animal bones (Nisar et al., 2017), Waste Shells of Mussel, Cockle, and Scallop (Buasri et al., 2013), etc. are some of the agricultural wastes derived heterogeneous catalyst with high catalytic activities.

2.13 ROBUST DESIGN

As the technical environment gets more and more competitive, industries require high-quality products. Unexpected departures from the planned function are induced by variances in various engineering processes. Robust design helps to prevent these situations. Robust design has been established in industrial engineering to increase the reliability and quality of products. Recently, a variety of design-related fields have utilized this technique. We start by going through the definition of a resilient design. It has been explained by several academics. When a technology, product, or process performs with the least amount of sensitivity to factors producing unpredictability (either in the production environment or the user's environment) and ageing at the lowest possible unit manufacturing cost, it is said to be robust. Taguchi, the father of robust design, defined robustness as the condition in which a technology, product, or process operates. Such describes a "robust design" as one having large tolerances for manufacturing and assembly-friendly design parameters and process aspects but still satisfies the functional requirements. This principle of robust design argues that the information content should be limited. In order to minimize a product's vulnerability to variation, Box states that "the process of robustifying a product requires establishing its criteria." Despite the fact that various words are used, their meanings are the same. The technical world defines the notion of resilient design as one that is insensitive to variances(Park, 2006).

2.13.1 TAGUCHI'S APPROACH TO PARAMETER DESIGN

In parameter design, a product's functional feature is impacted by two kinds of elements: control factors and noise factors. Control considerations for an injection moulding process include easily managed factors including as temperature, cycle time, and material choice. the difficulty, cost, or lack of ability to regulate noise components. Between-product noise, interior noise, and outside noise are three main categories of noise variables. Examples of each type of noisy component and manageable factor in product and process design are illustrated in Figure 2.13. When a product's performance deviates from the desired value, noise issues are frequently to blame.



	Product Design	**Process Design**
Outer Noise	Consumer's usage conditions Low temperature High temperature Temperature change Shock Vibration Humidity	Ambient Temperature Humidity Seasons Incoming material variation Operators Voltage change Batch to batch variation
Inner Noise	Deterioration of parts Deterioration of material Oxidation (rust)	Machinery aging Tool wear Deterioration
Between Product Noise	Piece to piece variation where they are supposed to be the same, e.g., Young's modulus shear modulus allowable stress	Process to process variation where they are supposed to be the same, e.g., variations in feed rate
Controllable Factors	All design parameters, e.g., • dimensions • material selection	All process design parameters All process setting parameters

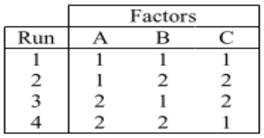
Figure 2. 11 Examples of Noise and Control Factors

As part of Taguchi's approach, each control parameter is carefully tweaked and tested at multiple levels employing design of experiments approaches, particularly Orthogonal Arrays (OAs). Among the regularly utilized OAs, Table 2.2 offers a list of the L4, L9, L12, L18, and L27. A thorough list of OAs is available by searching for text comparable to. The columns in the OA denote the factor and its corresponding values, and each row in the OA represents an experimental run that was carried out at the stated factor settings. Factors 1 and 2 are, for instance, at Levels 2 and 3, respectively, in experimental run #3 ofTable 2.2.(Simpson, 1989).

The experimental designer must determine the right factor levels for each control factor; normally, 2 or 3 levels are chosen for each component. The selection of the proper levels and amounts requires the majority of the work in arranging good design testing. Equation(1) can be used to compute the number of runs C = (A-1) B + 1

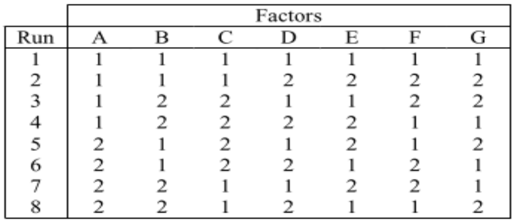
(Fadara & Engineering, 2021)(1).

Where C is the total number of experiments, A is the number of levels, and B is the number of factors



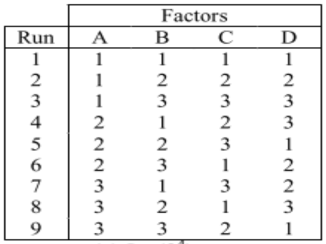
	Factors		
Run	A	B	C
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	1

(a) L_4 (2^3) array



	Factors						
Run	A	B	C	D	E	F	G
1	1	1	1	1	1	1	1
2	1	1	1	2	2	2	2
3	1	2	2	1	1	2	2
4	1	2	2	2	2	1	1
5	2	1	2	1	2	1	2
6	2	1	2	2	1	2	1
7	2	2	1	1	2	2	1
8	2	2	1	2	1	1	2

(b) L_8 (2^7) array



	Factors			
Run	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

(c) L_9 (3^4) array

To execute robust design, Taguchi advises combining a "inner array" with a "outer array" method. The settings for the noise factors compose the "outer array," whereas the settings for the control factors comprise the "inside array" and are the subject of the current study. The "product array" is made up of the "inner array" and the "outer array," also known as the "full parameter design-layout."

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 MATERIALS

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

Table3. 1 materials and reagents used for WCB production

MATERIALS	SOURCE	USES
Waste Cooking Oil	It was gotten from a restaurant in Warri Delta State Nigeria.	It is a feedstock for biodiesel production
Clam Shell	It was gotten from Agge in Delta State Nigeria.	It is a feedstock for the basic precursor of the heterogeneous Bi-functional catalyst
Cocoa Pods	It was obtained locally from the western part of Nigeria	It is the Feedstock for the acid precursor of the heterogeneous Bi-functional catalyst.
Sulphuric acid (H_2SO_4)	Chemical Engineering Lab, UNIBEN.	It is for the pre-treatment of the acid precursor

Potassium Hydroxide (KOH)	Chemical Engineering Lab, UNIBEN.	It is for the pre-treatment of the basic precursor and to determine the acid value of WCO and biodiesel.
Benzene (C_6H_6)	Chemical Engineering Lab, UNIBEN.	It is for the determination of the acid values of both the WCO and biodiesel produced
Chloroform ($CHCl_3$)	Chemical Engineering Lab, UNIBEN.	It is used for determination of the peroxide and iodine values of WCO
Ethanol (C_2H_5OH)	Chemical Engineering Lab, UNIBEN.	It is used for determining acid and saponification values of WCO and acid value of biodiesel produced
Methanol (CH_3OH)	Chemical Engineering Lab, UNIBEN.	It is used to stimulate the simultaneous esterification and transesterification of WCO to produce biodiesel.

Acetic Acid	Chemical Engineering Lab, UNIBEN.	Determination of the peroxide value of the WCO.
Sodium thiosulphate ($Na_2S_2O_3$)	Chemical Engineering Lab, UNIBEN.	For determination of the iodine and peroxide values of the WCO.
Distilled water (H_2O)	Central Research Lab, UNIBEN	For preparation of the standard solution and for washing biodiesel.
Phenolphthalein (indicator)	Chemical Engineering Lab, UNIBEN.	For titration
Starch indicator	Chemical Engineering Lab, UNIBEN.	For determination of the iodine value of the WCO.
Potassium iodide (KI)	Chemical Engineering Lab, UNIBEN.	For determining the iodine Value of the WCO.

Wij’s reagent	Chemical Engineering Lab, UNIBEN.	For determining the iodine value of the WCO.

APPARATUS AND THEIR USES

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

Table3. 2 list of apparatus used for biodiesel production

APPARATUS	**SOURCE**	**USES**
Microwave Oven	Chemical Engineering Lab, UNIBEN	Supplying heat needed for esterification and transterification of WCO.
Volumetric flask	Chemical Engineering Lab, UNIBEN	For volumetric measurement of solvent
Reflux Condenser	Chemical Engineering Lab, UNIBEN	Condensation of methanol which escapes as a vapor to liquid and sent back to the reactor.

Conical Flask	Chemical Engineering Lab, UNIBEN	It serves as a reactor.
Beakers	Chemical Engineering Lab, UNIBEN	As a container for substances.
Magnetic Stirrer	Chemical Engineering Lab, UNIBEN	For continuous stirring and heating of reactants.
Measuring Cylinder	Chemical Engineering Lab, UNIBEN	For Volumetric measurement of solvent.
Burette	Chemical Engineering Lab, UNIBEN	For titration.
Retort stand	Chemical Engineering Lab, UNIBEN	For holding burette and separating funnel.
Furnace	Energy Centre, UNIBEN	For calcination of Clam shells and carbonization of Cocoa pods.
Centrifuge	Chemical Engineering Lab, UNIBEN	Used to separate the biodiesel mixture obtained after reaction.

Weighing balance	Chemical Engineering Lab, UNIBEN	For measurements.
Pipette	Chemical Engineering Lab, UNIBEN	For titration.
Oven	Chemical Engineering Lab, UNIBEN	Determination of the moisture content of the WCO and drying.
Crucible	Chemical Engineering Lab, UNIBEN	Used to determine the moist content of WCO.
Separating funnel	Chemical Engineering Lab, UNIBEN	For separation and washing of biodiesel.
Flash Point Tester	Energy Centre, UNIBEN	To ascertain the flash point of the biodiesel generated..
Kinematic Viscometer	Chemical Engineering Lab, UNIBEN	Ascertaining the viscosity of both biodiesel and WCO.

3.2 METHODS

3.2.1 OIL CHARACTERIZATION

To ascertain the physiochemical characteristics of the waste cooking oil (WCO), including the specific gravity, acid value, saponification value, peroxide value, and iodine number, several analyses were conducted. The following lists the several techniques used to ascertain the oil's characteristics:

3.2.1.1 DETERMINATION OF THE ACID VALUE

This test was used to measure the acidity of the waste cooking oil both before and after. The acid value is the quantity of potassium hydroxide required to neutralize one milligram of waste cooking oil's free fatty acid content, or one gram. Free fatty acids are a close predictor of rancidity since they are regularly created during the breakdown of triglycerides.

The acid value of waste cooking oil was determined by titrating it against a standard potassium hydroxide (KOH) solution in an alcoholic medium.2.0g of Waste cooking Oil was measured into a conical flask using a weighing balance, 10ml of benzene, 10ml of ethanol and two drops of phenolphthalein indicator is added before being titrated against a standard 0.05M KOH solution. (Otoikhian et al., 2020).The color change is from white to pink.

The equation used for finding the acid value is;

$$\textbf{Acid Value} = \frac{\boldsymbol{Titration\ value \times KOH\ Normality \times 56.1}}{\boldsymbol{Weight\ of\ WASTE\ COOKING\ OIL\ \ used}}$$

Titration value= T_W-T_S

Where: T_w = Titrate value of the waste cooking oil

T_s = Titrate value of blank solution.

The weight percentage of fatty acids present in the oil is known as the free fatty acid (FFA) content, can be calculated using

$$\textbf{FFA (\%)} = \frac{\boldsymbol{Acid\ Value}}{\mathbf{2}}$$

3.2.1.2 DETEERMINATION OF THE IODINE VALUE

The proportional degree of un-saturation in oil components, as measured by the uptake of halogen, is expressed as the iodine value. Iodine Value offers an estimate of these quality criteria since the degree of un-saturation has a relationship with the melting point and oxidative stability. There is more un-saturation and increased oxidation susceptibility with increasing iodine values.

The iodine value of Waste Cooking Oil was tested by placing 1gram of the oil in a conical flask, adding 10 milliliters of chloroform (CCl4), gently heating the mixture, and allowing it to cool for duration of 10 minutes. 25mL of Wij's reagent (Iodine tri-chloride solution) was added into the flask and swirled vigorously; the mixture was left in the dark for 30 minutes to avoid any reactions with sunlight. After the designated amount of time, the mixture was titrated against sodium thiosulphate until a yellow color appears. This will be followed by the addition of 20mL of 10% KI and 150mL of distilled water. The resultant yellow mixture was titrated against sodium thiosulphate using a 1-percent starch solution as an indicator until an indigo/black color to colorless transition will be obtained (end point). The identical circumstances will be used for a blank test.

The value can be calculated with the Equation below:

$$\textbf{Iodine Value} = \frac{12.69 \times N \times (V_1 - V_2)}{Weight\ of\ WASTE\ COOKING\ OIL}$$

Where: V_1 = Sodium Thiosulphate Blank titrate

V_2 = Sodium Thiosulphate titrate of Waste Cooking Oil

N = Normality of Sodium Thiosulphate (Na_2SO_3)

3.2.1.3 DETERMINATION OF THE KINEMATIC VISCOSITY

The waste cooking oil's kinematic viscosity was determined using a calibrated capillary calorimeter, the kinematic viscosity of both the oil and the biodiesel would be determined. The equipment was turned on and a 200g of oil was measured in a beaker and placed under the calorimeter to take the readings.

