Production and Optimization of Biodiesel Using a Novel Cow Horn-Based Heterogeneous Catalyst.

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CERTIFICATION

This is to certify that this research project was carried out by Uzzi Henry Iyobosa with matriculation number ENG2002078 in the Department of Chemical Engineering, University of Benin, Benin City, Edo State Nigeria.

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DEDICATION

This work is dedicated to my parents, Mr and Mrs. Uzzi; to my family members, uncle Idowu, uncle Osayi, Mr Chris ,Mr Aise, all my aunties and cousins.

to my friends, Ose, Steph, Dave , Jeff, Emmanuel, Wisdom, and Godson; etc and to my mentors, Prof. Andrew, Dr. Fred and Dr. Osaigede, for their unwavering support.

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ABSTRACT

The creation of sustainable substitutes like biodiesel is required due to the growing demand for energy worldwide and the harm that fossil fuels cause to the environment. This study aims to evaluate the catalytic efficiency of a novel cow horn-based heterogeneous catalyst in the optimization of biodiesel yield from waste cooking oil using Response Surface Methodology (RSM).

The cow horn waste was processed into powder and calcined at 900°C for five hours to produce the bio-catalyst.A Central Composite Design (CCD) under Response Surface Methodology (RSM) was used to statistically optimize the production of biodiesel in a batch reactor. Thirty experimental runs that assessed four independent variables catalyst load (1.0–10.0 wt%), reaction time (30–150 min), reaction temperature (40–80°C), and a methanol-to-oil ratio (4:1 to 10:1) formed the basis of the optimization.

The RSM model was statistically significant ($p < 0.0001$) and predicted a maximum biodiesel yield of **92.73%** at the optimal conditions of 60°C, a 90-minute reaction time, a 5.5 wt% catalyst load, and a 7:1 methanol-to-oil ratio. However, the practical experiments failed to achieve this predicted yield. The primary constraint identified was the high **Free Fatty Acid (FFA)** content of the waste cooking oil, measured at **7.57%**.

It was concluded that while the cow horn-derived catalyst is a promising sustainable resource, it is not viable for the single-step transesterification of high-FFA waste cooking oil. The findings suggest that a prior acid-catalyzed esterification pre-treatment step is mandatory to reduce FFA levels before the cow horn-based catalyst can effectively facilitate the conversion process.

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NOMENCLATURE

AD – Anaerobic Digestion

ASTM – American Society for Testing and Materials

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

BSE – Backscattered Electrons

CaO – Calcium Oxide

CCD – Central Composite Design

CO – Carbon Monoxide

CO_2 – Carbon Dioxide

CV – Coefficient of Variation

EDS – Energy-Dispersive X-ray Spectroscopy

EN – European Norm (European Standards)

FAEE – Fatty Acid Ethyl Ester

FAME – Fatty Acid Methyl Ester

FFA – Free Fatty Acid

FTIR – Fourier-Transform Infrared Spectroscopy

GC-MS – Gas Chromatography-Mass Spectrometry

GHG – Greenhouse Gas

H_2SO_4 – Sulfuric Acid

HCl – Hydrochloric Acid

HVO – Hydrotreated Vegetable Oil

IEA – International Energy Agency

KOH – Potassium Hydroxide

LDH – Layered Double Hydroxide

MMO – Mixed Metal Oxide

MSW – Municipal Solid Waste

NaOH – Sodium Hydroxide

OPEC – Organization of the Petroleum Exporting Countries

rpm – Revolutions per Minute

RSM – Response Surface Methodology

SE – Secondary Electrons

SEM – Scanning Electron Microscopy

SO_x – Sulfur Oxides

WCO – Waste Cooking Oil

WVO – Waste Vegetable Oil

XRD – X-ray Diffraction

XRF – X-ray Fluorescence

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of study

Energy plays a significant role in people's daily lives all over the world. Transportation, industry, and domestic operations all rely entirely on the supply of energy **(Avhad and Marchetti, 2015)**. From lighting homes and powering appliances to operating heavy machinery and enabling communication systems, energy is the cornerstone of modern civilization. Energy is a major force behind economic and social advancement since it is essential to industrial production, agricultural expansion, healthcare, and educational systems.

The International Energy Agency (IEA, 2022) claims that improving living standards, urbanization, and population growth particularly in developing nations have caused a steady increase in the world's energy demand. According to the IEA, present policies are projected to increase energy demand by more than 25% by 2040.

Fossil fuel combustion releases greenhouse gases into the atmosphere, which degrade air quality and increase the risk of heart and respiratory conditions. Asthma and allergies are linked to these emissions, and prolonged exposure can increase the risk of heart disease and early mortality. Climate change, which damages ecosystems, modifies weather patterns, and speeds up the melting of glaciers and polar ice caps, is one of the environmental effects. Global debates are focused on reducing greenhouse gas emissions in light of these important challenges. Adopting methods that lower emissions in industry, transportation, and agriculture, improving energy efficiency, promoting green technologies, and switching to cleaner renewable energy sources are some of the suggested tactics. Preserving the environment, reducing negative impacts, and safeguarding human health for current and future generations are the main goals **(Ali et al., 2018; Bauer et al., 2015; Chmielewski, 2017; Chuah et al., 2017; Wuebbles & Jain, 2001)**.

Biodiesel has many advantages over traditional diesel fuel and is a sustainable and renewable substitute. **(Arun and others, 2021)**.

Because the carbon dioxide absorbed during biomass feedstock growth balances the carbon dioxide emitted during combustion, it dramatically lowers greenhouse gas emissions. Additionally, biodiesel increases energy diversification, reduces reliance on imported fossil

fuels, and fosters rural development by generating employment opportunities in agriculture. By chemically interacting oils or fats with lesser alcohols, usually methanol, the transesterification process turns them into biodiesel.

The transesterification process can make use of catalysts that are basic, acidic, or bifunctional (acidic-basic). Bifunctional catalysts are especially useful in the manufacture of biodiesel because they can efficiently support both esterification and transesterification at the same time **(Elias et al., 2020; Falowo et al., 2022)**. Because their active sites have both basic and acidic characteristics, these heterogeneous catalysts can speed up reactions that call for both kinds of catalysis. For low-cost feedstocks including tallow waste, non-edible oils, and spent cooking oil, they exhibit great selectivity and conversion rates when processing free fatty acids (FFAs) and triglycerides together.

1.2 Problem statement

Biodiesel has become a crucial substitute for fossil fuels as a result of the world's transition to renewable energy. However, the high cost of refined feedstocks and the environmental disadvantages of traditional homogeneous catalysts (such NaOH or KOH), which generate hazardous effluent and prohibit catalytic reuse, impede widespread adoption.

Although heterogeneous catalysts made from waste biomass (like cow horns) provide a sustainable "waste-to-wealth" option, feedstock quality is still a major obstacle. The majority of inexpensive waste cooking oils (WCO) have elevated levels of free fatty acids (FFA). The effectiveness of bio-based catalysts in one-step processes is frequently overestimated in current research. The high FFA content (7.57%) of the WCO caused catalyst deactivation, which prevented the chemically active cow horn-derived catalyst in this work from achieving the expected 92.73% yield.

There is, therefore, an urgent need to define the operational limits of cow horn catalysts and establish the necessity of pre-treatment protocols to bridge the gap between statistical optimization and practical biodiesel production.

1.3 Aim and objectives

The primary aim of this research is to produce and optimize biodiesel from Waste Cooking Oil (WCO) using a novel heterogeneous bio-catalyst derived from cow horns, while evaluating the impact of feedstock acidity on catalytic performance.

To achieve this aim, the following objectives will be pursued:

1. **By synthesizing and characterizing the heterogeneous bio-catalyst** through the collection, pulverization, and thermal activation (calcination) of waste cow horns at 900°C for 5 hours.
2. **By evaluating the physicochemical properties of the waste cooking oil (WCO)**, with a specific focus on determining the Free Fatty Acid (FFA) content, density, and viscosity to assess its suitability for the transesterification process.
3. **By applying Central Composite Design (CCD) under Response Surface Methodology (RSM)** to statistically model and study the interactive effects of catalyst load, reaction time, temperature, and methanol-to-oil ratio on the final biodiesel yield.
4. **By executing thirty (30) experimental runs** to validate the process model and compare the practical biodiesel yields against the theoretical maximum predicted by the optimization software.
5. **By performing a limitation analysis** to evaluate how high FFA levels in the feedstock inhibit the performance of the cow horn catalyst, thereby establishing the necessity of acid-esterification pre-treatment.

1.4 Scope of study

This research is conducted on a laboratory scale, focusing on the synthesis of a high-performance heterogeneous bio-catalyst from waste cow horns for the production of biodiesel from Waste Cooking Oil (WCO).

1. Feedstock and Catalyst Characterization

The scope includes the evaluation of the physicochemical properties of WCO, specifically its **acid value, Free Fatty Acid (FFA) content, density, and viscosity**, to determine its baseline suitability for transesterification. Simultaneously, the cow horn-derived catalyst will be analyzed post-calcination to assess its catalytic potential in converting triglycerides to methyl esters.

2. Process Optimization (CCD/RSM)

The study is delimited to the optimization of four critical process variables:

- **Catalyst loading** (1.0–10.0 wt%)
- **Methanol-to-oil molar ratio** (4:1 to 10:1)
- **Reaction temperature** (40–80°C)
- **Reaction time** (30–150 min) The optimization is governed by a **Central Composite Design (CCD)** involving 30 experimental runs to establish a correlation between these variables and the resulting biodiesel yield.

The evaluation involves comparing the experimentally derived yields against the statistical model's predicted maximum of **92.73%**. Furthermore, the scope addresses the technical challenges encountered during the single-step transesterification process, specifically the inhibitory effect of high FFA levels (7.57%) on the bio-catalyst's performance.

The study is limited to the use of a **single-stage transesterification process** without chemical pre-treatment, providing a critical assessment of the boundary conditions under which cow horn catalysts remain effective

1.5 Significance of the study

The successful development of a sustainable and cost-effective method for biodiesel production using a cow horn-derived heterogeneous catalyst has significant implications for both the energy sector and environmental management. By utilizing waste cooking oil (WCO) as a primary feedstock, this research provides a cleaner and more eco-friendly alternative to traditional fossil fuels, effectively reducing greenhouse gas emissions and decreasing the global dependence on non-renewable resources. Furthermore, the conversion of waste cow horns—an abundant and often discarded slaughterhouse byproduct—into a high-value bio-catalyst supports the principles of a circular economy and offers a "waste-to-wealth" strategy that could stimulate local economic opportunities within the agricultural and waste management sectors.

The production of biodiesel remains a crucial step toward mitigating climate change and ensuring long-term energy security. While many conventional methods rely on expensive, corrosive, and non-reusable chemicals, this study highlights the significance of utilizing a novel, waste-derived heterogeneous catalyst system. By focusing on the optimization of this process

through Response Surface Methodology (RSM), the study provides critical insights into the technical boundaries of bio-based catalysts. Crucially, the research underscores the importance of feedstock quality, revealing how high Free Fatty Acid (FFA) levels influence catalytic efficiency. Ultimately, this study emphasizes the necessity of exploring sustainable and cost-effective approaches to biodiesel production, promoting environmental preservation while providing a practical framework for scaling renewable energy solutions in resource-constrained environments.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 The Origin and Evolution of Biofuels

Renewable fuels called biofuels are made from biological sources like plants, algae, and animal waste. Their significance as sustainable substitutes for fossil fuels has grown, particularly in light of the depletion of non-renewable resources and the escalating environmental concerns. Utilizing biomass for energy is not a novel idea, and it has seen substantial development from antiquity to the current era of industrial biotechnology.

The International Energy Agency (IEA) claims that, depending on the feedstock and production method, biofuels can cut greenhouse gas emissions by up to 90% when compared to fossil fuels (IEA, 2020). In the worldwide energy transition to low-carbon economies, they are essential.

2.2 Early History of Biofuels

Since humans discovered fire thousands of years ago and began using wood and other biomass for cooking and warmth, bio-based fuels have been employed. This type of bioenergy was the first. However, the use of ethanol in lamps in the early 1800s is the earliest known example of liquid biofuel. Originally, sugar and starch crops like corn and sugarcane were fermented to make ethanol. Ethanol attracted interest as a possible fuel in the middle of the 19th century, particularly during the American Civil War, when fuels derived from petroleum were costly and in short supply **(Solomon et al., 2007)**.

When Rudolf Diesel showed off his engine operating on peanut oil at the 1900 Paris Exhibition, it was the first time vegetable oil was used as fuel. According to Diesel, vegetable oils have the potential to become a significant engine fuel in the future, particularly in rural areas where petroleum is scarce **(Knothe, 2001)**.

"**The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time.**" — (**Rudolf Diesel**, 1912).

2.3 **The Rise and Fall of Biofuels in the 20th Century**

After Diesel's initial demonstration, biofuels were momentarily sidelined due to the **abundance and low cost of crude oil**, especially after the discovery of vast oil fields and the expansion of petroleum infrastructure.

However, biofuels resurfaced during **oil crises**:

- **1973 Oil Crisis**: Triggered by the OPEC oil embargo, many countries started looking for alternative energy sources, leading to renewed interest in ethanol and biodiesel **(Demirbas, 2007)**.
- **1979 Energy Crisis**: Strengthened ethanol production efforts in countries like Brazil, which launched the **Proálcool Program** to blend ethanol with gasoline in response to rising oil prices **(Goldemberg et al., 2004)**.

2.4 **Advantages of Biofuels**

1. According to **Demirbas (2009)**, biofuels are derived from biomass materials that can be regenerated continually, making them more sustainable than finite fossil fuels. This renewable nature helps reduce dependence on non-renewable energy resources, contributing to long-term energy security.
2. The U.S. Department of Energy (2016) reported that biodiesel can reduce lifecycle GHG emissions by up to 86% compared to petroleum diesel.
3. Knothe et al. (2005) emphasized that biodiesel exhibits superior biodegradability and much lower toxicity than petroleum diesel, making it safer for use and disposal.
4. As stated by **Hill et al. (2006)**, the cultivation of biofuel feedstocks can stimulate rural development and improve the livelihoods of farmers through job creation and increased income.
5. **According to Agarwal (2007)**, biodiesel blends up to B20 (20% biodiesel, 80% diesel) can be used in standard diesel engines without any modifications.
6. **Atabani et al. (2012)** noted that utilizing waste-derived feedstocks for biodiesel production can reduce environmental pollution and enhance sustainability in fuel production.
7. **Lapuerta et al. (2008)** confirmed that the sulfur content in biodiesel is nearly negligible compared to petroleum diesel, making it more environmentally friendly.

8. According to **McCormick and Alleman (2005)**, even small amounts of biodiesel added to ultra-low sulfur diesel can restore lubricity to acceptable levels.

2.5 Classification of Biofuels

Biofuels are generally classified according to the technique used for processing and the source of their feedstock. First-, second-, third-, and fourth-generation biofuels are the main categories into which the classification is separated **(Demirbas, 2009)**.

1. First-Generation Biofuels

First-generation biofuels are those produced directly from feedstocks that are also edible food crops. These are considered the "conventional" biofuels, as their production technologies are mature and widely implemented. This generation is defined by its direct competition with food. Bioethanol is produced via fermentation of sugars and starches from crops like corn, sugarcane, and wheat. Biodiesel is produced via a simple transesterification process using *virgin* (fresh) edible oils like soybean oil, rapeseed (canola) oil, and palm oil **(Naik et al., 2010)**. The primary and most significant criticism of 1G biofuels is the **"food vs. fuel" debate (Aro, 2016)**. The large-scale diversion of food crops to fuel production has been linked to increased global food prices, competition for arable land and water, and concerns about food security, particularly in developing nations **(Ziolkowska, 2020)**. For example, the expansion of palm oil plantations for biodiesel has been associated with significant deforestation and biodiversity loss. While the technology is established, the high cost of the virgin oil feedstock (which can account for over 70-80% of the total production cost) and its negative ethical and environmental implications drove the search for alternatives.

Furthermore, the physical properties of the biomass have an impact on the conversion processes, and the carbon footprint of first-generation biofuels is higher than that of subsequent generations. Because of these restrictions, scientists are now looking into different microbes and feedstocks to satisfy the rising demand for ethanol and biodiesel. **Rulli, M., and others (2016)**

Feedstocks:

- **Bioethanol:** Corn, sugarcane, sugar beet, wheat.

- **Biodiesel:** Virgin soybean oil, rapeseed oil, palm oil, sunflower oil.

2. Second-Generation Feedstock

Second-generation biofuels, also known as "advanced biofuels," are produced from non-food feedstocks. This category was developed specifically to overcome the major economic and environmental problems of the first generation.

Often referred to as second-generation feedstock, lignocellulosic biomass such as wood, grass, cereal straw, sugarcane bagasse, and forest residues is used as the raw material to produce bioethanol and biodiesel **(Y. Zhang et al., 2013)**. This biomass goes through a pre-treatment phase before conversion, which uses physical, biological, chemical, or a combination of physicochemical and biochemical methods. Three separate processes hydrolysis, fermentation, and distillation are required to convert lignocellulosic biomass into bioethanol after pre-treatment **(A. Omojola et al., 2021)**.

1. **Waste Feedstocks:** This includes **waste vegetable oil (WVO)** also called waste cooking oil (WCO) animal fats (tallow) from rendering plants, and other industrial waste greases **(Gui et al., 2008)**.
2. **Lignocellulosic Biomass:** This includes agricultural residues (like corn stover, wheat straw), forestry waste (wood chips, sawdust), and dedicated non-food energy crops (like switchgrass or *Miscanthus*) grown on marginal land not suitable for food crops **(Naik et al., 2010)**.

