PRODUCTION OF BIODIESEL USING CALCINED CALCIUM PHOSPHATE SCUM FROM SUGAR REFINING INDUSTRY AS A SOLID HETEROGENEOUS CATALYST.

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FACULTY OF ENGINEERING

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BENIN CITY.

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A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING, FACULTY OF ENGINEERING, UNIVERSITY OF BENIN, BENIN CITY, IN PARTIAL FULFILLMENT OF AWARD OF BACHELOR OF ENGINEERING DEGREE IN CHEMICAL ENGINEERING

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CERTIFICATION

This certifies that I, **NKEENAM BARITONDUM JERRY,** of the Chemical Engineering department of the Faculty of Engineering, University of Benin, Benin City, Edo State, Nigeria, with matriculation number **ENG1508322,** completed and assembled the project work.

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DEDICATION

First and foremost, I want to thank God Almighty for this project's success, followed by my wonderful parents, Mr. and Mrs. Nkeenam, for their invaluable support and assistance during my studies and project work.

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ABSTRACT

Transport powered by fossil fuels is becoming more dependent on global industrialization, which is accelerating the loss of these resources and exacerbating climate change. Beyond environmental issues, this dependence impedes socio-economic progress and the Sustainable Development Goals. Using calcined calcium phosphate effluent from sugar refining as a solid heterogeneous catalyst, this research aims to manufacture biodiesel.

To optimize crucial process variables, this work utilized EDX analysis Response Surface Methodology (RSM) to convert waste cooking oil (WCO) into biodiesel. The catalyst, calcium phosphate scum, is derived from the sugar refining industry and is heterogeneous. After 29 iterations with a 5-level-4 factor Central Composite Design, a quadratic polynomial model was finalized. Reaction time (60-90 min), catalyst-to-oil weight ratio (1-4%), reaction temperature (40-70 °C), and methanol-to-oil ratio (6:1-18:1) were all fine-tuned in the study. It was proven that under these perfect conditions, used cooking oil may be transesterified.

Calcium zinc hydrogen phosphate (47%), fluorapatite (33%), osumilite (13.8%), and quartz (6.5%) were the solid mineral components found in the catalyst characterization results. These components were calcined to calcium oxides at a temperature of 1000℃. A significant pore capacity of 0.213cc/g and a high surface area of 235.505m2/g were found in the catalyst, respectively, according to the analytical analysis. This allows reactants to permeate quickly into the catalyst's interior. Based on the catalyst's elemental makeup, we know that it contains 50.4% silicon oxide (SiO2) and 41.436% aluminum oxide (Al2O3). FTIR study of catalyst indicated a medium stretch peak of methyl (C-H) group. SEM microscopy showed homogeneous spherical particles. EDS examination of catalyst revealed the presence of calcium and phosphorus in weight concentration at 62.67% and 25.99% respectively. Other elements were in trace levels.

With a reaction temperature of 55°C, a catalyst-to-oil weight ratio of 5%, a reaction time of 90 minutes, and a methanol to oil ratio of 12:1, numerical optimisation gave a maximum biodiesel yield of 93.2%.Notably, the reaction was highly impacted ($p < 0.0001$) by the catalyst concentration, time, and methanol-to-oil ratio. Consequently, it was found that Calcium Phosphate Scum derived from sugar refining businesses offers a cost-effective and efficient substitute for calcium oxide heterogeneous catalysts in biodiesel synthesis.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The increasing use of fuel-based energy in transportation is a direct outcome of global industrialization, which in turn leads to the depletion of fossil fuel supplies and a notable acceleration in the rate of global warming (Nguyen et al., 2021). Beyond ecological problems, this dependence on traditional energy sources affects socioeconomic aspects and slows down the advancement of the Sustainable Development Goals (SDGs) (Jaiswal et al., 2022). The necessity of transitioning toward sustainable and renewable energy options to comply with SDG targets is underscored by the predicted 40, 70, and 200-year lifetimes of fossil fuel reserves, which include coal, oil, and gas, respectively (Das et al., 2023). In an effort to combat fuel scarcity and pollution, renewable fuels are gaining popularity as a viable energy option (Ban et al., 2022). Goal 7 of the SDGs, which calls for the promotion of clean, cheap energy, is compatible with the adoption of renewable energy sources (Tilde, 2023). According to Jaiswal et al. (2022), this shift helps with both short-term issues like pollution and resource scarcity and long-term goals like sustainable and fair development (Jaiswal et al., 2022).

Fatty acid methyl ester (FAME), a biodiesel, has the potential to replace traditional petroleum fuel (Tilde, 2023) in future vehicles. Its compatibility with the existing petroleum infrastructure is one of its key selling points. Biodiesel is an attractive bioenergy option due to its low carbon dioxide emissions, diesel engine compatibility, and high combustion efficiency. This has led to a rise in biodiesel production around the world, which can replace fossil fuels (Uprety et al., 2017). In contrast to fossil fuels, FAME demonstrates tremendous environmental benefits, such as very

low sulfur content (up to 57.7%), little toxicity, and greatly reduced emissions of carbon monoxide (up to 58.9%) and carbon dioxide (up to 8.6%) (Lin et al., 2011). Apart from its biodegradable nature and renewability, they are additional qualities (Ao et al., 2023; Gebremariam & Marchetti, 2018). Furthermore, according to (Das et al., 2023), it possesses amazing fuel properties such as a high cetane number, low emissions, better lubricity, and higher combustion efficiency.

Biodiesel is created using a variety of techniques, including pyrolysis, transesterification, direct and indirect utilisation, micro emulsification, and the dilution method (Seffati et al., 2020b; Shaafi et al., 2022). Transesterification stands out as the most economical and straightforward technology for biodiesel synthesis. Using a sufficient catalyst, this method transforms triglycerides into methyl esters (using methanol) or ethyl esters (using ethanol) (Das et al., 2023). The process of transesterification reactions that produce fatty acid alkyl esters can be assisted by acids, bases, and enzymatic catalysts. As a co-product, glycerol is formed, constituting approximately 10% (w/w) of the manufactured biodiesel (Parthasarathy & Narayanan, 2014). Extensive research efforts have been spurred by the significance of biodiesel as a sustainable energy source, with a special emphasis on enhancing its production processes (Brahma et al., 2022). Central to this investigation is the creation of catalysts that are both efficient and eco-friendly, as they play a crucial part in the transesterification process (Das et al., 2023).

Conventional catalysts, like homogeneous acids or bases, have showed potential but typically come with downsides including increased costs, toxicity, and a considerable quantity of waste production. (Oliveira et al., 2021). Homogeneous base catalysts like NaOH and KOH experience difficulty in converting spent cooking oils and inedible oils into biodiesel because of their high Free Fatty Acid (FFA) levels, resulting in the creation of soap (Math & Chandrashekhara, 2016).

Moreover, the purification of biodiesel takes a significant amount of water, resulting in enormous wastewater formation (Zabeti et al., 2009). Additionally, the recovery and reuse of the catalyst pose issues (Uprety et al., 2016). To solve these hurdles, the creation of a heterogeneous catalyst has emerged as important, using its variety of advantages. These benefits comprise streamlined catalyst retrieval and reusability. This unique strategy not only handles the aforesaid difficulties but also enriches the complete process, ensuring heightened economic efficiency (Saifuddin et al., 2015). Several investigations have dug into biodiesel manufacturing utilizing various heterogeneous catalysts, including acids, bases, and enzymes (Das et al., 2023). Enzyme and acid catalysts demand enhanced working conditions, such as a high methanol-to-oil ratio, increased temperature, and extended reaction durations (Das et al., 2023). Hence, the preference frequently veers towards applying a basic catalyst in biodiesel generation. The use of a heterogeneous base catalyst serves to surmount problems such saponification, which limits glycerol separation from the methyl ester layer—an issue typically encountered with homogeneous base catalysts. Notably, these catalysts exhibit better catalytic efficacy even under mild circumstances (Wang et al., 2019). Heterogeneous base catalysts offer various benefits, including non-corrosiveness, eco-friendliness, and minimum disposal worries. Moreover, they are easily extractable from the reaction environment and can be modified to enhance activity, selectivity, and lengthen catalyst lifespan (Rizwanul Fattah et al., 2020).

Nevertheless, the synthesis of several heterogeneous base catalysts, such as alkaline earth metal oxides including MgO, BaO, SrO, CaO, zeolites, and KNO3 loaded on Al2O3, frequently includes multiple phases (Amirthavalli et al., 2022). This intricacy contributes to the entire procedures being delayed, arduous, and intricate. Furthermore, the total product cost is further exaggerated because to the high chemical expenses related with the precursors (Brahma et al.,

2022). Hence, utilizing waste materials as a heterogeneous base catalyst not only mitigates environmental concerns but also bolsters the economic sustainability of biodiesel production (Das et al., 2023).

1.2 STATEMENT OF PROBLEM

Conventional fossil fuels generate enormous issues, producing greenhouse gases that inhibit the accomplishment of Sustainable Development Goals (SDGs), particularly hurting Climate Action (SDG 13) and Clean Air and Water (SDGs 14 and 15) (Pestisha et al., 2023). The production and transportation of fossil fuels entail environmental concerns, including oil spills, harming ecosystems and biodiversity (SDG 15). Geopolitical conflicts over resource-rich regions impede Peace, Justice, and Strong Institutions (SDG 16). Concerns about resource depletion and energy security underscore the need for sustainable alternatives, aligning with Affordable and Clean Energy (SDG 7). Alternative biodiesel production faces hurdles like high costs and scalability issues, impacting Industry, Innovation, and Infrastructure (SDG 9) (Pestisha et al., 2023).

Also adding to the high cost are homogeneous catalysts, which are faced with challenges of high costof utilization and regeneration, toxicity, waste generation, competition with used oils, leading to soap formation and wastewater. Recovery and reuse of homogeneous catalysts present is challenging. Synthesized heterogeneous catalysts involve complex processes with high-cost precursors, increasing production complexity and expenses. An low-cost preferably waste-derived heterogeneous catalysts may potentially offer an environmentally sustainable and economically efficient alternative, which can address the challenges associated with conventional fuels and homogeneous catalysts.

1.3 AIM AND OBJECTIVES

This study aims to produce biodiesel using calcined calcium phosphate scum from sugar refining industry as a solid heterogeneous catalyst.

The study aims to achieve the following objectives:

i. To characterize the Waste Cooking oil
ii. To calcine and characterize the heterogeneous catalyst.
iii. To optimize biodiesel production using the Response Surface Method (RSM).
iv. To investigate the impact of variables such as molar ratio, catalyst concentration, reaction time, temperature, and mixing rate on biodiesel yield.
v. To produce biodiesel and characterize it.

1.4 SCOPE OF STUDY

This study encompasses both fieldwork and experimental investigations within its scope.

This study will cover the following:

(i). Obtaining calcium phosphate scum from sugar refining industry.

(ii). Calcining the calcium phosphate scum at a ramping temperature of 900^0C for a period of 2 hour for it's utilization as a heterogeneous catalyst.

(iii). Characterization of the heterogeneous catalyst using FTIR, SEM-EDX, BET, and XRF analysis.

(iv). Utiliing production variables such as time, temperature, catalyst loading, and methanol to oil ratio to investigate the yield of the biodiesel production.

(v). Characterization of the produced Biodiesel using XRD analysis.

1.5 RELEVANCE OF STUDY

This study presents sustainable strategies to reduce environmental pollution from traditional fossil fuels, which helps for accomplishing the Sustainable Development Goals (SDGs) (Das et al., 2023). Offering cleaner energy options promotes Sustainable Development Goal 13's call for global action against climate change, which is in accordance with Sustainable Development Goal 7 (Ensuring availability of reliable, modern, and inexpensive energy for all). The study also provides an alternate, sustainable use for surplus scum from Nigeria's sugar refining firms, which contributes to Sustainable Consumption and Production Goal 12 (Responsible Consuming and Production). The study advances SDG 15 (Life on Land) by providing an environmentally advantageous alternative to the typical waste scum disposal technique. Furthermore, the implementation of this alternative not only mitigates environmental hazards but also helps achieve SDG 8 (Decent Work and Economic Growth) by creating wealth from trash and supporting economic development in the region (Brahma et al., 2022).

CHAPTER 2

LITERATURE REVIEW

2.1 ENERGY; RENEWABLE AND NON-RENEWABLE SOURCES

The crucial element underlying economic advancement is energy, serving as a fundamental motor in sustaining contemporary economies and society (Mathew, 2013). The trajectory of our future economic advancement rests heavily upon the sustained, continuous accessibility of energy obtained from sources that are not only easily available but also secure as well as cost-effective (Oyedepo, 2012). A crucial aspect of this is the recognition that the global economy has witnessed a substantial surge in energy demand(Irena, 2022). Projections indicate an anticipated 84 percent increase in energy consumption by 2035, especially within the developing nations(Ahmad & Zhang, 2020). This surge underscores the growing importance of securing energy resources to meet the evolving needs of expanding economies, emphasizing the imperative for accessibility, safety, and affordability in energy sources to foster sustained global economic growth(Oyedepo, 2012). Also, while renewable energy sources can be replenished naturally over time and are not depleted when used, non-renewable energy which is derived from finite resources that cannot restore themselves over a short period and diminish over time. Renewable energy sources are considered sustainable and environmentally friendly while non-renewable energy is not considered sustainable in the long term due to the extended time required for its formation(Flórez-Orrego et al., 2015; Güney, 2019).