3.2.1.4 DETERMINATION OF OIL DENSITY

For determination of the density of WASTE COOKING OIL (WCO) 50mL density bottle of known weight was filed with WCO. The new weight of the density bottle is noted, the weight of WASTE COOKING OIL contained in the 50mL bottle is gotten by subtracting the known weight of the density bottle from its new weight. The density is calculated with the Equation below, measured in Kg/m^3.

$$\textbf{Density} = \frac{Weight\ of\ WASTE\ COOKING\ OIL}{Volume\ of\ WASTE\ COOKING\ OIL}$$

3.2.1.5 DETERMINATION OF MOISTURE CONTENT OF SHEA BUTTER OIL.

5.00g of WASTE COOKING OIL was weighed into a crucible of known weight and then placed in an oven at 150 ^{0}C temperature for 4 hours. The crucible was reweighed within an interval of 1 hour for the 4 hours to note the difference in weight of the crucible till the weight becomes stable. It is calculated using the Equation below:

$$\textbf{Moisture Content} = \frac{\textit{Initial weight of WCOO} - \textit{Final weight of WCO}}{\textit{Initial weight of WASTE COOKING OIL}} \times \mathbf{100}\%$$

3.2.1.6 DETERMINATION OF SAPONIFICATION VALUE

An alkali is used in the saponification process to break down or degrade a neutral fat into fatty acids and glycerol. The saponification number is the milligrams of potassium hydroxide (KOH) required to saponify one gram of fat. (Odoom & Edusei, 2015) It is clear that alkali is used to neutralize all of the free fatty acids and other reactive ester-like compounds, such as lactones, as well as to saponify all of the triglycerides, diglycerides, and monoglycerides in the sample.

The saponification equivalent of a fat or ester represents the amount that can undergo saponification with one mole (56.104 grams) of potassium hydroxide. Consequently, the equation can be expressed as 56.104 = saponification value x saponification equivalent. The saponification value of the waste cooking oil was gotten by measuring 1.00g of Waste Cooking Oil into a conical flask and adding 25mL of ethanolic KOH. Reflux heating was used to finish the product for an hour. The mixture was then combined with 0.5mL of phenolphthalein, and it was titrated against a 0.5M HCL solution until it becomes colorless. To conduct a blank (distilled water) test, the same circumstances will be employed.

The saponification value can be calculated using the Equation below

Saponification Value$= \frac{\mathbf{56.1 \times M \times (T_B - T_{WCO})}}{\mathbf{Weight\ of\ WASTE\ COOKING\ OIL}}$

Where: T_B = Blank titration

$T_{\text{WASTE COOKING OIL}}$ = WASTE COOKING OIL titration

M = Molarity of HCL

This equation can be used to determine the average Molecular of WASTE COOKING OIL.:

Mw = $\frac{\mathbf{168300}}{\mathbf{SV-AV}}$

Where: SV = Saponification Value

AV = Acid Value

3.2.1.7 DETERMINATION OF PEROXIDE VALUE

The condition of unsaturated oils and fats is indicated by the Peroxide Number (PV). Oxidation turns unsaturated fats and oils rancid, generating peroxides(YSI, 2019). The PV can be used to track the production of peroxides during the initial phases of oxidation(Popa et al., 2017). The millimoles of peroxide or milliequivalents of oxygen that are present per 1000 g of fat are measured as the peroxide value (1 mm = 2 meq.).Fresh oils are those that have POV values well below 10meq/kg. As soon as the peroxide value reaches between 20 and 40meq/kg, a rancid taste can be detected.

The concentration of hydro-peroxide, the main byproduct of oxidation, is determined by the peroxide value (PV). The idea is that potassium iodide releases iodine when peroxides are present., i.e.

$ROOH + KI \rightarrow ROH + KOH + I_2$

The amount of iodine generated is then measured by titrating sodium thiosulfate and employing a starch indicator to ascertain the amount of ROOH:

I_2+Starch+ $2Na_2S_2O_3$ (blue) → 2NaI +Starch+ $Na_2S_4O_6$ (Colorless)

The quantity of sodium thiosulfate (Na2S4O6) ingested is used to compute the number of peroxides. Peroxide value (PV) is the amount of mill equivalents (meq) of peroxide per kilogram of food-extracted fat.(Kong & Singh, 2011).

2.00g of WASTE COOKING OIL and 12mL of acetic-chloroform (3:2) was weighed into a conical flask to calculate the peroxide value. 0.2mL of saturated potassium iodide was added to the mixture and stirred for a minute. After that, distilled water was added. With 1mL of starch solution as an indicator, the resultant mixture was titrated against 0.1 N sodium thiosulphate until the blue-grey hue in the aqueous top layer vanished. The same procedures were followed for blank.

This value can be calculated with Equation below:

$$\textbf{Peroxide Value} = \frac{10 \times (N_1 - N_2)}{Weight\ of\ WASTE\ COOKING\ OIL}$$

Where: N_1 = Sodium Thiosulphate Blank titrate

N_2 = Sodium Thiosulphate titrate of WASTE COOKING OIL

3.2.1.8 DETERMINATION OF SPECIFIC GRAVITY (S.G).

The WASTE COOKING OIL S.G was calculated using the density bottle. A 50mL container that is clean, dry and weighed (W_0) is filled with Waste Cooking Oil, the stopper is placed, and the weight is again recorded to provide (W_1). Water is put to the container to replace the oil and grease after it has been cleaned and dried (W2). The specific gravity expression is provided by the Equation

$$\mathbf{S.G} = \frac{\boldsymbol{W1 - W0}}{\boldsymbol{W2 - W0}}$$

3.2.1.9 GCMS

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

During GC-MS analysis, as the sample mixture is introduced into the chromatograph, differential flow rates cause it to fractionate into its constituent parts. This process facilitates both quantitative assessment of component parts and generation of a mass spectrum for each component. GC-MS finds application in sample identification, environmental analysis, fire and explosives investigation, as well as drug detection. The three primary advantages of GC/MS analysis are its ability to identify organic components within complex mixtures, conduct quantitative analysis, and detect traces of organic contamination.

3.2.2 CATALYST PREPARATION

The optimization studies of biodiesel production from Waste Cooking Oil will use Clam Shells (mercenaria) and Cocoa Pods (Theobroma cacao) as basic and acid precursor feedstock respectively for the synthesis of heterogeneous bi-functional catalysts. In order to effectively transesterify the triglycerides contained in the Waste Cooking Oil and esterify the free fatty acids; heterogeneous bi-functional catalysts will be used in the process. Through kinetics studies and process optimization, these catalysts will be used to create biodiesel in a cleaner and more economical way.

3.2.2.1 PREPARATION OF THE ACID PRECURSOR

The cocoa pods are prepared by first cleaning, then chopping them into smaller pieces and sun-drying them for roughly seven days. Once sufficiently dried, the cocoa pods are manually crushed using a wooden mortar and pestle. Subsequently, the crushed material is carbonized by heating it to 250°C in a furnace, a process that lasts for 1 hour. After the carbonization procedure, the carbonized cocoa pod is removed from the furnace and left to cool to room temperature and then sun dried for a day. Subsequently, it is sieved using a 0.075mm mesh size to attain a consistent particle size distribution. The next step involves sulphonation of the sieved and carbonized cocoa pod material. This is accomplished by subjecting it to heat while reacting with a 1.5M standard solution of H_2SO_4 at a temperature of 150°C for duration of 3 hours, with periodic stirring to ensure uniform sulphonation. Finally, the sulphonated sample is left to stand for 48 hours before being washed with distilled water to eliminate sulphate ions(Akhabue et al., 2020). This process is referred to as "sulphonation." It then goes through a filtration procedure to remove contaminants and free ions, respectively, using distilled water and a filtering net. After that, the leftover sulphonated pod material is dried for eight hours at 200 °C in an oven before being sealed in an airtight container.

3.2.2.2 PREPARATION OF BASIC PRECURSOR

The Clam shells were washed in warm water to get rid of any contaminants, they were left to dry for two days in the sun. The shells were pulverized and then calcined at 900°C for six hours. Following calcination, they were soaked for 48 hours in 1M KOH, filtered, and then washed with distilled water. After that, the sample was dried in an oven for three hours at 150°C. After drying, the sample is removed from the oven and allowed to be cooled to room temperature and kept in an airtight container.(Akhabue & Ogogo, 2018) and (Akhabue et al., 2022).

3.2.2.3 CATALYST IMPREGNATION

To create a wet combination, the acid and basic precursors were combined in a beaker in a desired ratio with a small amount of water added. The final mixture was dried at 150 ^{0}C in the oven, crushed using a wooden mortar and pestle, and then heated once more for five hours in the muffle furnace at 300 ^{0}C. After that, the sample is taken out and allowed to cool in a desiccator before being transferred to an airtight container.

3.3 CATALYST CHARACTERIZATION

3.3.1 Surface Morphology of the Processed Catalyst

A strong analytical tool for analyzing a variety of materials at high magnifications and producing high-resolution images is scanning electron microscopy (SEM) or SEM analysis. SEM is based on the detection of high energy electrons that are released from a sample's surface following exposure to a very concentrated electron beam from an electron cannon. The SEM objective lens is used to concentrate this electron beam into a tiny area of the sample surface. To obtain the best quality images, variables such as the accelerating voltage utilized, the size of the aperture used, and the working distance (the distance between the sample and the electron gun) can be optimized. There are two ways to detect electrons, each of which provides essential insights through various imaging and processing techniques. It is possible to identify backscattered electrons in an image to provide contrast depending on the various chemical compositions present. The surface topography is revealed by secondary electrons that are released in close proximity to the sample's surface.(*Scanning Electron Microscopy (SEM) Analysis and Imaging - TWI*, n.d.)

SEM involves scanning the sample's surface with a low-energy electron beam that is directed towards the material. As the beam approaches and penetrates the material, a number of distinct interactions take place, causing photons and electrons to be emitted from or close to the sample surface.(Omidi et al., 2017) These signals, which result from the complex interactions between the electron beam and the sample, provide important details on the specimen's surface properties, chemical composition, crystalline structure, and alignment of its constituents. The wealth of data obtained from these interactions allows for a comprehensive analysis of the sample's properties.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

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

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

3.3.3 BET Surface Area Analyzer

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

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

3.3.4 Electron Dispersive X-Ray Spectroscopy (EDX)

Analytical methods for elemental analysis or chemical characterization of a sample utilize energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS), also referred to as energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA). EDS analysis enables mapping the elemental composition of individual spots or the lateral distribution of elements within the imaged area. Moreover, it can gather compositional data on quasi-bulk specimens (utilizing high accelerating voltage and low SEM magnification), as well as on specific particles, morphologies, or isolated regions on filters or within deposits.(Ismail et al., 2019)

Electrons colliding with bionanomaterials to produce X-rays are the basis of EDX's operation. Effective characterization of the elements is a function of each element's unique atomic structure, which forms a unique set of peaks on the X-ray spectrum. Sometimes, SEMs are used with EDX ray detectors to assess the elemental makeup of nanoparticles. The EDX technology detects the X-rays that are directed towards the NPs sample, allowing the EDX ray detector to quantify the amount of released X-rays in relation to their energy.(Akintelu et al., 2023)

3.3.4 X-Ray Diffraction (XRD)

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

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

3.3.6 Thermo gravimetric Analysis (TGA/DTGA)

Another type of thermal analysis method being utilized to ascertain how the mass of materials chemical and physical characterize changes is TGA. Usually, TGA measurements are conducted either over time, with consideration given to constant temperature and mass loss, or with a constant heating rate while monitoring temperature rise. TGA enables the exploration of physical events such as second-order phase transitions, vaporization, desorption, and chemical phenomena like dehydration, breakdown, etc. It facilitates the evaluation of mass changes in samples due to processes like oxidation, degradation, or loss of volatile substances.In addition, the standardized TGA testing protocols can also be used to quantify the materials thermal stability, or the resistance they provide against thermal breakdown or degradation.(Parameshwaran et al., 2018)

3.4. OPTIMISATION OF BIODIESEL PRODUCTION.

The biodiesel was produced using waste cooking oil, methanol and a bi-functional catalyst which was synthesized from cocoa pods and clam shells. The waste cooking oil is first sieved to remove particles, then the oil is measured using an electrical weighing balance into a round bottom flask and the catalyst and methanol is added as stated by the optimizing condition. It is then placed inside the microwave; the magnetic stirrer and microwave are then set to the various optimizing conditions. The reaction takes place producing the biodiesel which is placed in a centrifuge to separate the glycerol, biodiesel and catalyst before putting it into a separating funnel. It is then left for some time inside the separating funnel before being separated and washed with warm water then heated using a magnetic stirrer.

Plate 3.1: wco placed inside the microwave

Plate 3.2separation in the separating funnel

Plate 3.3: drying of biodisel

plate 3.4: clean biodiesel obtained after drying

Figure 3.1 Biodiesel obtained during optimization(a) shows wco placed inside the microwave (b) shows when the resulted mixture was being separated in the separating funnel, (c) shows when the obtained biodiesel was being dried after washing with warm water in the separating funnel and (d) shows the clean biodiesel obtained after drying

3.5 CATALYST REUSABILITY STUDY

The optimum condition obtained from the optimization study was used to carry out the reusability study, a larger amount of oil (250g) was used and the methanol and corresponding catalyst calculated for. At the end of each run the catalyst gotten was washed with methanol and dried in an oven at 70°C (since the boiling point of methanol is at 60°C) before being weighed and the equivalent methanol and oil for the next run measured. This process was done continually for five consecutive runs before the catalyst stopped producing; it was observed that the yield kept on reducing while the acid value increased for throughout the process.

CHAPTER FOUR

4.0 RESULTS AND DISCUSION

4.1 OIL CHARACTERIZATION

4.1.1 PHYSIOCHEMICAL PROPERTIES OF WASTE COOKING OIL

The physical and chemical properties of the waste cooking oil (WCO) were analysed as in the previous chapter according to ASTM standard. Table 4.1 presents the results obtained from the characterization of the WCO.

