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BIODIESEL SYNTHESIS FROM NEEM SEED OIL USING FISH SCALES AND CABBAGE BACK AS A NOVEL BIFUNCTIONAL CATALYST:

OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY

BY

IDAHOSA MICHAEL ENG1904995

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CERTIFICATION

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

ENGR. PROF. C. E. AKHABUE **DATE**

PROJECT SUPERVISOR

ENGR. PROF. S. E. UWADIA **DATE**

PROJECT COORDINATOR

ENGR. PROF. (MRS) E.T. AKHIHIERO **DATE**

HEAD OF DEPARTMENT

EXTERNAL SUPERVISOR **DATE**

DEDICATION

I dedicate this project work to the Almighty God for his mercy, love, grace, faithfulness, provision and strength given to me to complete this work.

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ABSTRACT

This study explores the synthesis of biodiesel from Neem Seed Oil (NSO) using a novel bifunctional catalyst derived from fish scales and cabbage back. The primary aim was to optimize the simultaneous esterification and trans-esterification processes through Response Surface Methodology (RSM) to enhance biodiesel yield and quality. The research also sought to address the challenges associated with conventional biodiesel production methods, such as high costs, environmental impact, and the need for sustainable catalysts. By utilizing waste materials as catalysts, this study aimed to promote a more eco-friendly and economically viable approach to biodiesel production.

The methodology involved the preparation and characterization of the bifunctional catalyst, which was synthesized from fish scales (basic precursor) and cabbage back (acid precursor). The catalyst was prepared through calcination, carbonization, and impregnation processes. Neem Seed Oil was characterized for its physicochemical properties, including acid value, saponification value, and viscosity, to ensure its suitability as a feedstock. The optimization of biodiesel production was conducted using RSM, with variables such as methanol-to-oil ratio, catalyst loading, reaction temperature, and time being systematically varied. The experimental design included 50 runs, and the resulting products were analyzed for biodiesel yield and quality.

The results indicated that no biodiesel formation occurred under the tested conditions, suggesting potential issues with the catalyst's effectiveness or the reaction parameters. Despite the lack of biodiesel production, the study provided valuable insights into the challenges of using waste-derived catalysts and highlighted the need for further optimization of catalyst preparation and reaction conditions. The characterization of NSO confirmed its potential as a viable feedstock, with properties suitable for biodiesel production. Future research should focus on refining the

catalyst synthesis process, optimizing reaction conditions, and exploring alternative feedstocks to achieve successful biodiesel production using sustainable and cost-effective methods.

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CHAPTER ONE

1.1 RESEARCH BACKGROUND

In view of the fact that fossil fuel consumption is linked to environmental problems and rising global energy demand, additionally, the combustion of fossil fuels has led to increased greenhouse gas emissions, which in turn has caused changes in the climate (Akhabue & Ewah, 2021.; Awogbemi, Inambao, & Onuh, 2020; Thangaraj, Solomon, Muniyandi, Ranganathan, & Lin, 2019). Biodiesel has gained acceptance as a sustainable fuel substitute, it also provides several advantages such as biodegradability, non-toxicity, and significant reduction in greenhouse gas emissions as compared to regular diesel. Diesel's interoperability with the current gasoline distribution system is one of its main benefits. Virgin vegetable oil, animal fats, non-edible oil, and leftover vegetable oil can all be used to make biodiesel. Additionally, the creation of biodiesel from leftover cooking oil cleans the waste stream and produces a useful product.

The concept of biodiesel originated in the mid-19th century, when J. Patrick and E. Duffy completed the first trans-esterification of vegetable oil in 1853. This predates the diesel engine invented by Rudolf Diesel, which was first intended to run on mineral oil but was able to run on peanut oil at the 1900 Paris Exposition. Vegetable oils have been the subject of varying degrees of interest over time, especially in periods of resource scarcity such as World War II.

Biodiesel is a renewable, sustainable, and bio-based substitute for the fossil diesel fuel and is produced primarily from vegetable oil, animal fats, or recycled cooking oils. The typical production process of biodiesel is the trans-esterification of triglycerides with a short-chain alcohol, which can be controlled by a different catalyst. Usually, methanol or ethanol is used as an alcohol and an alkali is the most common catalyst. In this manner, an equilibrium movable chemical reaction takes place, which directly results in both biodiesel as fatty acid alkyl esters and glycerol as one by product.

The main advantage of using heterogeneous catalysts in the production process for biodiesel is their reusability and recover ability. Most of the time, heterogeneous catalysts are solid materials which can be easily withdrawn from reaction mixture after trans-estrification process. This can be done by minimal filtration or centrifugation, hence it significantly decreases the large costs related to catalyst recovery performances. By contrast, homogeneous catalysts (which are soluble in the reaction medium) typically need to be separated via more resource-intensive techniques such as distillation or neutralization — a factor that makes them less suitable for large-scale applications (Knothe et al., 2017).

Heterogeneous catalysts are usually thermally stable than homogeneous ones. This means that their wider stable operating temperatures and condition support them from deactivate. For example, most of heterogeneous catalysts do not have thermostable property; in contrast many homogeneous catalysts can respond at higher temperature which worst treatment for homemade processes. This feature improves biodiesel production as a whole and also more consolidated in the choice of the process roof according to Bansal et al. (2020).

As heterogeneous catalyst provide a high selectivity towards desired products with minimal by-product formation. These catalysts are amenable to a design that could be shaped according to the requirements of different reactions in biodiesel synthesis, e.g. trans-esterification [21]. This selectivity is very important since it helps to increase the biodiesel yield and thus minimize purification stages that would be needed if any byproducts were produced during dehydration (Zhang et al., 2021).

This has a positive impact on the environment as well, for example in using them as heterogeneous catalysts. Because they are sometimes much more abundant materials and could be recycled for use many times, versus homogeneous catalysts that need to be discarded after just a few use. This waste generation reduction can also make heterogeneous systems far less wasteful. Moreover, most of the heterogeneous catalytic processes run under much milder conditions compared to harsher operating conditions in biodiesel production that could result in energy savings and decreased greenhouse gas emissions (Mansir et al., 2022).

There is increasing attention paid to alternative sources of a feedstock as they are competitive in price and are not in the competition with food production. Such sources include microalgae, waste cooking oils, and animal fats. Microalgae are especially promising, as they have a very high content of lipids, and their biomass grows quickly under different conditions.

Research is still concentrated on establishing integrated biorefineries that combine the production of biodiesel with other biofuels or bioproducts, boosting yield efficiency through sophisticated catalytic processes, and optimizing growth conditions for microalgae culture. Furthermore, life cycle analyses are becoming more and more crucial in determining how sustainable various biodiesel manufacturing routes are.

Production Methods

There are several methods employed during the biodiesel production process. Among them are the following:

1. Trans-esterification: the most common method, where the reaction of triglycerides with alcohol takes place, which is catalyzed by either homogeneous or heterogeneous catalysts.

2. Supercritical fluid processing: it is a way of biodiesel production that does not involve catalysts, where in both cases, the produced biodiesel is supercritically filtered by methanol or ethanol.
3. Enzymatic trans-esterification: this method when biodiesel production is catalyzed by enzymes is more environmentally friendly, although is areally slower than chemical processes.
4. Ultrasound-assisted trans-esterification: the use of ultrasonic waves enhances mass transfer during the reaction.

1.2 PROBLEM STATEMENT

Biodiesel production encounters various challenges that can impede its effectiveness, cost-efficiency, and sustainability. These challenges encompass the following aspects:

1. Availability and Cost of Feedstock: The availability of suitable feedstocks, such as vegetable oils, animal fats, or waste oils, poses a significant challenge. High-quality feedstocks can be costly and may compete with food production, raising ethical concerns about food security.

2. Efficiency of the Production Process: Conventional biodiesel production methods often involve trans-esterification processes that necessitate catalysts, typically sodium hydroxide or potassium hydroxide. These processes can be ineffective and produce by-products that complicate purification.

3. Environmental Impact: The environmental footprint of biodiesel production needs to be taken into account, including land use changes for feedstock cultivation, water usage, and emissions associated with the production process.

4. Waste Management: Effectively managing the disposal of by-products from biodiesel production presents additional challenges. Efficient management of these by-products is crucial to minimize environmental impact.

5. Catalyst Development: Developing efficient catalysts that can operate under mild conditions and are derived from sustainable sources remains a challenge in biodiesel production.

1.3 AIM

The aim of this experiment is to synthesize biodiesel from Neem Seed Oil (NSO) using a novel bifunctional catalyst derived from fish scales and cabbage back, and to optimize the simultaneous esterification and trans-esterification processes through Response Surface Methodology (RSM) to enhance biodiesel yield and quality. The study also seeks to address the challenges associated with conventional biodiesel production methods, such as high costs, environmental impact, and the need for sustainable catalysts, by utilizing waste materials as catalysts.

Objectives:

1. Catalyst Development: To prepare and characterize a bifunctional catalyst derived from fish scales (basic precursor) and cabbage back (acid precursor) for biodiesel production.

2. Feedstock Characterization: To analyze the physicochemical properties of Neem Seed Oil (NSO), including acid value, saponification value and density, to ensure its suitability as a feedstock for biodiesel production.

3. Process Optimization: To optimize the simultaneous esterification and trans-esterification processes using Response Surface Methodology (RSM) by varying key parameters such as methanol-to-oil ratio, catalyst loading, reaction temperature, and reaction time.

4. Biodiesel Production: To produce biodiesel from NSO using the synthesized bifunctional catalyst and evaluate the yield and quality of the biodiesel produced.

5. Environmental and Economic Assessment: To assess the environmental and economic viability of using waste-derived catalysts for biodiesel production, focusing on sustainability and cost-effectiveness.

1.4 SCOPE OF RESEARCH

This is a laboratory-scale study. Neems seed oil was chosen for the production of biodiesel using a bifunctional catalyst of calcium and cellulose source obtained from waste materials.

1.5 SIGNIFICANCE OF STUDY

Neem oil, extracted from the seeds of the neem tree (Azadirachta indica), has become popular for its wide-ranging uses in agriculture, medicine, and beauty products. Its insecticidal properties, antifungal effects, and potential as a natural pesticide have drawn attention. The growing demand for organic products has sparked interest in sustainable methods for producing neem oil.

1. Significance of Sustainable Production Methods

Conventional neem oil extraction methods often involve the use of chemical solvents or high energy inputs, which can be harmful to the environment and economically impractical. Therefore, it is essential to develop sustainable production methods. Production on a laboratory scale using waste materials not only addresses environmental concerns but also promotes resource efficiency by utilizing materials that would otherwise create waste.

2. Role of Bifunctional Catalysts

Bifunctional catalysts are capable of facilitating multiple reactions simultaneously, which can enhance the efficiency of the extraction process. In the context of neem oil production, these catalysts can improve yield and purity while reducing reaction times and energy consumption.

Using bifunctional catalysts derived from waste materials aligns with green chemistry principles by minimizing hazardous substances and promoting the use of renewable resources.

3. Economic Implications

The laboratory-scale production of neem oil using waste-derived bifunctional catalysts can significantly reduce production costs. By utilizing low-cost raw materials that are readily available as waste products, researchers can create a more economically viable process for neem oil extraction. This approach not only benefits producers but also makes neem oil more accessible to consumers.

4. Environmental Benefits

Using waste materials as catalysts contributes to waste reduction and promotes circular economy principles. This method minimizes landfill contributions and reduces the carbon footprint associated with traditional extraction processes. Furthermore, producing neem oil sustainably helps preserve biodiversity by reducing reliance on synthetic pesticides that may harm non-target species.

5. Contribution to Research and Development

This research area opens avenues for further studies on optimizing catalyst performance and exploring other potential applications for waste-derived bifunctional catalysts in various chemical processes. The findings could lead to innovations in both agricultural practices and industrial processes, fostering advancements in green technology.

CHAPTER 2

LITERATURE REVIEW

2.1 ENERGY

The fundamental principle of thermodynamics states that energy cannot be created or destroyed; rather, it can only be converted from one form to another.

Energy is a fundamental aspect of our everyday existence, influencing how we live, work, and engage with our surroundings. Simply put, energy is the ability to do work or create change, and it comes in many forms like thermal, electrical, mechanical, chemical, biomass and radiant energy. Grasping the concept of energy is vital, especially as we confront urgent issues such as climate change, energy security, and the need for sustainable development.

At its essence, energy is all about transformation. It cannot be created or destroyed, but it can shift from one form to another. This principle is captured in the law of conservation of energy, which asserts that the total energy in a closed system remains constant. For example, when we burn fossil fuels to generate electricity, we convert the chemical energy stored in the fuel into thermal energy, and then into electrical energy that powers our homes and businesses. However, this process has significant consequences. Burning fossil fuels releases greenhouse gases, which contribute to global warming and climate change (Intergovernmental Panel on Climate Change [IPCC], 2021).

As the global population continues to expand, so does our energy demand. Factors such as urbanization and industrialization contribute to this rising need. The International Energy Agency (IEA, 2022) predicts that global energy consumption will increase by nearly 25% by 2040, largely due to emerging economies striving to enhance living standards. This growing demand presents serious challenges, including heightened carbon emissions and environmental degradation.

In light of these challenges, there is an increasing focus on renewable energy sources like solar, wind, and hydropower. These alternatives provide a sustainable solution by harnessing natural processes to generate energy without depleting finite resources or emitting harmful pollutants. For instance, solar energy captures sunlight and converts it into electricity or heat, offering a clean and limitless energy source (Lund, 2020). Wind energy, on the other hand, utilizes the kinetic energy of wind to produce electricity, helping to reduce our dependence on fossil fuels.

Transitioning to renewable energy represents not only an environmental necessity but also an economic opportunity. The renewable energy sector has experienced remarkable growth in recent years, generating jobs and attracting investments. The International Renewable Energy Agency (IRENA, 2021) reported that the sector employed over 11 million people globally in 2018, with the potential for even more job creation as technologies improve and costs decline. This shift towards cleaner energy sources can enhance energy independence, bolster economic resilience, and improve public health by reducing air pollution.

Moreover, energy is closely tied to social equity and justice. Access to reliable and affordable energy is crucial for economic progress and enhancing quality of life. Unfortunately, millions of people around the world still lack electricity, which limits their opportunities for education, healthcare, and economic advancement (World Bank, 2020). Addressing energy poverty is essential for achieving the United Nations Sustainable Development Goals, particularly Goal 7, which aims to ensure access to affordable, reliable, sustainable, and modern energy for everyone.