Renewable energy adheres to the tenets of environmental sustainability by providing a cleaner and more enduring alternative to non-renewable sources. Unlike non-renewable sources that lead

to environmental degradation and are finite, renewable energy sources offer a sustainable solution (Kabeyi & Olanrewaju, 2022).

2.2 SUSTAINABLE DEVELOPMENT GOALS (SDGs) AND ENERGY EFFICIENCY

Energy is a critical component that drives the Sustainable Development Goals (SDGs) and affects many aspects of human life, including economic prosperity, agricultural output, general well-being, education, gender parity, empowerment, access to clean water, sanitation, and employment opportunities (Santika et al., 2019). Energy also plays a pivotal role in reshaping economies and societies. Although the Sustainable Development Goals (SDGs) are globally applicable goals, they are typically implemented within national and local frameworks, which has a notable impact on the energy landscape. Energy dynamics will unavoidably be impacted by the SDGs' incorporation into regional and national development plans (Santika et al., 2019). Specifically, using more energy will be required to solve issues with poverty reduction, hunger elimination, health enhancement, education advancement, gender equity, and the provision of clean water and electricity as well as the achievement of other SDGs. Research validates the complex relationship between energy requirements and achieving sustainable development goals (Santika et al., 2019).

Concerns have been raised by the recent increase in CO2 emissions and energy use. Anwar et al., 2020 and Osobajo et al., (2020) credit this tendency to the growing urban population (Anwar et al., 2020; Osobajo et al., 2020), while Zakari et al. (2022) speculate that the production of products and services may play a role (Zakari et al., 2022). Whatever the reason, the utilization of energy has emerged as a critical component of sustainable development. According to

projections, the world's industrial energy consumption could increase by almost 30% by 2050 (Larsson, 2009; Yu et al., 2022). The consumption of final products is expected to surpass 310 quadrillion BTUs. The aforementioned rise in energy use is expected to have implications for the economic, societal, and environmental domains. Thus, in order to reduce CO2 emissions, governments and policymakers need to give priority to implementing cleaner energy options (Zakari et al., 2022).

Aim 7 promotes universal access to affordable, clean energy by supporting renewable energy sources including wind and solar energy. In line with the SDGs' objectives for eradicating poverty, promoting health, and protecting the environment, renewable energy integration promotes economic growth, environmental sustainability, and social well-being (Mccollum, 2018). In order to achieve SDG 7, which is to ensure that everyone has universal access to affordable, dependable, sustainable, and modern energy, renewable energy is essential. By lowering greenhouse gas emissions, it combats climate change (SDG 13) and fosters economic growth (SDG 8) through employment creation (Santika et al., 2019). The 17 Sustainable Development Goals (SDGs) include gender equality, health, education, clean water, and peace in addition to the eradication of poverty. These objectives are met by renewable energy, which promotes sustainable development while reducing the effects of climate change (Gielen et al., 2019).

2.3 BIODIESEL; A SUSTAINABLE ENERGY SOURCE

Over the last twenty years, biodiesel has developed as a compelling alternative to fossil fuels, establishing itself as a realistic replacement for petrodiesel due to its similar qualities (Nath et al.,

2019). Biodiesel has various advantages over regular petrodiesel, including as decreased viscosity, a higher flash point, an enhanced cetane number, good lubricating characteristics, biodegradability, non-toxicity, and a lowered greenhouse gas emission profile. Furthermore, biodiesel boasts a reduced ignition delay time and excellent combustion efficiency, which contribute to lengthening engine life (Manigandan, Atabani, et al., 2020; Manigandan, Gunasekar, et al., 2020; Manigandan, Sarweswaran, et al., 2020; Ong et al., 2014; Wakil et al., 2015). This adaptable fuel can be used directly in diesel engines or combined with petrodiesel with few changes necessary (Gumus & Kasifoglu, 2010). As a result, biodiesel has attracted the attention of the scientific community, motivating various researchers to study its potential and work towards establishing its sustainability for wider application(Brahma et al., 2022).

Choosing biodiesel as an alternative fuel has several benefits over fossil fuels, particularly in its adaptability for diesel engines. Its low carbon content offers it as a possible alternative to heating oil(Mathew, 2013). Biodiesel aids in carbon cycle, preventing the release of stored carbon into the atmosphere(brahma et al., 2022). Formed from foundamental elements-sunlight and carbon dioxide – biodiesel shows a favourable energy balance, which is the ratio of energy stored in the fuel to the energy needed for growth, processing, and distribution. With an energy balance ratio surpassing 2.5 to 1, biodiesel successfully collects solar energy(tiele et al., 2017).

2.3.1 Historical Background of Biodiesel

The publication of "The Theory and Construction of a Rational Heat Engine" by German inventor Dr. Rudolph Diesel in 1893 marked a pivotal moment in the development of the diesel engine. Vegetable oil was initially utilized when Rudolph Diesel successfully operated the first diesel engine on peanut oil at the 1900 World's Exhibition in Paris.. Oilseed crops were the main source of the huge growth in biodiesel output. Diesel engines were commonly powered by

vegetable oils until the 1920s. The advantages of vegetable oils, including profitability, availability, low sulfur and aromatic content, biodegradability, and renewability, positioned them as superior to diesel fuel (Mathew, 2013). However, the current higher market values and challenging applications have limited the widespread use of crops for biodiesel production.

2.3.2 Importance of Biodiesel as a Renewable Fuel

Petro-diesel's qualities are mirrored in biodiesel, which is a refined fuel derived from organic sources (Hazrat et al., 2020). Serving as a secure substitute for traditional petroleum fuel, biodiesel stands out as an eco-friendly solution. This environmentally sensitive fuel provides clean combustion and offers high lubricity. Originating from renewable sources, biodiesel emulates the performance of petroleum diesel while dramatically lowering air pollution. Its biodegradable nature matches with eco-friendly methods, reinforcing its safety for the environment (Adipah, 2018). The creation of biodiesel involves numerous processes, providing flexibility in manufacturing. According to (Jamil et al., 2018) this fuel is a mono alkyl ester of fatty acids obtained from animal fat, edible and non-edible vegetable oils, and other biofuels such as ethanol and methanol. Thus, using biodiesel offers a feasible option for conventional diesel fuels derived from petroleum, encouraging ecologically friendly and sustainable energy practices (Huang et al., 2012).

2.4 PROPERTIES OF BIODIESEL

For the production of biodiesel, often referred to as fatty acid methyl esters (FAME), triacylglycerol and other molecules, along with vegetable and animal fats, can be utilized (Ngamcharussrivichai et al., 2010). FAME is a product of the metabolism of methanol. But a

fatty ester's overall characteristics are shaped by the interaction between the fatty acid chain and the alcohol group (Yu et al., 2022). For the purpose of producing fatty acid alkyl esters (FAAE) for biodiesel synthesis, the characteristics modified by alternative alcohols are therefore worthy of evaluation. Among the important characteristics that are being discussed are lubricity, kinematic viscosity, cetane number (CN), cold flow, and oxidative stability (Knothe, 2016).

2.4.1 Cetane Number and Combustion

Cetane Number (CN) acts as a critical measure of diesel fuel (DF) quality, reflecting its igniting behavior. Higher CN levels correspond with shorter ignition delay durations, indicating quick ignition upon injection into the cylinder(Knothe, 2016). Standards like ASTM D613 and ISO 5165 guide CN determination globally. Hexadecane, with a CN of 100, sets the high-quality benchmark, while 2,2,4,4,6,8,8-heptamethylnonane (HMN) at CN 15 reflects low ignition quality due to greater branching and reduced chain length. CN diminishes with shorter chains and increased branching. Petrodiesel standards necessitate a CN minimum of 40, whereas biodiesel requires 47 (ASTM D6751) or 51 (EN 14214). The old CN determination method involves extensive fuel utilization, leading the invention of the Ignition Quality Tester™ (IQT™). It offers a derived cetane number (DCN) corresponding with traditional CNs. DCN values of less saturated compounds exhibit higher consistency in literature due to the non linear connection between CN and ignition delay time (Knothe, 2016). Despite greater CNs of fatty molecules, biodiesel operation generally increases NOx emissions(Ladommatos et al., 1996). The CN's intricate relationship with engine emissions encompasses elements including injection pressure and combustion temperature. CN study of biodiesel, initially conducted with palm oil ethyl esters, indicated a relationship between compound structure and CN, exhibiting CN decrease with increased unsaturation and chain length. Branched esters give superior low-temperature

characteristics. The CN of biodiesel blends can be determined using a summation equation, with chain length determining heat of combustion (HG), an important feature for diesel fuels (Knothe, 2016).

$$CN_{mix} = \sum A_c \times CN_c \quad \ldots \ (1.1)$$

The notation "CNmix" symbolizes the Cetane Number (CN) that defines the biodiesel mixture, where "Ac" marks the amounts of each constituent, and "CNc" specifies the individual Cetane Number of each component in the blend (Knothe & Steidley, 2011).

2.4.2 Oxidative Stability

In addition to cold flow difficulties, the oxidative stability of biodiesel is a key concern, especially when kept for a lengthy period of time. The effects of heat, air, metal traces, antioxidants, and peroxides on the oxidation of biodiesel are noted by a number of researchers. Oxidation is catalyzed by components like air, high temperatures, and metals (Knothe, 2016). The Rancimat method, often used to determine oxidative stability, measures conductivity changes during air bubbling at 110°C (Botella et al., 2014). Biodiesel standards, including ASTM D6751 and EN 14214, demand minimum oxidative stability times (Kivevele et al., 2011). Oxidative stability is tested using a variety of methodologies, such as pressurized DSC and acid value. The rate of auto-oxidation, which is related with fatty substances, is dependent on the quantity and location of double bonds in the chain. Polyunsaturated fatty acids, such as linoleic and linolenic acids, which are particularly prone to auto-oxidation, have an effect on the oxidative stability of biodiesel. (Bokhari et al., 2014).

2.4.3 Viscosity

Viscosity has a significant impact on engine deposit formation by atomizing fuel during injection into the combustion chamber. Higher viscosity exacerbates these issues, making transesterified oils, such as biodiesel, more prone to atomization challenges and engine deposit formation compared to their parent oils(Ghurri et al., 2012). Neat vegetable oils, with their high viscosity, have been largely abandoned as alternative diesel fuels due to these concerns. Kinematic viscosity, a key parameter, is included in biodiesel standards like ASTM D445 and ISO 3104 (Blin et al., 2013). Research has explored the effects of blending petrodiesel and biodiesel on viscosity, resulting in the construction of forecasting models. The length of the chain and the level of fatty material saturation both raise viscosity, including the alcohol moiety (Wang et al., 2019). Factors like double bond orientation effect viscosity, with cis double bonds providing lower viscosity than trans (Dharma et al., 2016). Branching in the ester moiety has negligible influence on viscosity, presenting a possible path for boosting low-temperature qualities without large modifications to other fuel parameters . While dynamic viscosity studies are prevalent, biodiesel standards primarily focus on kinematic viscosity values (Pullen & Saeed, 2014).

In a way analogous to the formula used for estimating the cetane number (CN) of compounds, the kinematic viscosity of a blend of fatty esters can be determined using the equation put forward by Knothe and Steidley in 2011 (Knothe & Steidley, 2011).

$$v_{\text{mix}} = \sum A_C \times v_C \quad \ldots(1.2)$$

In this case, v_{mix} is the biodiesel sample's kinematic viscosity; A_c is the amount of each individual ester present; and v_c is the kinematic viscosity of each compound in the mixture independently.

2.4.4 Lubricity

The emergence of low-sulfur petroleum-derived fuels has underscored the significance of lubricity in diesel fuels (DFs). Conventional petrodiesel desulfurization processes diminish or eliminate its natural lubricity, crucial for the optimal performance of engine components like fuel pumps and injectors (Dimitrakis, 2003). Studies highlight oxygen- and nitrogen-containing compounds as pivotal for petrodiesel's lubricating properties, supported by investigations on specific C-3 compounds. Biodiesel and fatty compounds have demonstrated the ability to enhance petrodiesel's lubricity, especially in low-sulfur variants, offering an advantage over typical lubricity additives. Free fatty acids, monoacylglycerols, and glycerol display higher lubricating characteristics due to their free hydroxyl (OH) groups, which promote lubricity in fatty acid chains (Silva e Mello et al., 2014). Commercial biodiesel, having components beyond methyl esters, largely promotes petrodiesel lubricity at low mix ratios. Although adding glycerol to plain esters fails to improve petrodiesel lubricity, the introduction of polar molecules such free fatty acids or monoacylglycerols boosts it, underlining their pivotal function in biodiesel-petrodiesel blends (Silva e Mello et al., 2014). However, lubricity testing standards, like ASTM D6079 or ISO 12156, have not yet incorporated lubricity assessments for biodiesel, despite its advantageous performance compared to petrodiesel in this regard (Knothe, 2016).