Table 4. 1 physiochemical properties of WCO

Properties	**Values**
Acid Value (mg KOH/g)	20.40
FFA (%)	10.20
Saponification Value (mg KOH/g)	224.23
Molecular Weight (g/mol)	825.32
Peroxide Value (mol/kg)	6.50
Viscosity at 32.4^{o}C (MPa.S)	15.00
Density (Kg/m^3)	920.83
Moisture Content (%)	0.316
Specific gravity	0.92
Iodine value (mg KOH/g of oil)	90.10

According to the analysis done the acid value and FFA of the waste cooking oil was gotten to be (Falowo, 2021) which was gotten to be 5 mg KOH/g. generally Oil's with acid value above 2 mg KOH/g are classified as high acid value oils this implies that just esterification reaction would not produce biodiesel but it should be followed by transesterification or carried out simultaneously. In the study carried out the molecular weight of WCO was gotten to be 825.32 g/mol and the density was determined to be 920.83 Kg/m^3. The viscosity was gotten to be 16 which is greatly affected by the molecular weight simply because the higher the molecular weight of an oil the larger the viscosity. Density of feedstock oil is a crucial parameter in biodiesel production that significantly affects fuel quality. Accurately predicting density is essential for formulating an optimal blend of raw materials. This ensures that the biodiesel produced meets quality standards while also optimizing production costs.(Pratas et al., 2011)

4.1.2 GCMS

The graph of relative abundance was plotted against retention time in fig(4.1) The Gas-Chromatography and Mass-Spectroscopy analysis carried out on the oil obtained showed that the oil contains Acetic acid with(component weight of 0.54 wt% and retention time of 4.50mins), 1-hexanol with(component weight of 3.02 wt% and retention time of 16.22 mins), 2-Propenoic acid,3-phenyl-,methyl ester, (E) with(component weight of 0.61 wt% and retention time of 18.84mins), 2-methylbutyl octanoate with(component weight of 7.46 wt% and retention time of 20.60mins), o-Cymene with(component weight of 2.45 wt% and retention time of 22.00mins), Undecane with(component weight of 1.41 wt% and retention time of 24.53mins),Tetradecanoic acid with(component weight of 2.14 wt% and retention time of 25.23mins), 9,12-Octadecadienoic acid (Z,Z) with(component weight of 6.50 wt% and retention time of 26.78mins), n-Hexadecanoic acid with(component weight of 6.29 wt% and retention time of 28.77mins), palmitoleic acid with(component weight of 3.62 wt% and retention time of 30.15mins), Octadecanoic acid with(component weight of 7.85 wt% and retention time of 32.50mins), Diethyl Phthalate with(component weight of 3.92 wt% and retention time of 33.50mins), 9-Octadecenal,(Z) with(component weight of 9.01 wt% and retention time of 34.50mins), Ethyl Oleate with(component weight of 7.23 wt% and retention time of 36.76mins), 11-Octadecenoic acid, methyl ester with(component weight of 5.89 wt% and retention time of 36.01mins), cis-Methyl 11- eicosenoate with(component weight of 4.48 wt% and retention time of 39.50mins), Oleic acid with(component weight of 14.81 wt% and retention time of 40.50mins), Docosanoic acid with(component weight of 4.54 wt% and retention time of 43.02mins), 22-Tricosenic acid with(component weight of 6.65 wt% and retention time of 44.96mins) as seen in table(4.18)

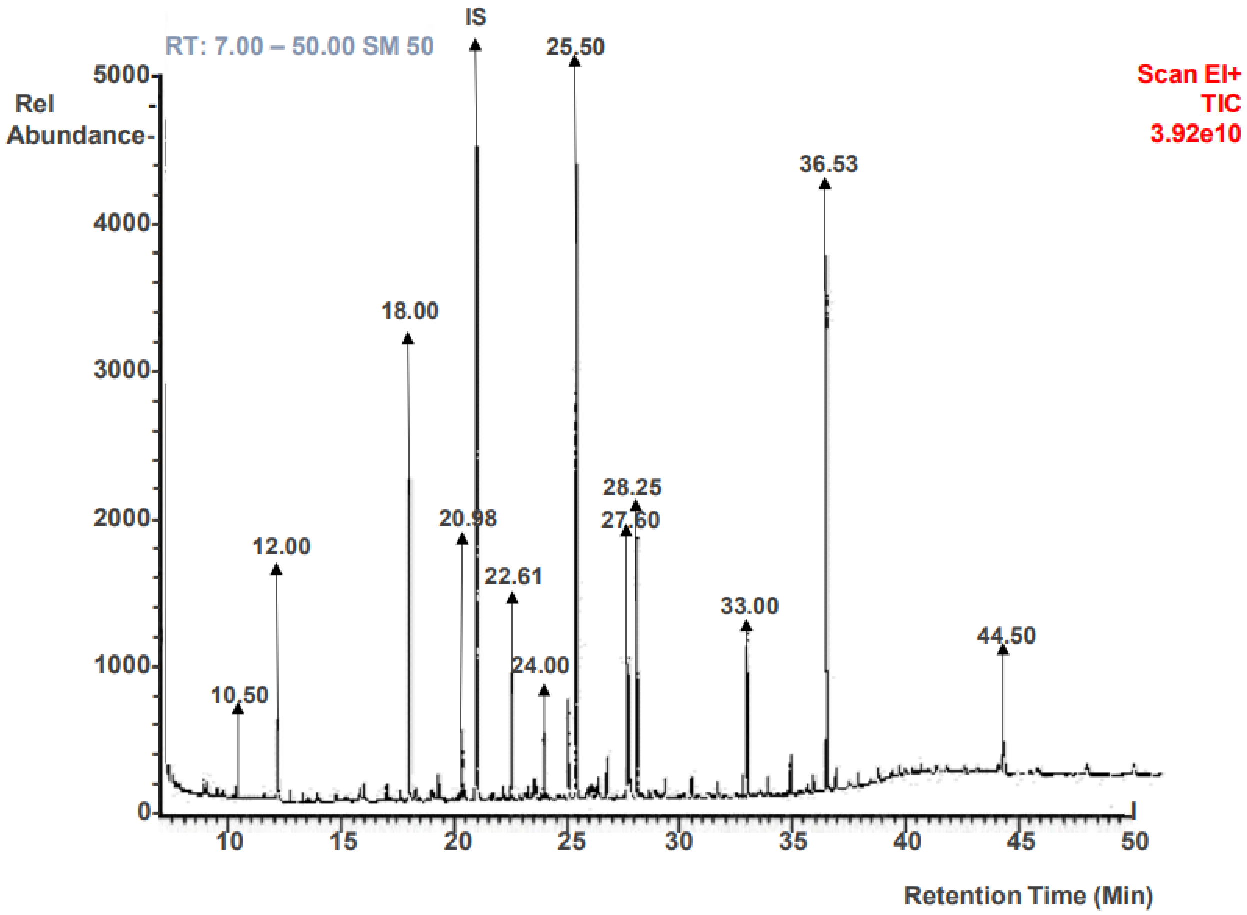


Figure 4. 1 GCMS result for waste cooking oil

4.2 CHARACTERIZATION OF CATALYST

The physicochemical features of the catalyst were thoroughly assessed. The analysis included a Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BHJ) technique for the evaluation of the catalyst's pore properties. Furthermore, the thermogravimetric analysis using a PerkinElmer TGA4000 equipment was utilized to evaluate the changed catalyst's sensitivity to temperature fluctuations. Energy Dispersive X-ray Fluorescence (EDXRF) was used to ascertain the oxide composition, and an X-ray diffractometer was used to identify the treated catalyst's crystal phase. Lastly, to look into the functional groups incorporated into the new catalyst, an FTIR spectrophotometer was used.

4.2.1. SURFACE MORPHOLOGY OF THE PROCESSED CATALYST

The Catalyst surface morphology was examined at different magnifications (500x and 2000x) using the scanning electron microscopy (SEM) which is illustrated in Figure 4.2.The images reveal the aggregation of the non-uniform particles, Figure 4.2a shows the formation of clusters at 500x magnification which showed large lumps. As the magnification increases, tiny particles become more prevalent as seen in Figure 4.2b meaning there is enough pore space which is very good.

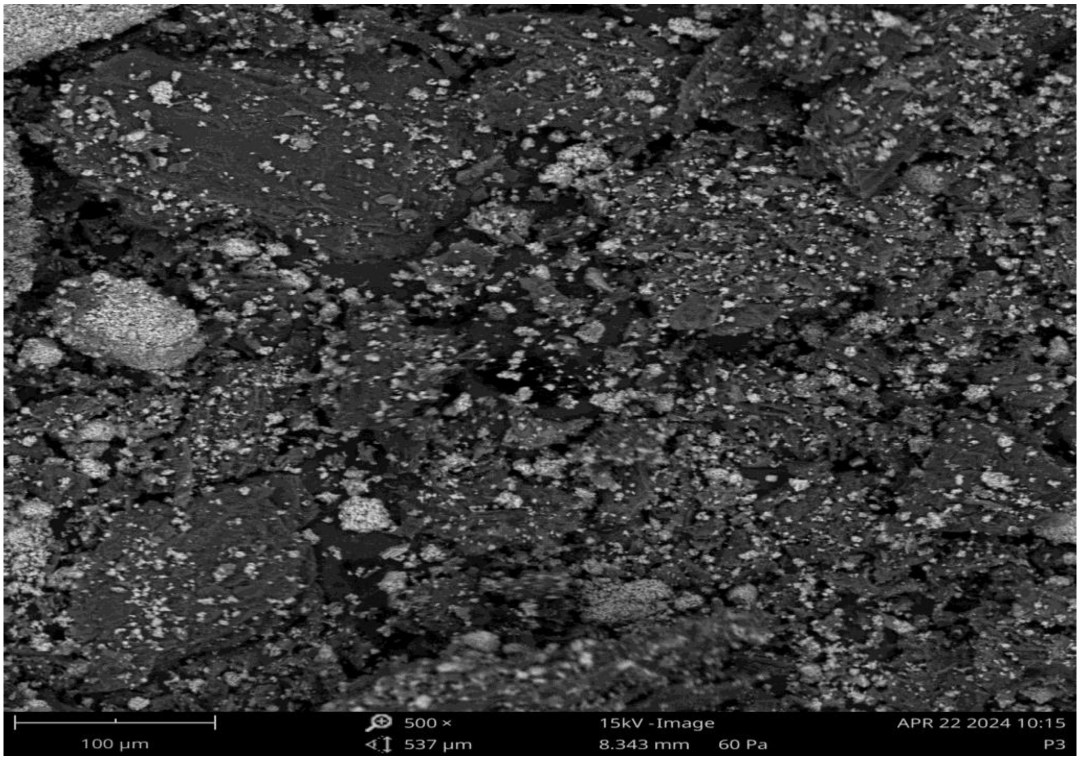
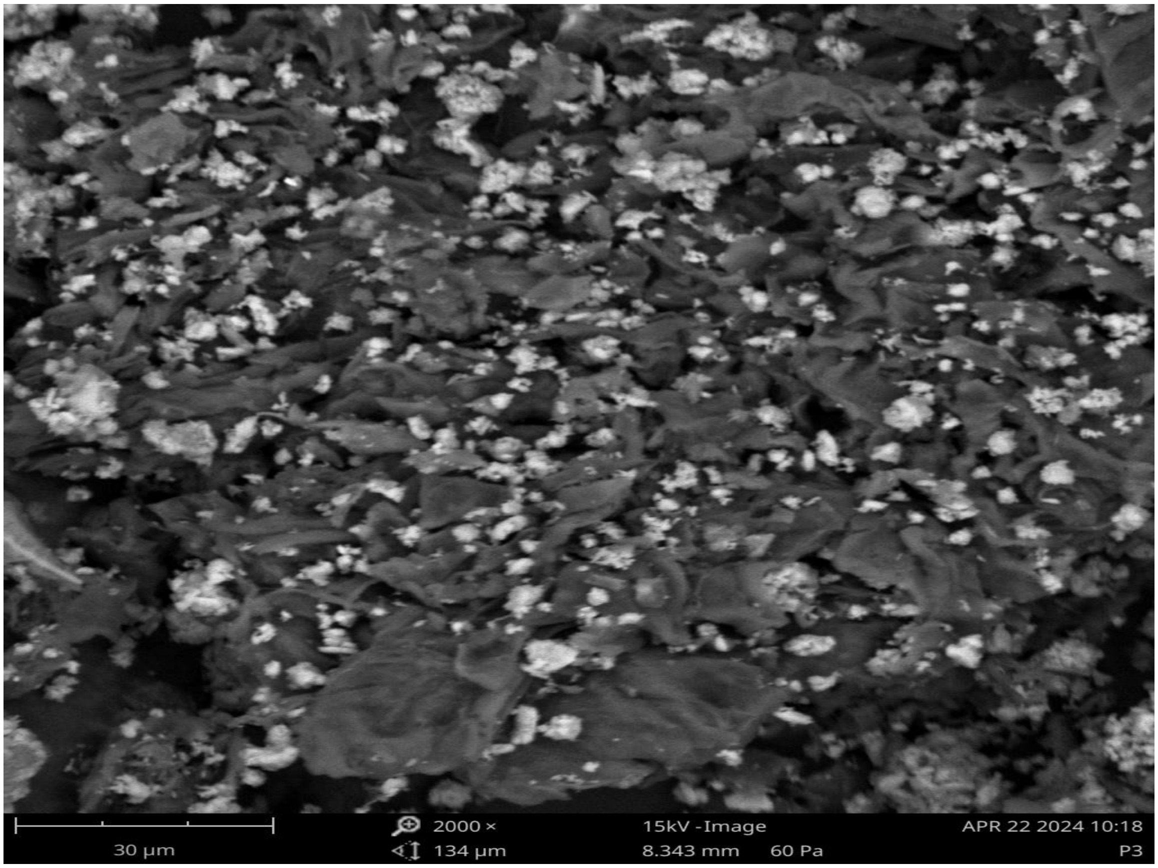


Figure 4. 2SEM analysis of catalyst *(a) 500x*

(b) 2000



4.2.2 ELECTRON DISPERSIVE X-RAY SPECTROSCOPY (EDX)

Table 4.2 presents the elemental composition of the bio-catalyst, as determined by EDX spectroscopy. Calcium (Ca) comprises the majority at 89.50 wt %, followed by Potassium (K) at 6.62 wt %, Sulphur (S) at 1.79 wt %, and Aluminium (Al) at 1.05 wt %. These elements' predominance underscores their pivotal roles as primary components in the processed catalyst.