2.1.1 SOURSES OF ENERGY

Energy comes from a variety of sources, each of which plays a vital role in fulfilling the needs of our contemporary society. Understanding these sources is crucial for creating sustainable energy policies and technologies. Generally, we can categorize energy sources into two main types: renewable and non-renewable.

RENEWABLE ENERGY SOURCES

Renewable energy sources are those that can naturally replenish themselves and are regarded as more sustainable due to their minimal environmental impact. The key renewable energy sources include; solar, wind, hydropower, biomass, geothermal energy, e.t.c.

NON-RENEWABLE ENERGY SOURCES

Non-renewable energy sources are finite and cannot be replenished on a human timescale. The main non-renewable energy sources include; fossil fuels, nuclear.

2.1.2 TYPES OF RENEWABLE ENERGY

2.1.2.1 GEOTHERMAL ENERGY

Geothermal energy is a fascinating renewable resource that taps into the heat stored beneath the Earth's surface. This heat comes from two main sources: the leftover heat from when the planet was formed and the natural decay of radioactive materials found in the Earth's crust. What makes geothermal energy particularly appealing is its ability to provide a stable and reliable energy source, unlike solar and wind energy, which can be influenced by changing weather conditions.

The heat beneath the Earth creates a temperature gradient that typically rises by about 25 to 30 degrees Celsius for every kilometer of depth, though this can vary depending on local geological conditions. Geothermal resources are generally classified into three types based on their temperature: low-temperature (below 150°C), medium-temperature (between 150°C and 200°C), and high-temperature (above 200°C). Understanding these classifications is essential for choosing the right technology and application for harnessing geothermal energy effectively (Lund et al., 2020)To make use of geothermal energy, various technologies are employed to convert the underground heat into usable energy. Geothermal power plants are primarily designed for generating electricity, drawing on steam or hot water from geothermal reservoirs. These plants come in three main types: dry steam, flash steam, and binary cycle plants, each with its unique method for turning thermal energy into the mechanical energy that generates electricity.

Besides electricity generation, geothermal energy can also be utilized for direct applications, such as heating and cooling buildings through geothermal heat pumps. These pumps take advantage of the relatively stable temperatures found just below the Earth's surface, making them a highly efficient and cost-effective option for reducing energy consumption (Garg et al., 2022).

Geothermal energy is often celebrated for its environmental benefits. Unlike fossil fuels, it produces significantly fewer greenhouse gas emissions, which is vital for combating climate change. The lifecycle emissions from geothermal energy are much lower than those associated with conventional energy sources, making it a compelling choice for reducing our overall carbon footprints (Hance et al., 2021). Additionally, geothermal energy can provide base load power, meaning it delivers a steady energy supply that isn't affected by the fluctuations seen with solar and wind energy.

The economic viability of geothermal energy is influenced by several factors, including resource availability, advancements in technology, and initial capital investments. While the costs related to exploration and drilling can be substantial, the long-term operational costs are generally lower than those of fossil fuel plants. This is due to reduced fuel needs and less frequent maintenance. The financial attractiveness of geothermal projects is further boosted by the long lifespan of these plants, which can operate effectively for decades with proper management (Lund et al., 2020).

However, geothermal energy isn't without its challenges. The geographical distribution of geothermal resources can limit access since suitable sites are often found in specific geological formations tied to tectonic activity. Moreover, the exploration phase carries certain risks, such as the possibility of dry wells, which can lead to financial losses for developers. There are also environmental concerns, including potential land subsidence and the careful management of geothermal fluids that may contain harmful minerals (Hance et al., 2021).

Looking ahead, the future of geothermal energy appears promising, especially as technology continues to advance. Enhanced geothermal systems (EGS) represent a significant area of research aimed at expanding the geographical reach of geothermal energy by artificially creating reservoirs in hot, dry rock formations. Additionally, combining geothermal energy with other renewable sources and energy storage systems can enhance its reliability, contributing to a more resilient energy grid (Garg et al., 2022).

2.1.2.2 HYDROELECTRIC ENERGY

Hydroelectric energy is a prominent form of renewable energy that generates power by utilizing the force of flowing or falling water. This energy is produced through the gravitational pull of water as it moves from higher altitudes to lower ones, making it a renewable resource capable of delivering consistent and reliable electricity. The importance of hydroelectric energy in the global energy mix is significant, as it supports energy security, fosters economic growth, and promotes environmental sustainability.

The generation of hydroelectric energy usually involves building dams across rivers or other bodies of water. When water accumulates in reservoirs behind a dam, it stores potential energy. Upon release, the flowing water drives turbines, converting potential energy into kinetic energy. The turbines' movement produces mechanical energy, which is then converted into electrical energy through generators. Various types of hydroelectric systems exist, such as run-of-the-river, reservoir-based, and pumped-storage systems, each with unique operational methods and uses (International Hydropower Association [IHA], 2021).

2.1.2.3 WIND ENERGY

Wind energy has emerged as a prominent renewable energy source, leveraging the kinetic energy of wind to generate electricity. As concerns regarding climate change and the depletion of fossil fuels intensify, wind power has gained significant traction, becoming a critical component in the transition to a more sustainable energy system. This renewable source not only contributes to reducing greenhouse gas emissions but also plays a vital role in enhancing energy security and fostering economic development.

The generation of wind energy involves the conversion of the kinetic energy present in wind into mechanical energy, which is subsequently transformed into electrical energy through the use of wind turbines. The operational principle of wind turbines is straightforward: when wind flows over the blades, it induces rotation. This rotational motion drives a generator, producing electricity. The efficiency of this energy conversion process is influenced by several factors, including the design of the turbine, wind speed, and local atmospheric conditions (Global Wind Energy Council [GWEC], 2021).

Wind turbines are primarily categorized into two types: horizontal-axis wind turbines (HAWTs) and vertical-axis wind turbines (VAWTs). HAWTs are the predominant design, characterized by two or three blades mounted on a tall tower. This configuration typically yields higher efficiency and is applied in both onshore and offshore wind farms. Conversely, VAWTs have blades that rotate around a vertical axis and, while less common, can be advantageous in specific applications, such as urban environments where wind directions can vary significantly (Liu et al., 2020).

2.1.2.4 SOLAR ENERGY

Solar energy is a renewable resource harnessed from the sun's radiation, providing a sustainable approach to meet the increasing global energy needs. The significance of solar energy has grown considerably due to its ability to lower greenhouse gas emissions, reduce dependence on fossil fuels, and address the challenges posed by climate change. There are two primary technologies for capturing solar energy: photovoltaic (PV) systems and solar thermal system.

Solar energy offers numerous benefits, including its renewability, low operating costs, and minimal environmental impact once systems are installed. Additionally, harnessing solar energy promotes energy independence, enabling regions to utilize local resources. The growth of solar technologies also fosters job creation in sectors such as manufacturing, installation, and maintenance (IRENA, 2020).

2.1.2.5 OCEAN ENERGY

Ocean energy refers to the renewable energy harnessed from various oceanic phenomena, including tides, waves, and thermal gradients. This resource is significant and largely underutilized, offering substantial potential for contributing to a sustainable energy future. Ocean energy technologies comprise several approaches, such as tidal energy, wave energy, and ocean thermal energy conversion (OTEC).

Ocean energy offers numerous advantages, including its renewable nature, minimal greenhouse gas emissions, and vast potential, particularly in coastal regions. Moreover, ocean energy technologies can enhance energy security, create jobs, and promote sustainable development in coastal communities.

Despite its benefits, ocean energy faces several challenges, such as high initial costs, technological development hurdles, and potential environmental impacts on marine ecosystems. To fully realize the potential of ocean energy, ongoing research, investment, and development are crucial (IEA, 2020).

2.2 BIOENERGY

Any type of energy obtained from biological processes is referred to as bioenergy. Bioenergy, which comes from biological materials, plays an important role in the global energy sector. This form of energy is generated from organic sources, including plants, agricultural leftovers, and waste products. As the world confronts the challenges of climate change and searches for sustainable energy options, bioenergy has become a vital part of the renewable energy mix.

One of the key advantage of bioenergy is its potential to lower greenhouse gas emissions, especially in sectors that are difficult to decarbonize, like aviation and heavy transportation. Recent research indicates that bioenergy can make a meaningful contribution to meeting the goals set by the Paris Agreement by offering a cleaner alternative to fossil fuels (Rogelj et al., 2018). Nevertheless, it’s crucial to take into account the lifecycle emissions related to bioenergy production, which can sometimes be higher than those of traditional fossil fuels due to factors such as land-use changes (DeCicco & Schlesinger, 2018).

2.2.1 SOURCES OF BIO-RENEWABLE ENERGY

Bio-renewable energy is derived from biological materials, offering a sustainable alternative to fossil fuels and contributing to a cleaner energy future. The primary sources of bio-renewable energy include biomass, agricultural residues, and organic waste.

Biomass is a major contributor to bio-renewable energy. It encompasses a wide range of organic materials, such as wood, crop residues, and energy crops specifically cultivated for energy production. Woody biomass, derived from trees and shrubs, is commonly used in the production of heat and electricity through combustion processes. In addition, energy crops like switchgrass and miscanthus are cultivated for their high yield and energy content, making them suitable for biofuel production (Renewable Energy Policy Network for the 21st Century [REN21], 2021).

Agricultural residues also play a crucial role in bio-renewable energy generation. These materials, such as straw, corn stover, and sugarcane bagasse, are often byproducts of food production. Instead of being discarded, they can be converted into bioenergy, thereby enhancing resource efficiency and reducing waste (Kumar et al., 2020). Utilizing these residues not only provides a renewable energy source but also helps in managing agricultural waste, contributing to a more sustainable agricultural system.

Organic waste, including municipal solid waste, food waste, and wastewater, represents another important source of bio-renewable energy. Through processes like anaerobic digestion, organic waste can be converted into biogas, a mixture of methane and carbon dioxide that can be used for heating, electricity generation, or as a vehicle fuel. This approach not only diverts waste from landfills but also reduces greenhouse gas emissions associated with waste decomposition (Mussatto et al., 2019).

2.2.2 BIOFUELS

Biofuels are renewable energy sources derived from organic materials, primarily designed to replace fossil fuels in transportation and energy generation. They are generally classified into two categories: first-generation biofuels, which come from food crops, and second-generation biofuels, sourced from non-food biomass. The growing need for sustainable energy alternatives has spurred extensive research and development in biofuel technologies.

The main sources of biofuels include a variety of feedstocks such as crops, agricultural byproducts, and waste materials. First-generation biofuels are mainly produced from food crops like corn, sugarcane, and vegetable oils. For example, ethanol is predominantly made from corn in the United States and sugarcane in Brazil, while biodiesel is often produced from vegetable oils like soybean and palm oil (Zhang et al., 2021).

In contrast, second-generation biofuels are obtained from non-food biomass, which includes agricultural residues (such as straw and corn stover), forestry byproducts, and dedicated energy crops like miscanthus and switchgrass. These feedstocks are beneficial as they do not compete with food production and can help reduce waste (Kumar et al., 2020). The utilization of lignocellulosic materials, rich in cellulose, hemicellulose, and lignin, has gained significant attention due to their availability and potential for producing high biofuel yields.

Catalytic processes play a critical role in biofuel production, as they are essential for converting biomass into usable fuel forms. The effectiveness of the catalysts used can greatly influence the efficiency and output of biofuel production. For biodiesel, the most common method is trans-esterification, which usually employs catalytic agents. Homogeneous catalysts like sodium hydroxide (NaOH) or potassium hydroxide (KOH) are often used, though these can be corrosive and complicate separation and purification processes (Demirbas, 2020).

As an alternative, heterogeneous catalysts have become increasingly popular because they are reusable and easier to separate. Solid acid and base catalysts, such as zeolites and ion-exchange resins, are being investigated for their potential to improve biodiesel production (Mansir et al., 2021). Additionally, enzymatic catalysis shows promise, especially for transforming lignocellulosic biomass into sugars, which can then be fermented into ethanol. Enzymes like cellulases and hemicellulases are crucial for breaking down complex carbohydrates into fermentable sugars (López et al., 2020).

2.2.2.1 BIOFUEL CLASSIFICATION AND USES

2.2.2.1.1 FIRST GENERATION BIOFUEL

First-generation biofuels are obtained from food crops, such as corn, sugarcane, and vegetable oils. Ethanol is commonly produced through the fermentation of sugars found in these crops, while biodiesel is generated through the trans-esterification of vegetable oils or animal fats. These biofuels are primarily utilized in the transportation sector, serving as substitutes for gasoline and diesel. Their integration into fuel markets is already significant; for example, ethanol is frequently blended with gasoline to lower emissions and improve fuel octane levels (Zhang et al., 2021).

2.2.2.1.2 SECOND GENERATION BIOFUEL

In contrast, second-generation biofuels are produced from non-food biomass, which includes agricultural residues, forestry byproducts, and specially grown energy crops. These biofuels are viewed as more sustainable since they do not compete with food supplies and can utilize waste materials. Lignocellulosic feedstocks, such as straw and wood chips, are processed to create bioethanol and biodiesel. The adoption of second-generation biofuels is increasing in both transportation and power generation, as they aid in reducing greenhouse gas emissions and enhancing energy security (Kumar et al., 2020).

2.2.3 BIODIESEL

Biodiesel is a renewable fuel made from various sources, including vegetable oils, animal fats, and recycled cooking oils. It serves as a greener alternative to traditional diesel, offering several advantages like lower greenhouse gas emissions and improved energy security. The primary method for creating biodiesel is called trans-esterification.

Biodiesel, often referred to as "green fuel," is a type of fuel composed of fatty acid ethyl esters or methyl esters. It is produced by combining animal fats or plant oils with short-chain alcohols such as methanol, utilizing either an alkaline or acidic catalyst (Akhabue et al., 2020).

Numerous studies have shown that biodiesel has a calorific value comparable to that of fossil fuels. Unlike traditional fossil fuels, biodiesel has a higher flash point, a better cetane number, improved lubricating qualities, and lower emissions. Because of their similar chemical and physical characteristics, biodiesel can effectively replace diesel fuel. Most modern biodiesel production systems primarily use refined vegetable oil as their main feedstock (Akhabue et al., 2020). Biodiesel can be utilized on its own in biodiesel engines or mixed with regular diesel, typically in proportions ranging from 5 to 20 percent, and it requires only slight modifications to be compatible with standard diesel engines.