2.5 TECHNIQUES FOR BIODIESEL PRODUCTION

Since the invention of the diesel engine and Dr. Rudolf Diesel's use of vegetable oil as fuel, the development of biofuels, particularly biodiesel, has been acknowledged (Tziourtzioumis & Stamatelos, 2012).

In an attempt to maximize product yields, improve fuel qualities, and lower production costs, a large number of researchers have made major strides in the advancement of biodiesel manufacturing techniques. The direct use of vegetable oils as fuels presents difficulties due to their high viscosity and low stability against oxidation (Brahma et al., 2022). of get over these issues, four distinct approaches of converting oils into biodiesel have been researched: pyrolysis, transesterification, micro-emulsification, and dilution (Robles-Medina et al., 2009). In order to develop sustainable biodiesel solutions, researchers have varied various techniques while keeping in mind the viability of large-scale manufacturing economically. The continued research demonstrates the dedication to improving biodiesel production methods for wider application and environmental advantages.

2.5.1 Dilution Method

This method involves mixing petrodiesel with vegetable or animal oils in a range of 10 to 40% (w/w) for use as fuel in diesel engines (Yatish et al., 2016). (Rezania et al., 2019a). The literature has reported successful vegetable oil-diesel blending; notable instances from World War II include the work of Nye et al. (Nye et al., 1983). By combining 10% vegetable oil with diesel in the pre-combustion chamber, Caterpillar Brazil Company demonstrated in 1980 that power maintenance could be accomplished without requiring engine modifications (Brahma et al., 2022). Successful results were reported in 1982 for a 20:80 vegetable oil to diesel ratio and a blend of 5% diesel and 95% used cooking oil (Ramadhas et al., 2004). Without experiencing any major operational difficulties, Pramanik et al. (2004) successfully ran an engine utilizing a 50% blend of Jatropha curcas oil (Ramadhas et al., 2004).

Following a number of study endeavors, a meeting in August 1982 in Fargo, North Dakota included a debate on the creation, methods, and limitations of using vegetable oil as fuel (Misra

& Murthy, 2010; Owolabi et al., 2012). Only liquid, portable diesel fuels with an approximate 80% heat content are suitable for blending. It should not be used with oils that have a high viscosity, a large unsaturated carbon chain, or low volatility. Using only vegetable oil in engines can lead to issues such coking, trumpet development, carbon deposition, oil ring sticking, thickening, and gelling of lubricating oil (da Costa & de Andrade Lima, 2021). Given these challenges, research into a more comprehensive technique to produce biodiesel economically is emphasized as a possible future fuel substitute (Leung et al., 2010; Ramadhas et al., 2004).

2.5.2 Micro-emulsification

Micro-emulsification (Brahma et al., 2022) is the process of dissolving vegetable or animal oils in alcoholic solvents and surfactants. A variety of alcoholic solvents, such as ethanol, methanol, butanol, and hexanol, are employed to create micro-emulsions that reduce the issue of high viscosity in vegetable oils. These solvents produce colloidal microstructures with sizes ranging from 1 to 150 nm (Rezania et al., 2019b). These micro-emulsions consist of transparent, clear, stable, optically isotropic colloidal dispersions including dispersed phase droplets or particles with sizes ranging from 100 to 1000 Å. According to Das et al. (2023), the dispersion components are oil, water, surfactant, and a tiny co-surfactant molecule.

Due to the high alcohol content in micro-emulsions, their heating values are lower than those of diesel fuels; but, by using the alcohols' high latent heat of vaporization to cool the combustion chamber, they help reduce nozzle coking. According to Yusuf et al. (2011), one example showed a drop in viscosity to 11.2 mm^2/s at 25°C when methanol was micellarly solubilized in triolin with soybean oil utilizing 2-octanol as an amphiphile. But issues with using a fuel for micro-emulsification that combines oil, methanol, 2-octanol, and cetane improver in a specific ratio have been reported (Srivastava & Prasad, 2000). One such issue is the accumulation of carbon

around injector nozzle tubes and valves. This fuel for micro-emulsification has a low cetane number, which could result in incomplete combustion (Leung et al., 2010). Thus, there is a pressing need for an improved biodiesel conversion method in addition to using micro-emulsification, particularly in the biorefinery sector.

2.5.3 Pyrolysis

Heating vegetable oil, animal fats, triglycerides, or portions of fatty acids to high temperatures (300–1300°C) in the absence of air or oxygen is known as pyrolysis (Yusuf et al., 2011). This leads to the generation of biodiesel.This process results in the structural modification of long-chain and saturated compounds, breaking chemical bonds and forming smaller molecules. A catalyst is not always necessary for thermal cracking to occur. Alkanes, alkadienes, aromatics, alkenes, and carboxylic acids are produced when vegetable oil is heated, along with trace amounts of gaseous byproducts. Conventional pyrolysis (550-900 K), fast pyrolysis (850-1250 K), and flash pyrolysis (1050-1300 K) are the three temperature-based categories for pyrolysis (Tziourtzioumis & Stamatelos, 2012). It's considered a waste-free, highly efficient, straightforward, and ecologically friendly method. Biodiesel generated through pyrolysis possesses favorable fuel properties, including low viscosity, elevated cetane number, reasonable copper corrosion rate, and low sulfur concentrations. Additionally, its water and sediment content remain below permissible limits (Jaiswal et al., 2022). However, the final product's high pour points, carbon residues, and ash content are undesirable (Atadashi et al., 2013). Because pyrolysis requires a large amount of energy and has associated limitations, scientists are searching for more economical ways to produce biodiesel.

2.5.4 Transesterification

Biodiesel is defined by the American Society for Testing and Materials (ASTM) as a blend of alkyl esters produced by transesterifying triglycerides from long-chain fatty acids (Chhetri et al., 2008). Transesterification is an extremely useful method that produces biodiesel by reacting alcohol with vegetable oil or any other triacylglycerol using a catalyst. The end products of this process are glycerol and alkyl esters, sometimes known as biodiesel. Because the reaction is reversible, too much alcohol is required to promote the desired products' formation. A stoichiometric 3:1 alcohol-to-oil ratio (ATOR) is required to complete it. Methanol, ethanol, propanol, butanol, and amyl alcohol are a few of the alcohols that are commonly utilized in transesterification to produce biodiesel (Humphrey et al., 2017). Methanol is the preferred choice due to its more affordable, polarity, and shorter chain length. Among the catalysts used in the synthesis of biodiesel are enzymes, homogeneous acids and bases, and heterogeneous solid acids and bases (Brahma et al., 2022). Base-catalyzed transesterification happens approximately 4000 times faster than acid-catalyzed transesterification. Important factors influencing the reaction are the type of catalyst, ATOR, load %, and reaction temperature (Misra & Murthy, 2011). Most researchers concur that the most effective method for creating biodiesel that meets ASTM D6751 and EN 14214 fuel property standards is transesterification. Notwithstanding its advantages, one significant drawback of transesterification is the requirement for more methanol (Leung et al., 2010). Therefore, finding the best transesterification conditions and developing affordable, environmentally acceptable, and efficient catalysts remain crucial challenges for the large-scale production of biodiesel (Ling et al., 2019). More focus will be on transesterification because it is the main technique used in this study to produce biodiesel.

2.6 PURIFICATION OF BIODIESEL

It is essential to purify biodiesel in order to get rid of pollutants, detergent, excess alcohol, free glycerol, and other impurities. (Postaue et al., 2022). These impurities not only affect engine performance but also complicate handling and storage. Purification guarantees adherence to quality standards such as ASTM D6751, lowering the water content to less than 500 parts per million. (Tâm et al., 2016). Also, purification enhances fuel quality, improving combustion efficiency and reducing harmful emissions(Atadashi et al., 2011; Banga & Varshney, 2010). Maheshwari et al. (2022b) state that this process is necessary to produce biodiesel that meets stringent performance and environmental requirements, ensuring the best possible engine performance and minimizing harmful effects on the environment and human health (Ali et al., 2013). Diverse techniques are utilised for this objective. Several methods that are frequently used are as follows:

2.6.1 Wet or Water Washing

Traditionally, the wet washing method is used to remove a variety of contaminants from raw biodiesel, including unreacted oil, excess catalyst, alcohol, salts, soaps, and organic contaminants (Rizwanul Fattah et al., 2020). Water is the cleansing agent used in wet washing; it might provide acid to neutralise any alkali catalyst that could still be present. The elimination of salt by-products from the transesterification process is made easier with the use of this technique. It's imperative to eliminate excess alcohol post-transesterification to minimize its presence in residual wastewater(Gokhan Demir & Soyhan, 2017). Some researchers advocate for the removal of excess alcohol following wet washing. They did this by using distilled water that was heated to between 50 and 60 degrees Celsius in order to stop saturated fatty acid esters from precipitating. Soft water washing encourages quick and thorough phase separation, which lowers

the development of emulsions. When hot distilled water is used, 99% pure biodiesel is produced. Although commercial biodiesel production employs both dry and wet washing methods, it is contended that only the wet washing procedure can effectively purify biodiesel to fulfil EN14214 criteria (Gokhan Demir & Soyhan, 2017).

Wet washing has advantages, but it also has drawbacks, such as longer separation times and lower product yields. Environmental worries are exacerbated when biodiesel leaks into the rinsing water, increasing pollutants in the effluent. Moreover, the substantial volume of wastewater generated during wet washing poses significant challenges for both the biofuel sector and the ecosystem(Catarino et al., 2020).

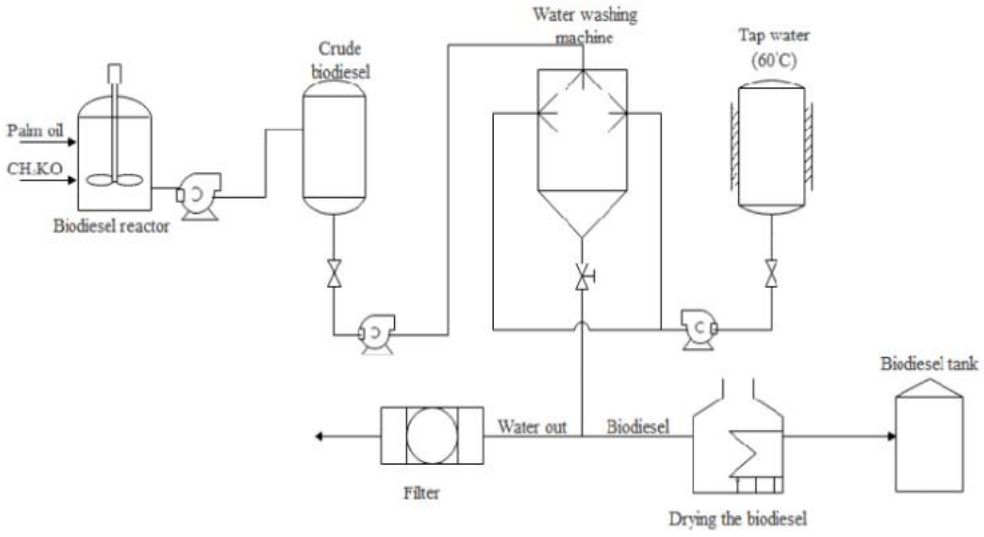

Figure 2.1. General scheme of the proposed biodiesel production process with an emphasis on biodiesel wash-water reuse.

2.6.2 Dry Washing

One technique that is commonly used in the purification of biodiesel is dry washing. It uses a variety of adsorbents, including activated carbon, activated fiber, activated clay, Magnesol,

cellulosics, Purolite, Amberlite, and Trisyl (Atadashi, 2015). Atadashi (2015) claims that these adsorbents include sites for both basic and acidic adsorption, which allows them to pull polar molecules like methanol and glycerol. To improve efficiency, a filter unit is included, as shown in Figure 1. Running at 65°C, it takes 20 to 30 minutes to complete (Leung et al., 2010). Dry washing produces a waterless process that improves fuel quality by drastically lowering levels of glycerides and total glycerol (Cavalcanti et al., 2022). In addition, it minimizes the wash tank's total surface area coverage, conserves space, expedites washing, eliminates waste water production, and is simpler to include into facilities that currently exist (Atadashi, 2015). Studies show that this process optimizes the refining of crude biodiesel by reducing production time and costs. By producing high-quality fuel without adding water, the biodiesel refinement process raises the possibility of meeting ASTM D6751's requirement for a water concentration of less than 500 ppm (Atadashi, 2015). In contrast, fuel water content from water washing techniques frequently exceeds 1000 parts per million, which makes water removal difficult and costly (Atadashi, 2015). Moreover, biodiesel produced from leftover frying oil was refined using rice husk ash (RHA) at various concentrations (1%–5% w/w), commercial adsorbent MagnesolÒ 1% (w/w), and conventional acid solution (1% aqueous H3PO4). RHA removed pollutants from biodiesel very effectively, especially at a 4% concentration, due to its high silica concentration and the presence of meso and macropores. As a result, rice husk ash, a byproduct of manufacturing rice, can be used in place of crude biodiesel.