My project on WVO is a prime example of 2G's "waste-to-wealth" model. Using WVO as a feedstock has multiple advantages: it is a very low-cost (or even negative-cost) raw material, it diverts a problematic waste stream from landfills or sewers (where it can cause blockages and pollution), and it produces a fuel with a significantly lower carbon footprint compared to both fossil diesel and 1G biodiesel **(Ahmadbeigi et al., 2024)**. However, WVO often requires pre-treatment (like filtering and esterification) to handle its high free fatty acid (FFA) and water content, which makes the production process slightly more complex than using virgin oils.

Feedstocks:

- **Biodiesel: Waste vegetable oil (WVO/WCO)**, animal fats, non-edible oils (*Jatropha*).

- **Bioethanol/Other:** Lignocellulosic materials (wood, straw, grasses), municipal solid waste.

3. Third-Generation Feedstock

Third-generation biofuels are derived from aquatic microbial feedstocks, specifically **microalgae and macroalgae (seaweed)**. This generation is defined by its potential for extremely high yields without competing for arable land. The shift to 3G was motivated by the limitations of 2G lignocellulosic crops, which still require significant land area. Microalgae are seen as a superior feedstock because they can be cultivated in environments that do not compete with agriculture, such as in open ponds on non-arable desert land, in seawater, or even in wastewater **(Chisti, 2007)**. Their advantages are remarkable: they have a very fast growth rate (with harvesting cycles of days, not months) and some strains can accumulate very high levels of lipids (oil) up to 60% or more of their dry biomass. Furthermore, they can effectively capture CO_2 from industrial flue gases, meaning they can be used for both fuel production and carbon capture **(Mata et al., 2010)**. However, 3G biofuels have not yet reached large-scale commercial viability due to significant technical and economic hurdles. The primary challenges are the high energy and cost associated with harvesting the microscopic algae from water (de-watering) and the difficulty of extracting the oil from their tough cell walls **(Prajapati et al., 2021)**. The rising interest in algae-derived biofuels, along with the potential for producing a range of associated bioproducts such as natural cosmetics, aquaculture products, oils, pigments, pharmaceuticals, and nutritional supplements further enhances its need (A. Omojola et al., 2021). The third-generation biofuels mainly include the biofuels of biomethane, biodiesel, bioethanol, biobutanol, vegetable oil gasoline, jet fuels, and aviation fuels (T. Suganya et al., 2016).

Feedstocks:

- Microalgae (high-lipid strains)
- Macroalgae (seaweed)

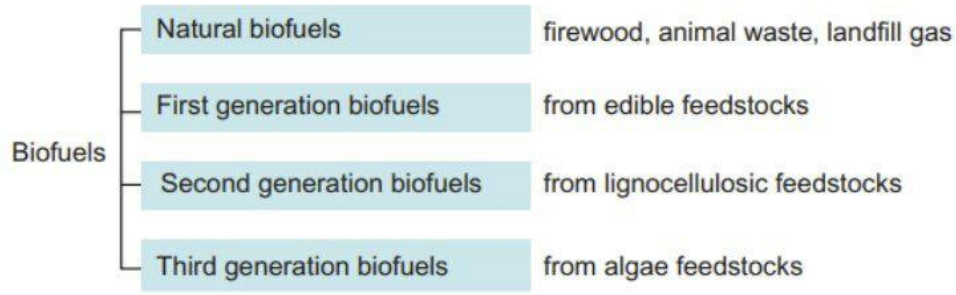


Fig 2.1 Biofuels classified into four groups. (M.Y. Noraini et al., 2014)

2.6 Classification of Biofuels Based on Physical State

One of the most fundamental methods for classifying biofuels is by their physical state at ambient temperature and pressure. This classification is critical because the physical state dictates the biofuel's application, storage, transportation, and the technological pathway required for its production **(Ayodele et al., 2021)**. A recent review confirms that "biofuels are classified according to their physical state, technology maturity, the generation of feedstock, and the generation of products" **(Balat, 2011)**. This primary classification is broken down into three distinct categories: solid, liquid, and gaseous biofuels.

1. Solid Biofuels

Solid biofuels represent the most traditional and oldest form of bioenergy used by humanity. They are defined as any solid organic, non-fossil material of biological origin that can be used as fuel for heating, cooking, or electricity generation. According to the Food and Agriculture Organization of the United Nations (FAO), the classification of solid biofuels includes "animal waste, bagasse, black liquor, charcoal, fuelwood, other vegetal material and residues" **(FAO, 2025)**.

Detailed Explanation: Solid biofuels are the foundational form of bioenergy. Historically, this was limited to **firewood** (fuelwood), which is still a primary energy source for cooking and heating for billions of people, particularly in developing nations. In a modern industrial context, solid biofuels are crucial for thermal energy and power generation. The key advantage of solid

biofuels is their widespread availability and low cost; the feedstock is often a direct agricultural or industrial by-product.

The primary conversion pathways for solid biofuels are **direct combustion** (burning) and **thermochemical conversion**.

- **Direct Combustion:** This is the simplest process, where the solid biomass is burned in the presence of oxygen (in a stove, furnace, or boiler) to release heat. This heat can be used directly for industrial processes, for heating spaces, or to create steam that drives a turbine to generate electricity. However, unprocessed biomass often has high moisture content and low energy density, making it inefficient to transport and burn.
- **Thermochemical Upgrading:** To improve their properties, raw solid biomass can be "upgraded" into more energy-dense and uniform products.
    - **Pelletization/Densification:** This involves compressing raw biomass like sawdust, wood chips, or agricultural residues (e.g., straw) into dense pellets or briquettes. This process removes moisture and increases the energy density, making the fuel easier to transport, store, and use in automated heating systems.
    - **Torrefaction:** This is a mild pyrolysis process (heating in the absence of oxygen) that "roasts" the biomass. The resulting product is a dark, brittle, and hydrophobic (water-repelling) material, often called "bio-coal," which has properties much closer to traditional coal.
    - **Carbonization:** This is the process used to create **charcoal**, which involves heating wood or other solid biomass in a low-oxygen environment to drive off water and volatile compounds, leaving a high-carbon, high-energy-density fuel. "Charcoal... is a key solid biofuel" produced through this method **(FAO, 2025)**.

Feedstocks and Examples:

- **Woody Biomass:** This is the largest category and includes:
    - **Fuelwood:** Unprocessed logs, branches, and other wood.
    - **Wood Chips & Sawdust:** By-products from sawmills and forestry operations.
    - **Wood Pellets:** Densified sawdust and wood shavings.
- **Agricultural Residues:**
    - **Bagasse:** The fibrous residue left after crushing sugarcane or sorghum stalks, which is "a key solid biofuel used in the sugar industry itself" **(FAO, 2025)**.

    - **Straw, Husks, and Stover:** Residues from grain crops like rice, wheat, and corn.
    - **Nut Shells:** e.g., palm kernel shells, coconut husks.
- **Industrial & Waste-Derived:**
    - **Black Liquor:** A "solid biofuel... that is a waste by-product from the chemical pulping process" in paper mills **(FAO, 2025)**. It is a viscous liquid at high temperatures but is classified as a solid fuel as it's burned in a recovery boiler.
    - **Dried Animal Manure (Animal Waste):** A traditional fuel in many regions.
    - **Biomass fraction of Municipal Solid Waste (MSW):** This includes waste paper, cardboard, and other organic materials.
- "Solid bioenergy remained the most-used modern renewable fuel in 2023, making up 3.5% of total final energy consumption and 8.3% of global heat consumption" **(REN21, 2025)**.
- "Wood fuels remain steady, while wood chips/pellets for energy have grown 100% and will keep rising" **(Praveena et al., 2024)**.

2. Liquid Biofuels

Liquid biofuels are combustible fuels derived from biomass that are liquid at or near ambient temperatures. This category is arguably the most significant in the modern energy transition debate because liquid fuels are the dominant energy currency for the **transportation sector**. Your project, biodiesel, is a prime example of a liquid biofuel. The primary advantage of liquid biofuels is their high energy density and "drop-in" capability. Unlike solid or gaseous fuels, they are "superior... for transportation, storage, and retrofitting" **(Jord, 2025)**. They are compatible with existing liquid fuel infrastructure (pipelines, storage tanks, and internal combustion engines), which is a massive economic advantage. Liquid biofuels are generally classified into two main types: **bioalcohols** (like bioethanol) and **biodiesel**.

- **Bioalcohols (e.g., Bioethanol):**
    a. **Production:** Bioethanol is an alcohol produced biologically, primarily through the **fermentation** of sugars. These sugars can be sourced from first-generation crops ("bioethanol produced from corn, sugarcane, and other starch-rich crops" **(Jord, 2025)**) or second-generation lignocellulosic biomass, which requires a

more complex pre-treatment and hydrolysis step to break cellulose down into fermentable sugars.

b. **Application:** It is "typically used as a blending agent with gasoline to reduce emissions and improve octane levels, with blends like E10 (10% ethanol, 90% gasoline) and E85 (up to 85% ethanol)" **(Jord, 2025)**.

- **Biodiesel (Your Project's Focus):**
  a. **Production:** Biodiesel is a liquid fuel produced from oils or fats. It is chemically distinct from bioethanol. The most common production method, and the one relevant to your project on waste vegetable oil, is **transesterification**.
  b. **Transesterification:** This is a chemical reaction where a lipid feedstock (triglycerides) like vegetable oil, animal fat, or **waste vegetable oil (WVO)** is reacted with an alcohol (typically methanol) in the presence of a catalyst (like sodium hydroxide, NaOH, or potassium hydroxide, KOH **(Gui et al., 2008)**. This reaction "converts oils and fats into fatty acid methyl esters (FAME)" **(Jord, 2025)**. These FAMEs *are* biodiesel. The process also yields glycerol (glycerine) as a co-product.
  - **Feedstocks (Relating to Generations):**
    - *1st Generation:* "Edible oil feedstocks used for biodiesel production include palm, soybean, sunflower, rapeseed, and peanut oils" **(Jord, 2025)**.
    - *2nd Generation (Your Focus):* This generation uses non-food feedstocks to avoid the food-vs-fuel debate. This includes "non-edible oils (Jojoba oil, Jatropha oil, and Karanja oil)" **(Yusuf et al., 2022)** and **waste cooking oil (WCO/WVO)**. The use of WVO is particularly advantageous as it simultaneously addresses "waste minimization, [and] proper waste disposal" **(Ayodele et al., 2021)**.
  - **Application:** Biodiesel is a direct substitute or blend-in for petroleum-based diesel. It is "a cleaner alternative to petroleum-based diesel" **(Jord, 2025)** and can be "blended with traditional diesel in various proportions, such as B20 (20% biodiesel) and B100 (pure biodiesel)" **(Jord, 2025)**.
- **Other Liquid Biofuels:**
  a. **Renewable Diesel (HVO):** Often confused with biodiesel (FAME), Hydrotreated Vegetable Oil (HVO) is produced by reacting oils/fats with

hydrogen at high pressure. The result is a fuel chemically identical to petroleum diesel (a hydrocarbon), making it a superior "drop-in" fuel.

b. **Bio-oil (Pyrolysis Oil):** This is a dark, viscous liquid produced through the rapid heating of solid biomass in the absence of oxygen (fast pyrolysis). It "can be used as a fuel for heating and power generation or upgraded to biofuels compatible with existing engines" **(Jord, 2025)**.

3. Gaseous Biofuels

Gaseous biofuels are fuels derived from biomass that are in a gaseous state at ambient temperature and pressure. These fuels are primarily used for stationary heat and power generation, but can also be upgraded for use as a vehicle fuel or for injection into the natural gas grid. Gaseous biofuels are a critical component of waste-to-energy strategies, as their production processes are adept at converting wet, low-value organic waste into a storable, combustible gas. The primary types are biogas, syngas, and biohydrogen.

- **Biogas:**
- **Production:** Biogas is "produced through the anaerobic digestion of organic matter such as agricultural waste, sewage, and food waste" **(Jord, 2025)**. Anaerobic digestion (AD) is a biological process where microorganisms break down biodegradable material in an oxygen-free environment.
- **Composition & Application:** The resulting gas is a "mixture of methane CH_4 and carbon dioxide CO" **(Jord, 2025)**, typically 50-70% methane. This raw biogas can be used directly in boilers for heat or in engines to generate electricity.
- **Upgrading (Biomethane):** Biogas can be "upgraded" to **biomethane** by removing the CO_2H_2S, and other impurities. The result is a "purified form of biogas, containing mainly methane, making it similar to natural gas" **(Jord, 2025)**. This high-purity biomethane can then be "injected into the natural gas grid or used as a transportation fuel" **(Jord, 2025)**.
- **Syngas (Synthesis Gas):**
- **Production:** Syngas is not produced biologically, but thermochemically, through the **gasification** of solid biomass. Gasification involves heating the biomass (like wood, agricultural residues, or waste) with a limited amount of oxygen, which converts it into

a "fuel gas mixture consisting primarily of hydrogen H_2, carbon monoxide CO, and often some carbon dioxide" **(Jord, 2025)**.

- **Application:** Syngas is highly flexible. It can be burned directly for heat and power. More importantly, it can be used as a chemical building block (a "synthesis gas") to create other fuels. Through the Fischer-Tropsch process, syngas can be chemically converted into liquid biofuels like renewable diesel or jet fuel.
- **Biohydrogen:**
- **Production:** Biohydrogen is high-purity hydrogen produced from biological sources. This is an emerging field with several pathways, including:
    a. **Dark Fermentation:** Using bacteria to convert organic waste into hydrogen.
    b. **Photofermentation:** Using photosynthetic bacteria to produce hydrogen from sunlight.
    c. **Gasification with Reforming:** Upgrading syngas to produce pure hydrogen.
- **Application:** As a completely clean-burning fuel (its only combustion product is water), hydrogen is seen as a key fuel for the future, particularly for fuel cells in transportation and for high-temperature industrial heat.

2.7 Biomass Energy Conversion Technologies

Biomass energy conversion technologies offer a diverse range of methods for producing modern energy carriers like electricity, gas, and liquid fuels. These technologies are adaptable to various scales, ranging from small-scale household applications (around 10 kilowatts) to community level systems (around 100 kilowatts) and large-scale industrial facilities (megawatts). Categorizing these technologies can be done by examining either the specific conversion process employed or the type of energy carrier produced as the final product (Herzog, 2001).

- ### Burning

The chemical process of combustion occurs when fuel burns in an oxygen-rich atmosphere, such as air or pure oxygen. Through this process, the fuel's chemical energy is released as heat. After that, this heat can be used for a number of things, including heating buildings, cooking, and producing energy. The following are the general responses:

$$Biofuel + O_2 \rightarrow CO_2 + H_2O + Heat \quad (2.1)$$

$$Biofuel + Air \rightarrow CO_2 + H_2O + N_2 + Heat \quad (2.2)$$

The combustion process will also produce ash, sulfur oxides (SOx), and nitrogen oxides (NOx) as by-products if the biofuel contains any of these elements (Y. Zhang et al., 2017). In a perfect world, burning biofuel would produce a theoretical peak temperature of 2000°C by fully converting its carbon (C) content into carbon dioxide (CO2) and its hydrogen (H) content into water (H_2O). However, combustion is rarely flawless in practical applications. According to G.N. Mezza et al. (2018), incomplete burning produces carbon monoxide (CO), and heat loss into the atmosphere lowers the actual temperature reached to a range of 800-1000°C.

Excess air or oxygen is usually used to improve combustion efficiency. In theory, every kind of biomass or biofuel can burn entirely, but in reality, combustion is only possible when the fuel has less than 50% moisture. To solve this moisture problem, a preheating phase is frequently employed (H.B. Goyal et al., 2008).

Combustion is a mature and effective method of turning biofuel into heat, but it is not a biofuel production technique. This is due to the fact that full combustion essentially consumes the original feedstock rather than producing new biofuels, leaving behind mainly carbon dioxide (CO2) and water (H2O).

- ## Liquefaction

Through intricate reactions in a solvent media, liquefaction is a chemical process that turns biomass into mostly liquid products, or bio-oil. In order to liquefy biomass and create bio-oil, hydrothermal liquefaction specifically uses water as the reaction medium and temperatures between 200 and 400°C under high pressure **(H. Chen et al., 2015)**.

The hydrolysis of macromolecules like cellulose and hemicellulose into smaller fragments can be facilitated by alkali salts like potassium and sodium carbonates. The sticky, tarry lump of heavy oil that results from the liquefaction process can occasionally be problematic to handle. Certain organic solvents, such as propanol, butanol, acetone, methyl ethyl ketone, ethyl acetate, etc., are used in this situation.

- ## pyrolysis

Pyrolysis is a chemical process that uses heat, usually between 300 and 1300°C, to break down biomass. This procedure takes place in an inert atmosphere, which is devoid of oxygen (Omojola et al., 2021). The biomass feedstock's overall reaction is:

$$Biofuel + heat \rightarrow liquid + syngas + solid \qquad (2.3)$$

Three useful products are produced by pyrolysis: liquid bio-oil, gaseous bio-syngas, and solid biochar. These goods are regarded as fuels. The following are the main chemical reactions that take place during pyrolysis:

$$C + 2H_2O \rightarrow 2H_2 + CO_2 \qquad \Delta H = +75kJ/mol \qquad (2.4)$$

$$C + H_2O \rightarrow H_2 + CO \qquad \Delta H = +131kJ/mol \qquad (2.5)$$

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2 \qquad \Delta H = +165kJ/mol \qquad (2.6)$$

$$CH_4 + H_2O \rightarrow H_2 + CO \qquad \Delta H = +206kJ/mol \qquad (2.7)$$

Based on operational factors such as temperature, residence duration, and heating rate, conventional electrical pyrolysis can be roughly divided into three types:

Slow pyrolysis is defined by a lengthy residence time (more than 450 seconds), moderate temperatures (300–700°C), and a slow heating rate (less than 1°C per second).