The following are some of the many different methods that may be used to produce biodiesel:

1. Pyrolysis

2. Dilution

3. Micro-emulsion

4. Preheating

5. Trans-esterification

The production of biodiesel is most effectively achieved through the trans-esterification process. This involves initially esterifying animal or vegetable fats with alcohol, followed by either esterification or trans-esterification to create biodiesel. Depending on the specific method employed, the reaction can be accelerated using either a heterogeneous or homogeneous catalyst. The trans-esterification process generally encompasses five stages in biodiesel production:

- Pretreatment stage
- Reaction stage
- Washing
- Alcohol recovery
- Glycerin purification stages

During the pretreatment stage, excess water and impurities, such as free fatty acids (FFA), are removed. After thoroughly mixing the alcohol and catalyst, the oil is introduced into the reactor while the mixture continues to be stirred. It is essential to wash the final product after using a homogeneous catalyst to eliminate any residual soap, glycerol, or other contaminants that may remain post-reaction. This washing process can be complicated by the use of water, which can lead to increased costs, challenges with solvent availability, emulsification issues, and water treatment concerns. In contrast, dry cleaning employs a chemical process, specifically ion exchange, to clean clothes. Once the product has dried, any unreacted components or byproducts can be recovered (A. B. Hassan & Ayodeji, 2019).

2.2.2.1 HISTORY OF BIODIESEL

The origins of biodiesel can be traced back to the late 19th century when Rudolf Diesel, the creator of the diesel engine, demonstrated his engine running on peanut oil at the 1900 World Exhibition in Paris. Diesel envisioned vegetable oils as a potential fuel source, advocating for the use of renewable energy derived from agricultural products. However, interest in biodiesel waned as petroleum and fossil fuels gained popularity in the early 20th century due to their lower costs and greater availability (Mofijur et al., 2020).

The modern resurgence of biodiesel began during the oil crisis of the 1970s, which reignited interest in alternative fuel sources. Researchers and entrepreneurs began to explore biodiesel as a sustainable energy option, particularly in light of fluctuating oil prices and increasing environmental concerns related to fossil fuel consumption. In 1978, the U.S. Department of Energy launched its first biodiesel research initiative, aimed at investigating the viability of using vegetable oils and animal fats as fuel for diesel engines (Knothe et al., 2010).

By the 1990s, advancements in biodiesel technology led to the establishment of commercial production facilities. The trans-esterification process, which transforms fats and oils into fatty acid methyl esters (FAME), was improved, making large-scale biodiesel manufacturing more achievable. The first commercial biodiesel plant in the United States began operations in Hawaii in 1991, marking a significant milestone in the development and acceptance of biodiesel as an alternative fuel (Zhang et al., 2021).

The early 2000s saw a notable increase in biodiesel production worldwide, fueled by government incentives and regulations that supported the growth of renewable energy sources. Both the European Union and the United States implemented policies to promote biodiesel use, leading to more investments in research and development. By 2005, biodiesel had gained considerable momentum, with production facilities set up in various countries (Mofijur et al., 2020).

Today, biodiesel is acknowledged as a key player in the renewable energy sector. It is made from various feedstocks, including vegetable oils, animal fats, and used cooking oils, and can be blended with conventional diesel or used as a standalone fuel. Ongoing improvements in biodiesel production techniques and increasing environmental awareness have cemented its position as a sustainable alternative to fossil fuel.

2.2.2.2 PROPERTIES OF BIODIESEL

Biodiesel can be classified using several criteria, with key factors that influence engine performance, suitability in cold weather, transport and storage properties, and the wear on engine components. These critical elements encompass various aspects of engine functionality. For instance, ease of starting, the formation of the fuel-air mixture, combustion efficiency, exhaust gas emissions, and heating value all play crucial roles. When it comes to cold weather performance, important considerations include cloud point, cold filter plugging point, and pour point. In terms of transport and storage, factors like oxidative stability, hydrolytic stability, and flash point are vital. Moreover, the wear on engine parts is evaluated through properties such as lubricity, viscosity, cleaning effects, and compatibility with the materials used in the engine. Collectively, these factors shape the classification of biodiesel and determine its appropriateness for diverse applications.

1. Flash Point: The flash point of biodiesel is an important property that greatly affects its safety and handling. Simply put, the flash point is the lowest temperature at which the vapor from a fuel can ignite when exposed to an ignition source. For biodiesel, this can vary widely, usually falling between 100°C and 170°C. Grasping the significance of the flash point is essential for several reasons. It influences how biodiesel is stored. A higher flash point typically means safer storage conditions. Consequently, biodiesel with a higher flash point can be kept in less regulated environments, lowering the chances of accidental fires. Furthermore, the flash point has implications for transport regulations. Biodiesel that has a lower flash point may require more stringent transportation rules, which can affect logistics and increase costs.

In addition, the flash point can impact engine performance. If the flash point is too low, it could create volatility issues, making it harder to start the engine, particularly in colder weather.

2. Density: Density is an essential characteristic of biodiesel that significantly impacts its functionality and usage. Obtained from plant oils or animal fats, biodiesel displays different density levels depending on its origin and how it's produced. Typically, biodiesel densities fall between 0.860 and 0.900 g/cm³, which can influence how well it mixes with standard diesel fuels. The density of biodiesel is affected by the volume of ester content and the residual alcohol, making the choice of vegetable oil a significant factor in determining this characteristic (Encinar et al., 2012)

Recognizing the importance of density is critical for various reasons, it affects the fuel's energy content. A denser biodiesel usually means more energy per unit volume, potentially boosting engine performance. On the flip side, if the density is too low, it can result in inefficient combustion, leading to lower effectiveness and higher emissions.

Additionally, density has an effect on the physical traits of biodiesel, including its viscosity. Viscosity impacts fuel injection and atomization in engines. It's crucial to strike a balance between density and viscosity to ensure peak engine operation. Biodiesel density can fluctuate with temperature changes. As temperatures increase, density generally decreases, which can pose challenges for fuel storage and handling.

3. Velocity: Viscosity indicates the amount of internal friction within a liquid, which directly influences how easily it flows. This property is particularly important when biodiesel is used as a substitute for its original oil. A high viscosity in fuel can pose significant challenges during combustion, leading to problems with atomization, increased smoke output, and incomplete combustion within the combustion chamber.

To guarantee the diesel injector operates effectively during fuel injection, biodiesel must possess a considerably lower viscosity. The greater the viscosity, the higher the chance of facing such operational difficulties. Transitioning to biodiesel can potentially lower the viscosity of vegetable oil, thus presenting a feasible alternative for enhancing engine performance.

4. Iodine Number: The iodine value (IV), often referred to as the iodine number, quantifies the degree of unsaturation in a blend of fatty substances. This measurement is crucial for assessing biodiesel's vulnerability to oxidation. Fats and oils high in unsaturated fats typically exhibit elevated iodine values. This can lead to polymerization, which may cause residue buildup on injector nozzles and piston rings. To prevent excessive polymerization of unsaturated fatty acids, it is crucial to limit their concentration in the fuel. If fuel leaks into the crankcase from the cylinder sides, it can create thick sludge within the engine's sump. Therefore, managing the iodine value is essential to ensure fuel stability and mitigate potential engine problems.

5. Cold Filter Flagging Point: Biodiesel provides enhanced lubrication compared to diesel derived from petroleum, which contributes to longer engine life and less wear. However, a fuel's

performance in cold weather is evaluated using its cold filter plugging point (CFPP). At lower temperatures, fuel may thicken or flow inconsistently, potentially affecting the operation of fuel pumps, lines, and injectors. Thus, maintaining an appropriate CFPP is essential for ensuring smooth engine functionality, particularly in colder climates.

6. Cloud Point and Pour Point: The cloud point and pour point are vital metrics for assessing biodiesel quality. The cloud point represents the temperature at which the fuel starts to crystallize. As temperatures decrease, the number and size of these crystals grow until the fuel eventually gels and becomes immobile. Conversely, the pour point indicates the temperature at which the oil ceases to flow. Both of these characteristics are crucial for determining fuel usability in colder conditions, especially during engine starts in frigid weather.

Reports suggest that biodiesel may exhibit higher cloud and pour points, making it necessary to keep these values sufficiently low to avoid operational challenges. Diesel boasts a very low cloud point of 4°C, allowing it to perform effectively even in cold environments. In contrast, elevated cloud points in biodiesel could hinder engine performance and increase emissions under low temperature conditions. Diesel's pour point is -40°C, and if vegetable oils reach this threshold, they may stop flowing, leading to issues such as clogged filters and fuel delivery problems. Therefore, ensuring low cloud and pour points is critical for biodiesel's reliable operation in cold weather.

7. Cetane Number: The cetane number of a fuel plays a crucial role in determining its ignition and combustion characteristics. Fuels with lower cetane numbers can cause noisy engine operation, increased smoke, and rough running. Conversely, fuels with higher cetane numbers lead to better combustion, less white smoke, and reduced emissions of carbon monoxide and hydrocarbons. This cetane rating has a direct influence on how easily the fuel ignites and its

overall combustion efficiency. It significantly impacts various aspects of engine performance, such as combustion stability, smoke generation, noise levels, and emissions of CO and hydrocarbons. Biodiesel, with its higher cetane number compared to conventional diesel, shows improved combustion efficiency.

2.2.2.3 BIODIESEL STANDARDS

Two crucial factors hold significant importance: the ester content, which must be at least 96.5%, and the acid value, capped at 0.5 mg KOH/g. The ester content is determined by the efficiency of the processing method and the type of feedstock used. The unsaponifiable fraction—comprising sterols, tocopherols, hydrocarbons, and more—accounts for about one to two percent of vegetable oils and helps keep the ester concentration of biodiesel between 98 and 99%.

Other important factors include the overall pollution levels, the presence of unreacted acylglycerols, phosphorus, alkali metals, and sulfur. Different regions, such as the EU and the USA, have specific requirements for oxidative stability. For example, biodiesel derived from rapeseed shows greater oxidation resistance compared to that from soy. Achieving these standards can be more difficult with various feedstocks, often necessitating additional pre- or post-treatment processes to ensure compliance with the required standards.

Biodiesel is eligible for commercial use and trade only if it meets established standards, specifically EN14214:2009 (EN) or ASTM D6751 (USA), as detailed in Table 2.1 below:

BIODIESEL PROPERTY SPECIFICATION			
Property	Units	ASTM D6751	EN 14214

		Tests	Limits	Tests	Limits
Flash point	°C	ASTM D93	130 minimum	EN ISO 3679	101 minimum
Cloud point	°C	ASTM D2500	−3 to −12	–	–
Pour Point	°C	ASTM D97	−15 to −16	–	–
Cetane number		ASTM D613	47 minimum	EN ISO 5165	51 minimum
Density at 15 °C	Kg/m ^{3}	ASTM D 1298	880	EN ISO 3675/ 12185	860–900
Kinematic viscosity at 40 °C	mm^2/s	ASTM D445	1.9–6.0	EN ISO 3104	3.5–5.0
Iodine number	g I_2/100 g	–	–	EN 14111	–
Acid number	mg KOH/g	ASTM D664	0.5 maximum	EN 14104	0.5 maximum
Saponification value	mg KOH/g	ASTM D5558	370 maximum	–	–
Boiling point	°C	ASTM D7398	100–615	–	–

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

Table 2.1: Biodiesel Production Specification

2.2.2.4 FEEDSTOCK FOR BIODIESEL PRODUCTION

Biodiesel production involves various natural and organic materials, including vegetable oils and animal fats. Prominent feedstock options for creating biodiesel include palm oil, soybean oil, and rapeseed oil, with soybean oil being a notable choice (Ambat et al., 2018). These feedstocks are categorized as first-generation biodiesel sources. Notably, biodiesel can be produced from feedstocks across different generations, ranging from the first to the fourth (Lee & Lavoie, 2013; D. Singh et al., 2020).

1. FIRST GENERATION FEEDSTOCK

The first generation of biodiesel feedstocks primarily consists of oils derived from edible crops and biomass (Lee & Lavoie, 2013). Examples include oils from palm, rapeseed, soybean, and sunflower plants. Using first-generation feedstocks is a common practice due to their ability to effectively meet biodiesel demand. However, their extensive use has resulted in rising food prices, as competition between the food and fuel sectors can lead to food insecurity. Furthermore, the profitability of producing biodiesel from first-generation feedstocks is often limited, given that the edible oil market can be more lucrative than the petroleum sector.

A significant issue linked to first-generation feedstock cultivation is its environmental impact. The large-scale farming of these crops contributes to various ecological problems, such as food insecurity, water shortages, deforestation, habitat destruction, and soil degradation (Jayakumar et al., 2017).

2. SECOND GENERATION FEEDSTOCKS

Second-generation biodiesel feedstocks, which do not come from food sources, can be sourced from a variety of materials (Lee & Lavoie, 2013a). These materials include waste vegetable oil, animal fats, greases, and oils from non-edible plants. Non-edible crops can be grown on smaller plots within mixed agricultural systems. Additionally, utilizing waste products, such as refuse, offers a viable option for producing second-generation feedstocks, helping to minimize landfill expansion and reduce harmful gas emissions from fossil fuels (Hums et al., 2016). When compared to first-generation feedstocks, second-generation options tend to be more economical. They are also believed to have a higher cetane number, be less corrosive, and generate fewer pollutants than biodiesel derived from first-generation sources (Sakthivel et al., 2018).

However, studies have highlighted some challenges linked to biodiesel made from second-generation feedstocks. These include lower fuel quality and yield, a lack of technology for large-scale production, biosecurity concerns regarding animal feedstocks, and issues related to poor cold flow characteristics (Alptekin & Canakci, 2011; Shah et al., 2018). Various oil-producing plant species, such as Pongamia pinnata (Karanja), Jatropha curcas (Jatropha), Bintangor (Calophyllum inophyllum), and Neem (Azadirachta indica), can be utilized as feedstocks for biodiesel production (Azam et al., 2005).

3. THIRD GENERATION FEEDSTOCK

The third generation of biomass feedstocks comes from microorganisms, particularly algae. Algae can be classified into two main types: microalgae and macroalgae (Shah et al., 2018b). Cultivating algae requires less land than traditional crops and has minimal ecological impact. They can flourish using basic resources such as sunlight, water, carbon dioxide, and some fertilizers. Moreover, algae can help mitigate greenhouse gas emissions since they absorb carbon dioxide during their growth.