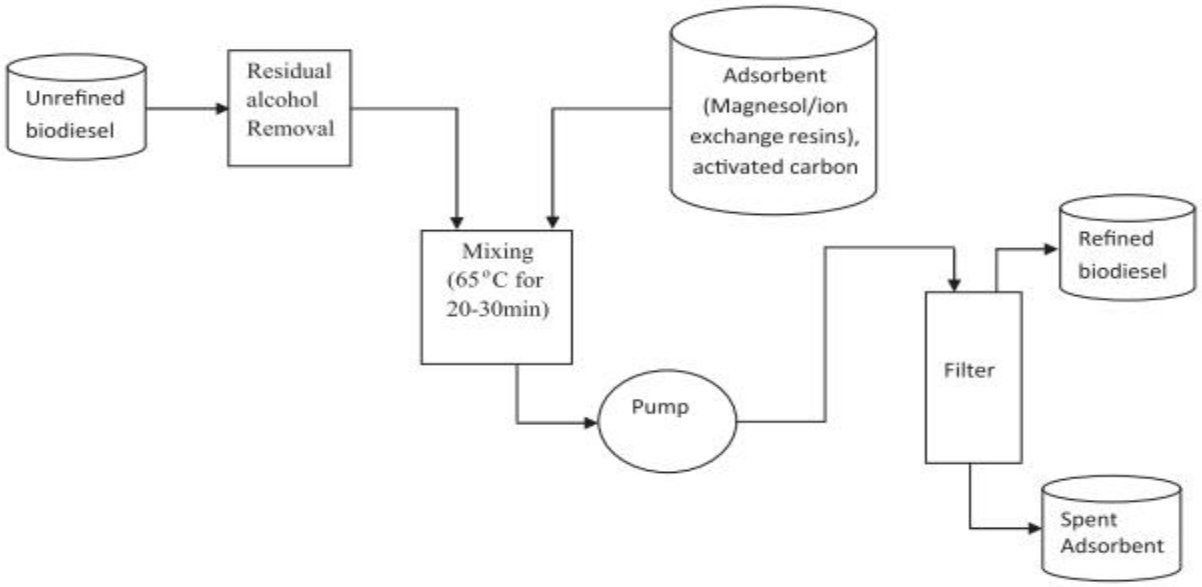

Figure 2.2. Diagram illustrating the method for biodiesel dry cleaning

2.6.3 Membrane Extraction

Membranes function as semi-permeable barriers that let some substances go through while keeping other species apart within a solution. Numerous properties, including homogeneity or heterogeneity, symmetry or asymmetry, solid or liquid composition, and fluctuating electrical charge, can be seen in these membranes. Convection and molecular diffusion, which are triggered by electric fields, concentration gradients, pressure differentials, and temperature changes, can both affect transport across membranes. Although membrane-based separations are commonly used in gas separation, protein isolation, and water purification, the treatment of non-aqueous fluids is still a developing field. They are mostly used in inert gasses and aqueous solutions for commercial purposes (Aziz et al., 2011).

Membrane extraction is a feasible technique for enhancing the standard of biodiesel fuel and is an efficient way to purify biodiesel. It entails separating components inside a solution selectively

using membranes as semi-permeable barriers (Atadashi, 2015). Recent studies have shown that membrane extraction can produce high-quality biodiesel with reduced impurities, contributing to improved engine performance (Atadashi, 2015). Along with other cutting-edge technologies like extraction using ionic liquids or deep eutectic solvents, this eco-friendly process is gaining popularity as a fresh approach to biodiesel purification (Ostojcic et al., 2020). Membrane processes offer a viable approach to both biodiesel production and purification, addressing the need for efficient and sustainable fuel production methods (Reis & Cardoso, 2016). Aziz et al. (2011) state that a number of factors, such as the composition of the membrane, temperature, flow velocity, operational pressure, and interactions between feed components and membrane surfaces, affect how effective membrane separation is.

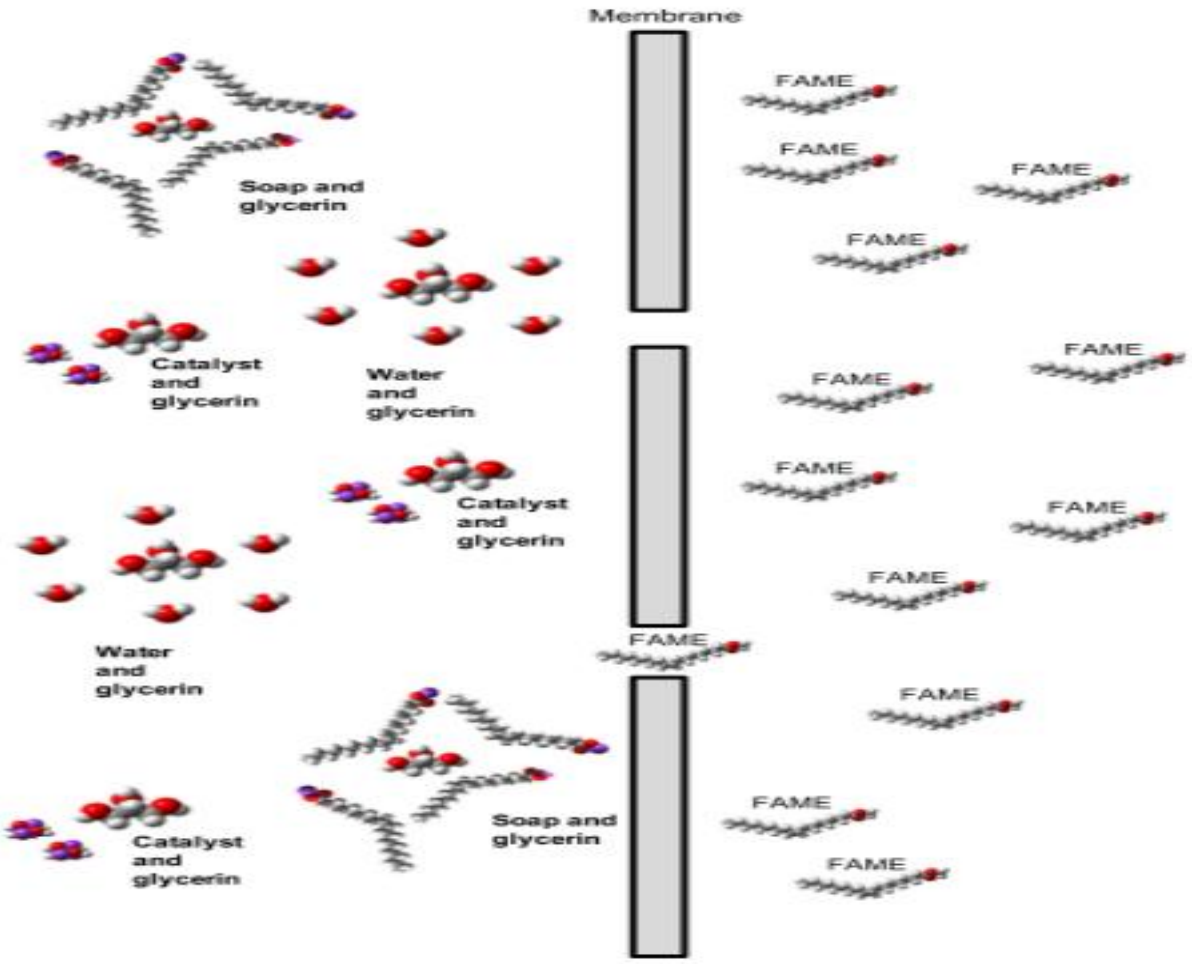

Figure 2.3 Membrane-based biodiesel impurity separation mechanism.

2.7 Feedstocks for the Production of Biodiesel

Four distinct categories of raw materials can be utilized in the production of biodiesel: feedstocks of the first, second, third, and fourth generations (Rahul et al., 2019).

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2.7.1 First-Generation Feedstocks

Numerous studies have looked into the process of producing biodiesel from popular edible vegetable oils, including rapeseed, soybean, palm, sunflower, and coconut oils. (Gaur et al.,

2021). This feedstock presents a financially viable substitute for traditional fossil fuels by providing highly scalable biodiesel manufacturing capabilities. But using it could start a fuel vs. food argument, which could raise the price of edible oils. The reliance on available arable land for cultivation raises concerns about deforestation, contributing to various environmental issues. The substantial land requirement for growing these feedstocks to meet global fuel demands not only poses ecological challenges but als o has the potential to disturb the balance of ecosystems, potentially leading to deforestation (D. Singh et al., 2020).

2.7.2 Feedstocks of the Second Generation

These non-edible feedstocks include oils and crops like mahua, jojoba oil, sea mango, tobacco seed, cotton seeds, jatropha, restaurant grease, waste cooking oil (WCO), and animal fats like pig lard and calf tallow that are unfit for human consumption (Utlu, 2007). These feedstocks are not deemed fit for human consumption because they contain toxic chemicals. Unlike edible oils, their use in the manufacturing of biodiesel allays concerns about the conflict between fuel and food because it doesn't directly impact the human food chain. The advantage of utilizing these feedstocks lies in their adaptability to growth in wastelands, requiring less farmland. Because multiple crops may be grown on a single piece of land, this method encourages environmental efficiency and is a more sustainable way to produce biodiesel. Furthermore, during the transesterification reaction, second-generation feedstocks produce important by-products (Suzihaque et al., 2022).

2.7.3 Feedstocks of the Third Generation

Microorganisms and algae are included in this group as feedstocks. Because they reproduce quickly, microalgae are a particularly good source of lipids for large-scale biodiesel synthesis (Jeswani et al., 2020). The swift growth of microalgae results in the generation of substantial

biomass, offering a viable alternative for biodiesel feedstock. With a high lipid content, microalgae can yield oil at a rate 25 times greater than traditional edible oils. Their adaptability to non-arable land makes them suitable for cultivation in areas unsuitable for conventional agriculture. Microalgae exhibit remarkable biomass doubling within approximately 24 hours without the need for herbicides or pesticides, ensuring high productivity in a short time frame (Davoodbasha et al., 2021). Furthermore, valuable by-products like carbohydrates and biopolymers are produced, serving various purposes such as feed or fertilizer. Despite these advantages, the significant capital expenses involved have prevented much study from being done in this field (Monika et al., 2023).

2.7.4 Feedstocks of the Fourth Generation

This group includes biomass that has undergone genetic modification with the goal of improving its ability to absorb solar energy and collect carbon dioxide. It consists of solar fuels utilizing photobiology and electrofuels, which are known for their low environmental impact and low level of debate (D. Singh et al., 2020). Although these feedstocks have many benefits, there hasn't been much research done on them because of their high upfront costs, low yields, and lengthy processing periods. These feedstocks of the future generation are characterised by their high energy content, affordability, easy availability, and inexhaustibility. This technology uses synthetic biology methods to produce biodiesel directly from solar energy and artificial photosynthesis.

This category includes waste cooking oil, which is a particularly good option for biodiesel conversion because it is renewable, economically feasible, and ecologically benign (Supraja et al., 2020). By using leftover cooking oil, problems over food and land availability are resolved, providing a long-term solution (Aboelazayem et al., 2018). Furthermore, because there is one

fewer step in the oil extraction process when producing biodiesel from leftover cooking oil, it is more economical than producing it from edible oil (Sendžikienė et al., 2018). Additional factors that enhance its effectiveness and affordability are the numerous sources of leftover cooking oil from different businesses, residences, and dining establishments.

2.8 WASTE COOKING OIL

The amount of waste cooking oil (WCO) produced has increased as a result of increased food consumption (Omar & Amin, 2011). According to Chhetri et al. (2008) and García-Martín et al. (2018), Spain, Canada, and the EU produce roughly 400,000, 135,000, and 700,000–1,000,000 tonnes of WCO annually, respectively. WCO, containing fatty acids, is commonly disposed of through land filling or river dumping, posing environmental risks (Chhetri et al., 2008). However, by transesterifying it with acidic, alkaline, or enzyme-based catalysts, it can be used again to produce biodiesel (Chongkhong et al., 2012). Heating oil generates free fatty acids (FFAs), glycerides, diacids, and polyacids, influencing transesterification efficiency (García-Martín et al., 2018). It's critical to keep an eye on the WCO acid index; if it rises beyond 2.5%, pre-esterification must occur before transesterification. Despite being thrown away, waste oil offers a financially viable alternative to virgin oil for the creation of biodiesel (Tanawannapong et al., 2013).