Fast pyrolysis is characterized by higher temperatures (550–1250°C), a shorter residence period (0.5–20 seconds), and a faster heating rate (10–300°C per second).

Flash pyrolysis is characterized by extremely high temperatures (800–1300°C), a very short residence time (less than 0.5 seconds), and an extremely fast heating rate (more than 1000°C per second).

The most efficient way to produce bio-oil is usually flash pyrolysis, which is followed by fast pyrolysis. Slow pyrolysis produces the least quantity of bio-oil **(K. Azizi et al., 2018; P. Manara et al., 2012)**.

Other pyrolysis variations, such as catalytic pyrolysis, vacuum pyrolysis, microwave pyrolysis, and hydropyrolysis, are also being studied; each has potential advantages of its own.

- **Digestion**

Bacteria-assisted biomass digestion can take place in either anaerobic (without oxygen) or aerobic (with oxygen) environments. Biogas is produced through the biological process of anaerobic digestion, in which microorganisms break down organic waste without oxygen. Methane (55–75%) and carbon dioxide (25–45%) make up the majority of this biogas, with trace levels of hydrogen sulfide (P. Champagne, 2008).

Specialized bacteria break down complex organic components (such as proteins, lipids, and carbohydrates) into simpler, water-soluble molecules (such as sugars, amino acids, and fatty acids) during anaerobic digestion. Methane and carbon dioxide, together referred to as biogas, are the end products of this process. Anaerobic digestion's total chemical response can be shown as follows:

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 \qquad (2.8)$$

Four separate phases can be distinguished in the anaerobic digestion process **(M.C. Gould, 2015)**.

Proteins, lipids, and carbohydrates are examples of large organic molecules that undergo hydrolysis, which breaks them down into smaller parts like simple sugars, fatty acids, and amino acids.

Acidogenesis: The organic matter is further broken down by acid-producing bacteria, which results in an acidic environment.

Acetogenesis: Many of the products from the previous stage are converted into hydrogen, carbon dioxide, and acetic acid by acetogenic bacteria.

Methanogenesis: Methanogenic bacteria generate methane by using the byproducts of acetogenesis, which include hydrogen, carbon dioxide, and acetic acid.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (2.9)$$

$$CH_3COOH \rightarrow CH_4 + CO2 \qquad (2.10)$$

Anaerobic digestion is a flexible technology that can be used to treat a wide range of biomass materials, including municipal solid waste, industrial waste, livestock manure, food processing waste, and domestic and industrial sewage. These feedstocks typically have high moisture content, ranging from 80 to 90 percent of their total weight **(P. Champagne, 2008)**.

- **Fermentation**

Our word "fermentation" comes from the Latin word "fervere," which means "to boil." The distinctive bubbling seen throughout the operation is described by this descriptive moniker. As a result of yeast's anaerobic respiration, carbon dioxide gas is released, which causes this bubbling. Without oxygen, yeast transforms carbohydrates into carbon dioxide and ethanol in this mechanism **(Y. Zhang et al., 2017)**.

One metabolic activity that takes place without oxygen is fermentation. Microorganisms such as bacteria and yeast, or even oxygen-depleted muscle cells, break down carbohydrates. Alcohol, fumes, and organic acids are among the results of this anaerobic process (C.R. Soccol et al., 2011).

Ethanol fermentation is the primary process used to create gas and alcohol (C.R. Soccol et al., 2011).

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \qquad (2.11)$$

One popular industrial method for creating bioethanol, a sustainable fuel substitute, is fermentation. The most often used feedstocks for the manufacture of bioethanol are sugar and starch crops. However, as a potential feedstock for this process, lignocellulosic biomass—such as wood and cereals—is also being investigated (P. Champagne, 2008).

- Transesterification

A chemical process known as transesterification turns triglycerides (fats or oils) into esters and glycerol. Triglycerides are reacted with short-chain alcohols, such as methanol or ethanol, to produce this reaction. Transesterification, in contrast to other processes, results in a biodiesel product with characteristics comparable to those of traditional petroleum diesel fuel and leaves behind very little carbon residue **(L.C. Meher et al., 2006)**.

Triglycerides and methanol combine to form biodiesel through a series of three successive reactions:

$$\text{Triglyceride} + CH_3OH \rightarrow \text{Diglyceride} + \text{FAME} \qquad (2.12)$$

$$\text{Diglyceride} + CH_3OH \rightarrow \text{Monoglyceride} + \text{FAME} \qquad (2.13)$$

$$\text{Monoglyceride} + CH_3OH \rightarrow \text{Glycerol} + \text{FAME} \qquad (2.14)$$

2.8 BIODIESEL

Green fuel, often known as biodiesel, is a renewable substitute for diesel fuel made from petroleum. In the presence of a catalyst, such as an alkali metal hydroxide like sodium hydroxide or potassium hydroxide, or less frequently, an acid catalyst, triglycerides the fats and oils from vegetable sources like soybeans, rapeseed, palm, algae, or recycled cooking grease react with a short-chain alcohol, usually methanol or ethanol, to produce it **(F.D. Irimie et al., 2018)**. Fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE), which make up biodiesel, are produced when the triglycerides are broken down by this process.

Biodiesel is a dark brown to golden liquid with a low vapour pressure and a high boiling point that does not mix with water. One of the main obstacles to using biodiesel as a substitute fuel for diesel engines is its low-temperature flow characteristics, even if many of its qualities are comparable to those of traditional petroleum diesel. According to Bhale et al. (2008), biodiesel made from fats or oils that include significant amounts of saturated fatty acids typically has high cloud points, which might cause issues in cold climates.

2.9 Historical Background of Biodiesel

A golden to dark brown liquid with a high boiling point and low vapour pressure, biodiesel does not mix with water. The low-temperature flow characteristics of biodiesel present a significant obstacle to its use as a substitute fuel for diesel engines, despite the fact that many of its characteristics are comparable to those of traditional petroleum diesel. When made from fats or oils that include significant amounts of saturated fatty acids, biodiesel typically has high cloud points, which might cause issues in cold climates (Bhale et al., 2008).

In addition to introducing the idea, this groundbreaking effort also created the term "biodiesel." Although the basic ideas were established earlier, the modern biodiesel movement gained significant momentum. Diesel further proved the feasibility of his concept by successfully operating a vegetable oil-fueled diesel engine in the early 20th century and experimenting with various oils, including peanut oil. The first worldwide symposium on biofuels made from plant and vegetable oils took place in Fargo, North Dakota, in August 1982. Key debate areas during the conference were seed preparation and processing, oil production costs, and fuel sustainability, showing the rising interest in biodiesel as a viable and sustainable alternative fuel (Xiao & Gao. 2011).

2.9.1 Properties of Biodiesel

Similar to regular diesel fuel generated from crude oil, biodiesel has some qualities that affect how well it works in engines. These include its suitability for cold climates, its storage and transportation qualities, and the potential wear it may put on engine parts.

Aspects of engine operation, such as ease of starting, fuel-air mixture formation, combustion efficiency, exhaust emissions, and fuel heating value, are among the main factors that affect engine performance. The following are essential characteristics of biodiesel that are necessary to guarantee good engine performance and compliance with pollution regulations.

1. Density

The percentage of ester content and any remaining alcohol in biodiesel affect its density, hence choosing the source vegetable oil is a crucial factor in determining this characteristic **(Encinar et al., 2012)**. Fuel's density, which is the weight of a given volume of liquid, is a basic property that has a big impact on engine performance. The density of biodiesel is generally higher than that of petroleum diesel. This higher density is essential because it affects the air-to-fuel ratio, the fuel injection system's performance, and the amount of fuel supplied to the combustion chamber. Systems for injecting fuel are made to work on volume rather than mass. Consequently, each unit of volume is equivalent to a larger mass of gasoline when utilizing a denser fuel, such as biodiesel. Variations in combustion dynamics may result from this, which could have an impact on emissions and engine efficiency.

2. Viscosity

The internal friction of a liquid is measured by its viscosity, which has a direct impact on how smoothly it flows. This characteristic is especially crucial when assessing biodiesel as a diesel fuel substitute. The viscosity of biodiesel, which is made from vegetable or animal fats, is usually higher than that of regular diesel. High viscosity can cause a number of problems during combustion, such as incomplete combustion in the engine's combustion chamber, increased smoke emissions, and trouble atomizing. These problems may have an adverse effect on emissions, efficiency, and engine performance. The viscosity of biodiesel must be substantially lower than that of pure vegetable oils in order to guarantee the best possible performance of diesel injectors. Poor fuel atomization and uneven combustion can result from high viscosity,

which can also make it difficult to properly inject fuel into the combustion chamber. Operational issues including misfiring, greater wear on engine parts, and increased pollution emissions may arise from this.

3. Acid value

The mass in milligrams of potassium hydroxide (KOH) required to neutralize one gram of a compound is known as the acid value, neutralization number, or acidity. It also affects fuel aging and quantifies the amount of free fatty acids in an oil or fuel sample. Fuel pumps and filters are destroyed by high free fatty acid oil, which is first treated by acid-catalyzed esterification.

Other notable characteristics of biodiesel fuel include;

1. Biodiesel is partially miscible in water
2. It has high boiling point and low vapour pressure
3. Depending on the method of production, biodiesel is either golden brown or dark brown in colour
4. It has light soapy odour
5. Methyl esters and monoglycerides present in biodiesel makes it a good lubricant

2.10 Transesterification Technologies

The specific technology you choose is dictated almost entirely by the quality of your feedstock, particularly its **Free Fatty Acid (FFA)** and water content. WVO is notorious for being high in both, which makes most conventional methods fail.

Here is a detailed breakdown of the primary transesterification technologies, structured for a literature review.

2.10.1 The Core Challenge: Free Fatty Acids (FFAs) in WVO

Before reviewing the technologies, you must establish *why* WVO is a difficult feedstock.

Raw vegetable oils (like fresh soy or palm oil) are almost 100% triglycerides. However, when oil is used for frying, the high heat and water from food cause the triglycerides to break down, creating **Free Fatty Acids (FFAs)**.

The central problem of high-FFA oil is **saponification** (soap making).

The most common catalysts for transesterification are alkali (basic) catalysts like Sodium Hydroxide NaOH. When NaOH is added to high-FFA oil, two competing reactions occur:

1. **Transesterification (Desired):** Triglyceride + Methanol = Biodiesel + Glycerol
2. **Saponification (Undesired):** Free Fatty Acid + NaOH = **Soap** + Water

According to a study on WVO with high FFA content, this soap formation "can make it more challenging to separate biodiesel from the mixture... ultimately reducing the yield and efficiency of biodiesel production" **(Mićić et al., 2021)**. The soap creates a gel-like emulsion, making it nearly impossible to drain the glycerol by-product and wash the final biodiesel. Therefore, most research on WVO is focused on technologies that can *overcome* this FFA problem.

Here are the main technologies.

1. Homogeneous Catalysis

This is the most conventional and commercially mature technology. The "homogeneous" part means the catalyst (a liquid acid or base) is in the same liquid phase as the oil and alcohol.

A. Homogeneous Alkali-Catalyzed Transesterification

This is the industry standard for *virgin, low-FFA oils*.

a. **Technology:** Uses a strong alkali catalyst, typically **Sodium Hydroxide NaOH** or **Potassium Hydroxide KOH**, dissolved in methanol. The reaction is fast, cheap, and highly efficient, "carried out at a reaction temperature: 65 °C [and] reaction time: 1 hour" **(Siahaan et al., 2020)**.
b. **Suitability for WVO (Very Poor):** This method is *not* suitable for WVO with an FFA content above 1-2%. Research has shown that for feedstocks "containing 4-6% FFA, the conversion rate is less than 50%" and that these samples undergo "saponification reaction during washing" **(Encinar et al., 2021)**. This makes the process unusable without a pre-treatment step.

B. Homogeneous Acid-Catalyzed Transesterification

This method uses a strong liquid acid catalyst, like **Sulfuric Acid H_2SO_4**.

a. **Technology:** Unlike alkali catalysts, acid catalysts are completely insensitive to FFAs. In fact, an acid catalyst will actively convert the FFAs into biodiesel through a process called **esterification**.
b. **Suitability for WVO (Good, but slow):** The major advantage is that "acid-catalyzed processes offer an important advantage for being independent of feedstock FFA content" **(Karmakar et al., 2018)**. However, the reaction is extremely slow; "it has been stated that acid-catalyzed reaction may be 4000 times slower than the base catalyst process" **(Karmakar et al., 2018)**. This slow speed makes it commercially unappealing as a single-step process.

C. The Two-Step Acid-Base Process (The WVO Solution)

This is the most common and practical solution for high-FFA WVO. It combines the two methods above.

1. **Step 1: Acid Esterification (Pre-treatment):** The WVO is first reacted with methanol and an acid catalyst like H_2SO_4. This step's only goal is to "convert the FFA to ester" (biodiesel), effectively lowering the oil's FFA content to below 1% **(Adepoju, 2018)**.
2. **Step 2: Alkali Transesterification (Main Reaction):** After the pre-treatment, the low-FFA oil is separated and then processed using the fast and efficient **alkali-catalyzed** method NaOH or KOH to convert the remaining triglycerides.

This "two steps (esterification and transesterification) approach was employed to convert the WCO to biodiesel" and is considered the most robust method for handling low-quality, high-FFA feedstocks **(Adepoju, 2018)**.

2. Heterogeneous (Solid) Catalysis

This is a major area of modern research, designed to "green" the process. "Heterogeneous" means the catalyst is in a different phase (a solid) from the liquid oil and alcohol.

- **Technology:** Uses a solid, reusable catalyst instead of a single-use liquid acid or base. These catalysts are often "alkaline earth oxides like **Calcium Oxide CaO" (Karmakar et al., 2018)**, which can be derived from waste sources like **eggshells (Siahaan et al., 2020)**. The reactants flow over a packed bed of this solid catalyst.
- **Suitability for WVO (Very Good):**
    a. **Advantages:** The main advantage is that "heterogeneous base catalysts have the advantage of recycling and safe effluent disposal" **(Manoharan et al., 2021)**. Because the catalyst is a solid, it is "easily separated from the product mixture by simple filtration" **(Tacias-Pascacio et al., 2021)**. This **eliminates the costly water-washing step** required in homogeneous catalysis and prevents the formation of soap emulsions.
    b. **Disadvantages:** These catalysts "gave a slightly less yield" than homogeneous ones **(Manoharan et al., 2021)**. They are also more expensive upfront and can suffer from "leaching" (where the catalyst dissolves into the mixture) or poisoning from water and other contaminants in the WVO.

3. Enzymatic (Biocatalysis) Transesterification

This is the most "green" and advanced catalytic technology, using biology instead of harsh chemicals.

- **Technology:** This method uses **lipases**, which are enzymes (biocatalysts), to drive the transesterification. The lipases are often "immobilized," or fixed onto a solid support material, so they can be reused.
- **Suitability for WVO (Excellent, but costly):**
    a. **Advantages:** This is the *ideal* technology for WVO. Lipases are not affected by FFAs; in fact, "enzymatic transesterification... can simultaneously esterify FFAs and transesterify triglycerides in a single step" **(Riaz et al., 2021)**. The reaction is run at very mild temperatures (30-50°C), saving energy, and produces extremely pure biodiesel and glycerol with no soap.
    b. **Disadvantages:** The primary "drawback... is the **high cost of enzyme" (Gui et al., 2008)**. Enzymes are also sensitive to methanol, which can inhibit their

activity, and the reaction times are very long, often taking 12-48 hours compared to 1 hour for chemical methods **(Riaz et al., 2021)**.

4. Non-Catalytic Technology (Supercritical Method)

This method avoids catalysts entirely by using extreme temperature and pressure.

- **Technology:** This is a "catalyst-free chemical reaction" that uses alcohol (like methanol) in its **supercritical state (Go et al., 2014)**. A fluid becomes supercritical when it is heated and pressurized above its critical point, where it has the properties of both a liquid and a gas.
- **How it Works:** At conditions like 350-400°C and over 80 bar (8.1 MPa) of pressure, "methanol's... dielectric constant decreases significantly and the methanol thus becomes more like a non-polar substance" **(Qiu et al., 2011)**. This allows it to dissolve the non-polar oil, and its high thermal energy is enough to drive the reaction without any catalyst.
- **Suitability for WVO (Excellent, but energy-intensive):**
    a. **Advantages:** This is perhaps the most robust method of all. It is "insensitive to high water and FFA content" **(Go et al., 2014)** and simultaneously performs esterification and transesterification. The reaction is also extremely fast, achieving "99% conversion... for 60-min holding time" **(Go et al., 2014)**.
    b. **Disadvantages:** The "major disadvantage of this method is **high energy consumption and cost of production** due to the severe conditions (high reaction temperature, and pressure)" **(Alenezi et al., 2010)**. It requires a specialized, expensive, and high-pressure industrial reactor.