Their significant mass fractions directly correspond to enhanced catalytic efficacy, crucial for effective conversions.

Table 4. 2 Elemental composition for bio-waste catalyst

Element Number	**Element Symbol**	**Element Name**	**Atomic Conc.**	**Weight Conc.**
20	Ca	Calcium	88.19	89.50
19	K	Potassium	6.68	6.62
16	S	Sulfur	2.21	1.79
13	Al	Aluminium	1.54	1.05
15	P	Phosphorus	0.89	0.70
14	Si	Silicon	0.49	0.35

4.2.2 BET ANALYSIS

The surface area of a catalyst directly affects its activity. An individual surface atom or a group of atoms with a distinct structure and set of properties is referred to as the "active site" where the catalyzed transformation occurs. Catalytic reaction processes are discussed from this perspective. The number of accessible active sites per unit mass of a catalyst or per unit volume of a reactor determines the catalytic process's efficiency. Since materials of a given kind often have about equal numbers of active sites per unit surface area, the amount of exposed surface area of a catalyst determines its overall activity. Even though there are many other factors that might affect the reaction kinetics in a catalytic reactor, such as diffusion kinetics, adsorption-desorption kinetics, and surface reactions equilibriums, it seems that the number of active sites is the main factor controlling the reaction rate. The bio-based catalyst's enormous surface area suggests that it is extremely catalytically active. These results imply that the catalyst's active site exists and that it can aid with diffusion problems because of the larger pore size and better flow channels on its exterior surface. This could speed up the reaction and accelerate how rapidly the reactants interact when combined(Tan et al., 2015). From the results in Table(4.3) to (4.8) It's apparent that the surface area, pore volume, and pore size of the unused catalyst exceed those of the used catalyst. The BET surface area of the catalysts measured 393.3 m^2/g for unused and 246.7 m^2/g for used catalysts. The larger surface area suggests high catalytic activity. The pore volume and diameter were 0.2349cc/g and 2.421nm for unused and 0.145cc/g and 2.108 nm for used catalysts. The micropore size was 5.520 nm in width and 0.1785cc/g in volume for unused and 5.878 nm in width and 0.1042cc/g in volume for used catalysts. The micropore surface area measured 502.1 m^2/g for unused and 293.3 m^2/g for used catalysts, indicating the presence of active sites that could enhance diffusion and reaction rates. These findings are detailed in Tables below;

Table 4. 3 surface area of unused catalyst

Methods	**Values (m^2/g)**
SinglePoint BET	301.1
MultiPoint BET	393.3
Langmuir Surface area	948.9
BJH method cumulative adsorption surface area	480.0
DH method cumulative adsorption surface area	509.0
t-method external surface area	393.3
DR method micropore area	502.1
DFT cumulative surface area	130.2

Table 4. 4 pore volume data for unused catalyst

Methods	**Values (cc/g)**
BJH method cumulative adsorption pore volume	0.2349
DH method cumulative adsorption pore volume	0.2395
DR method micropore volume	0.1785
HK method micropore volume	0.08909
SF method micropore volume	0.03323
DFT method cumulative pore volume	0.1429

Table 4. 5 pore size data for unused catalyst

Methods	**Values (nm)**
BJH method adsorption pore diameter (mode Dv(d))	2.421
DH method adsorption pore diameter (mode Dv(d))	2.421
DR method micropore pore width	5.520
DA method pore diameter (mode Dv(d))	2.680
HK method pore diameter (mode Dv(d))	0.3675
SF method pore diameter (mode Dv(d))	0.4523
DFT method pore diameter (mode Dv(d))	2.647

Table 4. 6 surface area for used catalyst

Methods	**Values (m^2/g)**
SinglePoint BET	171.4
MultiPoint BET	246.7
Langmuir Surface area	768.4
BJH method cumulative adsorption surface area	296.3
DH method cumulative adsorption surface area	314.7
t-method external surface area	246.7
DR method micropore area	293.3
DFT cumulative surface area	69.33

Table 4. 7 pore volume data for used catalyst

Methods	**Values (cc/g)**
BJH method cumulative adsorption pore volume	0.145
DH method cumulative adsorption pore volume	0.1481
DR method micropore volume	0.1042
HK method micropore volume	0.04776
SF method micropore volume	0.01387
DFT method cumulative pore volume	0.00811

Table 4. 8 pore size data for used catalyst

Methods	Values (nm)
BJH method adsorption pore diameter (mode Dv(d))	2.108
DH method adsorption pore diameter (mode Dv(d))	2.108
DR method micropore pore width	5.878
DA method pore diameter (mode Dv(d))	2.820
HK method pore diameter (mode Dv(d))	0.3675
SF method pore diameter (mode Dv(d))	0.4523
DFT method pore diameter (mode Dv(d))	2.647

4.2.3 XRD ANALYSIS

Figure 4.3 provides a detailed XRD analysis plot highlighting the rich crystalline structure of the treated catalyst, revealing crucial insights into its chemical makeup and possible catalytic action. The plot reveals obvious peaks that unmistakably correspond to the hexagonal lattice pattern characteristic of calcite Ca(CO3), as indicated by pronounced peaks occurring at 2θ values of 23.32°, 29.593°, 36.192°, 39.572°, 43.339°, 43.339°, 47.65°, 48.73°, 57.56°, and 60.82°. These unique peaks serve as robust markers of the presence and placement of calcite inside the catalyst structure.

Moreover, beyond the main calcite phase, the XRD study revealed the coexistence of various minerals and chemicals within the catalyst matrix. Notably, the identification of Quartz, Albite, and Muscovite alongside calcite deepens the characterization of the catalyst's composition, allowing a more nuanced knowledge of its chemical makeup. These supplemental findings increase the breadth of grasp about the catalyst's molecular structure, perhaps exposing synergistic effects or impurities that could influence its catalytic activity.

The identification of Quartz, Albite, and Muscovite within the catalyst not only adds to understanding its complex composition but also holds major consequences for its catalytic activity in specific chemical reactions. Each additional mineral or compound discovered gives chances for complicated interactions and catalytic pathways, influencing the catalyst's behavior and efficiency in specified activities. Consequently, this better understanding of the catalyst's composition supports informed optimization tactics and enables targeted adjustments to amplify its catalytic efficacy in desired applications. Thus, the XRD analysis, reinforced by the identification of various mineral phases, emerges as a vital tool for uncovering the nuances of catalyst chemistry and leading developments in catalytic design and performance.

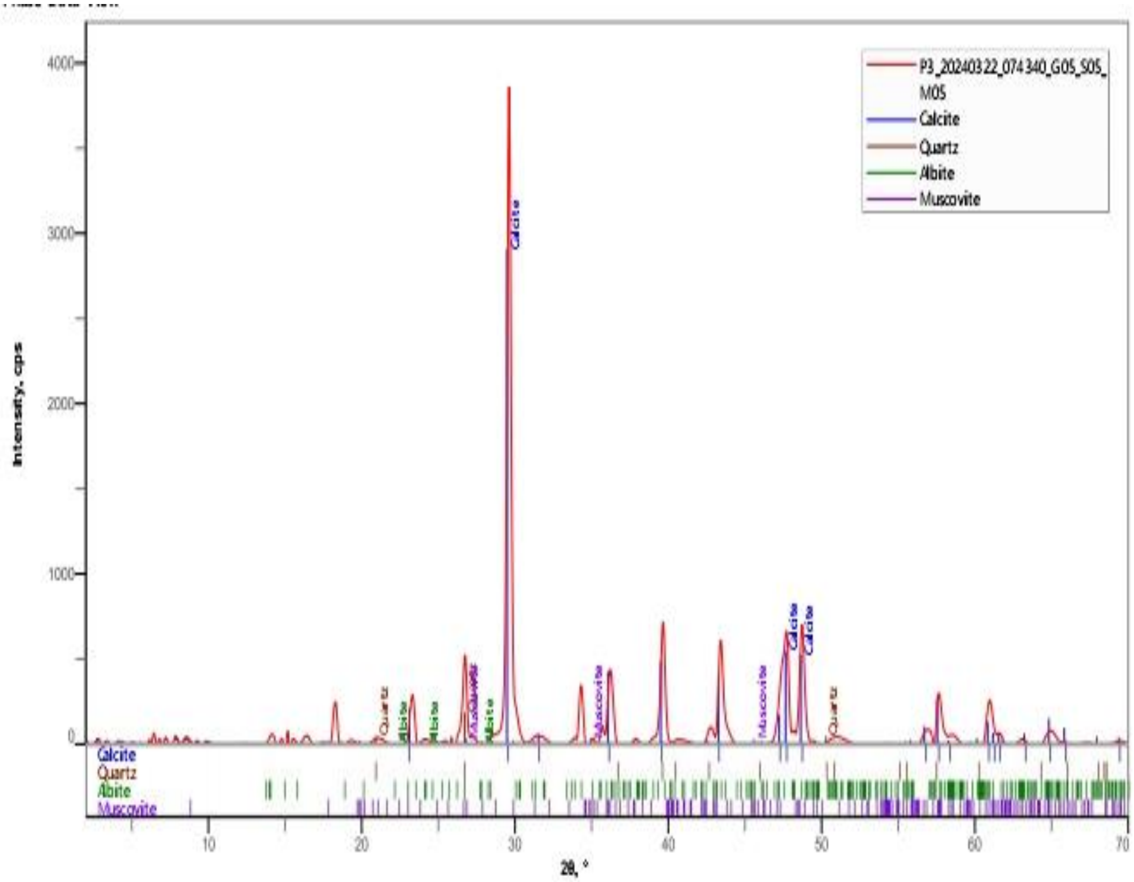


Figure 4. 3 XRD Plot of the processed catalyst

4.2.4 XRF ANALYSIS

The results on the XRF analysis of the bio-waste catalyst on the various oxides are shown in Table 4.9 along with the associated processed catalyst concentrations as found in the EDXRF analysis. The two most common oxides in the processed catalyst, as shown in the Table, were calcium oxide (68.431%), phosphorus pentoxide (13.522%) and sulphur trioxide(4.153%) with trace amounts of other oxides are SiO_2 (1.215%), Al_2O_3 (3.653%),Fe_2O_3(0.337%) and SnO_2 (0.764 %). The high amount of CaO gotten from the analysis was duly anticipated because calcium carbonate which is the major component of clam shell is broken down to calcium oxide.Other oxides found in traces throughout the sample are listed in the Table.

Table 4. 9 XRF analysis

Oxides	***Results (%)***	***Elements***	***Results(%)***
Silicon oxide (SiO_2)	1.326	O	33.526
Vanadium pentoxide (V_2O_5)	0.000	Mg	0.000
Chromium oxide (Cr_2O_3)	0.002	Al	1.933
Manganese Oxide MnO	0.046	Si	0.568
Iron (iii) oxide (Fe_2O_3)	0.139	P	5.901
Cobalt tetraoxide (Co_3O_4)	0.000	S	1.663
Nickel Oxide (NiO)	0.011	Cl	0.659
Copper Oxide (CuO)	0.143	K	5.468
Niobium pentaoxide (Nb_2O_3)	0.006	Ca	48.908
Molybdenum trioxide (MoO_3)	0.007	Ti	0.057
Tungsten oxide (WO_3)	0.000	V	0.000
phosphorus oxide (P_2O_5)	6.244	Cr	0.003
Sulphur (vi) oxide (SO_3)	3.400	Mn	0.039
Calcium oxide (CaO)	79.982	Fe	0.236
Magnesium oxide (MgO)	0.000	Co	0.001
Potassium (i) oxide (K_2O)	4.583	Ni	0.010
Barium oxide (BaO)	0.073	Cu	0.139
Aluminum oxide (Al_2O_3)	2.348	Zn	0.028
Tantalum pentaoxide (Ta_2O_5)	0.006	Zr	0.036
Titanium oxide (TiO_2)	0.078	Nb	0.017
Zinc oxide (ZnO)	0.028	Mo	0.010
Silver oxide (Ag_2O)	0.002	Ag	0.007
Chlorine (Cl)	1.218	Sn	0.602
Zirconium oxide (ZrO_2)	0.026	Ba	0.154
Tin oxide (SnO_2)	0.332	Ta	0.035

4.2.5 FTIR ANALYSIS

Figure 4.4 shows the FTIR spectrum of the processed catalyst. The functional groups present in the catalyst were analyzed between 4000 and 700 cm-1 in wavelength. The carbonyl functional group (C=O) is responsible for the peak at 1729.5 cm-1, while the stretching vibrations of the hydroxyl groups (-OH) of the Ca(OH)2 present in the processed catalyst are responsible for the broad bands between 32922.2 cm1 and 1481 cm-1 wavelengths. Because the catalyst was exposed to air for a period during the FTIR study, surface carbonate and hydroxyl species developed; the XRD also identified these species. The FTIR results unequivocally demonstrate CaO's propensity to react with airborne moisture and CO2.