2.9 TRANSESTERIFICATION METHOD

Transesterification has gained popularity recently as a method for turning vegetable oils into fuel products with improved technical suitability. Reducing the viscosity of feedstock/vegetable oils to levels more similar to traditional fossil-based diesel is an essential step in the manufacturing of biodiesel (Math & Chandrashekhara, 2016). One ester is changed into another through the exchange of the alkoxy moiety in this chemical process. Transesterification is an

equilibrium reaction that characterizes the alcoholysis of carboxylic esters, according to Mumtaz et al. (2012) and Rashid & Anwar (2008). Standard catalysts like NaOH and KOH are typically used to catalyze transesterification (Anwar et al., 2020). This procedure helps with equilibrium adjustment, which raises ester yields. Vegetable oils have an alkyl moiety linked to glycerol, which is a structurally diverse triglyceride molecule. When these triglyceride molecules are transesterified using short-chain alcohols and the right catalyst, they produce glycerol and fatty acid methyl esters (Anwar et al., 2020). Three consecutive reversible stages can be used to explain the general transesterification process (Mumtaz et al., 2017).

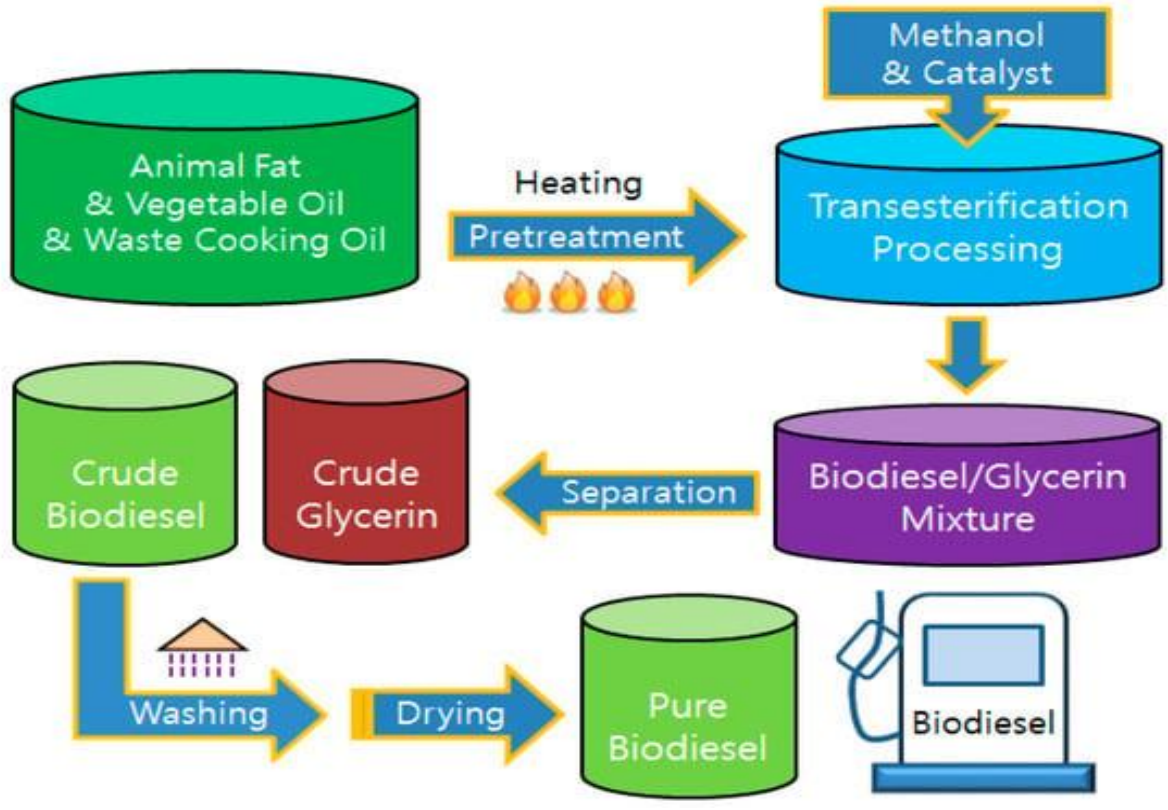


Figure 2.4 The particular transesterification procedure used to produce biodiesel

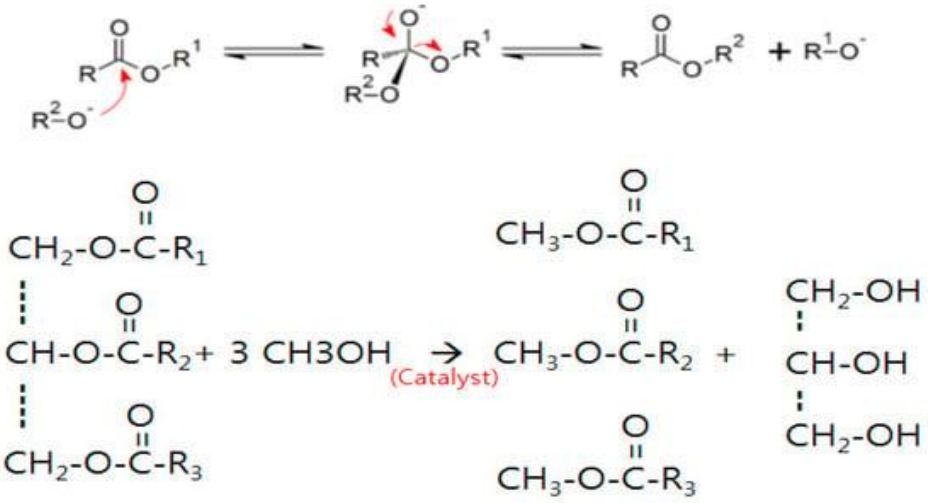


Figure 2.5 The lengthy hydrocarbon chains, also known as the fatty acid chains, are represented by the letters R1, R2, and R3 in the schematic depiction of the transesterification process. (Ge et al., 2017).

2.9.1 Transesterification of Waste Cooking Oils

A significant amount of waste cooking oil is produced by a number of establishments, such as eateries, slaughterhouses, and vegetable oil refineries. Making biodiesel from this material is a financially viable option. Cooking oil waste is primarily composed of triglycerides, however transesterification can transform them into glycerol and alkyl esters in the presence of a catalyst like NaOH or KOH. This reaction produces high-purity Fatty Acid Methyl Esters (FAME) when there are low quantities of free fatty acids present (Shu et al., 2011). But for better yield and purity, increased free fatty acid levels sometimes call for the use of acid catalysts such H2SO4 (Ambawatte et al., 2020). Three phases make up the transesterification process: first, triglycerides are formed under agitation from triglycerides and methanol, and then, monoglycerides and glycerin are converted. For better miscibility and ideal reaction kinetics, mass transfer is enhanced by stirring, with one mole of oil reacting with three moles of alcohol, a stoichiometric ratio. Adjustments in alcohol molar ratio may be necessary based on oil type,

catalyst, and process parameters (Abd Rabu et al., 2013). Reaction temperature typically ranges from 50–75 °C under atmospheric pressure, ideal for biodiesel production.

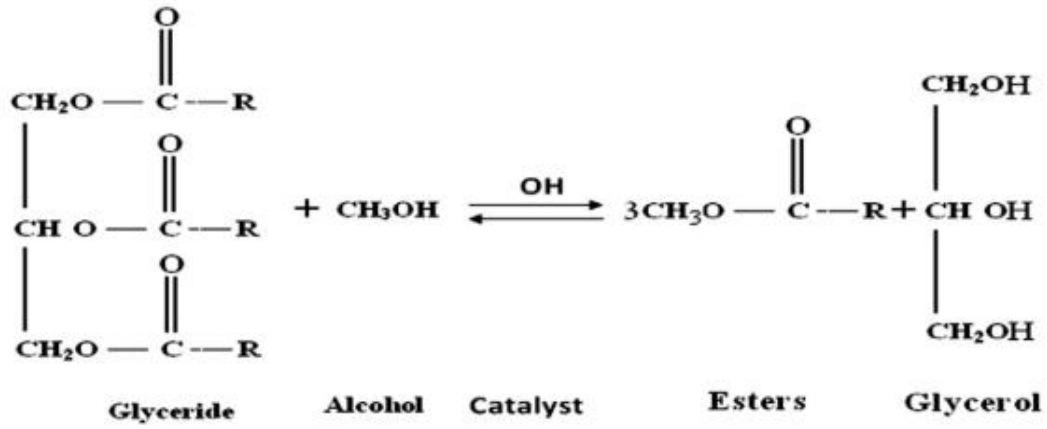


Figure 2.6 Transesterification process.

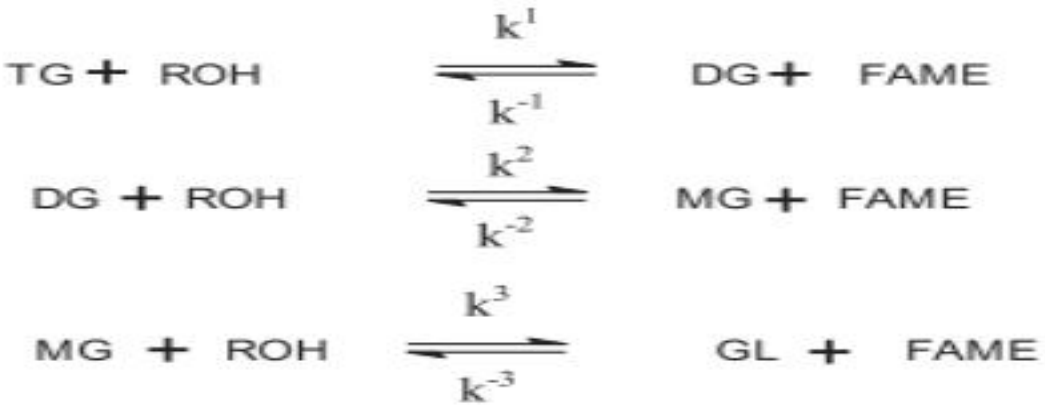


Figure 2.7 Overall transesterification reaction

2.10 CATALYSIS IN TRANSESTERIFCATION

Triglycerides, the feedstock oils, and alcohol often do not combine, producing a single-phase reaction mixture with a limited transesterification surface area. As a result, the rate of response is slow. Using a catalyst increases the area of contact between the reactants, which accelerates the

reaction. Chemical or biological catalysts may be used in catalytic transesterification processes. Chemical catalysts can be classified as heterogeneous (solid acids, bases, or acid–base bifunctional catalysts) or homogeneous (alkali or acid) nanocatalysts. Homogeneous chemical catalysts can accomplish greater conversion rates, but soap production makes recovery and purification more difficult (Thangaraj et al., 2019). Right now, enzyme catalysts are preferred due to their specificity, capacity to halt the production of soap, and simplicity in the purifying process. Biological catalysts can be free or immobilized lipase; the latter on nanomaterial support shows great promise (Jambulingam et al., 2019). The choice of catalyst is influenced by several factors, such as oil quality, free fatty acid concentration, operating conditions, required catalyst activity, cost, and availability (Tacias-Pascacio et al., 2019).

2.10.1 Homogeneous Chemical Catalyst

The process of selecting a catalyst affects how economically biodiesel is made. The kind of catalyst that should be employed depends on the concentration of free fatty acid (FFA) in feedstock oils. In the past, homogenous catalysts that coexist in the same phase as the reactants were used to create biodiesel.

2.10.1.1 Homogeneous Alkali Catalyst

Through the transesterification process, homogeneous alkali catalysts such as NaOH, KOH, CH3ONa, CH3OK, and NaOC2H5 are commonly used in the industrial biodiesel synthesis process. Their quick reaction times and favorable reaction conditions make them advantageous (Postaue et al., 2022). When processing extra-pure virgin oils with low free fatty acid (FFA) content and acid values below 0.5% and 1 mg KOH/g, respectively, these catalysts show exceptional efficiency and purity. High-fat oils are used to make soap, which lowers output and makes product separation more difficult (Jamil et al., 2018). Upon examining several alkali

catalysts, (Catarino et al., 2020) discovered that waste oils generated 92% of the biodiesel, whereas virgin oils produced 97%. Temperature, feedstock oil to alcohol molar ratio, vegetable oil purity, and catalyst concentration are all factors that affect the generation and purity of biodiesel (Catarino et al., 2020). Increased catalyst concentration causes soap formation, which leads to longer reaction times and the dilution of biodiesel with glycerol (Vicente et al., 2007). Efavi et al. (2018) reported that biodiesel yielded 70% when using a 0.13g NaOH catalyst, but dropped to 49% when the catalyst was raised to 0.18g.