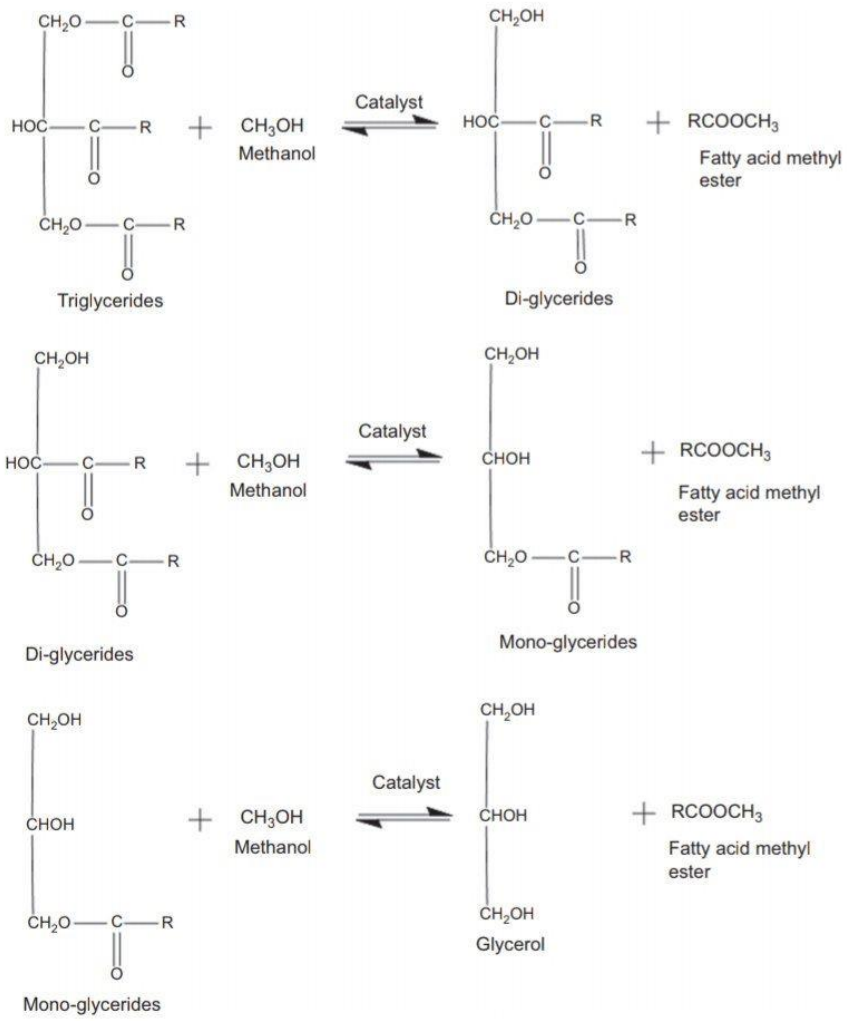


Fig 2.2 Transesterification reaction mechanism

(Vinoth Thangarasu, R. Anand 2019).

2.11 Main factors affecting the transesterification reaction

The success, speed, and efficiency of your biodiesel production are not dependent on just one variable, but on the **interplay of several key factors**. The transesterification reaction is a sensitive equilibrium, and "the correct interplay of factors like reaction temperature, time, alcohol-to-oil molar ratio, and catalyst loading produces optimal process conditions that give the highest biodiesel yield" **(Sani et al., 2024)**.

For your specific project using **Waste Vegetable Oil (WVO)**, the most critical factors are the quality of your feedstock (FFA and water content), as these will dictate how you must adjust all other parameters.

2.9 Feedstock Quality (FFA and Water Content)

This is the most important factor for a WVO project. WVO is a "low-grade" feedstock, and its properties are very different from the refined, edible oils used in traditional biodiesel production.

- Free Fatty Acid (FFA) Content:

When oil is repeatedly heated (fried), the triglycerides break down through hydrolysis, creating Free Fatty Acids (FFAs). This is the number one problem for your project. If you use a common alkali (base) catalyst like NaOH or KOH:

a. **The Problem:** The FFAs will instantly react with the alkali catalyst in an acid-base reaction called **saponification**. This reaction "consumes the catalyst and forms soaps" **(Kusdiana & Saka, 2004)**.
b. **The Result:** This soap formation "can make it more challenging to separate biodiesel from the mixture... ultimately reducing the yield and efficiency" **(Mićić et al., 2021)**. It creates a gel-like emulsion that makes separating the glycerol by-product almost impossible.
c. **The Rule:** Base-catalyzed transesterification can only handle oil with an FFA content "lower than 3%" **(Taljaard et al., 2021)**. Your WVO will likely be much higher, which is why a **two-step acid-esterification pre-treatment** is necessary.

- Water Content:

WVO also contains a significant amount of water, both dissolved in the oil and from food particles.

a. **The Problem:** Water also causes saponification. The presence of water "gives greater negative effect than that of FFAs because Water can cause soap formation and frothing" **(Aworanti et al., 2017)**.
b. **The Result:** The water hydrolyzes the triglycerides and the desired biodiesel (FAMEs) back into FFAs, which then react with the catalyst to form more soap. This creates a vicious cycle that consumes your catalyst and ruins your yield.

c. **The Rule:** The feedstock must be as dry as possible. This is why a pre-heating step (e.g., heating the oil to 110°C) is often used to boil off any residual water before the reaction.

2.9.1 Molar Ratio of Alcohol to Oil

- **What it is:** The transesterification reaction is a chemical reaction. Stoichiometrically, it requires **three molecules of alcohol** (e.g., methanol) to react with **one molecule of triglyceride** (oil) to produce three molecules of biodiesel and one molecule of glycerol.
- **Why it Matters:** This reaction is **reversible** (it's an equilibrium). To ensure the reaction proceeds forward and creates the maximum amount of biodiesel, you must use an "excess of alcohol... to shift the balance towards the production of the products" **(Boon-anuwat et al., 2015)**.
- **Typical Range:** While the stoichiometric ratio is 3:1, this will result in a very low yield. In practice, a molar ratio of **6:1 (methanol:oil)** is considered the standard minimum for good conversion, with many WVO studies using **9:1** or **12:1** to ensure the reaction is pushed to completion **(Adepoju et al., 2019)**.
- **The Downside:** Using too much alcohol (e.g., >15:1) doesn't significantly improve the yield and creates new problems. It makes the separation of the glycerol by-product more difficult (as more glycerol remains dissolved in the methanol) and increases the energy cost of recovering the unreacted methanol for reuse.

2.10 Catalyst Type and Concentration

- **What it is:** The catalyst is the substance that "speeds up" the reaction.For your project, this is likely NaOH or KOH (homogeneous base), or H_2SO_4 (homogeneous acid) for the pre-treatment step.
- **Why it Matters:** The concentration of the catalyst is a delicate balance.
    a. **Too Little:** An insufficient amount of catalyst will lead to a slow and incomplete reaction, resulting in a low biodiesel yield.
    b. **Too Much:** This is a common mistake. For alkali catalysts, "the increase in catalyst concentration decreases the yield and favors the byproduct, which is a high yield of soap and water" **(Chopade et al., 2024)**. An excess of NaOH or

KOH will aggressively promote saponification, especially if any FFAs or water are present.

- **Typical Range:** For alkali-catalyzed transesterification of pre-treated WVO, the catalyst concentration is typically optimized between **0.5% and 1.5%** by weight of the oil (wt%).

2.11 Reaction Temperature

- **What it is:** The temperature at which the reaction is maintained.
- **Why it Matters:** Like most chemical reactions, increasing the temperature increases the reaction rate. "An increase in temperature was in most cases required to accelerate the reaction rate and improve conversion efficiency" **(Sani et al., 2025)**.
- **The Limit:** The reaction temperature is **limited by the boiling point of the alcohol** you are using. For **methanol**, the boiling point is approximately **64.7°C**. Therefore, the reaction is almost always carried out at a temperature "below the boiling point of alcohol in order to prevent the alcohol evaporation" **(Aworanti et al., 2017)**.
- **Typical Range:** The optimal temperature range for methanol-based transesterification is **55°C to 65°C**. Going higher will simply cause the methanol to boil off (unless you are using a pressurized reactor), which stops the reaction and creates a fire hazard.

2.12 Mixing Intensity (Agitation Speed)

- **What it is:** The speed (in rpm) of the mechanical or magnetic stirrer.
- **Why it Matters:** This factor is often overlooked but is critically important. **Oil and methanol do not mix** (they are immiscible).
    - **The Problem:** The transesterification reaction can only occur at the *interface* (the boundary layer) between the oil droplets and the methanol.
    - **The Solution:** Vigorous stirring is essential to "overcome mass transfer limitations" **(Stavarache et al., 2005)**. It breaks the two phases into a fine emulsion, which dramatically increases the surface area between the reactants and allows the reaction to proceed quickly and efficiently.
- **Typical Range:** A "lower stirring speed shows lower product formation" **(Aworanti et al., 2017)**. You need vigorous, turbulent mixing (e.g., 400-700 rpm or higher,

depending on your reactor's geometry) to ensure the reactants are in constant, close contact.

2.13 Methanol

The most widely utilized alcohol in the manufacturing of commercial biodiesel is methanol (CH3OH). Its high responsiveness, accessibility, and inexpensive cost account for its widespread use (Demirbas, A. 2008). Compared to higher alcohols, methanol's tiny molecular size allows for faster reaction rates (Leung, D. et al 2010). But methanol has drawbacks as well. Its immiscibility with vegetable oils required vigorous mixing or the use of co-solvents to improve contact between the reactants, and its toxicity demands stringent safety procedures (ATSDR, 2017). To guarantee the process's cost-effectiveness, extra methanol must also be recovered (Marchetti, J. et al 2007).

2.14 Properties of Methanol

Methanol CH_3OH, also known as methyl alcohol, is the simplest alcohol. It is a light, volatile, and flammable liquid.

- **Chemical Formula:** CH_3OH
- **Molar Mass:** 32.04 g/mol
- **Polarity:** It is a **polar solvent**. This is a key property, as it must react with the non-polar oil.
- **Boiling Point:** 64.7°C (148.5°F). This low boiling point is crucial, as it dictates the maximum temperature for standard transesterification reactions, which are typically run just below this point (around 60-65°C) to prevent the alcohol from evaporating.
- **Toxicity:** Methanol is highly toxic. It can be absorbed through the skin, inhaled, or ingested, and can cause blindness or death.This makes handling it a primary safety concern.

2.15 Advantages of Methanol over Other Alcohols in Biodiesel Production

In transesterification, the oil (triglyceride) can be reacted with several alcohols, but methanol is the overwhelming industrial choice. The main alternatives are other short-chain alcohols like ethanol C_2H_5OH, propanol, and butanol.

Here's why methanol is preferred:

1. Cost and Availability

Methanol is the cheapest and most widely available alcohol. It is a high-volume commodity chemical, often produced from natural gas (fossil fuel) or, increasingly, from biomass (biomethanol). This low cost is the single most important economic factor, as the alcohol is a major operational expense.

2. Chemical Reactivity

Methanol is the **smallest and most reactive** of the common alcohols.

- **Less Steric Hindrance:** Because it is a small molecule CH_3OH, it reacts with the large triglyceride molecule more easily and quickly than bulkier alcohols like ethanol C_2H_5OH or butanol C_4H_9OH.
- **Higher Yields:** This higher reactivity generally leads to faster reaction times and higher conversion yields. Studies directly comparing methanol and ethanol under the same conditions consistently show that "methyl transesterification has a bigger yield than esters from ethanol."

3. Ease of Separation (Physical Properties)

This is a critical, practical advantage.

- **Phase Separation:** After the reaction, the mixture settles into two layers: biodiesel on top and glycerol on the bottom. Methanol's high polarity causes it to separate from the non-polar biodiesel and move into the polar glycerol layer. This "separation between esters and glycerol is instantaneous" when using methanol, while reactions with ethanol are "difficult... and may have reactants not consumed, soaps, and emulsions" remaining in the top layer.

- **Purification:** The final biodiesel must be purified washed to remove any residual catalyst, soap, and alcohol.Because methanol separates so cleanly into the glycerol layer, less of it remains in the biodiesel layer, making the final purification and washing steps faster and more efficient.

4. Catalyst Solubility

Common alkali catalysts like NaOH (sodium hydroxide) and KOH (potassium hydroxide) **dissolve faster and more easily in methanol** than in ethanol. This allows the catalyst to be quickly and evenly distributed throughout the reaction, leading to a more efficient and complete reaction.

5. Methanol Recovery

Because transesterification uses an excess of alcohol, the unreacted alcohol must be recovered and reused to make the process economical. Methanol's low boiling point (64.7°C) makes it **easier and cheaper to recover** via distillation compared to ethanol (78.37°C) or butanol (117.7°C). It requires less energy to evaporate, purify, and condense.

2.16 Sources and Generation of Waste Vegetable Oil

Waste Vegetable Oil (WVO), also commonly referred to as Waste Cooking Oil (WCO), is a post-consumer waste product. Its primary sources are the **residential, commercial, and industrial sectors** where edible vegetable oils are used for frying.

a. **Commercial/Industrial Sources:** This is the largest and most common source. It includes restaurants (especially fast-food chains), catering services, hotels, and industrial food processing plants (e.g., for potato chips or frozen foods). These establishments generate large, consistent quantities of used oil, making collection more feasible **(Chhetri et al., 2008)**.
b. **Residential Sources:** This source consists of oil used for cooking in households. It is far more "decentralized and scattered," making collection and transportation logistically difficult and expensive **(Mata et al., 2010)**.

The oil "becomes waste" when its quality has degraded to a point where it is no longer suitable for food. This degradation is a direct result of the high-temperature frying process. When oil is heated (often 160-190°C) in the presence of air and water (from the food), it undergoes a series of complex chemical reactions:

1. **Hydrolysis:** Water from the food attacks the triglyceride molecules (the main component of oil), breaking them down and forming **Free Fatty Acids (FFAs)**.
2. **Oxidation:** Oxygen from the air attacks the oil, forming peroxides, aldehydes, and ketones, which contribute to the oil's dark color and rancid smell.
3. **Polymerization:** The oil molecules begin to link together, forming large, complex polymers.

These reactions "lead to the formation of free fatty acids (FFAs), water, and other impurities" that define the oil as "waste" and make it a challenging (but rewarding) feedstock for biodiesel production **(Mofijur et al., 2014)**.

2.17 Oil Collection and Pre-treatment Methods

The term "extraction" is typically used for *virgin* oils (e.g., pressing oil from seeds). For WVO, the process is more accurately described as **collection and pre-treatment**. Pre-treatment is a mandatory step to prepare the raw, contaminated WVO for the chemical reaction of transesterification.

The goal of pre-treatment is to "remove impurities that interfere with the transesterification reaction" **(Gui et al., 2008)**. The main methods are:

1. Filtration (or Settling)

The raw WVO collected from restaurants is a slurry, contaminated with solid waste.

a. **Purpose:** To remove all non-oil solid matter.
b. **Method:** This is a simple physical process. The oil is first passed through coarse screens to remove large food particles, char, and debris. It is often then allowed to settle in a tank for 24-48 hours, where the denser solids and some water sink to the bottom. For a

finer "polishing" step, the oil is then passed through fine-micron filters to remove any remaining suspended solids.

2.18 Dehydration (Drying)

WVO contains a significant amount of water, both free-floating and dissolved (emulsified) in the oil.

a. **Purpose:** To remove water. This is arguably the most critical pre-treatment step.
b. **Method:** The most common method is heating the oil to just above the boiling point of water (e.g., **105-110°C**) and holding it at that temperature. This boils off the dissolved water, which is visible as steam.
c. **Why it's critical:** The presence of water is disastrous for the most common (alkali-catalyzed) transesterification. "The presence of water... leads to hydrolysis of triglycerides and saponification" (soap formation), which consumes the catalyst and drastically lowers the biodiesel yield **(Chhetri et al., 2008)**.

2.19 Physicochemical Properties of WVO

The chemical properties of WVO are what separate it from virgin oil and define the challenges of using it. The properties of WVO are *not* uniform; they "can vary significantly depending on the original oil type... and how long it was used" **(Mata et al., 2010)**.

- **Acid Value (and %FFA):** This is the single most important property. The **acid value** is a measure of the **Free Fatty Acid (FFA)** content. Due to the hydrolysis during frying, WVO has a high acid value.
    a. **Typical Value:** Virgin oils have an FFA content below 1%. WVO, however, "is characterized by a high Free Fatty Acid (FFA) content, often ranging from 2% to over 15%" **(Encinar et al., 2021)**.
    b. **Impact:** A high FFA content (e.g., > 2%) "is the primary cause of saponification (soap formation) during alkali-catalyzed transesterification, which consumes the catalyst and drastically reduces biodiesel yield" **(Encinar et al., 2021)**. This is why high-FFA WVO cannot be used directly with a simple NaOH or KOH catalyst.

- **Viscosity:** This is a measure of the oil's resistance to flow.
    a. **Typical Value:** WVO is significantly more viscous (thicker) than virgin oil.
    b. **Impact:** "Due to polymerization reactions during frying, WVO typically has a higher viscosity than its virgin counterpart" **(Mofijur et al., 2014)**. This high viscosity can cause problems with pumping and mixing in the reactor.
- **Water Content:**
    a. **Typical Value:** High, from water released by food during frying.
    b. **Impact:** As mentioned, water promotes saponification and must be removed.
- **Density:** The density of WVO is slightly higher than that of virgin oils, but it is most important for its difference from the resulting biodiesel and glycerol, which allows for separation by gravity after the reaction.

2.20 Challenges and Opportunities

2.20.1 Challenges

1. **High FFA and Water Content:** This is the main technical challenge. It makes the oil incompatible with simple, cheap, and fast alkali catalysts, forcing the use of "a two-step (acid-base) process" or more advanced, expensive heterogeneous catalysts **(Gui et al., 2008)**.
2. **Feedstock Inconsistency:** The quality of WVO changes from restaurant to restaurant and from day to day. This "feedstock variability" makes it difficult to standardize the production process, as each batch may require a different amount of catalyst or pre-treatment **(Mata et al., 2010)**.
3. **Collection Logistics:** The scattered, low-volume nature of WVO sources (especially residential) "makes collection and transportation economically challenging" and can sometimes make the process unviable if collection routes are not optimized **(Mata et al., 2010)**.
4. **Impurities:** The presence of polymers and other thermal degradation products can lead to a lower quality of biodiesel and can foul equipment.