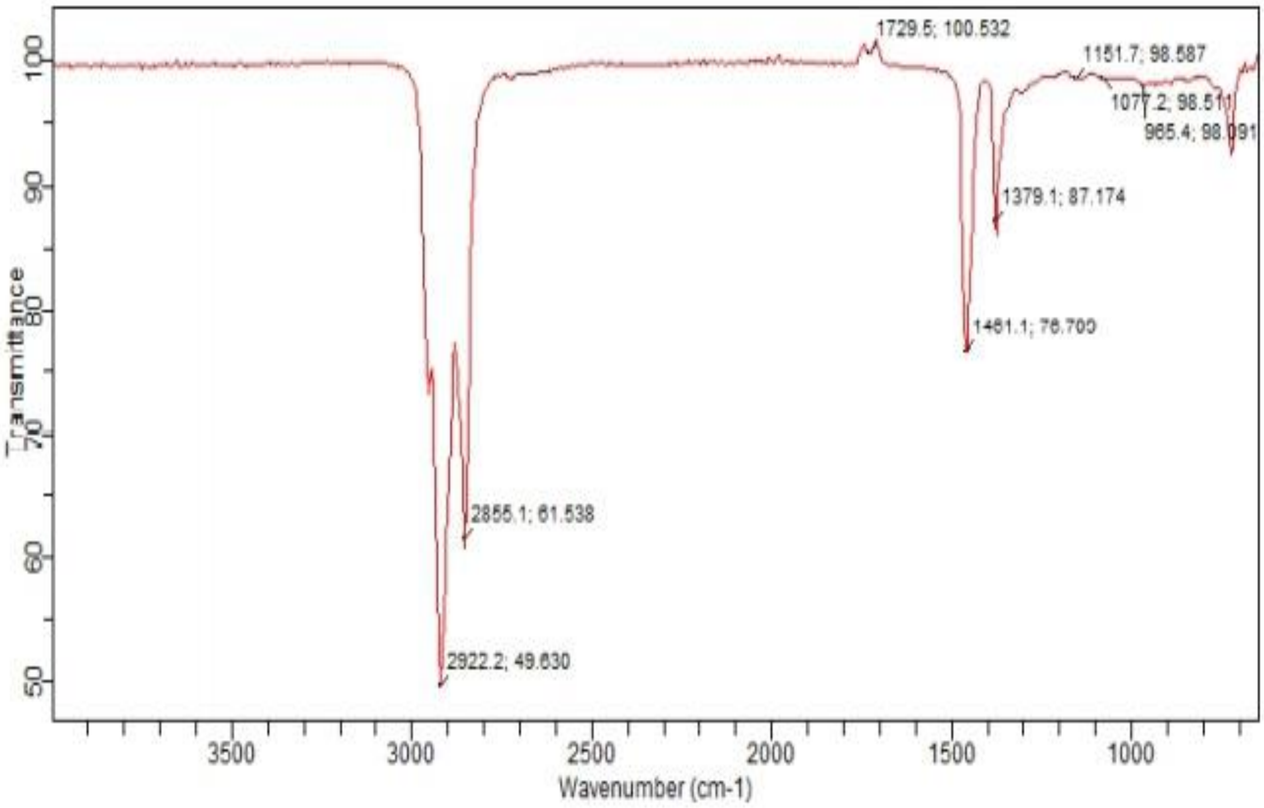


Figure 4. 4FTIR Spectrum for the processed catalyst

4.3 MODELLING OF SIMULTANEOUES ESTERIFICATION AND TRANSESTERIFICATION

4.3.1. STATISTICAL ANALYSIS OF VARIANCE

We employed a Robust Design approach, specifically the Taguchi L16 orthogonal array, to perform a statistical analysis of the concurrent esterification and transesterification of Waste Cooking Oil (WCO). In this procedure, a dual-purpose catalyst produced from a blend of Clam Shell and Cocoa Pod was employed. We carried out the experimental planning utilizing Design Expert 13.0 software.

Equation (4.1) outlines the calculation for determining the total number of experiments required, which is contingent upon the number of levels and factors involved.

$R = (L-1)\,F + 1$ (Fadara & Engineering, 2021)(4.1).

In this context, R represents the total count of experiments, L stands for the quantity of levels, and F denotes the quantity of factors. The specific values and the corresponding outcomes are presented in Table 4.10.

Table 4. 10 Experimental design matrix developed by Taguchi L16 orthogonal array

RUNS	ME:OH	CATALYST %	POWER	TIME	STIRRER SPEED	BIODIESEL YIELD	ACID VALUE
1	15:1	4	360	5	500	86.73	0.593
2	15:1	3	600	2	2000	93.74	0.712
3	9:1	4	800	2	1000	87.31	0.671
4	12:1	4	Defrost(180)	3	2000	83.37	0.774
5	12:1	3	800	4	500	82.71	0.672
6	15:1	5	Defrost(180)	4	1000	87.56	0.593
7	6:1	5	800	5	2000	85.63	0.514
8	6:1	3	360	3	1000	81.48	0.638
9	6:1	4	600	4	1500	84.72	0.482
10	12:1	2	600	5	1000	90.29	0.413
11	15:1	2	800	3	1500	86.93	0.475
12	6:1	2	Defrost(180)	2	500	77.63	0.785
13	9:1	3	Defrost(180)	5	1500	83.37	0.631
14	12:1	5	360	2	1500	87.48	0.574
15	9:1	2	360	4	2000	88.92	0.526
16	9:1	5	600	3	500	81.93	0.597

After the WCO was simultaneously esterified and trans-esterified, the variation in WCB yield and AV were statistically investigated to establish the optimum model to utilize. The collected data were then analyzed using analysis of variance (ANOVA) to determine the influence of various factors on the responses.

Table 4.11 and 4.12 presents the outcomes of the analysis of variance (ANOVA). WCB yield and Acid value, respectively, in 4.11 and 4.12

Table 4. 11 results for the analysis of variance (ANOVA) for WCB yield

Source	***Sum squares***	***Df***	***Mean Square***	***F-value***	***p-value***	
Model	224.84	12	10.74	70.49	0.0024	significant
A-MeOH:Oil	82.01	3	27.34	102.84	0.0016	
C-Power intensity	45.77	3	15.26	57.40	0.0038	
D-Reaction Time	26.26	3	8.75	32.93	0.0085	
E-Speed	70.82	3	23.61	88.81	0.0020	
Residual	0.7974	3	0.2658			
Cor Total	225.66	15				

Table 4. 12 results for the analysis of variance (ANOVA) for WCB AV

Source	***Sum of squares***	***Df***	***Mean Square***	***F-value***	***p-value***	
Model	0.1671	12	0.0139	76.71	0.0022	Significant
B-Cat.%	0.0333	3	0.0111	61.07	0.0035	
C-Power intensity	0.0485	3	0.0168	92.49	0.0019	
E-speed	0.0350	3	0.0117	64.31	0.0032	
Residual	0.0005	3	0.0002[			
Cor Total	0.1677	15				

The sum of squares and associated F-value can be used to characterize the impact of any factor. Elevated F-values and the sum of squares indicate that a certain element is essential to the process's reaction. The significance of each component to the result was also ascertained using the probability value (P-value). When the P-value is less than 0.0500, the model terms are considered significant.Values greater than 0.1000 indicate that the model terms are not significant. If a model has a lot of irrelevant terms, it can be made better by reducing its number.

The ANOVA model in this study yielded sum of squares for WCB Yield and Acid Value of 224.86 and 0.1671, respectively, with F-values of 70.49 and 76.71 and P-values of 0.0024 and 0.0022. Based on the results of the analysis of variance conducted on the WCB yield and Acid Value, it is evident that the methanol to oil ratio, reaction speed, reaction power and reaction time had a significant impact on the WCB yield, with the methanol to oil ratio having the greatest impact(Falowo, 2021) with a sum of squares value of 82.01, F-value of 102.84, and P-value of 0.0016. The acid value was significantly influenced by the reaction time and the power intensity, with the latter contributing more with a sum of squares value of 0.0504, F-value of 92.49, and P-value of 0.0019.

Utilizing the important variables, mathematical models were developed to forecast the acid value and WCB yield under the given circumstances. Because these models are expressed in terms of coded factors, reaction predictions for particular factor concentrations are made simpler. High values are shown as +1 in this coded equation, and low values are shown as -1. This coding method makes it possible to compare factor coefficients and assess each component's significance.

Biodiesel Yield $=85.6125-3.2475A[1] -0.23A[2]+0.35A[3]-2.63 C[1]+0.54C[2]+ 2.0575C[3]+ 0.927499999999999D[1] -2.185D[2] + 0.365D[3]+3.3625E[1]+1.0475E[2]+0.012500000000004 E[3]$

Acid Value =0.603125-0.053375B[1]+0.060125B[2]+0.026875B[3]+0.092625C[1]-0.020375C[2]-0.052125C[3]+0.082375D[1]+0.017875D[2]-0.034875D[3]

4.3.2. PREDICTED VERSUS ACTUAL VALUES OF WCB YIELD AND ACID VALUE

The graphs showing the expected and actual values for the WCB yield and AV of the WCB are shown in Figures 4.6 and 4.5, respectively. The fact that most of the data points in both plots were close to the line indicates how highly relevant the models are.

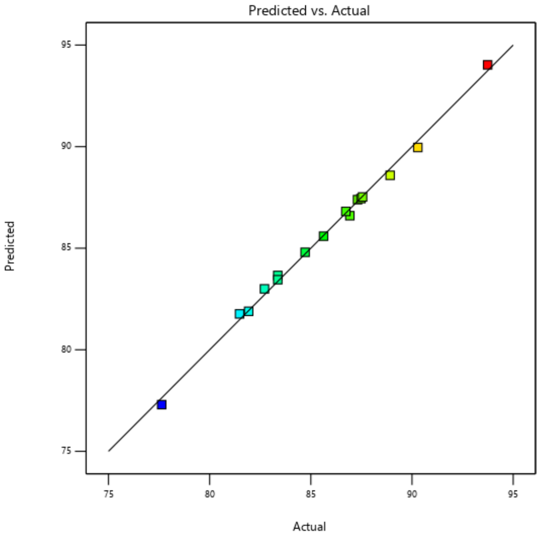


Figure 4. 6 predicted and actual values for the WCB yield

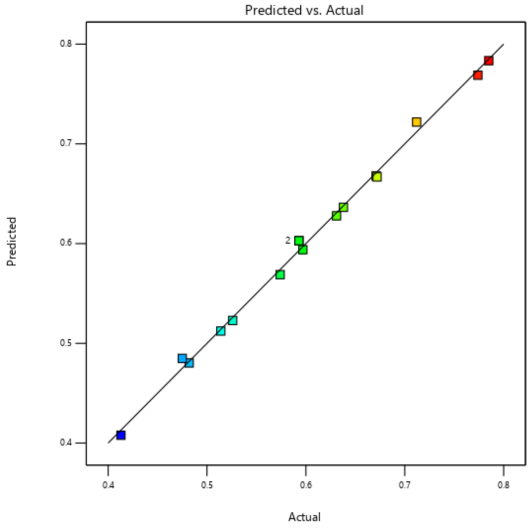


Figure 4. 5 predicted and actual values for the WCB AV

Table 4. 13 Values of predicted versus actual WCB yield

	Factors					Actual Value	Predicted Value
Run	A	B	C	D	E		
	MeOH:Oil (g)	Catalyst Loading (%)	Power Intensity (Watt)	Reaction Time (Minutes)	Stirrer Speed (RPM)		
1	15:1	4	360	5	500	86.73	86.81
2	15:1	3	600	2	2000	93.74	94.03
3	9:1	4	800	2	1000	87.31	87.39
4	12:1	4	Defrost(180)	3	2000	83.37	83.45
5	12:1	3	800	4	500	82.71	83.00
6	15:1	5	Defrost(180)	4	1000	87.56	87.52
7	6:1	5	800	5	2000	85.63	85.59
8	6:1	3	360	3	1000	81.48	81.77
9	6:1	4	600	4	1500	84.72	84.80
10	12:1	2	600	5	1000	90.29	89.96
11	15:1	2	800	3	1500	86.93	86.60
12	6:1	2	Defrost(180)	2	500	77.63	77.30
13	9:1	3	Defrost(180)	5	1500	83.37	83.66
14	12:1	5	360	2	1500	87.48	87.44
15	9:1	2	360	4	2000	88.92	88.59
16	9:1	5	600	3	500	81.93	81.89

Table 4. 14 actual versus predicted values for WCB AV

	Factors						
Run	A	B	C	D	E	Actual Value	Predicted Value
	MeOH:Oil (g)	Catalyst Loading (%)	Power Intensity (Watt)	Reaction Time (Minutes)	Stirrer Speed (RPM)		
1	15:1	4	360	5	500	0.5930	0.6029
2	15:1	3	600	2	2000	0.7120	0.7219
3	9:1	4	800	2	1000	0.6710	0.6679
4	12:1	4	Defrost(180)	3	2000	0.7740	0.7689
5	12:1	3	800	4	500	0.6720	0.6669
6	15:1	5	Defrost(180)	4	1000	0.5930	0.6029
7	6:1	5	800	5	2000	0.5140	0.5124
8	6:1	3	360	3	1000	0.6380	0.6364
9	6:1	4	600	4	1500	0.4820	0.4804
10	12:1	2	600	5	1000	0.4130	0.4079
11	15:1	2	800	3	1500	0.4750	0.4849
12	6:1	2	Defrost(180)	2	500	0.7850	0.7834
13	9:1	3	Defrost(180)	5	1500	0.6310	0.6279
14	12:1	5	360	2	1500	0.5740	0.5689
15	9:1	2	360	4	2000	0.5260	0.5229
16	9:1	5	600	3	500	0.5970	0.5939

4.3.3. FIT STATISTICS

Goodness of fit refers to how well a statistical model predicts observed data. It's a measure used to gauge how closely the predicted values match the actual ones. Essentially, it quantifies the difference between what the model predicts and what is actually observed.. The results for this study is shown in Table 4.15.