Nevertheless, challenges exist with third-generation feedstocks, similar to those encountered with previous generations. Algae cultivation requires substantial amounts of water, making it difficult to grow in some areas (Lee & Lavoie, 2013b). Additionally, the science surrounding algae cultivation is still relatively new, and the process of producing algae-based biodiesel on an industrial scale remains complex and expensive due to limited technological advancements (Lee & Lavoie, 2013b).

4. FOURTH GENERATION FEEDSTOCK

Recent advancements in synthetic biology have opened up new possibilities for creating fourth-generation feedstocks. By harnessing solar energy alongside genetically modified biological systems, it is now possible to produce biodiesel feedstock that is both sustainable and economically feasible (Abdullah et al., 2019). Fourth-generation biodiesel feedstocks can be produced through three main methods: (i) using specialized photosynthetic microorganisms, (ii) combining photovoltaics with microbial fuel systems, and (iii) developing synthetic cells. These groundbreaking techniques offer significant potential for the future of biodiesel production.

2.2.2.5 ALCOHOL IN BIODIESEL PRODUCTION

Alcohol plays a crucial role in the production of biodiesel, primarily serving as a reactant in the trans-esterification process. This chemical reaction involves the conversion of triglycerides, found in fats and oils, into biodiesel (fatty acid methyl esters, FAME) and glycerol. Alcohols, typically methanol or ethanol, are used to facilitate this reaction. The choice of alcohol significantly influences the efficiency, yield, and properties of the resulting biodiesel. Methanol is the most commonly used alcohol in biodiesel production due to its low cost, high reactivity, and ability to produce biodiesel with favorable properties. Methanol's molecular structure allows it to react efficiently with triglycerides, yielding a high percentage of biodiesel. However, safety concerns related to methanol handling and toxicity have prompted some producers to explore ethanol as an alternative. Ethanol, derived from renewable sources, can provide a more eco-friendly option, although it may result in slightly lower yields and require longer reaction times compared to methanol (Knothe, 2020).

The type of alcohol used in biodiesel production directly affects the fuel's characteristics, such as cetane number, viscosity, and cold flow properties. Biodiesel produced with methanol typically exhibits better combustion properties, while ethanol-based biodiesel may offer improved oxidative stability. Additionally, the use of ethanol may lead to biodiesel with higher cloud and pour points, which can impact performance in colder climates (D. Singh et al., 2020).

Recent research has focused on optimizing the trans-esterification process by exploring various alcohols and their effects on biodiesel properties. Studies have shown that using various alcohols, including butanol and propanol, can also yield biodiesel with distinct characteristics that may enhance fuel performance and environmental sustainability (Mansir et al., 2021). Furthermore, advancements in catalytic processes and enzyme technologies have the potential to increase the efficiency of alcohol use in biodiesel production, making it a more viable option for large-scale applications.

2.2.2.6 BIODIESEL PRODUCTION TECHNIQUES

Biodiesel production consists of several methods, each utilizing different approaches and technologies to convert various feedstocks into biodiesel. Among these methods, trans-esterification is the most widely recognized, along with supercritical fluid processing, enzymatic trans-esterification, micro-emulsion, and pyrolysis. This discussion will provide an in-depth exploration of each technique, with a particular emphasis on trans-esterification.

1. TRANS-ESTERIFICATION

Trans-esterification is the primary method used for biodiesel production. It involves a chemical reaction between triglycerides (fats and oils) and alcohol, typically methanol or ethanol, facilitated by a catalyst such as sodium or potassium hydroxide.

This process generates fatty acid methyl esters (FAME), the key components of biodiesel, along with glycerol as a by-product.

Process Overview

The trans-esterification process can be divided into several key steps:

Feedstock Preparation: The initial step is selecting and preparing the feedstock. Common options include vegetable oils (like soybean, palm, and canola oil) and animal fats. The quality of the feedstock is crucial; oils with high free fatty acid (FFA) content may need pre-treatment methods, such as acid-catalyzed esterification, to lower FFA levels before proceeding with trans-esterification (Fukuda et al., 2001).

Mixing and Reaction: The prepared feedstock is combined with the chosen alcohol and catalyst. This reaction typically occurs at elevated temperatures (around 60-70°C) and lasts for several hours. The efficiency of the reaction can be influenced by factors such as the alcohol-to-oil molar ratio, temperature, catalyst concentration, and reaction duration (Knothe, 2005).

Separation and Purification: Following the reaction, the mixture separates into two distinct layers: biodiesel (FAME) and glycerol. The denser glycerol settles at the bottom and can be easily removed. The biodiesel layer may require further purification steps, including washing with water to eliminate residual catalyst and impurities, as well as drying to remove any moisture (Demirbas, 2008).

Factors Affecting Yield and Quality

Various factors influence the yield and quality of biodiesel produced through trans-esterification:

Feedstock Quality: Impurities such as water, free fatty acids, and phospholipids can impact the reaction's efficiency. High FFA levels can lead to soap formation, complicating the purification process and reducing overall biodiesel yield (Fukuda et al., 2001).

Alcohol Type: Methanol is the most commonly used alcohol due to its low cost and high reactivity, while ethanol is also gaining traction, especially in regions where ethanol is produced from agricultural sources. The choice of alcohol can significantly affect the biodiesel's properties, such as cold flow characteristics and oxidative stability (Knothe, 2009).

Catalyst: The type and amount of catalyst used are critical for optimizing the reaction. While alkaline catalysts are most prevalent, acid catalysts can handle feedstocks with high FFA content. Acid-catalyzed trans-esterification typically requires longer reaction times and higher temperatures but can accommodate a wider range of feedstocks (Srinivasan et al., 2016).

Trans-esterification remains the most prominent technique for biodiesel production due to its efficiency and established methodology. As the demand for biodiesel continues to rise, ongoing research and innovation focused on optimizing this process, improving feedstock utilization, and exploring alternative catalysts are essential for enhancing the sustainability and economic viability of biodiesel production.

2. SUPERCRITICAL FLUID PROCESSING

Supercritical fluid processing utilizes supercritical alcohol, often methanol, to convert triglycerides into biodiesel. This method operates at temperatures and pressures above the critical point of the alcohol, which enhances the solubility of the reactants and accelerates the reaction rate.

This technique eliminates the need for a catalyst, thus reducing complications associated with catalyst recovery and waste management. However, the high energy requirements and costs related to the necessary equipment can limit its application on a large scale.

3. ENZYMATIC TRANS-ESTERIFICATION

Enzymatic trans-esterification uses lipases as catalysts to convert triglycerides and alcohol into biodiesel. This method operates under milder conditions and effectively processes feedstocks with high FFA content, making it suitable for waste oils and animal fats.

While enzymatic trans-esterification offers several environmental benefits and produces high-quality biodiesel, it is often slower and more expensive than chemical catalysis, which limits its application in large-scale biodiesel production. Ongoing research aims to enhance enzyme stability and reduce costs, making this technique more feasible.

4. MICRO-EMULSION

Micro-emulsion involves creating a stable mixture of biodiesel, water, and surfactants, which reduces the interfacial tension between immiscible phases. This technique enhances the dispersion of biodiesel in water and allows for the direct use of high-FFA feedstocks.

Micro-emulsion can facilitate the trans-esterification process and improve biodiesel yield. However, the complexity of the process and the need for surfactants may pose challenges for large-scale implementation.

5. PYROLYSIS

Pyrolysis is a thermochemical process that decomposes organic materials at high temperatures in the absence of oxygen. This method converts feedstocks into bio-oil, char, and syngas, with bio-oil being further refined into biodiesel.

Pyrolysis allows for the utilization of various feedstocks, including agricultural residues and waste materials. While it offers the potential for high energy yields, the variability of the bio-oil quality requires additional processing steps to produce biodiesel that meets industry standards.

2.2.2.7 CHEMISTRY OF BIODIESEL

The creation of biodiesel involves a series of chemical processes that convert triglycerides (oils and fats) into fatty acid methyl esters (FAME) and glycerol through specific reactions. The main chemical process for producing biodiesel is trans-esterification, which entails the reaction between triglycerides and alcohol (commonly methanol or ethanol) in the presence of a catalyst.

Triglycerides consist of glycerol and three fatty acid chains. When an alcohol and a catalyst are present, the ester bonds in the triglyceride are broken, converting the fatty acids into methyl or ethyl esters (FAME) and releasing glycerol as a by-product.

REACTION CONDITIONS

Several factors affect the efficiency and outcomes of the trans-esterification reaction:

Molar Ratio: The alcohol-to-triglyceride ratio is crucial. A higher alcohol ratio (typically around 6:1 or more) can drive the reaction toward FAME formation and improve yields. However, excessive alcohol may complicate the separation processes afterward (Knothe, 2009).

Temperature: The reaction typically occurs at elevated temperatures (60-70°C). Higher temperatures can accelerate the reaction rate, but exceeding certain limits may lead to unwanted side reactions or vaporization of the alcohol (Srinivasan et al., 2016).

Reaction Time: The duration of the reaction also plays a significant role in yield. Typical reaction times range from 1 to 8 hours, depending on the specific catalyst and conditions used.

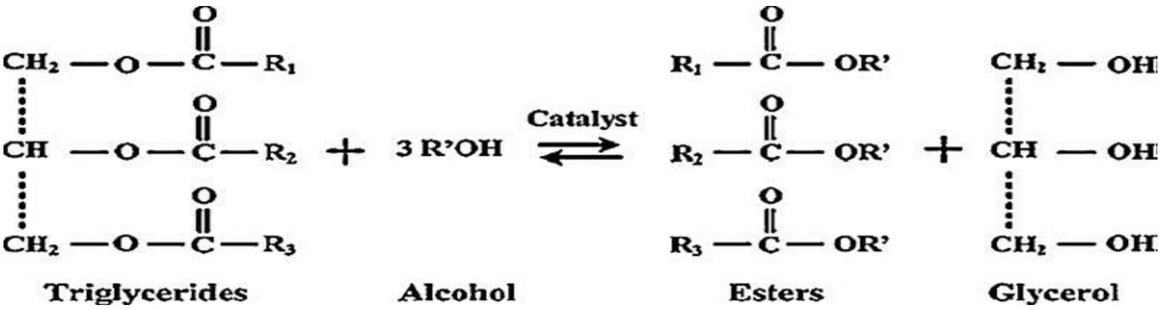

Figure 2.1 Trans-esterification Reaction

2.2.4 CATALYST STRUCTURE AND PREPARATION

Catalysts are essential in the production of biodiesel, greatly affecting how efficiently the process works, as well as the quality and yield of the biodiesel produced. Understanding the structure and preparation of these catalysts is crucial for optimizing their performance. In this section, we will explore different types of catalysts used in biodiesel production, their structural characteristics, preparation methods, and how these factors influence their effectiveness.

TYPES OF CATALYSTS

In biodiesel production, catalysts can be divided into two main categories: homogeneous catalysts and heterogeneous catalysts.

Homogeneous Catalysts: These types of catalysts, like sodium hydroxide (NaOH) and potassium hydroxide (KOH), are dissolved in the reaction mixture. They are popular because they tend to act quickly and efficiently, leading to faster reaction times. However, one drawback is that separating the biodiesel from these catalysts after the reaction can be tricky, which may result in contamination of the final product (Fukuda et al., 2001).

Heterogeneous Catalysts: Unlike homogeneous catalysts, heterogeneous catalysts exist in a different phase from the reactants. Examples include solid acid and base catalysts, such as ion-exchange resins and metal oxides. These catalysts offer the advantage of easier separation and can be reused multiple times, making them appealing for large-scale biodiesel production (Knothe, 2009).

The structure of a catalyst is vital in determining how effective it is in facilitating reactions. Some important structural features include:

Surface Area: A larger surface area means more active sites where reactions can occur. Generally, catalysts with higher surface areas perform better. Materials like zeolites and metal oxides are often designed to have increased surface areas to boost their effectiveness (Almeida et al., 2020).

Porosity: A porous structure aids in the movement of reactants and products during the reaction. Catalysts with mesoporous silica, for example, provide an ideal environment for catalytic reactions due to their porous nature (Wang et al., 2019).

Active Sites: The distribution and nature of active sites on the catalyst's surface are critical for its catalytic properties. For trans-esterification reactions, the presence of basic sites is especially important when using heterogeneous base catalysts (Knothe, 2009).

The way a catalyst is structured and prepared has a direct impact on how well it performs in biodiesel production:

Reactivity: Catalysts with higher surface areas and suitable pore sizes enhance the accessibility of reactants to active sites, leading to improved reactivity and higher conversion rates (Mansir et al., 2021).

Selectivity: The specific functional groups and arrangement of active sites on a catalyst can influence how selective it is for desired products, reducing side reactions and maximizing biodiesel yields (Knothe, 2009).

Stability and Reusability: The stability of a catalyst during reactions is crucial for maintaining its performance over time. Heterogeneous catalysts tend to be more stable and can be reused multiple times without significant loss of activity, making them a cost-effective option for industrial applications (Fukuda et al., 2001).

METHODS OF PREPERATION

1. Wet Impregnation Method: The preparation of catalysts can be effectively accomplished through the wet impregnation technique. This process begins by adding the precursors, which can be in the form of either salts or oxides, to a beaker filled with distilled water. The mixture is stirred for about five to six hours. Following this, the slurry is left to soak for twenty-four hours, and then it is dehydrated by roasting at 110 degrees Fahrenheit for a full day. After the drying phase, the sample is subjected to calcination in a high-temperature oven (Mahesh et al., 2015).

Wet impregnation is a simple method for catalyst preparation. In this technique, beakers containing distilled water and the required precursors are combined and stirred for a specific duration. Once the soaking and drying stages are completed, the catalyst is calcined in a furnace.

2. Precipitation Method: This method is often favored due to its cost-effectiveness and ease of execution. However, it demands considerable labor because product separation is necessary after precipitation, along with the requirement for large amounts of salt-containing solutions. Typically, the pH of the solution is adjusted by adding a different solution until precipitation takes place. Lyophilic precipitates are distinct from lyophobic ones, as the former appear as gels that may be amorphous or weakly crystallized, while the latter exhibit a crystalline structure. Nucleation refers to the process where solid seed crystals may develop in the mother liquid, either in a homogeneous or heterogeneous manner, depending on the specific conditions present.