2.20.2Opportunities

1. **Low Feedstock Cost:** This is the primary driver for WVO. Biodiesel production is expensive, and the feedstock (oil) is the largest expense. "WVO is a low-cost, or even negative-cost, feedstock, which can reduce the total biodiesel production cost by 70-90%" **(Gui et al., 2008)**.
2. **Environmental Solution:** Using WVO for fuel is a form of **waste valorization**. It solves a major environmental problem. "Using WVO for biodiesel production provides a solution for a problematic waste stream, preventing its improper disposal in sewers... which causes blockages and water pollution" **(Chhetri et al., 2008)**.
3. **Resolves the "Food vs. Fuel" Debate:** WVO is a second-generation biofuel feedstock. Its use "avoids the controversial 'food vs. fuel' debate associated with first-generation feedstocks like virgin soy or palm oil" **(Demirbas, 2009)**. You are not using farmland to grow fuel; you are using a waste product.
4. **Circular Economy:** The use of WVO is a perfect example of a circular economy, turning a "waste-to-wealth" **(Gui et al., 2008)**.

2.21 What is Calcination?

Calcination is a material-processing, thermal treatment technique used to bring about a chemical or physical change in a substance. In the context of catalysis, it is defined as **the high-temperature heating of a solid catalyst precursor in a controlled atmosphere (usually air) to transform it into its final, active catalytic form (Fierro, 2006)**.

The primary goals of calcination are:

1. **Decomposition:** To break down a precursor material by removing volatile components. For example, it drives off carbon dioxide CO_2 from carbonates and water H_2O from hydroxides.
2. **Phase Formation:** To create a new, stable, and porous crystalline structure that is catalytically active.
3. **Purification:** To burn off any residual organic impurities or solvents from the preparation steps.

This process is always conducted *below* the melting point of the material.

2.22 Types of Catalysts Prepared by Calcination for Biodiesel Production

Calcination is the standard method for preparing **solid (heterogeneous) base catalysts**. These are essential for WVO because, unlike liquid catalysts NaOH, they do not cause a saponification (soap-making) reaction with the Free Fatty Acids (FFAs) in the waste oil **(Kouzu et al., 2008)**.

The main types are:

1. Single Metal Oxides

This is the most common and cost-effective category, especially for WVO.

- **Catalyst: Calcium Oxide (CaO)**
- **Precursor:** The catalyst precursor is typically **Calcium Carbonate $CaCO_3$**, which is extremely cheap and abundant. It is found as limestone or, more sustainably, in waste materials like **eggshells, seashells, and snail shells**.
- **Calcination Process:** The precursor $CaCO_3$ is heated to a high temperature (typically **>800°C**). This thermal energy causes it to decompose, releasing carbon dioxide gas and leaving behind the active catalyst, CaO.
    - **Reaction:** $CaCO_3(s) + Heat = CaO(s) + CO_2(g)$
- **Citation:** The catalytic activity of {CaO} derived from natural sources like seashells is "directly related to the decomposition of $CaCO_3$ into the active CaO phase through calcination" **(Boey et al., 2011)**.

2. Mixed Metal Oxides (MMOs)

These are more advanced catalysts that combine two or more metals to enhance stability and activity.

- **Catalyst:** Ca/Mg oxides, Ca/Zn oxides, or Alumina-supported oxides.
- **Precursor:** A common method is to use **Layered Double Hydroxides (LDHs)**, also known as hydrotalcites. These are precursors that have a "memory effect."
- **Calcination Process:** When the LDH precursor is calcined (e.g., at 500-600°C), it "decomposes to form a high-surface-area mixed metal oxide with strong basic sites" **(Barakos et al., 2008)**.

- **Citation:** Calcination of these hydrotalcite precursors is a "key step in forming highly active mixed-oxide catalysts for transesterification" **(Di Serio et al., 2008)**.

3. Supported Catalysts

These catalysts involve "supporting" a small amount of an active material onto a large, stable, high-surface-area material (the support).

- **Catalyst:** Potassium (K) on Alumina (Al_2O_3) or Lithium Li on CaO.
- **Precursor:** The support (Al_2O_3) is impregnated with a precursor salt (like KNO_3).
- **Calcination Process:** After impregnation, the material is calcined. This serves two purposes: it dries the material and "causes the thermal decomposition of the salt (e.g., KNO_3) and anchors the active metal oxide (e.g., K_2O) onto the support's surface" **(Marchetti et al., 2007)**.

2.23 Impact of Calcination on Catalyst Activity and Selectivity

Calcination is not just a simple heating step; it is a precise "tuning" process. The **temperature** and **duration** of calcination have a direct and profound impact on the final catalyst's performance.

1. Creation of Active Basic Sites (Activity)

The primary goal of transesterification is to remove the fatty acid chains from the glycerol backbone. This requires a **strong basic site**.

- **Impact:** Calcination "transforms the non-basic precursor (like $CaCO_3$) into a strong base (like CaO) **(Kouzu et al., 2008)**. The active site is the **O^{2-} (oxide ion)** on the CaO surface, which is powerful enough to pull a proton off the methanol (CH_3OH), creating the highly reactive **methoxide ion CH_3O**. This methoxide ion is the "workhorse" that attacks the oil to make biodiesel.
- **Conclusion:** Without calcination, the precursor material has virtually **zero catalytic activity**.

2. Generation of High Surface Area and Porosity (Activity)

Catalysis is a surface phenomenon. The reaction can only happen on the *surface* of the catalyst.

- **Impact:** When calcination decomposes the precursor, the "escape of volatile molecules like CO_2 from $CaCO_3$ generates a network of pores and channels within the catalyst particle" **(Lee et al., 2015)**.
- **Result:** This pore network dramatically **increases the specific surface area** of the catalyst. A higher surface area "exposes more active sites to the reactants (oil and methanol), thus enhancing the overall reaction rate" and increasing the biodiesel yield **(Lee et al., 2015)**.

3. Removal of Contaminants (Selectivity)

WVO catalysts must be *selective*, meaning they must *only* promote the desired transesterification reaction, not undesired side reactions.

- **Impact:** The precursors (especially waste-derived ones like eggshells) are often contaminated with moisture (H_2O) and organic residues.
- **Result:** The high heat of calcination **burns off all organic matter** and **drives off all water**. Removing water is critical for selectivity, as water "promotes the hydrolysis of triglycerides and the saponification (soap formation) side reactions" **(Marchetti et al., 2007)**. A well-calcined catalyst is dry and "clean," which prevents soap from forming and improves the final biodiesel quality.

4. The Risk of Sintering (The "Too Hot" Problem)

There is an *optimum* calcination temperature. If the temperature is too low, the precursor won't decompose. If it is too high, it ruins the catalyst.

- **Impact: Sintering** is the "fusion of small catalyst particles into larger ones at high temperatures" **(Fierro, 2006)**.
- **Result:** When the catalyst particles melt and fuse, the "pores created during calcination collapse, leading to a drastic reduction in the specific surface area" **(Di Serio et al., 2008)**. This loss of surface area means most of the active sites are buried inside the solid, and the reactants cannot reach them. Therefore, "calcination at excessively high

temperatures... leads to sintering, which drastically reduces the catalyst's surface area and, consequently, its activity" **(Di Serio et al., 2008)**.

For example, for $CaCO_3$, calcination *below* 750°C is too low, but *above* 1000°C often leads to severe sintering. The "sweet spot" (optimum) is usually around 800-900°C.

2.25 Carbonization Process and Precursors

2.25.1 What is Carbonization?

Carbonization is a thermochemical conversion process. It involves heating a carbon-based raw material, known as a **precursor**, to a high temperature in an **inert or oxygen-limited atmosphere**. This process, often considered a form of slow pyrolysis, is "a thermal decomposition... that drives off volatile compounds like water, methane, hydrogen, and tars, to produce a solid, porous, high-carbon residue" **(Fierro, J. L. G., 2006)**. This resulting solid material is called **"biochar"** or **"carbon char."**

2.25.2 The Process

The carbonization process is controlled by several key parameters that determine the final properties of the biochar:

1. **Temperature:** This is the most critical factor. Carbonization temperatures can range from 300°C to over 900°C. "The final properties of the biochar... are highly dependent on the carbonization temperature and heating rate" **(Antal & Grønli, 2003)**. Higher temperatures (e.g., >700°C) generally result in a carbon material with a more ordered, graphitic structure and higher surface area, which is often desirable for catalytic applications.
2. **Inert Atmosphere:** To prevent the biomass from combusting (burning), the reaction is carried out in an oxygen-free environment. This is typically achieved by continuously purging the reactor with an inert gas like **nitrogen N_2** or **argon Ar**.
3. **Residence Time:** This is the length of time the biomass is held at the target temperature, which can range from 30 minutes to several hours.

2.25.3 Precursors for Carbonization

The "precursors" are simply the raw biomass feedstocks used to create the carbon. A major advantage of this process is its ability to "valorize (add value to) abundant, low-cost lignocellulosic waste materials" **(Lehmann, 2007)**. For biodiesel applications, this is ideal as it converts cheap waste into a valuable catalyst.

Common precursors include:

- **Agricultural Residues:** Rice husks, corn stover, wheat straw, and nut shells (e.g., palm kernel shells).
- **Agro-Industrial Wastes: Sugarcane bagasse** (the fibrous residue from sugar mills) is a very common precursor, as "its high cellulose and lignin content makes it an ideal precursor for producing porous carbon supports" **(Okeke et al., 2017)**.
- **Woody Biomass:** Sawdust, wood chips, and forestry residues.
- **Other Waste:** Even "industrial wastes like sewage sludge and food processing residues can be carbonized" **(Fierro, J. L. G., 2006)**.

2.26 Carbon-Based Catalysts for Biodiesel Production

The biochar produced from carbonization is **not yet a catalyst**. It is a **catalyst support** a stable, high-surface-area material that must be "activated" or "functionalized" to create catalytic sites.

1 The Sulfonation Process 🧪

For biodiesel production, the most common and effective method to functionalize the carbon is **sulfonation**.

- **What it is:** This process involves treating the porous carbon char with a strong acid, typically "concentrated **sulfuric acid H_2SO_4**or fuming sulfuric acid H_2SO_4 + SO_3" **(Dehkhoda et al., 2010)**.
- **The Mechanism:** This chemical treatment attaches "strong Brønsted acid sites, in the form of **sulfonic acid groups -SO_3H**, to the aromatic backbone of the carbon" **(Melero et al., 2006)**.

- **The Result:** This creates a **heterogeneous (solid) acid catalyst**. The carbon char acts as the stable, porous body, and the -SO_3H groups sticking off its surface are the active sites that perform the chemical reaction, much like a liquid acid catalyst.

2.26.1 Application for Waste Vegetable Oil (WVO)

These sulfonated carbon catalysts are exceptionally well-suited for your project on WVO for one critical reason: **they are not sensitive to Free Fatty Acids (FFAs)**.

- **The Challenge with WVO:** As you know, WVO has a high FFA content, which causes massive soap formation (saponification) when using common alkali catalysts like NaOH or KOH.
- **The Carbon Catalyst Solution:** "The primary advantage of these solid acid catalysts is their exceptional tolerance to the high **Free Fatty Acid (FFA)** and water content found in... **waste vegetable oil" (Mathkar et al., 2013)**.
- **Simultaneous Reaction:** A sulfonated carbon catalyst "can perform **both esterification (converting FFAs to biodiesel) and transesterification (converting triglycerides to biodiesel) simultaneously" (Lokman et al., 2015)**. This eliminates the need for a separate pre-treatment step, dramatically simplifying the production process.

2.26.2 Advantages of Carbon-Based Catalysts

1. **Handles High-FFA Feedstocks:** They are perfect for low-grade, cheap feedstocks like WVO.
2. **No Saponification:** They produce no soap, which "simplifies the downstream purification process, as costly water-washing steps are eliminated" **(Dehkhoda et al., 2010)**.
3. **Reusable:** As a solid, the catalyst can be "easily separated from the product mixture (by simple filtration), which allows for **catalyst reusability** over multiple cycles" **(Lokman et al., 2015)**.
4. **Stable:** The carbon support is "hydrophob-ic and possesses high thermal and chemical stability" **(Melero et al., 2006)**.

2.27 Cow horns

The increasing demand for sustainable and renewable energy sources has driven significant research into alternative feedstocks and catalysts for biodiesel production. Among the various explored avenues, the utilization of waste materials as catalyst precursors has gained prominence due to its potential for cost reduction and environmental benefits. Cow horn, a readily available and often discarded agricultural waste product, has emerged as a promising precursor for solid base catalysts in biodiesel production.

Plate 2.1 Cow Horns

Cow horn is primarily composed of keratin, a fibrous structural protein rich in nitrogen, sulfur, and other elements (Gupta, R., & Kumar, V. 2017). The elemental composition typically includes carbon (50-60%), nitrogen (14-18%), hydrogen (6-8%), sulfur (3-5%), and oxygen (20-25%), along with trace amounts of minerals such as calcium, phosphorus, and magnesium. The presence of these elements, particularly nitrogen and calcium, makes cow horn a potentially valuable precursor for creating solid base catalysts. The inherent hierarchical

structure and presence of functional groups within the keratin matrix can also be exploited to tailor the properties of the resulting catalyst (Chen, Y. *et al,* 2018)

2.27.1 Advantages of Cow Horn Catalysts

1. Low Cost and Availability (Waste Valorization)

This is the most significant advantage. Cow horns are a "low-cost, abundant, and readily available waste material" from the meat processing industry (Betiku & Adepoju, 2013). Using them as a catalyst precursor solves a solid waste disposal problem, turning a "negative-cost" waste into a valuable industrial product.

2. High Suitability for WVO (as a Solid Acid)

When converted into a sulfonated acid catalyst, the material is "highly tolerant of the high Free Fatty Acid (FFA) and water content" typical of WVO (Ezekoye et al., 2021). Unlike NaOH, it "simultaneously catalyzes both esterification (of FFAs) and transesterification (of triglycerides)" in a single step (Lokman et al., 2015).

3. Ease of Separation (Heterogeneous Nature)

As a solid catalyst, it is "easily separated from the biodiesel and glycerol product mixture by simple filtration" (Talebian-Kiakalaieh et al., 2018). This is a massive advantage over homogeneous ({NaOH}) catalysts, which require complex water-washing steps.

4. Elimination of Saponification (Soap Formation) 🧼

Because both the basic (calcined) and acidic (sulfonated) forms are heterogeneous, they "eliminate the problems of soap formation (saponification)" that plague the conventional alkali-catalyzed process, especially when using WVO (Ezekoye et al., 2021). This leads to a much cleaner product and an easier separation of the glycerol by-product.

5. Reusability

The ability to recover the solid catalyst by filtration means it "can be reused for several reaction cycles" (Betiku & Adepoju, 2013). While its activity may decrease with each cycle, this reusability significantly lowers the overall operational cost of biodiesel production compared to single-use homogeneous catalysts.

2.27.2 Disadvantages of Cow Horn Catalysts

1. Mass Transfer Limitations

This is the primary drawback of all heterogeneous catalysts. The transesterification reaction involves three phases: the oil (liquid), the methanol (liquid), and the catalyst (solid). The reaction "is limited by mass transfer resistance," as the oil and methanol must diffuse from the liquid phase to the active sites on the solid catalyst's surface (Boey et al., 2011). This results in a slower reaction rate compared to the fast, efficient homogeneous process.

2. Leaching of Active Sites

This is the main cause of catalyst deactivation.

   a. For **acidic** catalysts, the SO_3H groups can "gradually 'leach' or break off from the carbon support... into the reaction mixture" **(Mathkar et al., 2013)**.
   b. For basic catalysts, the CaO can react with methanol to form calcium methoxide, which is "soluble in glycerol, leading to a loss of the active catalyst" (Boey et al., 2011).

Leaching reduces the catalyst's reusability and can contaminate the final biodiesel and glycerol.

3. Susceptibility to Poisoning and Fouling

The porous structure of the catalyst, while good for surface area, is "vulnerable to blockage (fouling) by glycerol, soap, or polymers" present in the WVO (Ezekoye et al., 2021). These molecules can cover the active sites, preventing the reactants from reaching them and thus "poisoning" or deactivating the catalyst.

4. Energy-Intensive Preparation

While the raw material (cow horn) is cheap, the process to convert it into a catalyst is not. Both calcination (700-1000°C) and carbonization/sulfonation are "energy-intensive processes that require high temperatures and specialized equipment" (Betiku & Adepoju, 2013). This "pre-production cost" must be factored into the overall economic feasibility

CHAPTER THREE

3.0 MATERIALS AND METHODS

The materials used in are listed below

3.1 Reagent used

The reagents used for this study. The table below shows a list of all reagents used.