Table 4. 15 FIT Statistics for the study

	VALUE	
	WCB YIELD	**ACID VALUE**
R^2	0.9965	0.9968
Adjusted R^2	0.9823	0.9838
Predicted R^2	0.8995	0.9076
Adeq. Precision	35.9938	30.9144
Std. Dev.	0.5156	0.0135
Mean	85.61	0.6031
C.V. %	0.6022	2.23

The results showed that both generated models' correlation coefficients (R^2) were higher than 0.90. Less than 0.2 separated the adjusted R^2 value from the expected R^2 value, indicating that the two numbers were reasonably congruent. Both models' signal-to-noise ratios were found to have a sufficient precision of greater than 4, as shown in the Table. The ideal ratio is greater than 4. The current study's model that depicts the WOME yield and AV, respectively, had appropriate precision of 35.9938 and 30.1944.

4.4 EFFECT OF INDIVIDUAL PROCESS PARAMETERS ON WCB YIELD AND ACID VALUE

It was investigated how specific process variables affected the WCB production and acid value in a significant way. It was shown that the WCB yield was significantly influenced by the reaction time, reaction speed, power of the reaction and the methanol to oil molar ratio. But the catalyst loading, reaction speed, power of reaction and reaction time were the factors that had the biggest influence on the AV of the WCB.

4.4.1 EFFECT OF METHANOL TO OIL RATIO

One of the key process variables that affect how much WCB is produced is the methanol to oil molar ratio. Since the reaction is reversible, more methanol is needed to support the forward process even though 3 mols of methanol are normally required to convert 1 mol of triglyceride into 1 mol of WCB. The methanol to oil molar ratio has an impact on the WCB yield, as demonstrated in Figure 4.6. The plot demonstrates that there is an increase in WCB yield as the methanol to oil mole ratio rises from 6:1 to 15:1, while maintaining catalyst loading, reaction power, stirrer speed and reaction duration at 2 wt.%, 600watts, 1000rpm and 5mins., respectively.

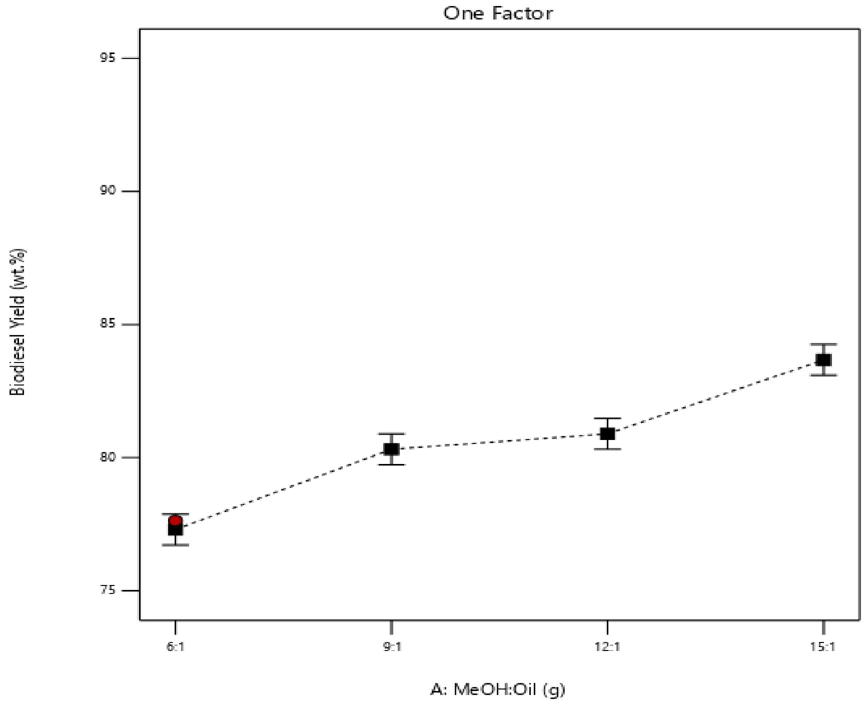


Figure 4. 7 effect of methanol to oil ratio on yield of WCB

4.4.2 EFFECT OF REACTION POWER

The effect of reaction power on the yield of the WCB was also investigated at four different levels;360, 600, Defrost(180) and 800, while holding the other process variables constant at a 15:1 methanol to oil molar ratio, a catalyst loading of 2 wt%, stirrer speed of 100rpm and a reaction duration of 5mins. The yields of the WCB increased steadily from Defrost(180) to 600watts before dropping drastically at 800watts as shown in Fig4.8. The AV for the WCB decreased very significantly as the power rose from Defrost(180) to 360watts then it also reduced from 360watts to 600watts but it wasn't that obvious but the increase from 600watts to 800watts was very notable.

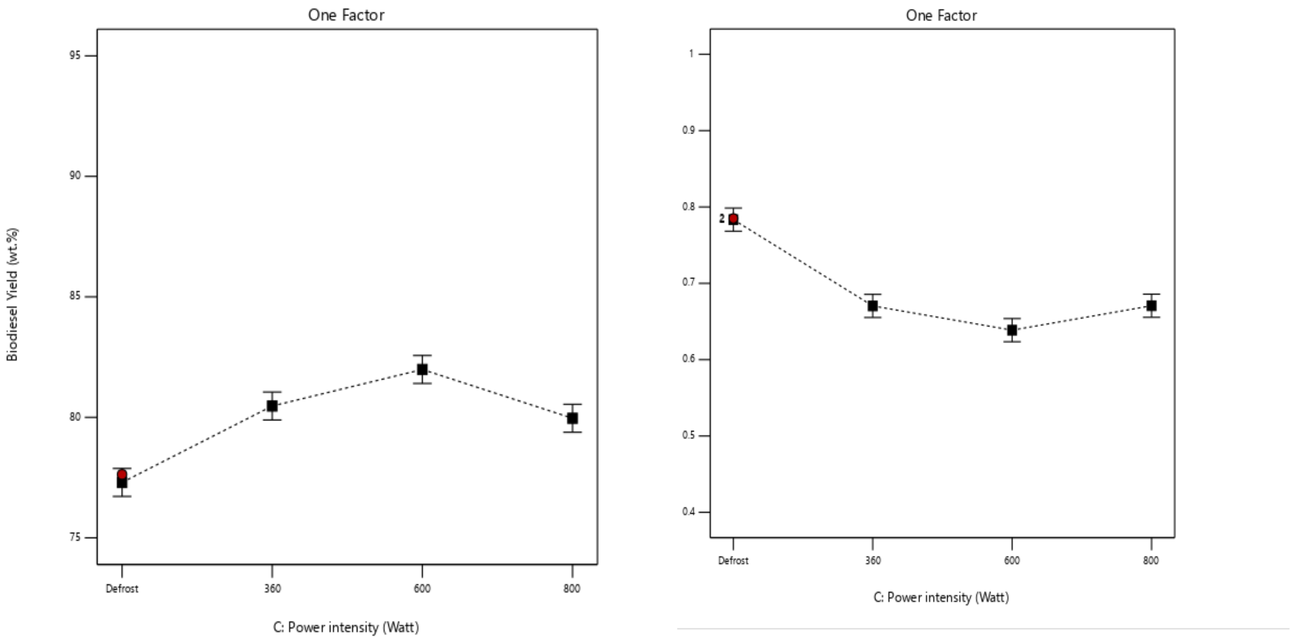


Figure 4. 8 effect of power(a)WCB yield (b)WCB AV

4.4.3 EFFECT OF REACTION TIME

According to Figure 4.9, under optimum conditions of a 15:1 methanol to oil molar ratio, a 2 weight percent catalyst loading, stirrer speed of 1000rpm and reaction power of 600watts, the effect of reaction time on WCB yield was also investigated at the three distinct levels of 2, 3, 4 and 5 min. When the reaction time was increased from 2 to 3 minutes, the amount of WCB produced reduced but as reaction time increased from the 3 to 5mins the WCB generated was increased steadily. The AV of WCB decreased steadily as the reaction time increased.

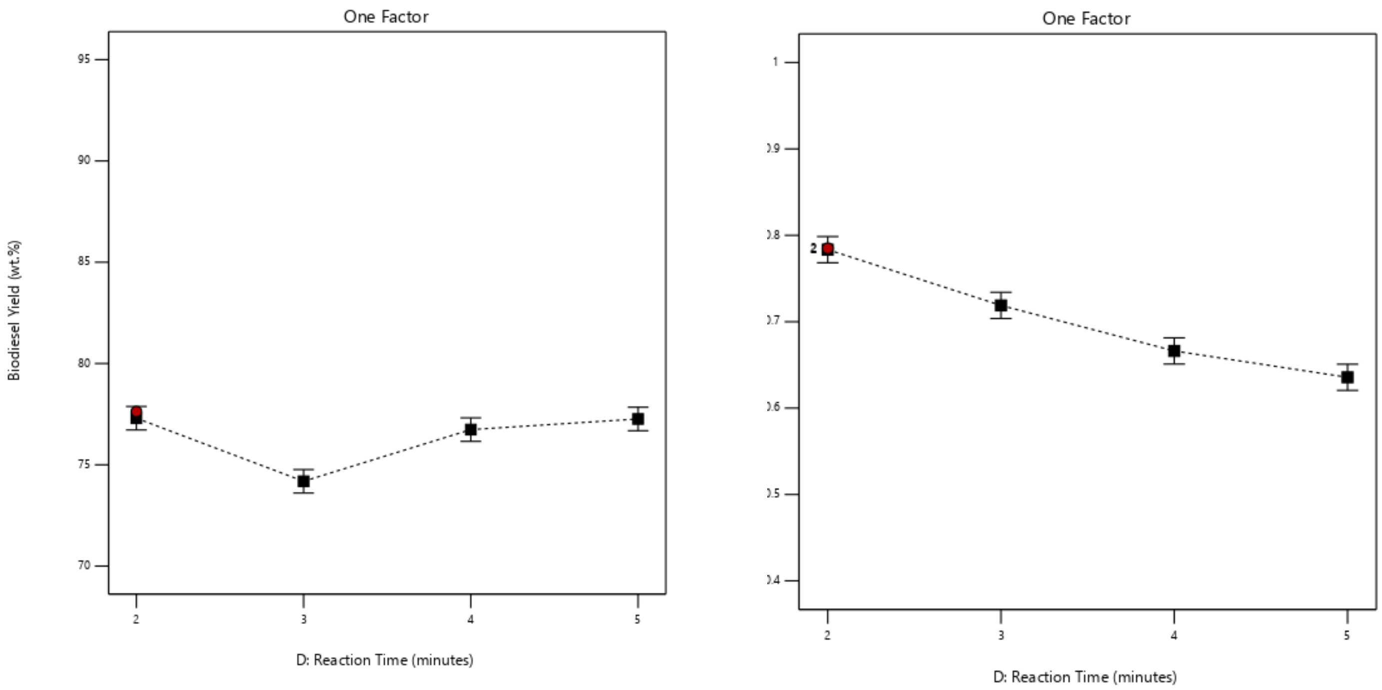


Figure 4. 9 effect of reaction time on (a)yield (b)AV

4.4.4 EFFECT OF STIRRER SPEED

The effect of stirrer speed on the yield of the WCB was also investigated at four different levels;500, 1000, 1500 and 2000 while holding the other process variables constant at a 15:1 methanol to oil molar ratio, a catalyst loading of 2 wt%, reaction power of 600watts and a reaction duration of 5mins. In Figure 4.9 (a) it can be seen that as the stirrer speed increases also the WCB generated increased while in (b) the AV consistently decreased from 500 to 1500 before a very significant increase at 2000rpm.