Processing methods such as heating, filtering, and removal of impurities, suspended particles, and inorganic debris from oil assist prevent the formation of unwanted byproducts. When heating oil above its boiling point, care should be used (Sheet, 2018). When added to the reaction mixture, co-solvents boost yield, shorten reaction durations, and minimize the generation of soap. Using methanol as a solvent and ethanol as a co-solvent in the KOH catalyst, (Jambulingam et al., 2019) created biodiesel from residual beef tallow (Mandari & Devarai, 2022). When utilized as a co-solvent, ethanol, a low-polarity active ester exchange agent, reduced reaction time by 61.11%, enhanced yield by 3.08%, and prevented the formation of soap (Mandari & Devarai, 2022). (Amirthavalli et al., 2022) reduced the amount of volatile solvent utilized in the biodiesel synthesis process by employing a special deep eutectic solvent and glycerol co-solvent, resulting in a higher yield of 98%.

Homogeneous alkali catalysts have several benefits since they are easily accessible, reasonably priced, and able to produce high-quality biodiesel fast. Sodium-based catalysts outperform KOH catalysts in methanol due to their faster solubility and higher yields (Mandari & Devarai, 2022). Base-catalyzed reactions have a reaction rate that is 4000 times faster than that of acid catalysts. However, this strategy may result in undesirable side effects including the creation of soap if the

FFA and water levels exceed 0.5% and 0.06 weight percent, respectively. There is also a limit to its feedstock flexibility. Because premium virgin oils are a major component of commercially approved base-catalyzed production, discussions concerning food vs fuel have arisen (Mandari & Devarai, 2022). The catalyst's irreversibility is a downside that requires neutralization and disposal as a salt waste stream. It also generates a significant amount of wastewater during the purification of biodiesel, creating environmental issues (Selvakumar & Sivashanmugam, 2017).

2.10.1.2 Homogeneous Acid Catalyst

One of the challenges associated with using homogenous alkali catalysts is the requirement for high-quality cooking oils and the difficulty in producing soap since feedstock oils have high FFA levels. When homogeneous acid catalysts are used, these drawbacks can be minimized. Acid catalysts are unaffected by the presence of FFA and, in contrast to alkali catalysts, can catalyze both esterification and transesterification reactions concurrently. Therefore, inexpensive raw materials high in FFAs, like animal fats, used cooking oils, and non-edible oils, can be efficiently employed as acid catalysts (Mandari & Devarai, 2022).

Due to their resistance to Free Fatty Acids (FFA), homogeneous catalysts provide improved access to active sites, which is especially advantageous. Cascao et al. (2013) list sulfuric acid (H2SO4), sulfonic acid (H2SO3), hydrochloric acid (HCl), and ferric sulphate (Fe2(SO4)3) as examples of bronsted acids. Sulfuric acid (H2SO4) is preferred because of its enhanced performance at medium temperatures and atmospheric pressure. An algal oil with 90% water content, Chlorella pyrenoidosa, produces 93.2% biodiesel when 0.5% H2SO4 is added. Furthermore, hydrochloric acid (HCl) shows promise (Ghurri et al., 2012). In certain conditions, it produces 90% more biodiesel than H2SO4. Utilizing affordable non-edible feedstocks like leftover cooking oil, the predicted cost of manufacturing biodiesel using acid and alkali catalysts

is US$0.8 and US$0.9 per litre, respectively. Comparatively speaking, the average cost per liter in Hong Kong is US$1.01 (Mandari & Devarai, 2022).

Acid catalysts mitigate soap formation issues encountered with alkali catalysts (Dall'Oglio et al., 2015). However, challenges persist, including water generation hindering transesterification and difficulties in catalyst recovery, product separation, and purification, leading to increased overall production costs (R. Singh et al., 2020).

2.10.2 Two-Step Transesterification

In order to overcome the shortcomings of the single-step homogeneous-catalyzed transesterification process, researchers have developed a novel two-step method for producing biodiesel utilizing either alkali or acid. This method uses both base and acid catalysts sequentially to speed up the process and prevent saponification. To get higher content non-edible oils' Free Fatty Acid (FFA) levels below 0.5–1%, they must first be esterified using an acid catalyst. Subsequently, a base catalyst aids in the completion of transesterification, increasing the yield of biodiesel. In a recent investigation, a semi-industrial pilot-scale microreactor was used. In the first phase, the FFA level was lowered using 1% H2SO4, and in the second, KOH was employed as a catalyst. Maximum yields of 97.2% in one minute and 98.26% in two minutes of residence time were achieved under ideal conditions, which included a 9.4:1 methanol to waste cooking oil (WCO) molar ratio, 1.16 wt% catalyst concentration, and 64.2°C temperature (Lemma et al., 2020).

Kivevele et al., (2011) produced an astounding 98% final biodiesel yield using a novel two-stage transesterification process, starting with a homogeneous base catalyst and switching to a heterogeneous catalyst in the second step (Kivevele et al., 2011). As oil seed is stored, the levels

of free fatty acid (FFA) increase. Rubber seed (Hevea brasiliensis) oil shows a notable increase in FFA content, from 2 to 45 weight percent, after two months at ambient temperature. Three processes were involved in the production of biodiesel from oil with a high FFA content: esterification, acidification, and saponification. For the purpose of saponification, the oil was heated to 68–70°C for 30 minutes while alcohol and NaOH were added. An HCl catalyst was added to the soap solution after the acidification stage in order to lower the concentration of FFA.

Finally, esterification with an acid catalyst was used to convert FFA to FAME. Slow esterification rates and long reaction times are disadvantages of this approach, even if it has the potential to produce more biodiesel. Furthermore, the two-step approach requires additional steps for the retrieval of the catalyst in each stage (Alves et al., 2014).

2.10.3 Heterogeneous Chemical Catalytic Transesterification

Often solid, heterogeneous catalysts perform their functions in separate parts of the reaction mixture, which is a liquid. In recent times, biodiesel has been produced using a wide variety of solid catalysts. Relevant to the feedstock is their capacity to withstand its water content and free fatty acid (FFA). The catalyst may be easily extracted from the reaction mixture thanks to the different phases, allowing for numerous cycles of reuse. The production of biodiesel is made more affordable because their utilization decreases the demand for soap (Wang et al., 2019). Continuous production in fixed bed reactors is made possible by the cost-effectiveness of heterogeneous solid catalysts. This, in turn, allows for expanded industrial-scale production (Wang et al., 2019).

2.10.4 Catalytic Transesterification by Heterogeneous Acid

Recent advances in catalysis have focused on developing a wide variety of durable catalysts for use in biodiesel synthesis. In the esterification and transesterification processes needed to make biodiesel, heterogeneous acid catalysts are used instead of the more conventional homogeneous acid catalysts. According to Guldhe et al. (2017), solid acid catalysts with Lewis and Brønsted acid active sites are more practical for industrial use than their homogeneous equivalents. Heterogeneous catalysts reduce problems like toxicity and corrosion of vessels in comparison to homogeneous catalysts. Furthermore, according to Mansir et al. (2017), they may withstand feedstock oils with high water levels and free fatty acids (FFAs) without the need for an acid pretreatment (Ajala et al., 2019). The invention of heterogeneous catalysts has enabled for the continuous manufacture of biodiesel while maximizing its economic feasibility by employing inexpensive raw materials such residual cooking oil and animal fat (Nata et al., 2017b).

2.10.5 Heterogeneous Catalytic Transesterification Using Alkali

Solid alkali catalysts are more catalytically effective than solid acid catalysts. Numerous studies have addressed the difficulties of producing biodiesel using homogenous alkali catalysts. Heterogeneous alkali catalysts are widely used because they offer a significant surface area for catalytic activity. These catalysts include hydrotalcite, metallic salts, zeolites, alkaline oxides, and alkaline earth metal oxides (Du et al., 2019). Alkaline earth metal oxides have strong basic characteristics and are inexpensive when used as solid alkali catalysts. Single metal oxides are useful for producing biodiesel, and dopants improve catalytic efficiency by increasing the surface area and properties of the catalyst (Atadashi et al., 2013).

Generally speaking, CaO and BaO are stronger than MgO. But according to (Huang et al., 2012), BaO is both poisonous and easily soluble in ethanol or methanol. Because of its decreased

solubility in methanol, wide availability, strong activity, and selectivity, CaO is considered a better heterogeneous catalyst that performs well under moderate reaction conditions. When producing industrial biodiesel, it is stable over long periods of time and economically feasible. Das et al. (2020) generated biodiesel using a cobalt-doped CaO catalyst derived from eggshells and calcined at various temperatures. The cobalt-doped CaO was produced using the co-precipitation method. The catalyst was used for three cycles, with a maximum generation of 98.3% biodiesel at a 1.5 weight percent catalyst loading at 60°C and a 12% yield decline in the third cycle due to catalyst poisoning (Das et al., 2020). (Jamil et al., 2018) looked at a number of alkaline earth metals, including MgO, BaO, SrO, and CaO. CaO shown superior catalytic activity for the production of biodiesel when added to pure carbon, with an ideal biodiesel yield of 94.27%. Catalytic activity dropped, though it remained steady, after six runs (Jamil et al., 2018).

Solid calcium diglyceride (CaDG) catalyst was used at a flow rate of 45 L/h at 50 °C for four hours, with a catalyst loading of 1.5 wt%, in a semi-continuous reactor to create 90% biodiesel (Malpartida et al., 2020). A 4:1 optimum methanol to oil ratio—which is almost stoichiometric—is desirable. However, limited mass transfer slows down the rate of reaction since methanol is weakly soluble in oil. To get around this problem, co-solvents can be added to the reaction mixture to increase the liquid-liquid interfacial area. Usually employed as co-solvents, ionic liquids and organic solvents must be entirely eliminated from the reaction to minimize risks and toxicity. Using crude biodiesel as a co-solvent eliminates the need for co-solvent recovery. After using crude biodiesel as a co-solvent for 1.5 hours, Todarovic and colleagues (2019) generated a 99.9% biodiesel yield. Salinas et al. (2012) reported a >90% yield with a catalyst loading of 6 weight percent and a methanol to oil ratio of 54:1 at 55 °C for five hours in their study of potassium-supported TiO2 catalysts for biodiesel generation. Despite the finding of catalyst

deactivation, a yield of 81 ± 6% was sustained in four cycles without treatment.CaO, a possible solid alkali catalyst, faces difficulties due to Ca2+ seeping into methanol, which causes soap formation with FFA and catalytic deactivation by CO2 and water (Li et al., 2020). On the other hand, MgO has a small surface area but remains active even when exposed to water. Including supplementary content makes it more engaging. For example, a carbon-based magnesium oxide catalyst produced 96.5% of the biodiesel (Du et al., 2019). β-strontium silicate yielded 97.88% biodiesel, consistent for six cycles. Because of catalyst recovery, heterogeneous alkali catalysts provide faster reactions, higher yields, and lower processing costs. On the other hand, disadvantages include the possibility of product contamination from active site leaching, sensitivity to FFA content, high methanol to oil ratio needs, and poisoning from air exposure (Engineering, 2015).

2.11 Heterogeneous Acid–Base Bifunctional Catalytic Transesterification

Bifunctional heterogeneous catalysts could be used to produce biodiesel. Researchers have recently focused a great deal of interest on metallic oxide catalysts due to their exceptional catalytic activity and durability. These catalysts feature both basic and acidic sites, resulting in high conversion rates and selectivity. This makes it possible for triglyceride transesterification and free fatty acid (FFA) esterification to occur simultaneously. They function well with inexpensive feedstock oils, including residual cooking oil, tallow wastes, and non-edible oils. Esterification is first employed in acid-catalyzed treatments to reduce the FFA concentration in order to create high-quality biodiesel. Transesterification using a base catalyst comes next. Moreover, heterogeneous bifunctional catalysts can be designed to satisfy specific physicochemical specifications, ensuring that neither a high FFA content nor the presence of water would hinder the transesterification process (Al-Saadi et al., 2020a; Farooq et al., 2013).

Jamil et al. (2020) investigated calcium and copper-based metal-organic framework (MOF) catalysts. Esterification was catalyzed by Cu-MOF, an acid, and transesterification by Ca-MOF, an alkali. The yields of Cu-MOF and Ca-MOF, which were synthesized independently using solvothermal and hydrothermal methods, were 78.3% and 78%, respectively.. But when these catalysts were combined, the output of biodiesel was 85%. According to Jamil et al. (2020), these catalysts showed good regeneration potential by being active for three cycles. Furthermore, Al-Saadi et al. (2020) created a unique acid-base bifunctional catalyst (SrO-ZnO/Al2O3), which, under ideal circumstances, produced 95.1% of biodiesel via transesterification and 71.4% via esterification (Al-Saadi et al., 2020b). Furthermore, because of their inexpensive and varied composition, naturally occurring clay minerals like bentonite were investigated for catalytic synergy.

Under particular reaction conditions, a graphene oxide/bentonite catalyst demonstrated improved accessibility to reactants, leading to a 98.5% biodiesel production (Ali et al., 2018).

2.12 CALCIUM PHOSPHATE SCUM AS A SOLID HETEROGENOUS CATALYST

Calcium phosphate scum from the sugar refining industry serves as an innovative and sustainable solid heterogeneous catalyst in the biodiesel production process (Mandari & Devarai, 2022). This catalyst is derived from waste material, making it cost-effective and environmentally friendly. Its unique properties make it an efficient catalyst for transesterification reactions, converting triglycerides into biodiesel. The calcination process enhances the catalytic activity of calcium phosphate scum, ensuring high conversion rates. Large-scale biodiesel production may also easily access it due to its abundance as a byproduct of the sugar refining industry. By recycling

industrial leftovers, the usage of this catalyst supports the circular economy and helps reduce waste.