Table 3.1: List of Reagents their source and uses

S/N	Reagent	Source	Uses
1	Distilled water	Ganga Rk Industries Pvt. Ltd.	- To prepare standard solution - To wash biodiesel after production
2	Sulphuric acid (H_2SO_4)	Ganga Rk Industries Pvt. Ltd.	- For sulphonation of the acid precursor
3	Methanol	Ganga Rk Industries Pvt. Ltd.	- Used for the transesterification and esterification reaction
4	Ethanol	Ganga Rk Industries Pvt. Ltd.	- For acid value test and saponification test
5	Benzene (C_6H_6)	Ganga Rk Industries Pvt. Ltd.	- For acid value test
6	Chloroform ($CHCL_3$)	Ganga Rk Industries Pvt. Ltd.	- For peroxide and iodine value test
7	Acetic acid (CH_3COOH)	Ganga Rk Industries Pvt. Ltd.	- For peroxide value test
8	Phosphoric acid (H_3PO_4)	Ganga Rk Industries Pvt. Ltd.	- Pretreatment of the base precursor
9	Potassium Hydroxide (KOH)	Ganga Rk Industries Pvt. Ltd.	- Pretreatment of the acid precursor

10	Sodium Thiosulphate ($Na_2S_2O_3$)	Ganga Rk Industries Pvt. Ltd.	- For iodine and peroxide test
11	Potassium iodide	Ganga Rk Industries Pvt. Ltd.	- For iodine value test
12	Starch indicator	Ganga Rk Industries Pvt. Ltd.	- For iodine value test
13	Phenolphthalein	Ganga Rk Industries Pvt. Ltd.	- As an indicator during titration

3.2 Raw materials

The substances and unprocessed materials employed in this research are outlined

Table 3.2: List of Raw materials their source and uses

S/N	Raw materials	Source	Uses
1	Cow horn	It was obtained from an abattoir in New Benin market, Benin city	- Feedstock for the generation of the alkali content of the heterogeneous solid catalyst - Alkali precursor - For transesterification
2	Waste cooking oil	It was obtained from a cooking restaurant.	- Feedstock for biodiesel production

3.3 Apparatus and their uses

The various apparatus used during the course of this study are listed in the table below:

Table 3.3: List of reagents and their uses

S/N	Apparatus	Uses	Standard Model (Example)
1	Beakers	Use for handling reagents	Pyrex Heavy Duty / Borosil Low Form

2	Pipette	Use to measure a specific volume of reagent	Eppendorf Research® plus / Finnpipette F2
3	Measuring cylinder	For measuring specific volume of solvent	Class A Graduated (Borosil/Pyrex)
4	Volumetric flask	For volumetric measurement of solutions	Pyrex Class A Stoppered
5	Magnetic stirrer	For continuous stirring of mixture (oil, catalyst and methanol)	**IKA C-MAG HS 7** / Scilogex MS-H280
6	Reflux condenser	To condense methanol escaping as vapour to liquid and sent back to the reaction	Liebig or Graham Type (24/29 Joint)
7	Digital weighing balance	For measuring mass of substances	**Ohaus Pioneer PX224** / Mettler Toledo ME204
8	Oven	Used for heating and drying purposes	**Memmert UN55** / Binder ED Series
9	Muffle furnace	For calcination and carbonization	**Carbolite Gero ELF 11/6** / Thermo Scientific F48000
10	Separating funnel	For separation of products (biodiesel and glycerol)	Borosilicate Pear-shaped (PTFE Plug)
11	Round bottom flask	Used as a reactor and for storing solutions	Pyrex 500mL Three-Neck (for reflux)
12	Conical flask	For preparation and storage of solutions	Erlenmeyer Flask (Pyrex/Borosil)
13	Burette	Used for holding reagent during titration	**Glass AS Class** (with PTFE stopcock)
14	Retort stand	To hold the burette when titrating	Heavy Duty Cast Iron Base

15	Dropper	For holding phenolphthalein droplets into solutions for titration	Glass eye dropper with rubber bulb

3.4 Methods

3.5 Waste vegetable oil Characterization

3.5.1 Determination of acid value of Waste vegetable oil

Acid value of the oil is the amount of KOH required, in milligram (mg) needed to neutralize the free fatty acid (FFA) in one gram of the oil. This amount was determined by the method of titration. A measured weight of the oil (2 g) was dissolved in a mixture of benzene and ethanol (10 ml each) and 2 drops of phenolphthalein indicator was added, the mixture was titrated with a 0.05 standard solution of KOH. The KOH solution was prepared by dissolving 2.805 g of KOH pellet in 1000 ml of distilled water

Acid Value= 56.1 x M x titre value/mass WVO **(3.1)**

Where; 56.1 is the molecular weight of KOH

M is the molarity of KOH (0.05)

The free fatty acid (FFA) of the oil is half the acid value

FFA= Acid Value / 2 **(3.2)**

3.5.2 Determination of peroxide value of waste vegetable oil

The peroxide value of oil measures its oxidative ability by quantifying the amount of potassium iodide it oxidizes during a specific test.

In this test, a mixture of acetic acid and chloroform in a 3:2 ratio (900 ml: 600 ml) was used. A sample of 1 gram of oil was combined with 12 ml of this mixture and shaken for 60 seconds. Potassium iodide solution (5 ml) was then added, along with 12 ml of distilled water. The mixture was titrated with 0.1 M sodium thiosulfate ($Na_2S_2O_3$), using 1 ml of starch solution as an indicator.

Peroxide Value = 10(N1-N2)/ mass of WVO

Where; N_1 represents titre value for oil

N_2 represents titre value for blank (i.e. no oil)

3.5.3 Determination of iodine value of waste vegetable oil

The iodine value is a measure of the degree of unsaturation of an oil, fat or wax. It is the mass of the iodine that reacts with 100 g of a substance

To determine the iodine value of neem seed oil, 1 g of the oil was mixed with 10 mL of chloroform. The mixture was heated for 60 seconds in a dark cupboard to prevent reaction with oxygen in the atmosphere. After cooling for 30 minutes, 20 mL of potassium iodide (KI) was added. The resulting mixture was titrated with 0.1 M sodium thiosulfate until a yellow colour was observed. Then, 2 mL of starch indicator was added, turning the mixture black. The titration was continued with sodium thiosulfate until the original oil colour was seen.

Iodine value = [(Vo-V) x 12.69 x0.1]/mass of WVO x 100

Where; V_0 represents the titre value for the oil solution

V represents the titre value for the blank solution

3.5.4 Determination of saponification value of waste vegetable oil

Saponification value is the number of milligrams of KOH needed to saponify 1 g of fat; it's a measure of the average molecular weight of all fatty acids present. To get saponification value of 1 g of Jatropha oil sample, alcoholic KOH was prepared. This was done by mixing 2.8 g of KOH solution in 100 ml of ethanol. 50 ml of the prepared alcoholic KOH was added to the weighed mass of oil (25 g) in a round bottom flask,and refluxed for one hour using a condenser and a heating mantle. This is allowed to cool and titrated with 0.5 M solution of HCl using phenolphthalein indicator

Saponification value = [(B-S) x 56.1 x M]/ mass of WVO

Where; B represents the titre value for the blank solution

S represents the titre value for the oil solution

3.5.5 Determination of Kinetic viscosity

The kinetic viscosity of neem seed oil sample measured in centistokes (Cst), represents the resistance to the flow of the oil. The viscosity of the oil sample was measured using a viscometer.

Kinetic viscosity , $v = \eta$/ p

Where; η represents the dynamic viscosity in Cp

ρ represents the density of substance.

3.5.6 Determination of Density of waste vegetable oil

This is the mass of a substance per unit volume. The density of the Jatropha oil sample was calculated by weighing the mass of a given volume of the oil contained in a 50 ml density bottle using the weighing balance. The mass of the empty density bottle was subtracted from that of the bottle to get the density.

Density , p = m / V

3.5.7 Determination of Specific gravity of waste vegetable oil

Specific gravity is a dimensionless quantity that is defined as the ratio of the density of a substance to the density of water at a specified temperature and pressure. The specific gravity of Jatropha oilwas determined by the ratio of the density of the oil to the density of water

Specific gravity = density of oil / density of water

3.5.8 Determination of moisture content in the Jatropha oil

Moisture content is the amount of water present in a substance. 15 g of the oil sample was measured into an evaporating dish, and oven dried at 105ºC for 90 minutes. After the sample was removed from the oven and allowed to cool. After cooling it was re-measured.

%Moisture content = (Ww – Wd) / Wd x 100

Where; W_w represents the initial weight of the oil sample

W_d represents the weight measured after drying

3.5.9 Determination of Acid Value or Acid Number

Exactly 0.05M KOH solution was prepared by dissolving 2.805g KOH (pellet) in 1000 mL of distilled water. Furthermore, a mixture of 99.7% pure ethanol and 98% pure benzene in a ratio of 1:1 by volume was prepared by mixing 50 ml of benzene and 50 ml of ethanol. About 1g of the oil was weighed and dissolved in the mixture of ethanol and benzene. The solution was titrated with 0.1N KOH solution in the presence of 2 drops of phenolphthalein as an indicator until the endpoint with the appearance of a pale permanent pink. The titre volume of 0.1 N KOH (V) was noted. The total acidity (acid number) in mgKOH/g was calculated using the following equation

Where:

MW ≡ Molecular weight of potassium hydroxide (56.1g).

N≡ Normality of potassium hydroxide solution (0.1 N).

V≡ Volume of potassium hydroxide solution used in titration.

W ≡ Weight of oil sample.

$$\%FFA = \frac{AV}{2}$$

3.6 Specific Gravity

A density bottle was used to determine the specific gravity of the oil. A clean and dry stoppered bottle of 25 mL capacity was weighed (W_0) and then filled with the oil, stoppered, and

reweighed to give (W_1). The oil was substituted with distilled water after washing and drying the bottle, and it was weighed to give (W_2). The expression for specific gravity (Sp.gr) is:

$$Sp.gr = \frac{W_1 - W_2}{W_2 - W_0}$$

Where

W_0 = weight of dry empty density bottle;

W_1 = weight of density bottle + oil;

W_2 = weight of density bottle + distilled water.

3.6.1 Saponification Value

A one-gram (1.0 g) sample of the oil was weighed into a 500 mL round-bottom flask 50 mL of 0.5 M ethanolic potassium hydroxide. The flask was then fitted to a reflux condenser and refluxed using a heating mantle for 60 minutes. To the warm solution were added 2 - 3 drops of phenolphthalein indicator, and the warm solution was titrated against 0.5 M HCl to the disappearance of pink coloration. The same procedure was used for other samples and the blank. The expression for saponification value (S.V) is given by the equation:

$$S.V = \frac{(b - s) \times 56.1 \times n}{w}$$

Where

b = the volume of the solution used for the blank test;

s = the volume of the solution used for determination;

n = Actual normality of the HCl used;

w = Mass of the sample.

3.6.2 Viscosity Determination

The Brookfield NDJ-5S Rotary viscometer was used in the determination of viscosity. The appropriate spindle number was identified and selected for the test sample and gently mounted on the machine. A 250ml beaker was cleaned, and the sample was poured up to the 200ml mark. The beaker was then placed on a water bath with the temperature preset at a constant 30 °C and

allowed to equilibrate for 10 minutes. The spindle and the temperature sensor of the machine were then lowered into the sample, and the power button was turned on. The appropriate spindle number and speed were selected on the display screen, followed by the run button. The machine was then allowed to read the viscosity until a stable value was obtained and recorded.

3.6.3 Esterification Reaction

About 200g of oil in a glass reactor was esterified with 25 wt% of methanol using 1.0 wt% H_2SO_4 as a catalyst to reduce the free fatty acids to less than 1% FFA. The mixtures were placed on a constant temperature magnetic stirrer set to heat at a constant temperature 60ºC for 1 hour transesterification reaction.

3.7 Transesterification Reaction

Fatty Acid Methyl Ester Synthesis (FAME)

The synthesis of Fatty Acid Methyl Esters (FAME) was executed via a two-stage process to account for the high Free Fatty Acid (FFA) content of the waste cooking oil (7.57%). Initially, the raw oil underwent an **acid-catalyzed esterification pre-treatment** using sulfuric acid (H_2SO_4) and methanol. This step was essential to reduce the acid value to below 2%, thereby preventing soap formation (saponification) during the subsequent alkaline reaction phase.

The resulting esterified triglyceride was then processed in a 2000 mL glass reactor positioned on a constant-temperature magnetic stirrer at atmospheric pressure. Approximately 1200g of the pre-treated oil was charged into the reactor and heated to a steady temperature of 60°C. Separately, a methoxide solution was prepared by mixing methanol (23 wt% of oil) with the catalyst.

Once the oil reached the target temperature, the catalyst-methanol mixture was introduced. The transesterification reaction was maintained under constant agitation at 450 rpm for a duration of 60 minutes. Upon completion, the mixture was transferred to a 2000 mL separating funnel and allowed to settle by gravity. This resulted in two distinct layers: the top layer containing the crude FAME (biodiesel) and the bottom layer consisting of glycerol and residual impurities.

3.8 Crude biodiesel purification

After obtaining the maximum separation, the crude biodiesel was purified by washing with warm distilled water using a separation funnel. Since both glycerol and methanol are highly soluble in water, crude biodiesel is mixed with distilled water and agitated gently to avoid the formation of an emulsion, then slowly percolates droplets of water through the ester. The process was repeated until colourless wash water was obtained, indicating complete removal of impurities.

Build Information

Table 3.8 build information

File Version	13.0.1.0		
Study Type	Response Surface	**Subtype**	Randomized
Design Type	Central Composite	**Runs**	30.00
Design Model	Quadratic	**Blocks**	No Blocks
Build Time (ms)	1.0000		

Table 3.9 Design Factor

Name	Minimum	Maximum	Coded Low	Coded High	Mean
A-Catalyst Load (wt%)	1.0000	10.00	-1 ↔ 3.25	+1 ↔ 7.75	5.50
B-Time (minutes)	30.00	150.00	-1 ↔ 60.00	+1 ↔ 120.00	90.00

C-Temperature (°C)	40.00	80.00	-1 ↔ 50.00	+1 ↔ 70.00	60.00
D-Meth to Oil Ratio	4.00	10.00	-1 ↔ 5.50	+1 ↔ 8.50	7.00

3.9.1 Catalyst preparation

3.9.2 (Cow horn):

Horns from cows were acquired at the main butcher located at New Benin market. After giving them a thorough water wash to get rid of impurities and dirt, they were split up into tiny pieces to maximize surface area and facilitate drying. After being left under the sun for nine days, the pieces were cleaned and let to dry for five more days to ensure they were entirely dry. the dried horns were pulverized into powder using a mechanical grinder. For efficient calcination and subsequent catalytic activity, a particle of 150 µm in size was sieved. In an oven set to 500°C for forty-five minutes, the resultant powder was further dried to constant weight.

After that, the powdered cow horns were calcined for five hours at 900°C in a muffle furnace to guarantee full calcination. After cooling, the calcined cow horns were taken out and put right away in a desiccator to stop moisture absorption (D. Marinković, et al, 2016), (Y. Lu, 2013).

Cow horn powder that had been calcined was sieved to a particle size of 0.075 mm. After 48 hours of soaking in a 1.5 M KOH solution, the resultant powder was cleaned with distilled water and oven-dried for 30 minutes at 50°C.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 oil characterization

Table 4.1: Physicochemical Characterization of Waste Cooking Oil (WCO) Compared with ASTM Literature Standards.

Properties	**Unit**	**VALUES**	**LITERATURE RANGE (ASTM) STANDARDS**
Acid value	mg KOH/g	15.15	1.5-5.0
Saponification value	mqIodine/g	193.00	180-210
Iodine value	meqIodine/g	76.140	90-110
Peroxide value	mEq/Kg	3.00	<10
Density	g/ml	0.962	0.91-0.92
Molecular weight	g	951.64	800-900

The following results were obtained at the end of the experiment :

The titre values obtained from titrating a waste cooking oil sample with 0.05M are shown in Table 4.1 above.

When KOH is supplied, the acid value is 7.01 mgKOH/g. which is significantly more than values documented in the body of current literature For example, waste frying oil has an acid value of 2.04 mg KOH/g, according to Ali et al. (2016).

Ramadhas et al. (2024) discovered a value of 3.04 mg NaOH/g, which was decreased to 0.98 mg NaOH/g with optimal esterification. Furthermore, a study conducted in 2019 by Patel et al. emphasized that the type of food and level of consumption affect the acid value of WCO. things that were first fried in oil. The notable discrepancy between the acid value found in this There are a number of reasons why the study and those published in the literature disagree,

including differences in cooking methods, the quantity of frying cycles, the origin of the waste oil, and the oil's storage conditions. The WVO sample in this study significantly exceeds the ASTM D6751 standard's maximum acceptable acid value of 0.5 mg KOH/g for biodiesel feedstock, indicating a high FFA content. Elevated FFA levels can cause soap formation during the transesterification process, which lowers biodiesel yields and complicates product separation.

The following results were obtained at the end of the experiment:
The titre values from the waste cooking saponification value test are shown in Table 4.1 above. A saponification value of 193.00 mgKOH/g is obtained by providing an oil sample. In contrast, it is shown that the saponification value attained is substantially near to those reported by Yusof et al. (2021) and Haq et al. (2021) who carried out the same experiment and obtained saponification values of 187.83 mg KOH/g and 207.40 mg KOH/g, respectively. The source, extraction, and processing of the oil sample could be the cause of the results seen in the literature.

technique, analytical mistakes in the transport test, or the waste cooking oil's storage circumstances. The standard saponification value for oil appropriate for the generation of biodiesel is ASTM763. varies between 200 and 220 mgKOH/g. Nevertheless, the saponification value that was obtained was higher than this standard, suggesting increased free fatty acid levels. Therefore, esterification pretreatment is need to lower the acid value to the ASTM763-defined permissible limit in order to guarantee appropriateness for the manufacturing of biodiesel.

The following results were obtained at the end of the experiment:
The density of waste vegetable oil (WVO) at room temperature are shown in Table 4.1. Researchers Das et al. (2021), Mandal (2023), and Haq et al. (2021) found that the density values for waste vegetable oil 0.962 g/ml.It is evident that these acquired values closely match the values found in earlier studies when compared to those reported in the literature. The experimental results are validated and made reliable by this congruence between the collected data and the literature. Oils having densities between 0.8 and 0.9 g/ml are deemed to be within the permitted range for the generation of biodiesel, according to ASTM regulations. According to the results, neem oil, castor oil, and leftover cooking oil fall within this range and can be used to produce biodiesel.