2.2.2.1 CATALYSTS FOR TRANS-ESTERIFICATION

A catalyst plays a crucial role in speeding up the conversion of one substance into another during chemical reactions. In the case of trans-esterification, there are three main types of catalysts that can be employed: base catalysts, acid catalysts, and enzymes (Boey et al., 2011). The classification of these catalysts as either acidic or basic is influenced by whether they are homogeneous or heterogeneous in nature.

Homogeneous catalysts dissolve completely with the reactants, resulting in a uniform mixture. In contrast, heterogeneous catalysts exist alongside the reactants, creating a suspension or separate physical phases. The primary difference between these two types lies in how they can be separated from the reaction mixture.

This inability to separate heterogeneous catalysts as easily means they can be reused multiple times, and they tend to be more resilient against the detrimental effects of feedstocks that have high levels of free fatty acids (FFA). However, it’s important to note that the reaction rates for trans-esterification using heterogeneous catalysts are generally slower when compared to those using homogeneous catalysts.

2.2.2.2.1 HOMOGENEOUS CATALYST

Homogeneous catalysts are crucial in the biodiesel production process, significantly influencing how efficiently the reactions occur and the overall yield of the product. These catalysts can be divided into two primary categories: acid catalysts and base catalysts. They fully dissolve in the reaction mixture, creating a uniform solution that helps convert triglycerides into fatty acid methyl esters (FAME) and glycerol.

1. HOMOGENOUS BASE CATALYSTS

Base catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), are frequently used in biodiesel production because they are effective for transesterifying oils with low free fatty acid (FFA) content. In this process, the catalyst deprotonates the alcohol, forming an alkoxide ion that reacts with triglycerides. One of the main benefits of using base catalysts is their ability to produce high reaction rates, which leads to shorter reaction times and higher yields (Fukuda et al., 2001).

However, there are some drawbacks to using base catalysts. They are sensitive to water and high levels of free fatty acids, which can cause soap formation during the reaction. The presence of soap complicates the separation of biodiesel from the glycerol by-product and can lower the overall yield (Knothe, 2009). Therefore, base-catalyzed trans-esterification is most effective for feedstocks that have low FFA content, such as refined vegetable oils.

2. HOMOGENEOUS ACID CATALYSTS

On the other hand, acid catalysts like sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are used for biodiesel production when the feedstocks contain higher FFA levels. Acid-catalyzed trans-esterification can effectively convert triglycerides and free fatty acids into biodiesel without producing soap. The reaction begins with a protonation step that activates the triglyceride, followed by a nucleophilic attack by the alcohol (Fukuda et al., 2001).

While acid catalysts can handle higher FFA levels, they generally have slower reaction rates compared to base catalysts. This slower pace means that longer reaction times are needed to achieve similar yields, potentially raising production costs (Srinivasan et al., 2016). Additionally, acid catalysts are often more expensive and require careful handling due to their corrosive properties.

2.2.2.2.2 HETEROGENOUS CATALYST

Heterogeneous catalysts are crucial in the biodiesel production process, offering distinct advantages like easier separation, reusability, and versatility with different feedstocks. These catalysts work in a different phase from the reactants, which allows for straightforward separation after the trans-esterification reaction. In this section, we will discuss the characteristics, benefits, and challenges associated with both acid and base heterogeneous catalysts in biodiesel production.

1. HETEROGENEOUS BASE CATALYSTS

Base heterogeneous catalysts, such as calcium oxide (CaO) and magnesium oxide (MgO), are gaining popularity for their effectiveness in converting triglycerides into biodiesel. These materials can be made from inexpensive and readily available resources, making them cost-effective options for biodiesel production. The process involves deprotonating alcohol to create alkoxide ions, which then react with triglycerides to produce fatty acid methyl esters (FAME) and glycerol (Zhang et al., 2020).

One of the key advantages of using base heterogeneous catalysts is their ability to handle higher free fatty acid (FFA) levels in feedstocks. Unlike homogeneous base catalysts, which can create soap when FFA levels are elevated, heterogeneous catalysts tolerate these conditions without significant loss of activity. This characteristic makes them suitable for processing waste oils and fats that often have higher FFA concentrations (Bafakeeh et al., 2021).

However, base heterogeneous catalysts do face some challenges. Their reaction rates are generally slower compared to homogeneous catalysts, primarily due to mass transfer limitations associated with their solid form. Researchers are actively looking for ways to improve this by optimizing the size of catalyst particles and enhancing agitation during the reaction to facilitate better mass transfer (Gonzalez et al., 2021).

2. HETEROGENEOUS ACID CATALYSTS

Acid heterogeneous catalysts, like sulfonic acid-functionalized materials and various solid acid catalysts such as zeolites and metal oxides, are particularly useful when working with feedstocks that have high FFA content. The mechanism involves protonating triglycerides, which then allows alcohol to react and convert both triglycerides and free fatty acids into biodiesel (Fukuda et al., 2001).

The main advantage of using acid heterogeneous catalysts is their ability to process feedstocks with high FFA levels without producing soap. This makes them suitable for a broader range of feedstocks, including used cooking oils and animal fats. Additionally, these catalysts can be reused multiple times, making them more economical for industrial applications (Knothe, 2009).

However, acid heterogeneous catalysts typically have slower reaction rates compared to base catalysts. This slower pace can be due to their solid-state nature and the potential for deactivation over time due to fouling or coking. Researchers are exploring more efficient solid acid catalysts with improved surface areas and active sites to enhance their performance (Kumar et al., 2021).

3. Activated Oxides of Alkali Earth Metals

Activated oxides of alkali earth metals, such as calcium (Ca), magnesium (Mg), beryllium (Be), boron (B), strontium (Sr), and barium (Ba), are commonly utilized as catalysts in biodiesel production. These oxides can be obtained in their pure forms or from naturally occurring mixed forms. Among these catalysts, calcium oxide (CaO) stands out due to its favorable characteristics, which include high basicity, low toxicity, minimal environmental impact, cost-effectiveness, and the ability to produce high-quality biodiesel with minimal input from CaO itself (Boro et al., 2012). Research indicates that CaO is more effective for trans-esterification compared to other catalysts like Mg-Al mixed oxide or anion-exchange resins. Although potassium-loaded catalysts showed faster reaction rates, their reusability was lower than that of CaO (Kouzu & Hidaka, 2012; Paterson et al., 2013).

Calcium oxide (CaO) is recognized as a highly active alkaline compound, known for its long catalyst lifespan and strong catalytic performance under mild reaction conditions (Kumar & A, 2012). However, its practical application in industrial settings may not always be economically viable due to certain limitations, such as susceptibility to degradation. Pure calcium oxide (CaO) can be extracted from used snail shells (Achatina fulica) under specific conditions of high heat and pressure (Linggawati et al., 2015).

Using discarded snail shells for biodiesel production is a promising option given their low cost (Fatimah et al., 2017). The waste from the common species, Achatina fulica, has also shown notable catalytic effectiveness (Fatimah et al., 2018). The pursuit of developing catalytic materials from inexpensive, renewable resources that are abundantly available has attracted considerable interest from researchers. This initiative aims to reduce catalyst production costs, minimize metal losses during reactions, and enhance the overall feasibility of catalytic processes (Bennett et al., 2016; Shan et al., 2016a).

2.2.2.2.3 ENZYME CATALYST

The challenges associated with using acid and base catalysts in biodiesel production have led to the development of enzyme catalysts, commonly referred to as biocatalysts. These biocatalysts are typically produced through fermentation processes and are derived from microorganisms (Semwal et al., 2011). Enzyme catalysts for biodiesel production are mainly classified into three types: free enzymes, intracellular lipases, and extracellular lipases (Bohlouli & Mahdavian, 2019; J. Yan et al., 2014a).

Extracellular lipases are sourced from purified lipase enzymes obtained from host microbes and are used directly in the trans-esterification process. This involves extracting the enzyme and immobilizing it on a supporting material (Ganesan et al., 2021). While this method offers high stability and selectivity in reactions, the production of extracellular lipase can be quite costly due to the labor-intensive nature of the extraction and purification processes (Yan et al., 2014a). On the other hand, intracellular lipases, also known as whole-cell lipases, are taken from microorganisms that produce lipases and are utilized as catalysts in biodiesel trans-esterification. Producing intracellular lipases is generally more cost-effective since it avoids the complex extraction and purification steps required for their extracellular counterparts (Ganesan et al., 2021; Guldhe et al., 2016).

Both intracellular and extracellular lipases face challenges related to mass transfer, and extracellular lipases tend to have a preference for glycerol. Some studies have explored the use of enzymes as a substrate (Guo et al., 2020; Pollardo et al., 2018). Research suggests that these challenges might be addressed by using free or liquid enzymes, which enhance mixing and mass transfer properties and could serve as a more cost-effective option compared to intracellular and extracellular lipases (Andrade et al., 2019). A study demonstrated that a genetically engineered strain of Aspergillus oryzae, which produces a free liquid lipase, was able to convert low-quality feedstocks with high FFA content into 97% biodiesel (Chang et al., 2021).

In general, enzyme catalysts require less energy, provide a straightforward process, can be reused, and are capable of handling high levels of FFA and moisture. This helps mitigate the saponification issues often seen with acid or base catalysts. The enzymatic trans-esterification process simplifies the purification of biodiesel (Meher et al., 2006). However, the production costs for enzymes and the slower reaction times associated with enzyme catalysts can be a drawback (Boey et al., 2011). Additionally, introducing methanol as a trigger for enzyme catalysts may reduce biodiesel yields (Magner, 2013).

2.2.2.2.4 COMPOSITE CATALYSTS FROM WASTE MATERIALS

Researchers are looking into using readily available and inexpensive Exploring various raw materials for the production of biodiesel with the aim of discovering a more cost-efficient and economically viable approach to fuel manufacturing (Mahmood Khan et al., as cited in Amenaghawon, Evbarunegbe, and Obahiagbon, 2021). As the demand for renewable energy continues to rise, there’s a growing interest in producing biodiesel using composite catalysts made from waste materials. This approach not only helps reduce production costs but also promotes sustainability by repurposing materials that would otherwise go to waste. In this discussion, we’ll explore the benefits and challenges associated with using composite catalysts derived from various waste sources for biodiesel production.

Composite catalysts can be created from a wide range of waste materials. These include agricultural residues, food waste, and industrial by-products. For example, waste cooking oil, animal fats, and biomass residues like rice husks and palm kernel cake are often transformed into effective catalytic materials. Research shows that we can convert these waste materials into catalysts through processes like carbonization, calcination, or chemical modification, which enhance their catalytic properties (Khalil et al., 2020).

One of the most significant advantages of composite catalysts from waste materials is their cost-effectiveness. By utilizing readily available waste products, we can significantly lower the overall costs of biodiesel production. Moreover, these catalysts often possess impressive catalytic performance due to their high surface area and porosity, which facilitate effective mass transfer during the trans-esterification process (Shan et al., 2019).

Another important benefit is the positive environmental impact. By repurposing waste materials, we help reduce overall waste and promote a circular economy. This approach aligns with sustainable development goals, as it minimizes the environmental footprint associated with biodiesel production (Bafakeeh et al., 2021).

While the advantages are clear, there are also challenges when it comes to using composite catalysts made from waste materials. One major issue is the variability in the composition and quality of the waste feedstock. This can lead to inconsistent catalytic performance, as impurities or differing chemical structures in waste materials might affect efficiency and selectivity during the trans-esterification process (Gonzalez et al., 2021).

Additionally, preparing these composite catalysts can be labor-intensive, and optimization may be required to achieve the desired catalytic activity. Researchers are actively exploring ways to improve the synthesis processes, such as adjusting conditions for carbonization or modifying the chemical structures of waste materials to enhance their catalytic properties (Kumar et al., 2021).

Recent studies have highlighted the potential of various composite catalysts from waste materials in biodiesel production. For instance, researchers have successfully created catalysts from agricultural residues like rice husk ash, demonstrating promising catalytic activity for trans-esterification (Anwar et al., 2020). Additionally, composite catalysts made from waste cooking oil combined with metal oxides have shown remarkable improvements in reaction rates and biodiesel yields compared to traditional catalysts (Raza et al., 2021).

The incorporation of nanotechnology has also emerged as an exciting area of research for developing advanced composite catalysts. By combining waste materials with nanomaterials, we can enhance both catalytic activity and stability, further improving the efficiency of biodiesel production (Alhassan et al., 2022).

2.2.2.2 CATALYST CHARACTERIZATION

Characterizing catalysts is essential in the biodiesel production process, as it directly impacts their efficiency, activity, and selectivity. Gaining insights into the physicochemical properties of catalysts can help optimize their performance during trans-esterification, a reaction that converts triglycerides into fatty acid methyl esters (FAME) and glycerol.

1. PHYSICAL CHARACTERIZATION

Physical characterization focuses on assessing the surface area, pore size distribution, and morphology of catalysts. These attributes are crucial because they significantly influence catalytic activity and mass transfer during biodiesel production.

BET Surface Area Analysis: The Brunauer-Emmett-Teller (BET) method is widely used to determine the specific surface area of solid catalysts. A higher surface area typically means better catalytic activity, as it provides more active sites for the reaction (Khan et al., 2021). Studies show that catalysts with larger surface areas can lead to significantly higher biodiesel yields.

Pore Size Distribution: The pore structure is equally important, as it affects how easily reactants can access active sites. Techniques such as nitrogen adsorption-desorption isotherms help analyze pore size distribution. Catalysts with mesoporous structures often demonstrate superior catalytic performance due to improved diffusion of reactants (Zhang et al., 2020).

Morphological Analysis: Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are key techniques for visualizing the morphology and particle size of catalysts. These methods can reveal the distribution of active sites and the overall structural integrity of the catalyst (Hossain et al., 2020). The morphology can significantly influence the reaction kinetics and the overall efficiency of the biodiesel production process.

2. CHEMICAL CHARACTERIZATION

Chemical characterization provides information about the catalyst's composition, functional groups, and interactions. This knowledge is vital for understanding the catalytic mechanism and optimizing reaction conditions.

X-ray Diffraction (XRD): XRD is used to determine the crystalline structure of catalysts. The level of crystallinity can influence catalytic properties; for example, more crystalline materials often exhibit better thermal stability and catalytic activity (Fukuda et al., 2001). XRD characterization can also identify phase changes that occur during catalyst synthesis.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectroscopy identifies functional groups present in the catalyst. Specific functional groups can significantly impact the catalytic mechanism. For instance, hydroxyl groups can enhance the adsorption of reactants on acidic catalysts, which influences the trans-esterification process (Mansir et al., 2019).