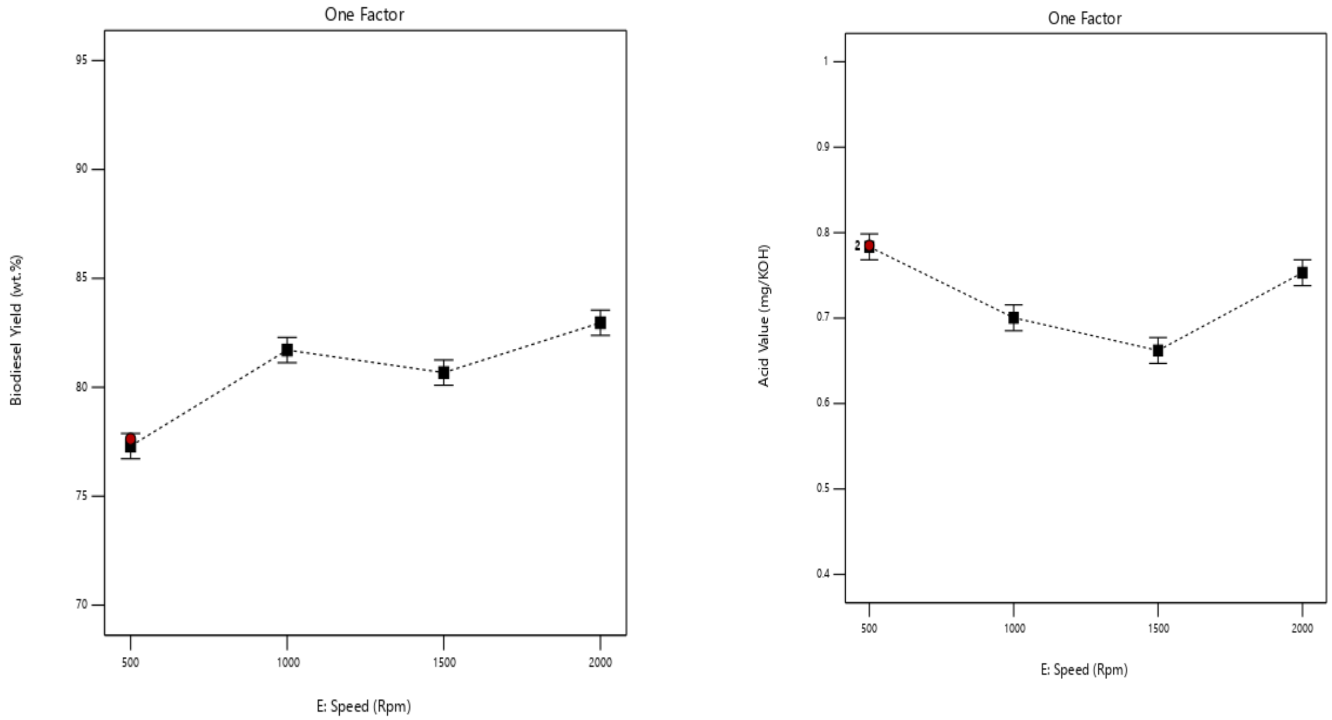


Figure 1 4.9effect of stirrer speed on WCB (a)yield (b)AV

4.4.5 EFFECT OF CATALYST LOADING

The effect of catalyst loading on the AV of WCB is seen in Figure 4.10. The remaining four variables were kept constant at a 15:1 methanol to oil molar ratio, stirrer speed of 1000rpm, reaction power of 600watts and a reaction duration of 5mins. The plot demonstrates that raising the catalyst load from 2 to 3 weight percent resulted in an increase in the AV of the WCB.

However, as the catalyst load was raised to 4 wt.%, the AV of the WCB somewhat dropped also for 5 wt.%. Because too much catalyst thickens the mixture and slows down the rate at which the triglyceride interacts with the catalyst's active sites, it usually leads to low conversion.

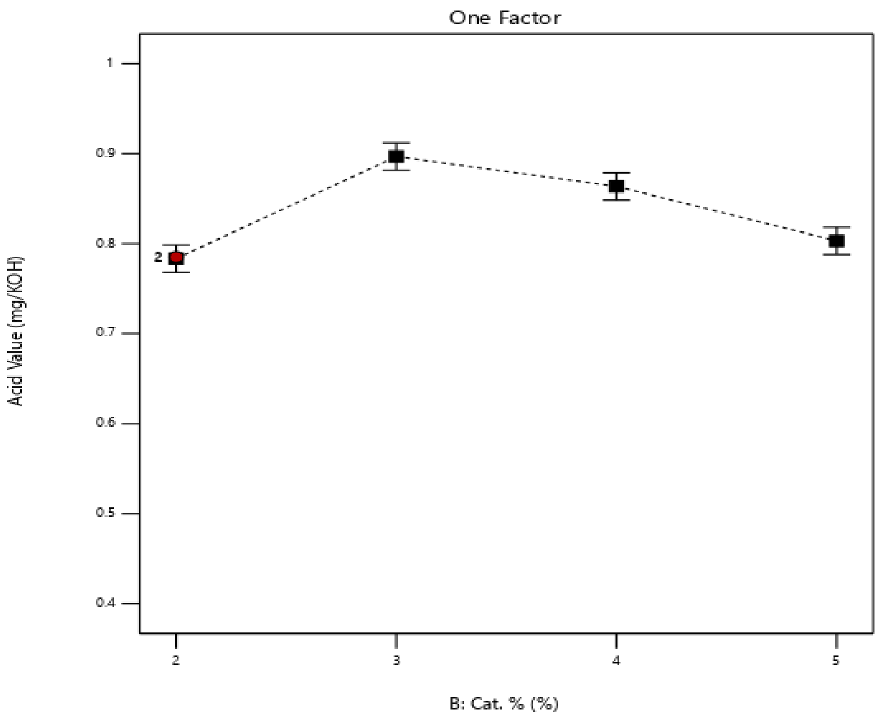


Figure 4. 10 effect of catalyst loadin

4.5 PROCESS PARAMETER OPTIMIZATION AND MODEL VALIDATION

With parameter values of 15:1 methanol to oil molar ratio, 2% catalyst loading, 600 watts power, 1000 rpm stirrer speed, and 5 minutes reaction time, the optimal condition was predicted using Robust Design (Taguchi L16orthogonal array). This produced a 92.737 weight percent WCB yield and 0.408 mg KOH/g AV. This prediction was verified by performing three test runs of the simultaneous reaction with 70g of WCO under the anticipated conditions. The average values of these runs produced 92.18 weight percent of WCB yield and an AV of 0.395 mg KOH/g. It was also reported that an average WCB yield of 95.68 weight percent and an AV of 0.393 mg KOH/g were produced after using 250g of WCO to carry out the reusability investigation under the anticipated conditions. The average production of biodiesel is very close to the expected yield, indicating that the model used in this study is able to predict the optimal values and provide an adequate description of the process.

4.6 PHYSIOCHEMICAL PROPERTIES OF THE WCB

To determine the fuel characteristics of the WOME produced under optimum reaction circumstances, characterization was done. The WCB's kinematic viscosity and density were found to be, respectively which is within the ASTM and EN biodiesel standard limits. The results showed that the WCB's AV, flash point, and calorific value. The resulting values for each WOME characterization are displayed in Table 4.16.

Table 4. 16 WCB Characterization results

PROPERTY	VALUE	ASTM D6751
Acid value (mg KOH / g)	0.393	Max. 0.5
Kinematic viscosity at 40^{o}C (mm^2/s)	4.64	1.9-6.0
Density at 40^{o}C (kg/m^3)	862	Max. 880
Iodine value (g I_2 / 100 g)	12.56	-
Saponification value (mg KOH / g)	198.52	Max. 370
Cetane number	70.94	Min. 47
Moisture content (%)	0.776	Max. 0.05
Higher heating (Calorific) value (MJ / kg)	41.10	Min. 38
Flash point (^{o}C)	151	Min. 130
Cloud point (^{o}C)	1.1	-3 to 12
Pour point (^{o}C)	-2	-15 to 16

In table 4.16 above the acid value of the WCB is seen to be 0.393 mg KOH / g which is a very notable drop from the acid value of the WCO feedstock which was 20.40 mg KOH / g. this significant difference seen shows that the microwave assisted technique which was employed in carrying out this experiment was successful in the trans-esterification of the oil. This acid value gotten aligns with the standard and is far less than that gotten by (Oyedoh et al., 2022) but close to that documented by (Falowo, 2021) which is 0.46. The major concern regarding the acid number in biodiesel is that the presence of fatty acids could lead to corrosion and deposits in fuel injectors by catalyzing polymerization in hot recycling fuel loops.

The values gotten for the density and viscosity of the biodiesel are 862 kg/m^3 and 4.64 mm^2/s respectively and these values fall within the ASTM D6751 standards. The density is similar to that gotten by (Monika et al., 2023) which was 865.5 kg/m^{3}and the viscosity to that of (Kawentar & Budiman, 2013) which was 4.971, a research also done by (Ulukardesler, 2023) using waste cooking oil showed a viscosity of 4.79 mm^2/s and density of 879 kg/m^{3}respectively. Biodiesel with high density greatly affects the performance of fuel pumps, fuel filters, and the air-fuel mixing behavior in compression ignition (CI) engines. The performance of fuel injection systems is influenced by viscosity, especially when it increases at low temperatures, affecting fuel fluidity. High viscosity leads to poor fuel spray atomization and less precise fuel injector operation. Biodiesel, with its lower viscosity, is easier to pump, atomize, and generates finer droplets.

The cetane number gotten from this study is 70.94 which is a very high value and it indicates that the biodiesel produced has a very high ignition power, it also satisfies the ASTM D6751 standards which states that the minimum value for cetane number is 47. The "flash point" is the lowest temperature at which a liquid releases enough vapor in a test container to create a combustible mixture with the air close to the liquid's surface(Santos et al., 2020).The minimum flash point accepted by ASTM D6751 is 130^{0}C, so the waste cooking biodiesel falls within the allowable range, the value gotten is close to that of (Gupta & Rathod, 2018)who also used the microwave assisted technique and got 165^{0}C.

The cloud point and pour point of the biodiesel was found to be 1.1^0C and -2^0C respectively and these values are within the ASTM D6751 standards. The cloud point is the temperature at which small, solid crystals start to form and become visible in the fuel as it cools down. The fuel will function more properly at temperatures above -2^0C this will enable the fuel to avoid clogging and flow more without solidifying so as not to affect the engine. The calorific value obtained for the WCB is 41.10 MJ / kg which satisfies the ASTM D6751 standards which allows for a minimum value of 38 MJ / kg. The calorific value is less than that of conventional diesel which is at 45 MJ / kg but the value is also very large compared to standards and thus indicates a high energy content making it a favorable choice for fuel. A key characteristic of a fuel is its calorific value, which measures the heat released during combustion and reflects the energy content of the fuel.

4.7 IMPACT OF REUSABILITY OF THE CATALYST ON WCB YIELD AND ACID VALUE

The investigation into the catalyst's commercial viability for biodiesel production involved assessing its reusability and its impact on WCO yield and Acid Value. The reusability test was conducted under optimal conditions determined through optimization, involving a series of five consecutive test runs where the catalyst was recovered and reused and treated using methanol. In the first run using 250g of WCO, the biodiesel yield was 95.68 wt.% with an Acid Value (AV) of 0.393 **mg**KOH/g. However, subsequent runs showed a decreasing trend in biodiesel yield and an increasing trend in AV. In the second run (144.6g of WCO), the biodiesel yield decreased to 92.18 wt.% with an AV of 0.438 mg KOH/g. This trend continued in the third run (104.4 g of WCO) with a biodiesel yield of 88.16 wt.% and an AV of 0.503 mg KOH/g. The fourth and fifth runs also followed this trend, with the fourth run (86.25 g of WCO) having an AV of 0.579 and a biodiesel yield of 83.27 wt.% and the fifth run (60.05 g of WCO) having an AV of 0.603 and a biodiesel yield of 76.45 wt.%. The decrease in Waste cooking oil Biodiesel (WCB) production and the consistent rise in Acid Value (AV) could be linked to the saturation of the catalyst's active sites due to the presence of glycerol or unreacted triglycerides. Table 4.17 illustrates the reusability result

Table 4. 17 Results for reusability study of WCB

RUNS	1	2	3	4	5
WCB YIELD (Wt. %)	95.68	92.18	88.16	83.27	76.45
ACID VALUE (mg KOH/g)	0.393	0.438	0.503	0.579	0.603
WCO MASS (g)	250	144.6	104.4	86.25	60.05

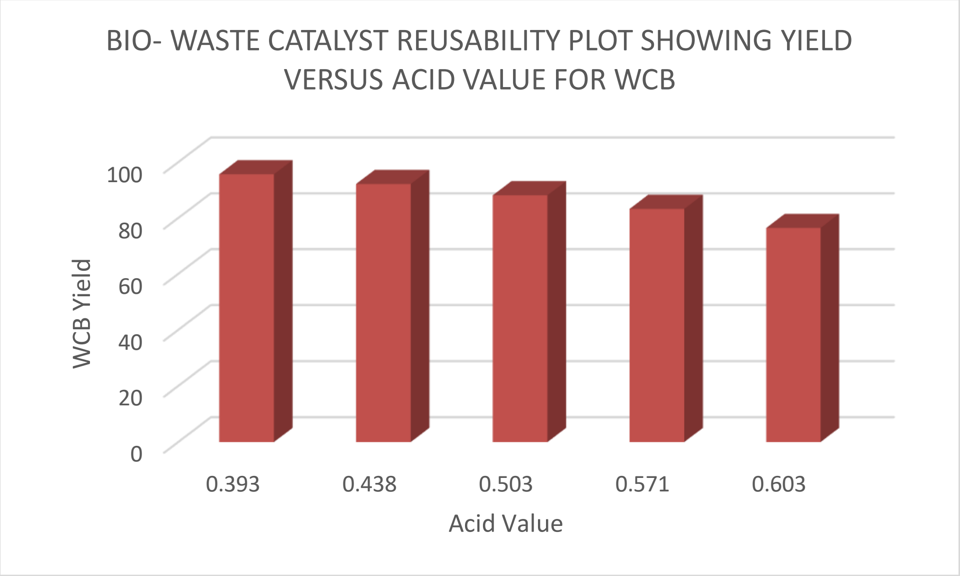


Figure 4. 11 bio-catalyst reusability plot

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The aim of this study which is the optimization of the microwave aided biodiesel production from waste cooking oil using a bio-waste catalyst derived from clamshell and cocoa pods via the Taguchi Optimization Approach was carried out successfully. Conclusion drawn from the characterization of the WCO, bio-waste catalyst, biodiesel, the analysis of variance and the reusability of the catalyst are as follows:

1. The bio-waste catalyst was found to be potent in carrying out the simultaneous esterification and transesterification of the WCO, where the BET analysis showed the catalyst to have a BET surface area of 393.3 m^2/g, Pore volume and diameter 0.02349 cm^3/g and 2.421 nm, respectively and the average micropore size calculated to be 5.520 nm in width and 0.1785 cc/g in volume, while the micropore surface area found to be 502.1 m^2/g. From the XRF result it is seen that calcium oxide has 68.431% followed by phosphorous pentoxide which contains 13.527%
2. The WCO was found suitable for the production of biodiesel even though it had a high acid value of 20.4 mg KOH/g and FFA was 10.4 %
3. The model terms were significant to the responses, according to the statistical analysis of variance, and the model's fit statistics demonstrated a high degree of predictive accuracy. The optimal combination of input variables identified for the procedure is a heating power of 600W, methanol:WCO of 15:1, time of 5 min, reaction speed of 1000rpm and Catalyst loading of 2 wt% with an optimum WCB yield of 92.737 wt.% and AV of 0.408 mg KOH/g.