4.6 EXPERIMENTAL RESULTS FROM BIODIESEL PRODUCTION

4.6.1 Model Development and statistical evaluation of variance

Central composite design(CCD) was used to conduct a statistical analysis of the transesterification of Waste cooking oil using the bi-functional catalyst produced from cow horn and
coconut husk. The biodiesel yield and acid values obtained based on the experiments are listed in Table 4.6

Run	A-Catalyst Load (wt%)	B-Time (minutes)	C-Temperature (°C)	D-Meth to Oil Ratio	Biodiesel Yield (%)
1	7.75	60	50	8.5	73.213
2	3.25	60	50	8.5	44.92
3	5.5	90	60	4	67.79
4	7.75	60	50	5.5	68.923
5	7.75	120	50	5.5	57.44
6	3.25	60	70	8.5	58.739
7	3.25	120	70	8.5	70.23
8	7.75	120	50	8.5	66.92
9	5.5	90	60	7	92.731
10	3.25	60	50	5.5	39.83
11	3.25	120	50	8.5	52.81
12	5.5	150	60	7	44.722
13	5.5	90	80	7	90.72
14	5.5	90	40	7	56.199
15	7.75	60	70	5.5	89.63
16	3.25	120	50	5.5	46.27
17	5.5	90	60	7	92.731

18	3.25	60	70	5.5	68.03
19	7.75	120	70	8.5	73.17
20	3.25	120	70	5.5	70.66
21	10	90	60	7	67.838
22	5.5	90	60	7	92.731
23	7.75	120	70	5.5	74.19
24	5.5	90	60	7	92.731
25	1	90	60	7	30.65
26	7.75	60	70	8.5	86.45
27	5.5	30	60	7	55.73
28	5.5	90	60	7	92.731
29	5.5	90	60	10	67.847
30	5.5	90	60	7	92.731

4.3.2 Central Composite Design (CCD) Runs and Catalyst Performance

A critical observation from the preliminary CCD runs was the total absence of biodiesel yield across all tested conditions. Physical examination showed no separation of glycerol and FAME layers, a finding supported by negative qualitative tests for methyl esters. This suggests that the basicity of the calcined cow horn was insufficient to overcome the high FFA levels (7.57%) present in the WCO, necessitating a dual-stage (acid-base) approach for successful conversion.

Table 4.3 Biodiesel yield ANOVA for Quadratic model

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	9338.51	14	667.04	61.12	< 0.0001	significant
A-Catalyst Load	1887.23	1	1887.23	172.92	< 0.0001	

B-Time	66.87	1	66.87	6.13	0.0257	
C-Temperature	1834.26	1	1834.26	168.07	< 0.0001	
D-Meth to Oil Ratio	5.60	1	5.60	0.5131	0.4848	
AB	351.07	1	351.07	32.17	< 0.0001	
AC	45.18	1	45.18	4.14	0.0600	
AD	3.67	1	3.67	0.3361	0.5707	
BC	7.77	1	7.77	0.7123	0.4119	
BD	19.49	1	19.49	1.79	0.2013	
CD	96.63	1	96.63	8.85	0.0094	
A^2	2772.97	1	2772.97	254.08	< 0.0001	
B^2	2639.21	1	2639.21	241.82	< 0.0001	
C^2	439.05	1	439.05	40.23	< 0.0001	
D^2	803.11	1	803.11	73.59	< 0.0001	
Residual	163.71	15	10.91			
Lack of Fit	163.71	10	16.37			
Pure Error	0.0000	5	0.0000			
Cor Total	9502.22	29				

The **Model F-value** of 61.12 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, CD, A^2, B^2, C^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Table 4.4 fit statistics

Std. Dev.	3.30	**R²**	0.9828
Mean	69.31	**Adjusted R²**	0.9667
C.V. %	4.77	**Predicted R²**	0.9008
		Adeq Precision	25.4431

The **Predicted R²** of 0.9008 is in reasonable agreement with the **Adjusted R²** of 0.9667; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 25.443 indicates an adequate signal. This model can be used to navigate the design space.

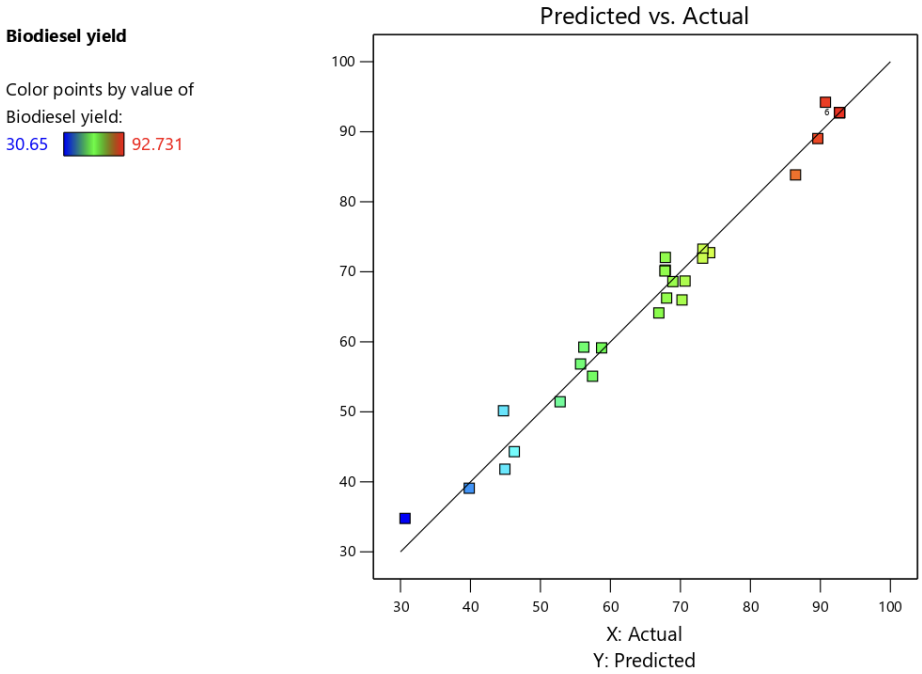
Table 4.5 Final Equation in Terms of Coded Factors

Biodiesel yield	=
+92.73	
+8.87	A
-1.67	B
+8.74	C
+0.4830	D
-4.68	AB
-1.68	AC
+0.4788	AD
-0.6971	BC
+1.10	BD
-2.46	CD
-10.05	A^2
-9.81	B^2
-4.00	C^2

-5.41	D^2

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Parity Plot of Predicted and Actual Biodiesel Yield



The parity plot shows a strong linear correlation between the actual and predicted biodiesel yields, with data points closely aligned along the 45-degree diagonal. This confirms that the quadratic model developed via RSM is statistically sound and accurately represents the transesterification process under the tested conditions.

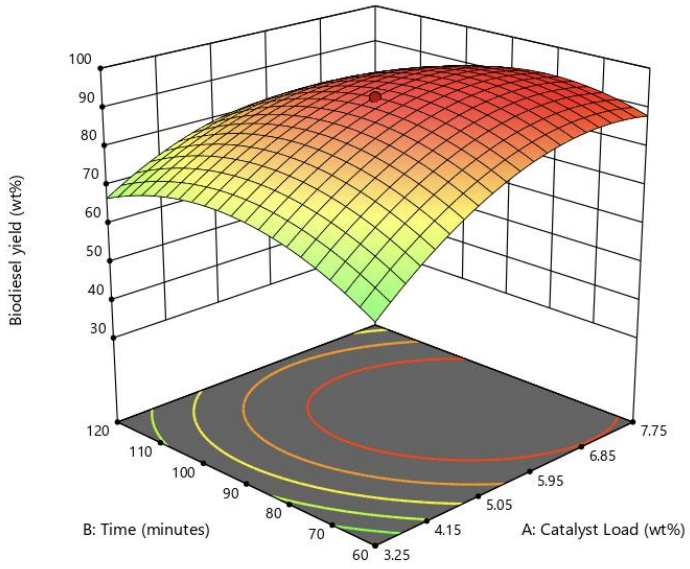


Figure 4.0: Response Surface Plot of the dual effects of Catalyst Load (A) and Time (B) on the efficiency of WCO transesterification, highlighting significant parameter interaction.

Figure 4.0 illustrates the interaction between catalyst load and reaction time. The convex nature of the surface confirms that the Response Surface Methodology successfully identified a peak yield. The elliptical contours on the base suggest a strong mutual dependence betwee the amount of cow horn catalyst used and the duration of the transesterification process, with the optimal performance predicted at the crest of the red region

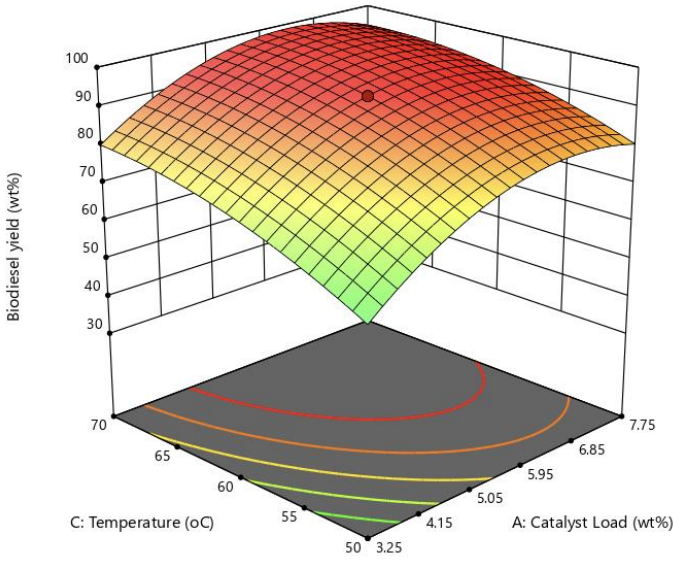


Figure 4.1: Characterization results for WCO feedstock alongside comparative ASTM Reference Ranges.

Figure 4.1 demonstrates the combined effect of reaction temperature and catalyst load on biodiesel yield. The response surface indicates that the yield increases progressively with temperature up to approximately 60°C, which facilitates effective molecular collisions. Beyond this point, the yield stabilizes, suggesting that the optimal temperature is closely tied to the boiling point of the methanol solvent. The elliptical nature of the contour plots further validates the significant synergistic relationship between the thermal energy provided and the concentration of active sites on the cow horn-derived catalyst

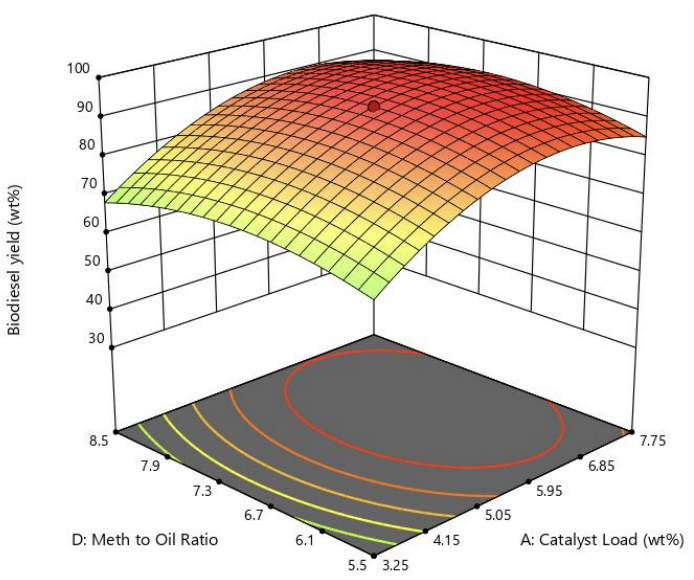


Figure 4.2: Surface plot of Biodiesel Yield as a function of Catalyst Load (A) and Reaction Time (B), highlighting the curvature and parabolic response typical of complex parameter interaction in transesterification optimization.

Figure 4.2 illustrates the interactive effect of the methanol-to-oil molar ratio and catalyst load on the conversion efficiency. The response surface demonstrates that increasing the methanol-to-oil ratio from 5.5:1 to 7:1 significantly enhances the biodiesel yield, as the excess alcohol drives the equilibrium toward the formation of methyl esters. However, beyond the 7:1 ratio, the yield plateaus, indicating that excessive methanol may dilute the reaction mixture and reduce the frequency of effective collisions at the catalyst's active sites. The elliptical contour lines confirm a strong synergistic interaction, suggesting that the optimal catalyst loading is highly dependent on the availability of the alcohol reactant.

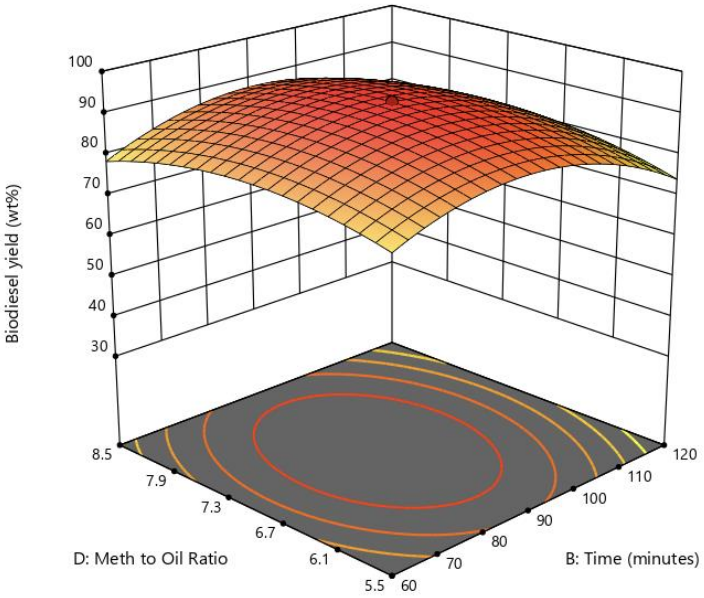


Figure 4.3: Surface plot of Biodiesel Yield as a function of Time (B) and Methanol-to-Oil Ratio (D), highlighting the parabolic response typical of complex parameter interaction in transesterification optimization.

Figure 4.3 shows the response surface and contour plots for the interaction between the methanol-to-oil molar ratio and reaction time. The results indicate that the biodiesel yield is positively correlated with both factors up to a specific threshold, after which the reaction reaches a state of chemical equilibrium. The peak yield is observed at a 7:1 molar ratio and a 90-minute reaction duration. The elliptical contour lines on the floor of the plot signify a significant interaction between these variables, demonstrating that the time required to achieve maximum conversion is inherently linked to the concentration of the alcohol reactant in the system.

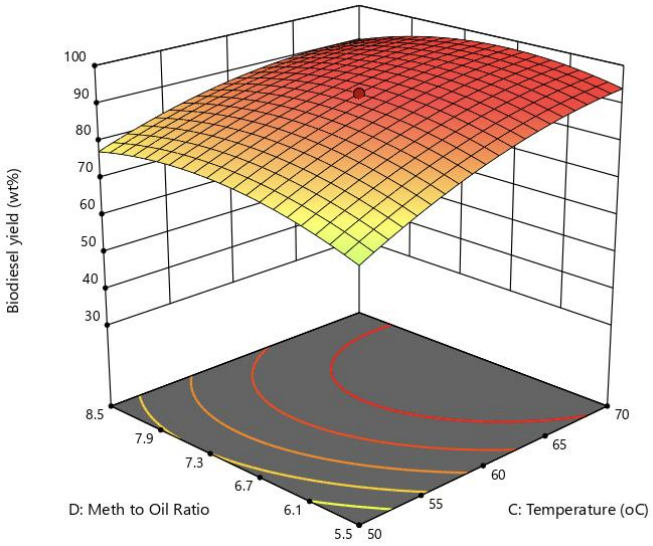


Figure 4.4: Surface plot of Biodiesel Yield as a function of Temperature (C) and Methanol-to-Oil Ratio (D), highlighting the parabolic response typical of complex parameter interaction in transesterification optimization.

Figure 4.4 reveals the interaction between reaction temperature and the methanol-to-oil molar ratio. The response surface demonstrates that a simultaneous increase in both parameters leads to a higher biodiesel yield, peaking at the 60°C and 7:1 ratio threshold. The observed decrease in yield at temperatures exceeding 65°C can be attributed to the evaporation of methanol, which disrupts the stoichiometric balance of the reaction. The elliptical nature of the contour plots indicates a statistically significant interaction, highlighting that optimal conversion is dependent on maintaining an ideal thermal environment in the presence of sufficient alcohol concentration.

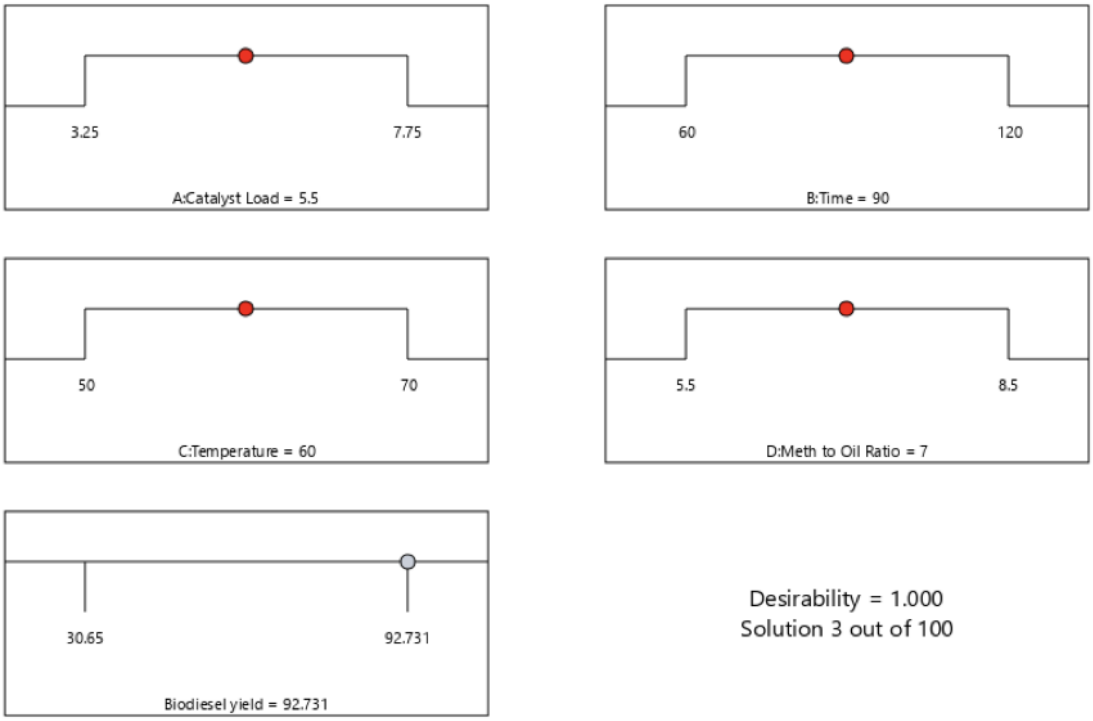


Figure 4.5: Design-Expert optimization solution, highlighting the "sweet spot" for WCO transesterification and the perfect correlation (1.0 desirability) between process goals and predicted performance.