Energy Dispersive X-ray Spectroscopy (EDX): EDX analyzes the elemental composition of catalysts. Understanding the distribution and concentration of different elements helps correlate their presence with catalytic activity. EDX can also provide insights into the metal loading in heterogeneous catalysts, which is crucial for their effectiveness (Kumar et al., 2021).

3. CATALYTIC ACTIVITY AND SELECTIVITY

Evaluating the catalytic activity and selectivity of catalysts under relevant reaction conditions is vital for biodiesel production.

Activity Tests: To assess catalytic activity, trans-esterification reactions are conducted under controlled conditions. The conversion rate of triglycerides to biodiesel is measured using gas chromatography (GC). High conversion rates indicate effective catalytic performance (Rojan et al., 2021).

Selectivity Tests: Selectivity refers to the catalyst's ability to convert certain substrates into the desired products. This can be evaluated by analyzing the product distribution after the reaction. A highly selective catalyst will favor the formation of biodiesel while minimizing by-products (Mansir et al., 2019).

4. THERMAL STABILITY AND REUSABILITY

Thermal stability and reusability are critical factors that influence the practical application of catalysts in biodiesel production.

Thermogravimetric Analysis (TGA): TGA measures weight changes in the catalyst as temperature varies. This technique helps evaluate the thermal stability of the catalyst and its resistance to decomposition at high temperatures, which is essential for maintaining performance during extended reactions (Khan et al., 2021).

Reusability Studies: Assessing the reusability of catalysts is important for determining their economic viability. Catalysts can be subjected to multiple reaction cycles, and their performance over time can be monitored. A catalyst that maintains its activity and selectivity after several uses is valuable for biodiesel production (Zhang et al., 2020).

2.2.5 DESIGN OF EXPERIMENT

The Design of Experiments (DOE) has proven beneficial across various scientific disciplines, particularly in enhancing process and product quality as well as optimizing products (Durakovic, 2018). The roots of DOE can be traced back to the agricultural studies conducted by Sir Ronald Fisher in the 20th century. Fisher, along with his collaborator Frank Yates, laid the groundwork for statistical methods used in designing and analyzing experiments. In 1951, Box and Wilson published a foundational study on response surface designs, aiming to identify optimal conditions by analyzing outputs as response functions.

Experimentation based on a statistical model offers an effective way to gather data. This method has long been employed to enhance both products and processes. By utilizing DOE, researchers can systematically conduct experiments that are later analyzed to identify significant factors and improve the phenomenon or process under investigation. Furthermore, incorporating DOE in product innovation (PI) can accelerate product design and development, making the process easier and more cost-effective, while also enhancing performance and reliability (Arboretti et al., 2022).

2.2.5.1 PRINCIPLE OF DOE

The fundamental elements of Design of Experiments (DOE) include identifying a set of variables that may affect the performance of a process, selecting appropriate levels for these variables, specifying combinations of these factor levels, and conducting experiments according to a predetermined plan. It is essential that the factors be tested at a minimum of two levels, and if there is interest in identifying curvature effects, additional levels may be required to assess the impact of each process variable. For a given number of factors (k) and levels (l), a full-factorial design will have a total of lk experimental runs, representing all possible combinations of factors and their levels. However, as the number of factors or levels increases, the number of required tests can quickly become impractical.

To address this issue, fractional factorial designs have been developed, which require fewer experimental runs than a full factorial design while still allowing for the estimation of many effects. Central Composite Design (CCD) and Box-Behnken Design (BBD) are commonly used methods to explore interactions and quadratic effects in experiments based on 2k factorial or fractional factorial designs. BBDs, in particular, incorporate 2k factorial designs into full-block designs, often resulting in more efficient experimental solutions compared to CCDs in terms of the number of runs needed. CCDs enhance 2k factorial or fractional factorial designs by adding axial runs and center points. Different design types, such as full factorials, fractional factorials, CCDs, and BBDs, are utilized in response surface methodology. Additionally, there are various design patterns used in this context that feature unique characteristics, including mixing patterns and constraints related to randomization.

2.2.5.2 RESPONSE SURFACE METHODOLOGY (RSM)

Response Surface Methodology (RSM) focuses on developing empirical models from experimental data collected according to the experimental design. It encompasses a range of mathematical and statistical techniques and serves as a multivariate statistical tool. By employing lower-order polynomials, RSM has proven to be a reliable statistical approach for chemical process applications. The Central Composite Design (CCD), which is suitable for fitting second-order polynomial equations, has been applied to optimize numerous research problems within the RSM field.

A CCD is composed of three categories of design points:

(a) Axial points, or star points, which are positioned at a specific distance (α) from the center and equal to two times the number of factors (2k), used to form quadratic equations.

(b) Two-level factorial or fractional factorial design points, which include various combinations of +1 and -1 factor levels, also totaling two times the number of factors (2k).

(c) Center points, which provide replicates and allow for a reliable and unbiased measurement of experimental errors.

Given these components, the estimated total number of experiments (N) in a CCD can be expressed as:

$N = k^2 + 2k + n$ where k represents the number of factors being studied, N is the total number of experiments, and n denotes the number of repeated tests. Typically, when implementing central composite design within the framework of RSM, software tools like Minitab or Design Expert are employed for effective execution.

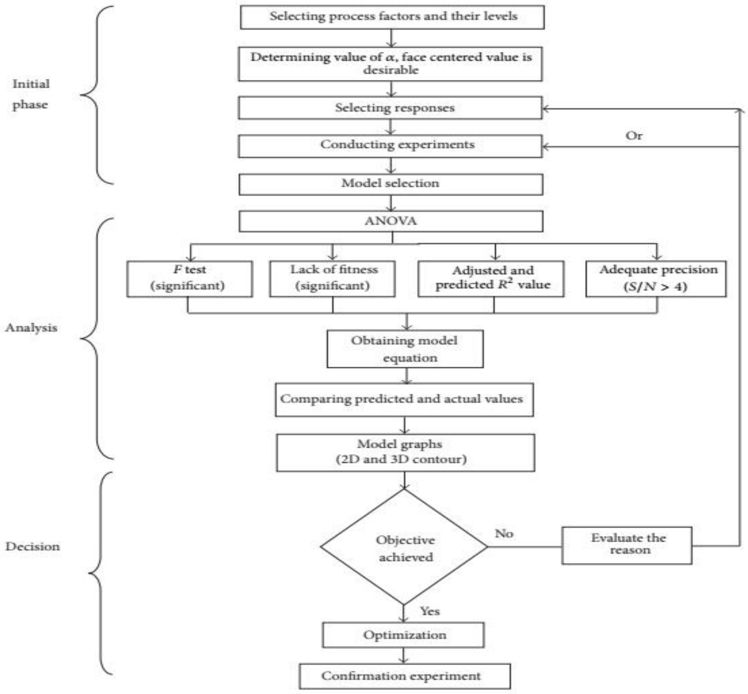

Figure 2. 1: Central composite design flow diagram (Asghar et al, 2014)

STEPS IN RSM METHODOLOGY IN BIODIESEL PRODUCTION

Response Surface Methodology (RSM) is a statistical approach used to optimize processes, including biodiesel production. The following steps outline the RSM methodology for biodiesel production:

1. Define Objective

Clearly articulate the goals of the biodiesel production process, such as maximizing yield, improving fuel quality, or reducing production costs.

2. Identify Variables

Determine the key factors that influence biodiesel production. Common variables include:

- Type of feedstock (e.g., vegetable oils, animal fats)
- Catalyst type (e.g., NaOH, KOH)
- Catalyst concentration
- Methanol-to-oil ratio
- Reaction temperature
- Reaction time

3. Select Experimental Design

Choose an appropriate RSM design, such as:

- Central Composite Design (CCD)
- Box-Behnken Design (BBD)

These designs allow for the efficient exploration of the relationships between factors while minimizing the number of experiments.

4. Conduct Preliminary Experiments

Perform initial experiments to gather baseline data on the effects of the factors. This helps in refining the levels for the RSM design.

5. Perform the Experiments

Execute the experiments according to the chosen RSM design. Ensure consistent conditions throughout the experiments and include replicates to assess variability.

6. Analyze Data

Use statistical software to analyze the experimental data. Fit a response surface model to describe the relationship between the independent variables (factors) and the dependent variable (biodiesel yield).

7. Optimize the Response

Utilize the response surface model to identify the optimal conditions for biodiesel production. This step may involve predicting responses at different combinations of factor levels.

8. Validate the Model

Conduct confirmation experiments under the predicted optimal conditions to validate the model's accuracy. Compare the results with the predicted values for reliability.

9. Interpret Results

Analyze the outcomes to understand the effects of different factors on biodiesel yield and quality. Summarize the findings and draw conclusions based on the data.

2.2.5.3 ARTIFICIAL NEURAL NETWORKS (ANN)

Artificial Neural Networks (ANNs) have increasingly become a vital tool in various fields, including the production of biodiesel. Their ability to model complex relationships and analyze large datasets makes them particularly useful. ANNs are inspired by the human brain's structure and function, consisting of interconnected nodes (or neurons) organized in layers.

At the heart of ANNs are several layers: an input layer, one or more hidden layers, and an output layer. Each neuron in these layers performs mathematical operations on the input data, applying weights and biases before passing the results through an activation function. The network learns by adjusting these weights and biases based on the errors it makes in its predictions, often using a method called backpropagation (Haykin, 2009).

Input Layer: This is where the network receives initial data, which might include various parameters related to biodiesel production, such as the type of feedstock, reaction conditions, and catalyst types.

Hidden Layer(s): These layers enable the network to learn intricate patterns in the data. The number of hidden layers and the neurons within them can significantly affect the network’s performance.

Output Layer: This is where the final predictions or classifications are made based on the input data. In the context of biodiesel production, the output might indicate the yield of biodiesel or its fuel properties.

ANNs have been applied in several ways within biodiesel production:

Predictive Modeling: ANNs can predict biodiesel yield based on various input parameters, like the type of feedstock and specific reaction conditions. By training on historical data, ANNs learn the relationships between these factors and can provide accurate predictions for new experiments (Santos et al., 2020).

Process Optimization: ANNs can work alongside optimization algorithms to find the best operating conditions for producing biodiesel. By simulating different scenarios, these networks help identify the ideal parameters that maximize yield while keeping costs down (Mansir et al., 2019).

Quality Assessment: ANNs can also predict important fuel properties, such as viscosity and flash point, which are crucial for ensuring the biodiesel produced meets industry standards (Bafakeeh et al., 2021).

2.2.5.4 TAGUCHI DESIGN OF EXPERIMENT

The Taguchi Design of Experiments (DOE) is a powerful statistical approach created by Dr. Genichi Taguchi, aimed at enhancing product quality and performance through systematic experimentation. This method is appreciated for its efficiency and effectiveness in identifying how various factors influence a process's outcome, enabling researchers and engineers to find optimal conditions with minimal experimentation.

Taguchi listed three conditions:

- On-target with little variance; (such as a component being joined within an assembly).
- Larger is better (for instance, in agricultural productivity),
- While smaller is preferable (for example, carbon dioxide emissions)

At the heart of Taguchi's methodology are several key concepts:

Orthogonal Arrays: Taguchi designs make use of orthogonal arrays to streamline the experimentation process. These arrays allow for the examination of multiple factors at different levels without requiring an overwhelming number of experiments. By organizing experiments this way, researchers can assess interactions between factors without needing a full factorial design, which can often be impractical for complex systems (Taguchi et al., 2005).

Control of Variability: A significant aspect of Taguchi's approach is the focus on controlling variability, rather than simply optimizing average performance. This methodology emphasizes robust design, aiming to make products and processes less sensitive to variations that are difficult or costly to manage, such as environmental factors (Taguchi, 1993). By prioritizing robustness, organizations can achieve more consistent outcomes and improved quality.

Loss Function: Taguchi introduced the idea of a loss function, which quantifies the economic loss associated with deviations from target values. This concept highlights that quality should not just be measured by how many products meet specifications but also by the costs incurred due to variations. By minimizing the loss function, companies can achieve better quality and reduce expenses (Taguchi, 1987).

Taguchi's design principles have found applications across various industries to boost quality and efficiency:

Manufacturing: In manufacturing settings, Taguchi DOE is widely used to optimize processes and identify key factors that influence product performance. Engineers can systematically evaluate the effects of different parameters on production techniques, such as machining, welding, and assembly (Montgomery, 2017).

Product Development: During product development, Taguchi designs help identify the optimal parameters that lead to better functionality and user satisfaction. By addressing the factors that affect product performance, teams can create items that better meet customer expectations (Phadke, 1989).

Quality Improvement: Taguchi's methodology is often integrated into quality improvement initiatives, such as Six Sigma and Total Quality Management (TQM). By employing Taguchi DOE, organizations can systematically identify and eliminate sources of variability, resulting in higher quality products and services.

2.2.5.4.1 TAGUCHI RULES FOR PRODUCTION

Dr. Taguchi concluded that the most effective way to eliminate variability in a product lies in the production process and its design. To address this, he developed a quality engineering methodology that can adapt to various situations, which consists of three essential stages (Karna, 2012):

I. System Design

This stage focuses on the conceptual design, emphasizing creativity and originality.

II. Parameter Design

Once the concept is established, standard engineering practices dictate that expected values for various dimensions and design factors should be determined.

III. Tolerance Design

After completing the parameter design and understanding how different parameters influence performance, the next step is to minimize and manage variations in critical dimensions.

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 REAGENTS AND RAW MATERIALS USED.

The substances and unprocessed materials employed in this research are outlined in Table 3.1.

MATERIALS	SOURCE	USES
Fish Scales	It was obtained locally from fish sellers.	Feedstock for the acid precursor of the heterogeneous Bifunctional catalyst.
Cabbage back (Brassica rapa)	It was obtained locally from Cabbage back (Brassica rapa) sellers.	Feedstock for the basic precursor of the heterogeneous Bifunctional catalyst.
Neem Seed Oil (NSO)	Local vendoe	Feedstock for biodiesel production.

Potassium Hydroxide (KOH)	JHD	For pre-treatment of the basic precursor and to determine the acid value of NSO and biodiesel.
Sulphuric acid (H2SO4)	JHD.	For pre-treatment of the acid precursor.
Acetic Acid	JHD.	For determining the peroxide value of the NSO.
Chloroform (CHCl3)	JHD.	For determining the peroxide and iodine values of NSO.
Benzene (C6H6)	JHD.	For determining the acid values of both the NSO and biodiesel produced.