Furthermore, its compatibility with transesterification reactions ensures the production of high-quality biodiesel with minimal environmental impact. By utilizing calcium phosphate scum as a catalyst, this project highlights the potential for sustainable and efficient biodiesel production methods. Overall, the use of calcined calcium phosphate scum represents a promising approach to advancing the sustainability of biodiesel production processes(Eng & Ukzn, 2020).

2.13 PREVIOUS RELATED STUDIES

Research	**Drawbacks**	**Citations**
An overview of current developments in the manufacturing of cleaner biodiesel	The manufacture of biodiesel by alkali catalysis has a number of disadvantages, including water washing and dehydration.	(Maheshwari et al., 2022)
Using calcined phosphate rock as a precursor to calcium oxide heterogeneous catalyst for the manufacture of biodiesel.	Non-utilization of raw materials as catalysts for biodiesel production	(Kiprono, Rutto, Seodigeng, et al., 2022)
Biodiesel production through transesterification over heterogeneous catalysts	Non-utilization of raw materials as catalysts for biodiesel production	(Ngamcharussrivichai et al., 2010)
A review of heterogeneous calcium oxide-based catalyst	Major industrial solid wastes such as Sugar Refining wastes not visited	(Ling et al., 2019)
Catalysis in biodiesel production—a review	No practical conducted	(Thangaraj et al., 2019)

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 Reagents and Raw Materials Used

The calcium phosphate scum used for the development of the heterogeneous catalyst was obtained from BUA sugar refineries in Nigeria.

Also, the waste cooking oil was acquired from restaurants and canteens around the school environment, the University of Benin, Benin City, Nigeria, and neighboringroadsidebean cake vendors around the school locality.

The reagents used are listed below;

(i). Distilled water

(ii). Methanol

(iii). Potassium hydroxide

(iv). Benzene

(v). Phenolphthalein indicator

(vi). Ethanol

(vii). Detergent

(viii). Hydrochloric acid

(ix). Iron chloride

(x). Nickel nitrate

3.1.2 List of Equipment / Apparatus

i. Digital scale
ii. Conical flask
iii. Dropper
iv. Syringe
v. Density bottle
vi. Laboratory pestle
vii. Laboratory mortal
viii. Hang gloves
ix. Stirrer
x. Magnetic stirrer
xi. Funnel
xii. Measuring Cylinder
xiii. Round bottom flask
xiv. Muffle furnace
xv. Oven
xvi. Crucibles
xvii. Beakers
xviii. Heating mantle
xix. Desiccator
xx. Retort stand
xxi. Viscometer

xxii. Pipette

xxiii. Centrifuge

xxiv. Burette

3.2 METHODS

3.2.1 The Physicochemical of theOil Used

3.2.1.1 Density

The exact addition of palm kernel oil to a density container with a defined volume marked the beginning of the testing procedure. The first thing that needed to be done was weigh the empty bottle using a high-precision weighing balance. After that, there was one more weighing that included the bottle and the oil. The measured values were recorded with great care. The resulting weight shift, which was calculated by deducting the empty bottle's original weight from the oil and bottle's combined weight, took on significant importance. This computed weight change was crucial in determining the oil's weight-to-mass ratio. Utilizing this established ratio, the next step involved the computation of the oil's density by dividing its mass by the known volume of the density bottle.

$$Density = \frac{Mass}{Volume} \qquad 2\text{-}1$$

3.2.1.2 Moisture content

The procedure involved introducing waste cooking oil (WCO) into a beaker with a predetermined mass. Using a precision balance, the total weight of the beaker and oil was measured before being allowed to evaporate for an hour at 120°C in the oven. Following the completion of the evaporation process, the weight of the beaker and the desiccated oil was re-

measured and recorded. The percentage of moisture content was computed employing the subsequent formula:

$$Moisture\ content\ = \frac{w_1 - w_2}{w_1 - w_0} \qquad 2\text{-}2$$

Where;

w_0 = weight of empty beaker

w_1 = weight of beaker and oil before evaporation

w_2 = weight of beaker and oil after evaporation

3.2.1.3 Acid Value

An initial analysis was carried out to determine the amount of free fatty acids present in the used cooking oil (WCO) before the biodiesel synthesis process was started. It was necessary to weigh out one gramme of residual cooking oil and pour it into a conical flask. After that, 10ml each of benzene and ethanol were added to the flask in equal amounts. Carefully stirring the ensuing amalgamation helped to facilitate the dissolution of the oil. The final step involved titrating the resulting solution against a 0.05N KOH solution. As part of the titration method, three drops of phenolphthalein were administered as an indicator. To start the titration process, the KOH solution was gradually added to the mixture of oil, alcohol, and phenolphthalein.

This addition was accompanied by thorough shaking until the solution maintained a continuous pink hue for a duration of 20 seconds.

$$Acid\ Value\ = \frac{N \times 56.1 \times (V_s - V_b)}{weight\ of\ oil\ of\ sample} \qquad 2\text{-}3$$

$$FFA = \frac{Acid\ Value}{2} \qquad 2\text{-}4$$

Where;

V_S = Volume of 0.05N KOH used with oil

V_b= Volume of 0.05N KOH used without oil (Blank)

N = Concentration of KOH

3.2.1.4 Saponification Value

The average molecular weight of the fatty acids present in a sample as triglycerides is determined by the saponification value. It shows the milligrams of potassium hydroxide (KOH) or sodium hydroxide (NaOH) needed to fully saponify one gramme of fat in accordance with particular recommendations (Bello et al., 2015). A conical flask was filled with an exact 2-gram quantity of the oil sample to start the procedure. Next, the liquid in the pipette was able to empty completely after carefully pipetting 5 ml of an alcohol potassium hydroxide solution into the flask. The mixture underwent heating and boiling on a sand bath under an air condenser setup for approximately 50 minutes. The solution exhibited a change in clarity and homogeneity during boiling, indicating the conclusion of the saponification process. A blank sample was analysed using a similar process. After boiling, the mixture was taken out of the sand bath and given a quick rinse with distilled water to make it easier for the parts that were attached to slide down the sides of the flask. After adding 1 ml of an indicator, the contents of the flask were allowed to cool. 0.5M HCl was added to the solution and titrated until the pink hue vanished. A particular relationship was used to determine the oil's saponification value.

$$Saponification\ Value\ =\ \frac{56.1\times N\times(V_b-V_s)}{weight\ of\ oil\ of\ sample} \qquad 2\text{-}5$$

Where;

V_S = Sample titre value

V_b= Blank titre value

N = Concentration of HCl

3.2.1.5 Kinematic Viscosity

The investigation into the rheological characteristics of the WCO specimen entailed employing a digital viscometer calibrated in milli-Pascal seconds to assess its dynamic viscosity. This experimental procedure was executed under controlled conditions with a temperature set at 30°C. Subsequently, the kinematic viscosity was determined through the application of the relevant formula, as outlined below:

$$Kinematic\ Viscosity\ (cSt) = \frac{n}{density\ of\ oil\ sample} \qquad 2\text{-}6$$

n = Dynamic Viscosity of oil in centipoise

3.2.1.6 Mean molecular mass

The mean molecular weight of WCO was determined by taking into account its acid value and saponification value through the application of the following formula:

$$Average\ molecular\ weight\ =\ \frac{56.1\times1000\times3}{SV-AV} \qquad 2\text{-}7$$

Where;

SV = saponification value of WCO

AV = Acid value of WCO

3.2.1.7 Specific gravity

A simple procedure was used to ascertain the waste cooking oil (WCO) sample's specific gravity. Initially, a dry, clean, 25 ml density container's mass was determined and noted as m1. The combined mass of the water and the bottle was measured and recorded as m2 after the addition of distilled water. The remaining vegetable oil was poured into the bottle, and the mass was measured in milliliters (m3). Next, the following formula was used to determine the oil sample's specific gravity:

$$Specific\ gravity = \frac{m_3 - m_1}{m_2 - m_1} \qquad 2\text{-}8$$

3.2.2 Preparation of Catalyst and Transesterification

Calcium Phosphate Scum waste from the sugar industry was used for the pro3duction of the heterogeneous catalyst

3.2.2.1 Calcination of the Calcium Phosphate Scum

The calcination was conducted according to Kiprono et al., (2022). Using a lab pestle and mortar, the phosphate scum was first ground into small particles and then sieved to provide a consistent size distribution. After that, the finely ground scum was put inside a crucible and heated to 1000 °C for eight hours in a furnace. This heat treatment was intended to facilitate the conversion of calcium carbonate, which was contained in the scum, into calcium oxide and release carbon dioxide as a gas. The sample was calcined for eight hours, and then it was gradually cooled in the furnace for one hour, until it reached room temperature (25 ºC). The thermal decomposition of the scum occurred within the furnace, as indicated by the following equation(Kiprono, Rutto, & Seodigeng, 2022):

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \uparrow$$

3.2.2.2 Preparation of bifunctional catalyst

The fabrication of a doped bifunctional catalyst employed the wet impregnation method. This was done according to (Amenaghawon et al., 2022). The process involved the creation of a slurry solution by introducing the Calcium Phosphate Scum into distilled water containing dissolved iron chloride and nickel nitrate. Subsequently, the mixture underwent stirring for approximately one hour, ensuring thorough blending. The resulting slurry solution was subjected to a heated magnetic stirrer operating at 80 degrees Celsius until complete evaporation of water, yielding a solid substance.This solid underwent sun drying for several hours, followed by an additional one-hour drying period in an oven set at 100 degrees Celsius. Subsequent to these initial stages, the doped catalyst experienced a stringent 6-hour calcination process at a high temperature of 900 degrees Celsius. Post-calcination, the catalyst was meticulously transferred to a desiccator to avert moisture absorption. Ultimately, it was stored in an airtight container, rendering it prepared for future utilization(Amenaghawon et al., 2022).

3.2.2.3 Transesterification procedure

The process of transesterification was carried out in accordance with (Kiprono, Rutto, Seodigeng, et al., 2022). Pretreatment of the oil was not essential because of its low free fatty acid concentration. One phase comprised the transesterification process. In order to eliminate moisture and reduce the likelihood of water-related catalyst issues impeding the production of biodiesel, waste cooking oil was first heated to temperatures above 150 °C (Kiprono, Rutto, Seodigeng, et al., 2022). Subsequently, the oil was filtered to eliminate food particle residues, acknowledging its cafeteria waste origin. Alcohol vaporisation was avoided during

transesterification by using a reflux condenser in a flask with three necks. The device was set up on a magnetic stirrer for hot plates that had a thermometer connected. A given amount of oil was weighed and heated to a set temperature beforehand. Following that, a particular quantity of catalyst and methanol were added, determined by suggested experimental values (Kiprono, Rutto, Seodigeng, et al., 2022). Throughout the experiment, stirring happened at a steady 400 revolutions per minute. The contents of the flask were transferred to a separating funnel and the reaction was stopped after a predefined period of time. Throughout the night, the mixture separated into three layers: the solid heterogeneous catalyst was at the bottom, glycerol, residual methanol, mono and diglycerides, and glycerol were in the middle, and the ester was at the top (Kiprono, Rutto, Seodigeng, et al., 2022). The catalyst was removed, cleaned, and dried so that it could be used again in later cycles of biodiesel production. The ester's glycerol layer was extracted separately. A pure methyl ester sample was obtained by repeatedly washing and heating the resultant ester at 100 °C to remove any remaining methanol and water (Kiprono, Rutto, & Seodigeng, 2022). The resulting sample was then weighed using the given procedure to determine the yield.

$$Yield\ of\ Biodiesel\ = \frac{grams\ of\ biodiesel\ produced}{gramsofoil\ used} \times 100\% \qquad 2\text{-}9$$

3.2.3 Characterization of Catalyst

Using various analytical methods, the catalyst's functional groups, surface morphology, structure, and surface area were evaluated. Functional group identification was made easy by FTIR Spectrophotometry, and surface shape was exhibited by SEM-EDX (Scanning Electron Microscopy-Energy Dispersive X-ray). The surface area was determined in part utilizing BET (Brunauer-Emmett-Teller) analysis. Furthermore, X-ray diffraction analysis, or XRD, was

employed to investigate the catalyst's crystalline structure. The oxide composition of the sample was measured by means of X-ray fluorescence (XRF) analysis.

This comprehensive approach involving multiple analytical methods ensured a thorough understanding of various aspects of the catalyst, encompassing its chemical composition, structural characteristics, and surface properties.