4. It was shown that the WCB yield was significantly affected by the reaction time, reaction speed, power of the reaction and the methanol to oil molar ratio while the catalyst loading, reaction speed, power of reaction and reaction time were the factors that had the biggest influence on the AV of the WCB.
5. After being reused for five runs with treatment with methanol, the bio-waste catalyst was determined to be industrially feasible and to continue producing a significant yield (over 76% WCB Yield).
6. The optimal factors produced with physiochemical parameters that complied with the biodiesel specifications of ASTM D6751 and EN 14214 after conducting a characterization of the WCB.
7. The microwave aided technique was found to be time efficient and effective in producing biodiesel.

5.2 RECOMMENDATION

This research work showed that there was a high yield of biodiesel using Waste Cooking Oil,clam shell and cocoa pods as catalyst for WCB production so government should focus on the encouragement for the improved cultivation of cocoa pods and utilization of waste clam shells more research work should also be done on their use. It could also be seen that production of biodiesel through the microwave aided technique showed its potency in time reduction and quality biodiesel production so more work should be done on this aspect by fabricating a bigger microwave together with a magnetic stirrer that can produce a larger amount of biodiesel at once.

Also it is highly recommended that biodiesel should be used in place of diesel because;

a) It provides lubricity and very good ignition which means greater engine efficiency and duration.

b) It generally reduces greenhouse effect which has adverse effect on the global climate by reducing the amount of CO emissions.

c) It doesn’t require any engine modifications.

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APPENDIX

- ACID VALUE OF WASTE COOKING OIL

Acid Value = $\frac{\boldsymbol{N*56.1056*(T_v-T_b)}}{\boldsymbol{weight\ of\ waste\ cooking\ oil\ sample\ (g)}}$

Where;

N = normality of KOH solution

56.1056g/mol = molecular weight of KOH

T_v = Titration volume of KOH solution with waste cooking oil

T_{B} = Titration volume of KOH solution without waste cooking oil (blank solution)

2.012g of WCO sample

Initial reading = 0ml

Final reading = 14.8ml

Blank reading = 0.2ml

AV = $\frac{\mathbf{0.05*56.1056*(14.8-0.2)}}{\mathbf{2.012\ (g)}}$

= 20.354mgKOH/g

2.052g of WCO sample

Initial reading = 14.8ml

Final reading = 30ml

Blank reading = 0.2ml

AV = $\frac{\mathbf{0.05*56.1056*((30-14.8)-0.2)}}{\mathbf{2.052\ (g)}}$

= 20.501mgKOH/g

AV_{avg} = $\frac{\mathbf{20.354+20.504}}{\mathbf{2}}$

= 20.4mgKOH/g

FFA present = $\frac{\mathbf{Acid\ Value}}{\mathbf{2}}$

$\frac{20.4}{2}$ = 10.2mgKOH/g

- IODINE VALUE OF WASTE COOKING OIL

Iodine Value = $\frac{\mathbf{N*12.69*(V_1-V_2)}}{\mathbf{weight\ of\ WASTE\ COOKING\ OIL\ (g)}}$

Where;

N = normality of sodium Thiosulphate = 1N

12.69 = constant value

V_1 = titration value of blank test

V_2 = titration value using waste cooking oil

Initial reading = 0ml

Final reading = 13.4ml

Blank reading = 20.5ml

IV = $\frac{\mathbf{1*12.69*(20.5-13.4)}}{\mathbf{1(g)}}$

= 90.099mgKOH/g

- PEROXIDE VALUE OF WASTE COOKING OIL

Peroxide value (PV) = $\frac{\mathbf{10*N*(N_1-N_2)}}{\mathbf{weight\ of\ waste\ cooking\ oil}}$

Where;

N_2 = Titre value using waste cooking oil

N_1 = Titre value of blank test

N = normality of sodium thiosulphate

Initial reading = 0ml

Final burette reading = 26.1ml

Blank reading = 32.6ml

PV = $\frac{\mathbf{10*0.1*(32.6-28.2)}}{\mathbf{1}}$

=6.5mol/kg

- SAPONIFICATION VALUE OF WASTE COOKING OIL

Saponification Value = $\frac{\frac{\mathbf{56.1056g}}{\mathbf{mol}}\mathbf{*N*(T_b-T_j)}}{\mathbf{weight\ of\ waste\ cooking\ oil\ (g)}}$

Where;

N = Normality of HCL solution

T_b = Titre value of blank test

T_j = Titre value of waste cooking oil sample

Initial reading = 0ml

Final reading = 24.1ml

Blank reading = 40.1ml

SV = $\frac{\frac{56.1056g}{mol}*0.5*(40.1-24.1)}{2(g)}$

= 224.2725mgKOH/g

Molecular weight = $\frac{168300}{(Saponification\ Value-Acid\ Value}$

$\frac{168300}{(224.2725-20.4}$ = 825.515g/mol

- KINEMATIC VISCOSITY

Rpm: 60

Temperature:32.4^{o}C

Viscosity: 15.0mpa.s

- MOISTURE CONTENT

Moisture content = $\frac{W_1 - W_2}{W_1}$* 100%

Where;

W_1= initial weight of crucible + WCO sample

W_2 = final weight of Crucible + WCO sample

W_1= 55.865g

W_2 = 55.815g

MC = $\frac{56.011 - 55.834}{56.011}$ * 100%

= 0.00316

- DENSITY

ρ = $\frac{weight\ of\ oil}{volume\ of\ bottle}$

$\frac{92.083g}{100ml}$ = 0.92083g/ml

=920.83kg/m^3

- SPECIFIC GRAVITY

SG = $\frac{\rho 1}{\rho 2}$

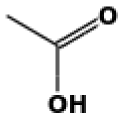
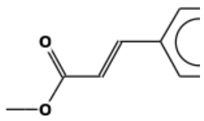
Where;

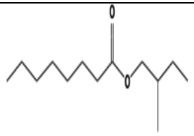
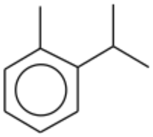
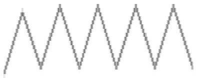
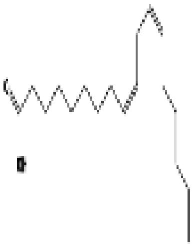
ρ_1 = Density Waste cooking oil at 25^{o}C

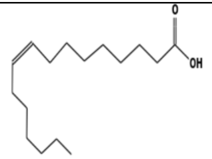
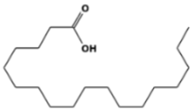
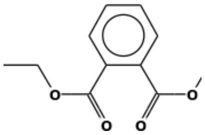
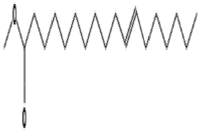
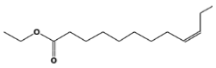
ρ_2 = Density of distilled water at 25^{o}C

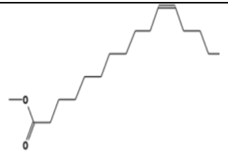
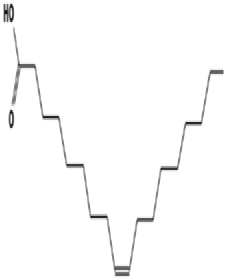
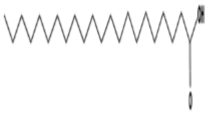
$\frac{920.83}{997.04} = 0.9236$

Table 4. 18 GCMSAnalysis result for WCO

Peak #	RT	Compound Detected	Mol. Formula	MW	Peak Area %	Comp. wt%	m/z	Structures
1	4.50	Acetic acid	$C_2H_4O_2$	60	0.59	0.54	43, 45, 60	
2	16.22	1-hexanol	$C_6H_{14}O$	102	3.20	3.02	43, 56, 102	
3	18.84	2-Propenoic acid, 3-phenyl-, methyl ester, (E)-	$C_{10}H_{10}O_2$	162	0.65	0.61	77, 131, 162	
4	20.60	2-Methylbutyl octanoate	$C_{13}H_{26}O_2$	214	7.93	7.46	57, 127,	

							214	
5	22.00	o-Cymene	$C_{10}H_{14}$	134	2.56	2.45	91, 119, 134	
6	24.53	Undecane	$C_{11}H_{24}$	156	1.51	1.41	43, 57, 156	
7	25.23	Tetradecanoic acid	$C_{14}H_{28}O_2$	228	2.28	2.14	60, 73, 228	
8	26.78	9,12-Octadecadienoi c acid (Z,Z)	$C_{38}H_{68}O_8$	242	6.85	6.50	67, 81, 280	
9	28.77	n-Hexadecanoic acid	$C_{18}H_{26}O$	256	6.71	6.29	43, 73, 256	
10	30.15	Palmitoleic acid	$C_{16}H_{30}O_2$	254	3.88	3.62	43,	

							57, 254	
11	32.50	Octadecanoic acid	$C_{18}H_{36}O_2$	284	7.31	7.85	43, 73, 284	
12	33.50	Diethyl Phthalate	$C_{12}H_{14}O_4$	222	4.15	3.92	65, 149, 222	
13	34.50	9-Octadecenal, (Z)-	$C_{18}H_{34}O$	266	8.59	9.01	41, 55, 266	
14	36.01	11-Octadecenoic acid, methyl ester	$C_{19}H_{36}O_2$	296	6.22	5.89	43, 74, 336	
15	36.76	Ethyl Oleate	$C_{20}H_{38}O_2$	310	6.54	7.23	43, 97, 310	
16	39.50	cis-Methyl 11-eicosenoate	$C_{21}H_{40}O_2$	324	4.48	5.78	43, 73,	

							324	
17	40.50	Oleic acid	$C_{18}H_{34}O_2$	282	14.81	14.52	41, 55, 282	
18	43.02	Docosanoic acid	$C_{22}H_{44}O_2$	340	4.79	4.54	57, 129, 340	
19	44.96	22-Tricosenoic acid	$C_{23}H_{44}O_2$	352	6.93	6.65	55, 69, 352	

CHARACTERIZATION OF WCO BIODIESEL

1. Iodine value

$$\text{Iodine Value} = \frac{N*12.69*(V_1-V_2)}{weight\ of\ jatropha\ biodiesel(g)}$$

Where;

N = normality of sodium Thiosulphate

12.69 = constant value

V_1 = titre reading of blank

V_2 = titre reading using WCO biodiesel sample

Initial reading = 0ml

Final reading = 10.6ml

Blank reading = 20.5ml

IV = $\frac{\mathbf{0.1*12.69*(20.5-10.6)}}{\mathbf{1(g)}}$

= 12.56 g iodine / 100 g

2. Saponification Value

Saponification Value = $\frac{\frac{56.1056g}{mol}*N*(T_b-T_j)}{weight\ of\ jtropha\ curcas\ oil\ (g)}$

Where;

N = Normality of HCL solution

T_b = Titre reading of blank

T_j = Titre reading of WCO biodiesel sample

Initial reading = 0ml

Final reading = 26.3ml

Blank reading = 40.1ml

$$\mathbf{SV} = \frac{\frac{56.1056g}{mol} * 0.5 * (40.1 - 26.3)}{1.95g)}$$

= 198.52 mg KOH / g

3. Cetane Number

$$CN = a + \frac{5458.3}{x} - 0.225y$$

Where;

x = saponification value

y = iodine value

$$CN = 46.27 + \frac{5458.3}{198.52} - (0.225 * 12.56)$$

= 70.94

4. Density

$$\boldsymbol{\rho} = \frac{\textbf{weight of biodiesel}}{\textbf{volume of bottle}}$$

$$\frac{86.22g}{100ml} = 0.862\text{g/ml}$$

= 862kg/m^3

5. Moisture Content

$$\text{Moisture content} = \frac{W_1 - W_2}{W_1} * 100\%$$

Where;

W_1 = initial weight of crucible + WCO biodiesel sample

W_2 = final weight of Crucible + WCO biodiesel sample

W_1 = 239.119g

W_2 = 237.264g

$$\mathbf{MC} = \frac{\mathbf{239.119-237.264}}{\mathbf{238.119}} * 100$$

= 0.776%

6. Higher Heating Value

HHV = 49.43 – {0.041(SV) + 0.015(IV)}

Where;

SV = saponification value of WCOB

IV = iodine value of WCOB

= 49.43 – {(0.041*198.56) + (0.015*12.56)}

= 41.10MJ/kg

7. Biodiesel Yield

$$\textbf{Yield (\%)} = \frac{\boldsymbol{weight\ of\ biodiesel}}{\boldsymbol{weight\ of\ oil}}$$