Ethanol (C2H5OH)	PROLABO.	For determining acid and saponification values of NSO and acid value of biodiesel produced.
Methanol (CH3OH)	PROLABO.	To stimulate the simultaneous esterification and trans-esterification of NSO to produce biodiesel.
Distilled water (H2O)	Chemistry Lab, University of Benin.	For preparing the standard solution and for washing biodiesel.
Phenolphthalein (indicator)	JHD.	For titrating.
Sodium thiosulphate (Na2S2O3)	JHD.	For determining the iodine and peroxide values of the NSO.

Potassium iodide (KI)	JHD.	For determining the iodine value of the NSO.
Starch indicator	Unbranded.	For determining the iodine value of the NSO.

Table 3. 1 Raw Materials and Reagents

EQUIPMENT	**SOURCE**	**USES**
Beakers	Chemical Engineering Lab, UNIBEN.	For containing substances.
Measuring Cylinder	Chemical Engineering Lab, UNIBEN.	Volumetric measurement of solvent.
Volumetric flask	Chemical Engineering Lab, UNIBEN.	For volumetric measurement of solvent.
Magnetic Stirrer	Chemical Engineering Lab, UNIBEN.	For continuous stirring of reactants.

Reflux Condenser	Chemical Engineering Lab, UNIBEN.	To condense methanol escaping as a vapour to liquid and sent back to the reactor.
Conical Flask	Chemical Engineering Lab, UNIBEN.	To serve as a reactor.
Weighing balance	Chemical Engineering Lab, UNIBEN.	For measuring mass.
Oven	Chemical Engineering Lab, UNIBEN.	For drying/ To determine the moisture content of the NSO.
Furnace	Chemical Engineering Lab, UNIBEN.	For calcination of fish scale and carbonization of cabbage back (Brassica rapa)
Separating funnel	Chemical Engineering Lab, UNIBEN.	For separating biodiesel and washing biodiesel.
Burette	Chemical Engineering Lab, UNIBEN.	For titration.
Pipette	Chemical Engineering Lab, UNIBEN.	For titration.

Retort stand	Chemical Engineering Lab, UNIBEN.	For holding burette and separating funnel.
Crucible	Chemical Engineering Lab, UNIBEN.	Used to determine the moist content of NSO.
Centrifuge	Chemical Engineering Lab, UNIBEN.	Used to separate the biodiesel mixture obtain after reaction.
Flash Point Tester	Chemical Engineering Lab, UNIBEN.	Used to determine the flash point of the biodiesel produced.
Kinematic Viscometer	Chemical Engineering Lab, UNIBEN.	Used to determine the viscosity of the biodiesel and NSO.

Table 3.2 The various apparatus and their function

3.2 METHODS

3.2.1 NEEM SEED OIL CHARACTERIZATION

3.2.1.1 DETERMINATION OF ACID VALUE

Determining the Acidity of Neem Seed Oil

Using this method, we will assess the acidity of Neem Seed Oil both prior to and following a specific process. The acid value refers to the quantity of potassium hydroxide (KOH) required to neutralize one gram of free fatty acids present in one milligram of Neem Seed Oil. Since free fatty acids are typically generated during the breakdown of triglycerides, this measurement serves as a reliable indicator of rancidity.

The figure illustrates the amount of fatty acids that have been hydrolyzed from glycerides due to factors such as moisture, temperature, or the action of the lipolytic enzyme lipase.

To determine the acid value of Neem Seed Oil, we will perform a titration using a standard KOH solution in an alcoholic medium. This involves taking 2.0 grams of Neem Seed Oil in a 250 mL conical flask and adding benzene, ethanol, and three drops of phenolphthalein indicator. The oil will then be titrated against a standardized KOH solution. The acid value can be calculated using Equation 1:

$$\text{Acid Value} = \frac{(\boldsymbol{T_v - T_B}) \times \boldsymbol{KOH\ Normality} \times \mathbf{56.1}}{\boldsymbol{Weight\ of\ NEEM\ SEED\ OIL\ used}} \qquad \mathbf{1}$$

Where: T_v = Titrate value of the Neem Seed Oil

T_B = Titrate value of blank solution.

The proportion of fatty acids by weight within the oil is referred to as the free fatty acid (FFA) content. This can be determined using Equation 2:

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

3.2.1.2 DETERMINATION OF SAPONIFICATION VALUE

This test aims to determine the saponification value of Neem Seed Oil both before and after the processes of esterification and trans-esterification. The saponification value indicates how much potassium hydroxide is required to react completely with every reactive unit in one gram of the sample. This process involves using an alkali to convert triglycerides, diglycerides, and monoglycerides present in the sample while also neutralizing free fatty acids and other reactive substances like lactones.

The saponification value, along with several related metrics, provides insight into the average molecular weight of the fatty materials, or more specifically, their equivalent weight. The saponification equivalent of a fat or ester refers to the amount that can be saponified by one mole (56.104 grams) of potassium hydroxide. This leads to the equation: 56104 = saponification value x saponification equivalent (Chakrabarty, 2003).

To determine the saponification value for Neem Seed Oil, 2.00 grams of the oil will be placed in a conical flask, and 25 mL of ethanolic KOH will be added. The mixture will then be refluxed for one hour to ensure the reaction completes. After this, 0.5 mL of phenolphthalein will be added to the mixture, and the color will be adjusted using a 0.5M HCl solution until it turns colorless. A blank test using distilled water will be conducted under the same conditions.

The saponification value can be calculated using Equation 3:

The saponification value can be calculated using Equation 3:

$$\textbf{Saponification Value} = \frac{\mathbf{56.1 \times M \times (T_B - T_{WCO})}}{\mathbf{Weight\ of\ NEEM\ SEED\ OIL}} \qquad \mathbf{3}$$

Where: T_B = Blank titration

$T_{\text{NEEM SEED OIL}}$ = Neem Seed Oil titration

M = Molarity of HCl

Equation 4 can be used to determine the average Molecular of Neem Seed Oil.:

$$\mathbf{Mw} = \frac{\mathbf{168300}}{\boldsymbol{SV - AV}} \qquad \mathbf{4}$$

Where: SV = Saponification Value

AV = Acid Value

3.2.1.3 DETERMINATION OF PEROXIDE VALUE

The presence of peroxides is the first indication that unsaturated fats and oils are beginning to go rancid. The peroxide value is defined as the number of millimoles of peroxide or milliequivalents of oxygen present per 1000 grams of fat (1 mm = 2 meq.).

To determine the peroxide value of Neem Seed Oil, 2.00 grams of the oil will be combined with 12 mL of a 3:2 mixture of acetic acid and chloroform in a conical flask. Next, 0.2 mL of saturated potassium iodide will be added, and the mixture will be stirred for one minute. Following this, distilled water will be added to the mixture. A 1 mL portion of starch solution will be used as an indicator during the titration process with 0.1 N sodium thiosulphate. The titration will continue until the blue-grey color in the upper aqueous layer disappears. The same procedure will be followed for the blank test.

The peroxide value can be calculated using Equation 5 below:

$$\textbf{Peroxide Value} = \frac{10 \times (N_1 - N_2)}{Weight\ of\ NEEM\ SEED\ OIL} \qquad 5$$

Where: N_1 = Sodium Thiosulphate Blank titrate

N_2 = Sodium Thiosulphate titrate of NEEM SEED OIL

3.2.1.4. DETERMINATION OF IODINE VALUE

This method is one of the most effective analytical techniques for assessing the unsaturation levels of fats and oils. The underlying principle involves introducing halogen to an unsaturated bond, where it reacts with the double bond.

To conduct the iodine value test for Neem Seed Oil, 0.25 grams of the oil will be placed in a conical flask, followed by the addition of 10 mL of chloroform ($CCl4$). The mixture will be gently heated and then allowed to cool for 10 minutes. After that, 25 mL of Wij's reagent will be added, and the mixture will be stirred vigorously yet carefully. It will then be left in the dark for 30 minutes to prevent any reactions caused by sunlight. Once the time has elapsed, the mixture will be titrated with sodium thiosulphate until a yellow color appears. Following this, 20 mL of a 10% potassium iodide (KI) solution and 150 mL of distilled water will be added. The resulting yellow mixture will undergo titration with sodium thiosulphate, using a 1% starch solution as an indicator. The titration will continue until the color changes from indigo/black to colorless, indicating the endpoint. The same conditions will be applied for the control test.

The iodine value can be calculated using Equation 6 below:

$$\textbf{Iodine Value} = \frac{12.69 \times N \times (V_1 - V_2)}{Weight\ of\ NEEM\ SEED\ OIL} \qquad 6$$

Where: V_1 = Sodium Thiosulphate Blank titrate

V_2 = Sodium Thiosulphate titrate of Neem Seed Oil

N = Normality of Sodium Thiosulphate (Na_2SO_3)

3.2.1.5 DETERMINATION OF KINEMATIC VISCOSITY

The kinematic viscosity of Neem Seed Oil will be measured using a capillary viscometer that has been calibrated according to the ASTM D445 standard. For this measurement, a clean and dry capillary viscometer will be utilized, and 200 mL of Neem Seed Oil will be timed between the two menisci—the lower and upper meniscus. The same method will be applied to measure the viscosity of biodiesel.

3.2.1.6 DETERMINATION OF OIL DENSITY

To determine the density of Neem Seed Oil, a 50 mL density bottle with a known weight will be filled with the oil. The new weight of the density bottle will then be recorded. By subtracting the known weight of the empty bottle from its new weight, the weight of the Neem Seed Oil in the 50 mL bottle can be calculated. The density will be determined using Equation 7 below, with measurements expressed in kg/m³.

$$\textbf{Density} = \frac{\boldsymbol{Weight\ of\ NEEM\ SEED\ OIL}}{\boldsymbol{Volume\ of\ NEEM\ SEED\ OIL}} \qquad \textbf{7}$$

3.2.1.7 DETERMINATION OF MOISTURE CONTENT OF NEEM SEED OIL

To determine the moisture content of Neem Seed Oil, 2.00 grams of the oil will be accurately weighed and placed into a crucible with a known weight. The crucible will then be heated in an oven at 150 degrees Celsius for four hours. During this time, the crucible will be reweighed at one-hour intervals to observe the changes in weight until it stabilizes. The moisture content will be calculated using Equation 8:

$$\text{Moisture Content} = \frac{\textbf{Initial weight of NSO} - \textbf{Final weight of NSO}}{\textbf{Initial weight of NEEM SEED OIL}} \times \mathbf{100}\%$$

3.2.1.8 DETERMINATION OF SPECIFIC GRAVITY (S.G.)

To determine the specific gravity (S.G.) of Neem Seed Oil, a density bottle will be used. First, a clean and dry 50 mL container will be weighed (W0) before filling it with Neem Seed Oil. After adding the oil, the stopper will be placed on the bottle, and the weight will be recorded again (W1). Next, the container will be cleaned and dried, and water will be added to replace the oil, providing a new weight (W2). The specific gravity can then be calculated using Equation 9:

$$\mathbf{S.G} = \frac{\boldsymbol{W1 - W0}}{\boldsymbol{W2 - W0}} \qquad \mathbf{9}$$

3.2.2 CATALYST PREPARATION

Fish scales and Waste cabbage back (Brassica rapa) will serve as the raw materials for creating diverse bifunctional catalysts. These catalysts will be employed in the process of catalyzing the production of biodiesel from neem seed oil, utilizing optimization and kinetics studies.

3.2.2.1 ACID PRECURSOR

The composition of cellulose, hemicellulose, and lignin in cabbage back (Brassica rapa) can vary, but general estimates for the percentage composition in the dry weight of cabbage back (Brassica rapa) back are as follows:

- Cellulose: 30-40%

- Hemicellulose: 20-25%

- Lignin: 5-10% (Zhang, et al, 2015)

The waste cabbage back (Brassica rapa) obtained from a nearby cabbage seller will be employed in creating the acidic active center of the dual-purpose catalyst. These waste cabbage back (Brassica rapa) are rinsed with hot water to remove dirts and left to dry under sunlight for a duration of one week. Afterwards, the dried waste cabbage back (Brassica rapa) will be carbonized in a muffle furnace at 300 °C for 4 hours. It will be allowed to cool before crushing it using a wooden mortar and then sieved to obtain ash.

The cabbage back (Brassica rapa) ash will be treated with a 1.5M standard solution of H2SO4 and then stir the mixture continuously on heat for 3 hours at 150 °C using a heating mantle. This is known as Sulphuration. Subsequently, the blend is covered and left undisturbed for 48 hours. Following this, it undergoes a thorough wash and filtration process using distilled water and a mesh filter to eliminate impurities and free ions. The residue of the sulfur-treated cabbage back (Brassica rapa) ash is then subjected to drying in an oven at 150 °C for a duration of 2 hours, after which it is stored in an air-tight container.

Fig 3.1: Treated cabbage back

3.2.2.3 BASIC PRECURSOR

Fish scales which are majorly composed of calcium salt, are sourced from the descaling of Croaker fish (Sciaenidae) are to be used in the synthesis of the basic active site of the bifunctional catalyst.

Waste fish scales will be thoroughly rinsed several times with hot distilled water to eliminate any remaining flesh and gelatinous substances. Following this, they will be dried in a hot air oven at 100 degrees Celsius for approximately 6 hours. Once dried, the scales will be grinded into a fine powder and then calcined in a muffle furnace at varying temperatures ranging from 600 to 800 degrees Celsius for 2 hours. It is then treated with a standard molar solution of 1.5 M of KOH, the blend is covered and left for 48 hours. It will be finally undergo washing and filteration like the acid precursor. It will finally be subjected to drying in an oven 150 °C for a duration of 2 hours, after which it is stored in an air-tight container.

Fig 3.2: Treated fish scale

3.2.2.3 CATALYST IMPREGNATION

In a beaker, the acid and basic precursors will be combined in a chosen ratio along with a small amount of water to create a wet mixture. This mixture will then be dried in an oven at 150 degrees Celsius. After drying, it will be ground using a wooden mortar and pestle, and subsequently heated in a muffle furnace at 600 degrees Celsius for 3 hours. Once this step is complete, the sample will be removed and placed in a desiccator to cool. Finally, it will be transferred to a sealed container for storage.