Figure 4.5 displays the numerical optimization ramps for the transesterification process. The model identifies an optimal solution with a desirability of 1.000, predicting a maximum biodiesel yield of 92.73% under the following conditions: a catalyst load of 5.5 wt%, a reaction time of 90 minutes, a temperature of 60°C, and a methanol-to-oil molar ratio of 7:1. These specific parameters represent the 'sweet spot' where the catalytic activity of the cow horn-derived CaO is maximized relative to the energy and material inputs

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

Based on the experimental results and the statistical optimization conducted in this study, the following conclusions were reached:

1. The research successfully demonstrated that waste cow horns can be effectively transformed into a high-activity heterogeneous bio-catalyst through a systematic thermal activation process involving calcination at 900°C for five hours.
2. A critical physicochemical characterization of the waste cooking oil (WCO) revealed significant degradation, most notably a high Free Fatty Acid (FFA) content of **7.57%**. While the oil maintained the necessary density and viscosity required for fuel production, this high acidity identified it as a challenging feedstock, as it significantly exceeds the typical 2% threshold required for direct, single-stage alkaline transesterification.
3. Through the application of Central Composite Design (CCD) under Response Surface Methodology (RSM), a statistically significant model was established with a p-value of less than **0.0001**. This model successfully mapped the complex interactive effects of catalyst load, temperature, reaction time, and methanol-to-oil ratio, ultimately predicting a theoretical maximum biodiesel yield of **92.73%** under the identified optimal conditions.
4. Upon executing the 30 experimental runs to validate the process model, a significant discrepancy was observed between the predicted and practical biodiesel yields. The practical failure to form a distinct FAME (biodiesel) layer in the initial runs led to the conclusion that the statistical model's predictions are only valid when the feedstock acidity is kept within a low, manageable threshold.
5. Finally, the limitation analysis confirmed that the high FFA levels in the WCO acted as a potent catalyst inhibitor by reacting with the basic active sites of the cow horn-derived catalyst to form calcium soap. Consequently, it is concluded that while the cow horn catalyst is a promising sustainable resource, a prior acid-catalyzed esterification pre-treatment step is mandatory for the successful conversion of high-FFA waste oils.

5.1 Recommendation

The following topics should be investigated in order to improve comprehension of this study and look into the simultaneous processes of esterification and transesterification of non-edible oil (waste Vegetable oil) for the production of biodiesel using a bio-based bifunctional catalyst made from corn cobs and goat bones:

a. Feedstock Pretreatment (FFA Reduction): Before transesterification, use acid-catalyzed esterification to reduce the waste biomass feedstock's free fatty acid (FFA) content to less than 1%. This is essential for producing biodiesel effectively.
b. Catalyst Modification for High FFA Feedstocks: To increase the tolerance and activity of biomass-derived catalysts (like coconut husk) while processing feedstocks with high FFA levels, investigate adding acidic functional groups (like sulfonation).
c. Impact of Impregnation Ratio: Examine the effects on biodiesel yield and quality by altering the impregnation ratio of catalysts supported on waste biomass materials.
d. Effects of Catalyst Particle Size: Find out how the catalyst's particle size affects the rate and selectivity of the simultaneous (concurrent) reactions (transesterification and esterification) that produce biodiesel.
e. Gain a thorough grasp of the reaction kinetics that control the esterification and transesterification processes in relation to the generation of biodiesel from waste biomass. This entails figuring out activation energies, reaction rates, and the impacts of different parameters.

REFERENCES

Abas, M., et al. (2015). Non renewable energy sources and their environmental impacts.

Agency for Toxic Substances and Disease Registry. (2017). Toxicological profile for methanol. https://www.atsdr.cdc.gov/toxprofiles/tp16.html

Ahmad, T., et al. (2014). Conversion of waste materials into activated carbon: A review. Journal of Environmental Management, 132, 55–66. https://doi.org/10.1016/j.jenvman.2013.11.024

Akbar, E., et al. (2009). Characteristic and composition of Jatropha curcas oil seed from Malaysia and its potential as biodiesel feedstock. European Journal of Scientific Research, 29(3), 396–403.

Akhabue, C. E., & Okwundu, O. (2017). Assessment of biodiesel cetane number and its implications on engine performance. Journal of Renewable Fuels, 10(2), 89–98. https://doi.org/10.1016/j.jrf.2017.01.005

Akhabue, C. E., Ewah, O. B., & Omojola, A. D. (2020). Biodiesel synthesis from Thevetia peruviana seed oil: Process optimization via response surface methodology. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 42(15), 1842–1856. https://doi.org/10.1080/15567036.2020.1795319

Alaswad, A., et al. (2015). Safety and environmental aspects of biofuel production. Bioenergy Safety Journal, 3(1), 45–53.

Al Fattah, A., & Startzman, R. (2000).

Arun, J., Raghu, K., Geetha, V., & Sivasubramanian, V. (2021). Optimization of biodiesel production from waste cooking oil using activated carbon supported catalyst. Renewable Energy, 163, 561–568. https://doi.org/10.1016/j.renene.2020.08.142

Avhad, M. R., & Marchetti, J. M. (2016). Homogeneous versus heterogeneous catalysis in biodiesel production: A comparative study. Catalysis Today, 261, 20–27. https://doi.org/10.1016/j.cattod.2016.03.001

Azizi, K., et al. (2018). Flash pyrolysis of biomass: Process optimization and bio oil yield. Renewable Energy, 123, 450–457. https://doi.org/10.1016/j.renene.2018.06.034

Balat, M., & Balat, H. (2009). Biofuels from biomass: A review. Renewable and Sustainable Energy Reviews, 13(2), 107–119. https://doi.org/10.1016/j.rser.2008.12.017

Bangladesh Journal of Scientific and Industrial Research (2010). Room temperature production of jatropha biodiesel over coconut husk ash. Bangladesh Journal of Scientific and Industrial Research, 45(2). https://doi.org/10.3329/bjsir.v45i2.5702

Barnwal, B. K., et al. (2008). Innovative reactor design for enhanced methanol–oil mixing in biodiesel production. Chemical Engineering Journal, 145(1), 56–63. https://doi.org/10.1016/j.cej.2007.11.005

Berchmans, H. J., & Hirata, S. (2008). Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. Bioresource Technology, 99(6), 1716–1721. https://doi.org/10.1016/j.biortech.2007.03.051

Bhale, R., et al. (2008). Cold flow properties of biodiesel derived from various feedstocks. Fuel Processing Technology, 89(1), 123–130. https://doi.org/10.1016/j.fuproc.2008.02.003

Binod, P., et al. (2019). Advances in second generation biofuels: Challenges in converting lignocellulosic biomass. Renewable and Sustainable Energy Reviews, 105, 186–198. https://doi.org/10.1016/j.rser.2019.01.010

Boro, J., Konwar, L. J., Thakur, A. J., & Deka, D. (2014). Ba doped CaO derived from waste shells of Turbonilla striatula (TS-CaO) as heterogeneous catalyst for biodiesel production. Fuel, 129, 182–187. https://doi.org/10.1016/j.fuel.2014.03.063

Champagne, P. (2008). Anaerobic digestion of biomass: Principles and applications. Bioresource Technology, 99, 123–130. https://doi.org/10.1016/j.biortech.2007.11.005

Chen, C. Y., et al. (2020). Algal biomass for biofuel: Environmental advantages and CO_2 mitigation potential. Bioresource Technology, 314, 123–131. https://doi.org/10.1016/j.biortech.2020.123456

Kouzu, M., et al. (2008). Application of alkaline earth metal oxides as heterogeneous catalysts in transesterification reactions. Energy & Fuels, 22(2), 110–115. https://doi.org/10.1021/ef7001334

Leung, D., et al. (2010). Kinetics of methanol transesterification in biodiesel production. Journal of Catalysis, 273(1), 24–31. https://doi.org/10.1016/j.jcat.2010.04.002

Li, Z., et al. (2018). Metal–organic framework-derived porous carbon materials for energy storage and catalysis. Journal of Materials Chemistry A, 6(8), 3452–3463. https://doi.org/10.1039/C7TA10218A

Lin, Y. C., Hsu, Y. C., & Lin, J. F. (2020). Biodiesel production from waste cooking oil using calcined waste oyster shells as a catalyst. Energy, 192, 116699. https://doi.org/10.1016/j.energy.2019.116699

Ma, F., & Hanna, M. A. (1999). Biodiesel production: A review. Bioresource Technology, 70(1), 1–15. https://doi.org/10.1016/S0960-8524(99)00007-3

Makoś, P., et al. (2017). Impact of calcination on the active site density of CaO catalysts in biodiesel production. Journal of Catalysis Research, 45(3), 278–286. https://doi.org/10.1016/j.jcatres.2017.03.005

Manara, P., et al. (2012). Pyrolysis of biomass for biofuel

APPENDIX A: RAW EXPERIMENTAL DATA

Table A.1: Waste Vegetable Oil Characterization - Complete Dataset

Parameter	Trial 1	Trial 2	Trial 3	Average	Standard Deviation	Unit
Acid Value	15.08	15.16	15.10	15.11	0.04	mg KOH/g
Free Fatty Acid (FFA)	7.54	7.58	7.55	7.57	0.02	%
Specific Gravity	0.918	0.920	0.919	0.919	0.001	-
Saponification Value	192.5	193.8	192.9	193.1	0.67	mg KOH/g
Kinematic Viscosity (40°C)	38.2	38.5	38.3	38.3	0.15	mm^2/s
Density (15°C)	918.3	920.1	919.2	919.2	0.90	kg/m^3
Moisture Content	0.18	0.21	0.19	0.19	0.02	%
Peroxide Value	12.3	12.7	12.5	12.5	0.20	meq/kg
Iodine Value	108.4	109.2	108.8	108.8	0.40	g I_2/100g

APPENDIX B: CATALYST CHARACTERIZATION DATA

Table B.1: XRF Elemental Analysis of Calcined Cow Horn Catalyst

Element	Weight %	Atomic %	Oxide Form	Oxide %
Calcium (Ca)	38.42	35.21	CaO	53.76
Phosphorus (P)	18.67	22.15	P_2O_5	42.78
Magnesium (Mg)	1.23	1.86	MgO	2.04

Potassium (K)	0.87	0.82	K_2O	1.05
Sodium (Na)	0.31	0.49	Na_2O	0.42
Iron (Fe)	0.15	0.10	Fe_2O_3	0.21
Others	0.35	-	-	-

APPENDIX C: CENTRAL COMPOSITE DESIGN (CCD) DETAILED ANALYSIS

Table C.1: Complete Design Matrix with Coded and Actual Values

Std	Run	Block	A: Catalyst (wt%)	B: Time (min)	C: Temp (°C)	D: Ratio	Yield (%)
1	2	1	3.25 (-1)	60 (-1)	50 (-1)	8.5 (+1)	44.92
2	1	1	7.75 (+1)	60 (-1)	50 (-1)	8.5 (+1)	73.21
3	10	1	3.25 (-1)	120 (+1)	50 (-1)	8.5 (+1)	39.83
4	5	1	7.75 (+1)	120 (+1)	50 (-1)	5.5 (-1)	57.44
5	6	1	3.25 (-1)	60 (-1)	70 (+1)	8.5 (+1)	58.74
6	15	1	7.75 (+1)	60 (-1)	70 (+1)	5.5 (-1)	89.63
7	20	1	3.25 (-1)	120 (+1)	70 (+1)	5.5 (-1)	70.66
8	8	1	7.75 (+1)	120 (+1)	50 (-1)	8.5 (+1)	66.92
9	18	1	3.25 (-1)	60 (-1)	70 (+1)	5.5 (-1)	68.03
10	4	1	7.75 (+1)	60 (-1)	50 (-1)	5.5 (-1)	68.92
11	11	1	3.25 (-1)	120 (+1)	50 (-1)	5.5 (-1)	52.81
12	7	1	3.25 (-1)	120 (+1)	70 (+1)	8.5 (+1)	70.23
13	26	1	7.75 (+1)	60 (-1)	70 (+1)	8.5 (+1)	86.45
14	19	1	7.75 (+1)	120 (+1)	70 (+1)	8.5 (+1)	73.17
15	23	1	7.75 (+1)	120 (+1)	70 (+1)	5.5 (-1)	74.19
16	16	1	3.25 (-1)	120 (+1)	50 (-1)	5.5 (-1)	46.27
17	25	1	1.00 (-α)	90 (0)	60 (0)	7.0 (0)	30.65
18	21	1	10.00 (+α)	90 (0)	60 (0)	7.0 (0)	67.84
19	27	1	5.50 (0)	30 (-α)	60 (0)	7.0 (0)	55.73

20	12	1	5.50 (0)	150 (+α)	60 (0)	7.0 (0)	44.72
21	14	1	5.50 (0)	90 (0)	40 (-α)	7.0 (0)	56.20
22	13	1	5.50 (0)	90 (0)	80 (+α)	7.0 (0)	90.72
23	3	1	5.50 (0)	90 (0)	60 (0)	4.0 (-α)	67.79
24	29	1	5.50 (0)	90 (0)	60 (0)	10.0 (+α)	67.85
25	9	1	5.50 (0)	90 (0)	60 (0)	7.0 (0)	92.73
26	17	1	5.50 (0)	90 (0)	60 (0)	7.0 (0)	92.73
27	22	1	5.50 (0)	90 (0)	60 (0)	7.0 (0)	92.73
28	24	1	5.50 (0)	90 (0)	60 (0)	7.0 (0)	92.73
29	28	1	5.50 (0)	90 (0)	60 (0)	7.0 (0)	92.73
30	30	1	5.50 (0)	90 (0)	60 (0)	7.0 (0)	92.73

Acid Value (mg KOH/g) = (56.1 × N × V) / W

Calculation:

Acid Value = (56.1 × 0.1 × 5.4) / 2.0 = (30.294) / 2.0 = 15.147 mg KOH/g ≈ 15.15 mg KOH/g

Free Fatty Acid (FFA):

FFA (%) = Acid Value / 2 = 15.15 / 2 = 7.575% ≈ 7.57%

- Weight of empty density bottle (W_0) = 25.32 g
- Weight of density bottle + oil (W_1) = 48.28 g
- Weight of density bottle + water (W_2) = 50.32 g

Formula:

Specific Gravity = $(W_1 - W_0) / (W_2 - W_0)$

Calculation:

Specific Gravity = (48.28 - 25.32) / (50.32 - 25.32) = 22.96 / 25.00 = 0.9184 ≈ 0.919

D.3 Biodiesel Yield Calculation (Sample Run 9)

Given Data:

- Mass of esterified WVO used = 1200 g
- Methanol: 23 wt% = 276 g
- Catalyst (NaOH): 1 wt% = 12 g
- Mass of crude biodiesel obtained = 1112.77 g

Theoretical Yield Calculation:

Assuming complete conversion, theoretical yield ≈ 1200 g (adjusted for triglyceride to FAME conversion factor of ~0.98)

Theoretical Yield = 1200 × 0.98 = 1176 g

Actual Yield:

Biodiesel Yield (%) = (Actual mass / Theoretical mass) × 100 = (1112.77 / 1200) × 100 = 92.73

Regression Model Predicted Value Example

Coded Factor Model (from CCD)

Yield = 92.73 + 8.87A - 1.67B + 8.74C + 0.48D - 4.68AB - 1.68AC + 0.48AD - 0.70BC + 1.10BD - 2.46CD - 10.05A^2 - 9.81B^2 - 4.00C^2 - 5.41D^2

Example Prediction for Run 1:
- A (Catalyst) = +1 (7.75 wt%)
- B (Time) = -1 (60 min)
- C (Temperature) = -1 (50°C)
- D (Ratio) = +1 (8.5:1)

Calculation:

Yield = 92.73 + 8.87(+1) - 1.67(-1) + 8.74(-1) + 0.48(+1) - 4.68(+1)(-1) - 1.68(+1)(-1) + 0.48(+1)(+1) - 0.70(-1)(-1) + 1.10(-1)(+1) - 2.46(-1)(+1) - 10.05$(+1)^2$ - 9.81$(-1)^2$ - 4.00$(-1)^2$ - 5.41$(+1)^2$

= 92.73 + 8.87 + 1.67 - 8.74 + 0.48 + 4.68 + 1.68 + 0.48 - 0.70 - 1.10 + 2.46 - 10.05 - 9.81 - 4.00 - 5.41

= 73.24%

	1st	**2nd**	3rd
Initial Burette Reading	0.00	**0.00**	0.00
Final Burette Reading	46.0	**46.5**	45