3.2.3 CATALYST CHARACTERISATION

3.2.3.1 SURFACE MORPHOLOGY OF THE PROCESSED CATALYST

Scanning Electron Microscopy (SEM) is an essential method for studying the surface structure of processed catalysts, offering high-resolution images that capture intricate details of the catalyst's design. This technique is particularly effective for examining aspects like pore size, surface texture, and the arrangement of active sites, all of which are crucial for how well a catalyst performs.

One of the key benefits of SEM is its capability to visualize the impact of different catalyst preparation techniques, such as calcination and impregnation, on the catalyst's surface characteristics. These processing methods can significantly change the morphology of the catalyst, and SEM enables researchers to evaluate these changes effectively (Zhou et al., 2021). By analyzing SEM images taken before and after processing, researchers can gain valuable insights into how these morphological variations affect catalytic activity.

Fig 3.3 The wet impregnation process

3.2.3.2 BET SURFACE AREA ANALYSER

The Brunauer-Emmett-Teller (BET) surface area analysis is a popular technique used to characterize the surface area of catalysts, a critical factor that affects their catalytic activity. This method involves measuring the physical adsorption of nitrogen gas onto the catalyst's surface at liquid nitrogen temperatures, which allows for the calculation of the specific surface area based on the amount of gas adsorbed.

BET analysis is based on the concept of multilayer adsorption of gas molecules on a solid surface. When nitrogen is adsorbed onto the catalyst, it forms several layers, and the amount of gas adsorbed at different relative pressures is recorded. The BET equation relates this amount to the catalyst's surface area, enabling the determination of specific surface area (Brunauer et al., 1938).

The surface area of a catalyst is crucial because it determines the number of active sites available for chemical reactions. Generally, a larger surface area results in higher catalytic activity, as more reactants can interact with the catalyst. Thus, measuring the BET surface area is essential for optimizing catalyst formulations and ensuring their effective performance in various applications, such as petrochemical processing, environmental cleanup, and fuel cells (Zhao et al., 2020).

BET analysis is conducted using specialized instruments known as BET surface area analyzers. The process typically involves several steps: preparing the sample, degassing it to remove moisture and impurities, and then measuring nitrogen adsorption. The data collected is analyzed to determine the BET surface area, pore volume, and pore size distribution of the catalyst, providing a detailed understanding of its textural properties (Liu et al., 2021).

3.2.3.3 ELECTRON DISPERSIVE X-RAY SPECTROSCOPY (EDX)

Electron Dispersive X-ray Spectroscopy (EDX or EDS) is an effective analytical method used for determining the elemental composition and chemical characteristics of materials. It is often combined with Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy

(TEM) to provide both qualitative and quantitative insights into the elemental makeup of samples at a micro- or nanoscale level.

The technique is based on the principle that when a sample is hit with high-energy electrons, it emits X-rays that are unique to the elements present in that material. Each element produces X-rays with specific energies, which allows for their identification. Additionally, the intensity of the emitted X-rays corresponds to the concentration of each element, enabling quantitative analysis (Williams & Carter, 2009).

EDX is extensively utilized in materials science, especially in catalysis, to analyze and understand the composition of catalysts and other materials. By generating detailed elemental maps and spectra, EDX provides insights into element distribution, impurity presence, and the overall makeup of catalysts, which is vital for enhancing their performance (Wang et al., 2021).

3.2.3.4 X-RAY DIFFRACTION (XRD)

X-ray Diffraction (XRD) is an essential analytical method used to investigate the crystalline structure of materials. The technique involves directing X-rays at a sample and measuring the angles and intensities of the X-rays that are diffracted by the crystal lattice. The resulting diffraction pattern reveals important information about the material's phase composition, crystallite size, and any internal strain.

When X-rays hit a crystalline material, they are scattered at specific angles based on how the atoms are arranged within the crystal. By analyzing these diffraction patterns, researchers can identify the different phases present in the sample and extract various structural details, such as lattice parameters and symmetry (Klug & Alexander, 1974).

3.2.3.5 THERMOGRAVIMETRIC ANALYSIS (TGA/DTGA)

Thermogravimetric Analysis (TGA) is a thermal analysis technique that measures the change in mass of a material as it is heated over time. This method provides critical information about the thermal stability, composition, and decomposition behavior of various substances, including polymers, metals, and catalysts. Differential Thermogravimetry (DTGA) is a related approach that focuses on measuring the rate of mass change, offering a more detailed perspective.

In TGA, a sample is gradually heated at a controlled rate while its mass is continuously recorded. As the temperature rises, any changes in the sample's weight indicate physical and chemical transformations, such as dehydration, oxidation, or decomposition. The resulting TGA curve, which plots weight loss against temperature, helps researchers identify specific thermal events and analyze how stable the material is (Yang et al., 2021).

TGA is frequently used in material science to characterize catalysts, polymers, and composite materials. In the field of catalysis, TGA assesses the thermal stability of catalysts and examines their decomposition profiles, which are essential for understanding how they perform under different conditions (Zhao et al., 2020). DTGA enhances this analysis by showing the rates of mass loss, making it easier to identify overlapping decomposition steps.

A significant benefit of TGA/DTGA is its ability to provide quantitative data regarding weight changes associated with thermal processes. This information is vital for determining material composition, evaluating the effectiveness of thermal treatments, and investigating the stability of new formulations. Additionally, TGA is relatively easy to conduct and can be applied to a wide variety of materials (Gao et al., 2020).

3.2.4.1 OPTIMIZATION OF BIODIESEL

The process of producing biodiesel includes utilizing Neem Seed Oil, methanol, and a biologically derived catalyst created from fish scale and cabbage back.The NSO is first sieved to remove particles, then added to a conical flask and addition of Methanol and processed catalyst. The reaction takes place at the optimizing condition producing biodiesel, Glycerol and catalyst mixture, which is then separated with the use of centrifuge (Catalyst) and separating funnel (Glycerol). The biodiesel is washed with the use of warm water and dried to obtain a clean biodiesel, while the glycerol is discarded. The optimization of concurrent esterification and trans-esterification of NSO was conducted using the RSM , incorporating four variables with three tiers and yielding two outcomes.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 PHYSIOCHEMICAL PROPERTIES OF NEEM SEED OIL (NSO)

The characteristics, both physical and chemical, of Neem Seed Oil (NSO) were evaluated using the methodologies described in the preceding section, adhering to the ASTM standard guidelines. The findings from the NSO characterization are presented in Table 4.1.

PROPERTIES	**VALUES**
Acid Value (mg KOH/g)	17.67
FFA (%)	8.835
Saponification Value	196.35
Molecular Weight (g)/mol	941.91
Peroxide Value	5
Density (Kg/m^3)	0.962

Table 4.1 Physiochemical Properties of NSO

4.2 MODELING OF SIMULTANEOUS ESTERIFICATION AND TRANS-ESTERIFICATION OF NSO

An RSM orthogonal array, under CCD, was employed to statistically analyze the concurrent esterification and trans-esterification of NSO using a dual-action catalyst derived from Fish scale and Cabbage back. Employing Design Expert 13.0, an experimental design using RSM was carried out.

Std	Run	Block	Factor 1 A: MeOH: Oil	Factor 2 B: Catalyst Load %	Factor 3 C: Power Inten Watt	Factor 4 D: Speed rpm	Factor 5 E: Time minutes
24	1	Block 1	15.00	5.00	800.00	500.00	5.00
16	2	Block 1	15.00	5.00	800.00	2000.00	2.00
47	3	Block 1	10.50	3.50	490.00	1250.00	3.50
41	4	Block 1	10.50	3.50	490.00	1250.00	2.00
10	5	Block 1	15.00	2.00	180.00	2000.00	2.00
30	6	Block 1	15.00	2.00	800.00	2000.00	5.00
21	7	Block 1	6.00	2.00	800.00	500.00	5.00
18	8	Block 1	15.00	2.00	180.00	500.00	5.00
29	9	Block 1	6.00	2.00	800.00	2000.00	5.00

40	10	Block 1	10.50	3.50	490.00	2000.00	3.50
46	11	Block 1	10.50	3.50	490.00	1250.00	3.50
42	12	Block 1	10.50	3.50	490.00	1250.00	3.50
19	13	Block 1	6.00	5.00	180.00	500.00	5.00
26	14	Block 1	6.00	5.00	180.00	2000.00	2.00
36	16	Block 1	10.50	2.00	180.00	2000.00	5.00
7	17	Block 1	6.00	5.00	490.00	1250.00	3.50
6	18	Block 1	15.00	2.00	800.00	500.00	2.00
2	19	Block 1	15.00	2.00	800.00	500.00	2.00
5	20	Block 1	6.00	2.00	180.00	500.00	2.00
23	21	Block 1	6.00	5.00	800.00	500.00	2.00
12	22	Block 1	15.00	2.00	180.00	2000.00	2.00
13	23	Block 1	6.00	2.00	800.00	500.00	2.00
44	25	Block 1	10.50	3.50	490.00	1250.00	3.50
50	26	Block 1	10.50	3.50	490.00	1250.00	3.50
38	27	Block 1	10.50	3.50	800.00	1250.00	3.50
31	28	Block 1	6.00	5.00	800.00	2000.00	5.00

37	29	Block 1	10.50	3.50	180.00	1250.00	3.50
43	30	Block 1	10.50	3.50	490.00	1250.00	3.50
4	31	Block 1	15.00	5.00	180.00	500.00	2.00
34	32	Block 1	15.00	3.50	490.00	1250.00	3.50
3	33	Block 1	6.00	5.00	180.00	500.00	2.00
22	34	Block 1	15.00	2.00	800.00	500.00	5.00
33	35	Block 1	6.00	3.50	490.00	1250.00	3.50
15	36	Block 1	6.00	5.00	800.00	2000.00	2.00
48	37	Block 1	10.50	3.50	490.00	1250.00	3.50
32	38	Block 1	15.00	5.00	800.00	2000.00	5.00
39	39	Block 1	10.50	3.50	490.00	500.00	3.50
14	40	Block 1	15.00	2.00	800.00	2000.00	2.00
1	41	Block 1	6.00	2.00	180.00	500.00	2.00
25	42	Block 1	6.00	2.00	180.00	2000.00	5.00
8	43	Block 1	15.00	5.00	800.00	500.00	2.00
27	44	Block 1	6.00	5.00	180.00	2000.00	5.00
49	45	Block 1	10.50	3.50	490.00	1250.00	3.50

9	46	Block 1	6.00	2.00	180.00	2000.00	2.00
28	47	Block 1	15.00	5.00	180.00	2000.00	5.00
20	48	Block 1	15.00	5.00	180.00	500.00	5.00
17	49	Block 1	6.00	2.00	180.00	500.00	5.00
35	50	Block 1	10.50	2.00	490.00	1250.00	3.50

Table 4.2. The Experimental design

The first four runs were conducted and there was no esterification or trans-esterification reaction in any of the runs leading to no formation of biodiesel.

At the end of each experiments, the product was spun using a centrifuge and kept in a separating funnel for 24 hours .The mixture formed two layers after 24 hours which are excess methanol at the top and the oil at the bottom.

DISCUSSION

The experimental results indicate that no biodiesel formation occurred during the simultaneous esterification and trans-esterification of Neem Seed Oil (NSO) using the bifunctional catalyst derived from fish scales and cabbage back. This lack of reaction suggests potential issues with the catalyst's effectiveness or the reaction conditions. Several factors could have contributed to this outcome. First, the catalyst preparation process, including calcination and impregnation, may not have achieved the desired catalytic activity. The catalyst's surface area, porosity, or active sites might have been insufficient to facilitate the reaction. Additionally, the reaction conditions, such as temperature, methanol-to-oil ratio, and catalyst loading, may not have been optimized for biodiesel production. The absence of biodiesel formation highlights the need for further investigation into the catalyst's properties and the optimization of reaction parameters to enhance its performance. Futher studies will focus on refining the catalyst synthesis process and conducting a more detailed analysis of its structural and chemical properties to identify and address the limitations observed in this study.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This study aimed to explore the synthesis of biodiesel from Neem Seed Oil (NSO) using a novel bifunctional catalyst derived from fish scales and cabbage back. The research focused on optimizing the simultaneous esterification and trans-esterification processes through Response Surface Methodology (RSM) to enhance biodiesel yield and quality. Despite the extensive experimental design and rigorous characterization of both the feedstock and the catalyst, the results indicated that no biodiesel formation occurred under the tested conditions.

The lack of biodiesel production suggests that the bifunctional catalyst, as prepared, may not have been effective in catalyzing the esterification and trans-esterification reactions. Several factors could have contributed to this outcome, including insufficient catalytic activity due to improper calcination or impregnation processes, suboptimal reaction conditions, or inadequate surface area and porosity of the catalyst. The absence of biodiesel formation underscores the complexity of biodiesel production and the critical role of catalyst design and reaction optimization.

However, this study provides valuable insights into the challenges associated with using waste-derived catalysts for biodiesel production. The characterization of Neem Seed Oil (NSO) revealed its potential as a feedstock, with properties such as acid value, saponification value, and viscosity falling within acceptable ranges for biodiesel production. The experimental design and methodology employed in this research lay a foundation for future studies aimed at refining the catalyst synthesis process and optimizing reaction conditions.

In conclusion, while the current results did not yield biodiesel, the findings highlight the need for further research into the development of efficient, sustainable catalysts from waste materials. Further work would focus on improving the catalytic activity of the bifunctional catalyst, exploring alternative preparation methods, and conducting more detailed optimization studies to achieve successful biodiesel production from Neem Seed Oil.

5.2 RECOMMENDATIONS

Based on the findings of this study, the following recommendations are proposed for future research:

1. Catalyst Optimization: Further investigation into the catalyst preparation process, including calcination temperature, impregnation techniques, and the ratio of acid to basic precursors, is necessary to enhance catalytic activity.

2. Reaction Condition Optimization: A more detailed optimization of reaction parameters, such as temperature, methanol-to-oil ratio, catalyst loading, and reaction time, should be conducted to identify the optimal conditions for biodiesel production.

3. Alternative Feedstocks: Exploring other non-edible oil sources or waste oils as feedstocks for biodiesel production could provide additional insights into the versatility of the bifunctional catalyst.

4. Reaction kinetics of the reactions involved.

5. The impact of the catalyst's particle size on the concurrent reaction.

By addressing these recommendations, future research can build upon the findings of this study to develop a more efficient and sustainable approach to biodiesel production using waste-derived catalysts.

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