3.2.4 GC-MS analysis

Following the transesterification reaction, the biodiesel sample was evaluated using a mass selective detector (MSD)-equipped gas chromatography-mass spectrometry (GCMS) system (Agilent 5977) (Supraja et al., 2020). The dimensions of the HP 5 ms ultra inert column were 30 m × 250 μm (ID) × 0.25 μm. A GC chamber was filled with a sample volume of around 1 μL, and helium was utilized as the gas carrier, flowing at a rate of 1 mL min−1 (Mandari & Devarai, 2022). A split-less injection approach was adopted. The specifications for the oven temperature program were as follows: it would begin at 80 °C and climb in increments of 10 °C min−1 up to 180 °C (1 min) and 15 °C min−1 up to 255 °C (2 min) (Mandari & Devarai, 2022). The peaks of FAMEs (fatty acid methyl esters) recorded at varied retention durations were examined (Mandari & Devarai, 2022).

3.2.5 Characterization of the biodiesel produced

According to the standard specifications provided in ASTM D 6751 and EN 14214, the biodieselsynthesised material was thoroughly characterised (Saad et al., 2023).

3.2.6 Experimental Design

The response surface methodology was utilized with the aim of improving the efficiency of biodiesel conversion. Using a Box-Behnken, the study incorporated four distinct design characteristics to assess their effects on biodiesel yield. The parameters that were evaluated included the catalyst concentration (%), reaction temperature (°C), reaction duration (min), and methanol-to-oil ratio (mol/mol). Notably, the trial method was conducted with the stirring speed being constant (Kiprono, Rutto, & Seodigeng, 2022).

Table 3.1 Experimental variable parameters

Factor	Variable	Unit	Minimum	Mean	Maximum
A	Reaction temperature	°C	40.00	55.00	70.00
B	Reaction time	min	60.00	75.00	90.00
C	Catalyst loading	Wt%	1.0000	3.00	5.00
D	Methanol to oil ratio	mol/mol	6.00	12.00	18.00

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF WASTE COOKING OIL

Table 4.1 summarizes the outcomes of an analysis done on the composition of waste vegetable oil. The percentage of FFA was 1.2975%. Research reveals that elevated levels of FFA reduce the efficiency of catalysts and lower the yield of manufacturing. Consequently, it is proposed that the proportion of FFA in WCO not transcend 1 weight percent (Tshizanga, 2015). On the other hand, heterogeneous catalysts have been found to catalyze oil with a high FFA content (6–15%) without the requirement for any prior preparation (Buasri et al., 2013). Prior investigations with WCO (FFA 6.6–6.8%) have exhibited good yield (90%) under comparable reaction conditions (60°C, 5h, 24:1 ratio, 4% catalyst loading). (Tshizanga, 2015). The moisture content of WVO (0.2 wt%) was smaller than the amount (≥0.5wt%) that has been stated in the literature to limit biodiesel yield (Tshizanga, 2015).

Table 4.1 Characteristics of leftover cooking oil used to produce biodiesel

Property	Value
Acid value (mg KOH/g oil)	2.595
FFA (%)	1.2975
Moisture content (%)	0.02
Dynamic viscosity @ 40 °C (mPas)	29.50
Saponification value (mg KOH/g oil)	300.135
Average molecular weight (g/mol)	565.638
Density @ 40 °C. (g/ml)	0.903
Specific gravity	0.9127

4.1.1 Catalyst characterisation

The physical and chemical parameters of the solid catalyst employed in the transesterification reaction are provided below. It was noticed that the features resulted in a considerable activity in the reactions. This supposition is supported by the SEM images of catalyst (Figure 4.2) (Buasri et al., 2013).

4.1.2 Bet analysis

Reactants were able to quickly permeate into the interior of the catalyst due to its large pore capacity (0.213cc/g) and high surface area (235.505m2/g) (table 4.2) (Tshizanga, 2015). (D. Singh et al., 2020) indicated that a greater pore diameter is advantageous for improved diffusion of reactant and product molecules. The observation is in keeping with that of Carreia et al. (2014) with a slightly greater (0.238cc/g) pore volume of CaO catalyst (Tshizanga, 2015).

Table 4.2 Properties of the calcined Catalyst

Calcined calcium phosphate scum	**Value**
Surface Area	235.505 m^2/g
Pore Volume	0.213 cc/g
Pore diameter	2.920 nm

4.1.3 Functional group of the catalyst

Carbon containing surface functional groups plays important role in influencing the surface properties and catalytic performance of the calcined scum. These groups can be formed during calcination where the calcium phosphate scum is heated to high temperatures to create new

chemical bonds and surface functionalities. The FTIR spectra obtained for the prepared adsorbent is revealed in Figure 4.1. The summary of the result is presented in the table 4.3 below.

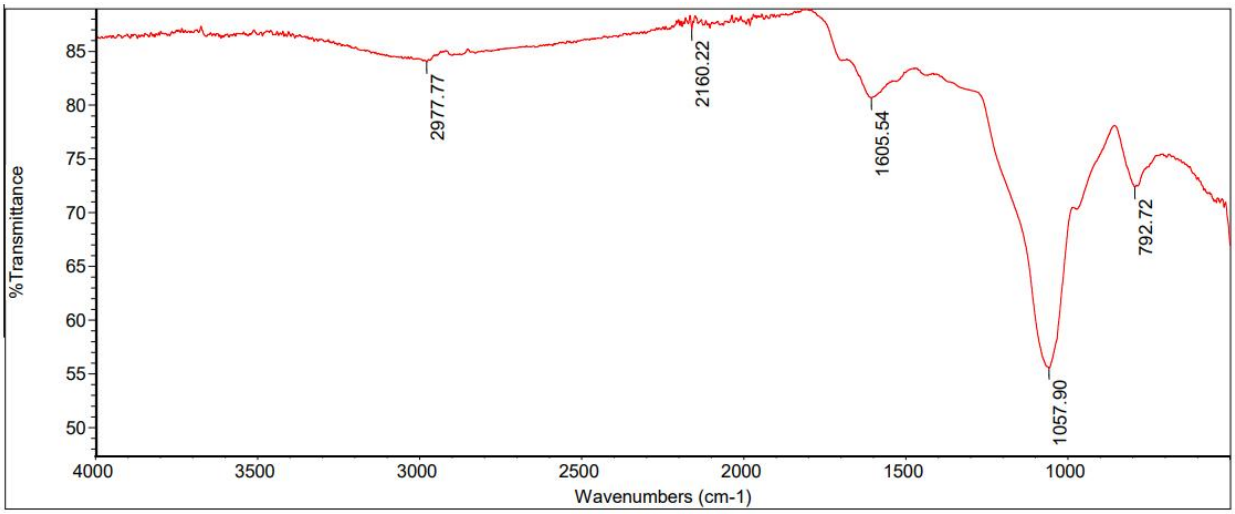


Figure 4.1 FTIR spectrum of catalyst

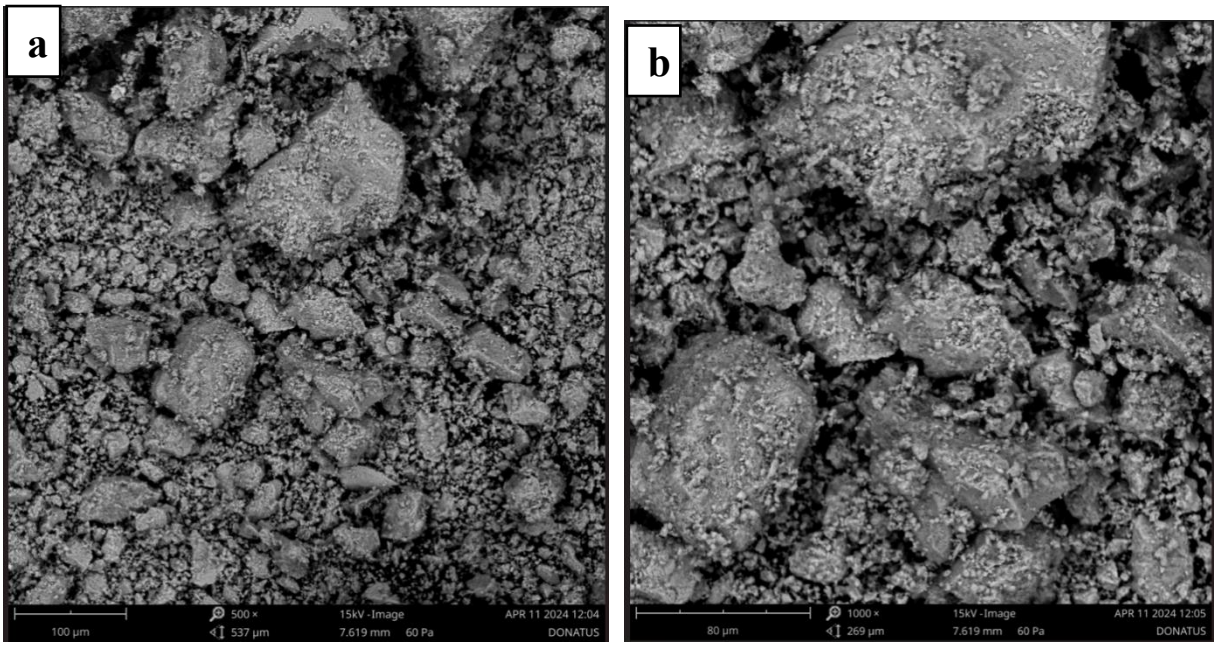
Table 4.3 Summary of Spectrum peaks of Catalyst

Peak Number	**position**	**Functional groups**	**Comment**
1	2977.7	Methyl (C-H)	Medium stretch
2	2160.22	Azide (N=N=N)	Strong strectch
3	1605.54	Conjugated Alkene (C=C)	Medium stretch
4	1057.90	Sulfoxide (S=O)	Strong stretch
5	792.72	Alkene (C=C)	bending

4.1.4 Surface morphology of catalyst

Micrograph of the catalyst obtained by the SEM images at 500x to 1500x magnifications are presented below in figure 4.2. Sample showed relatively unifo rm spherical particles in the

size range of 20μm (Wang et al., 2019). It is worth mentioning that these particles' surface was rough. Rough surfaces are known to posses more micropores and thus more efficient catalytic activities (Wang et al., 2019).



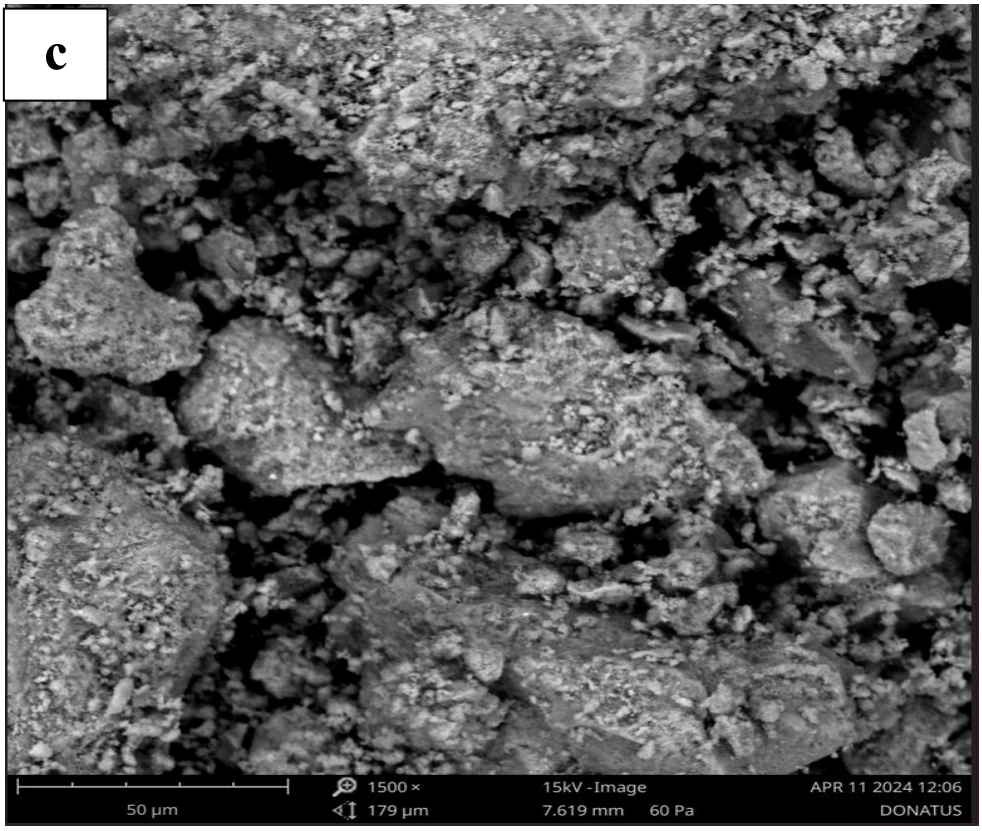


Figure 4.2 Micrograph of catalyst at (a) 500xx, (b) 1000xx of magnification and (c) 1500xx of magnification

Table 4.4 EDS Elemental composition, atomic conc and weight conc of elements in the catalyst

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
20	Ca	Calcium	57.41	62.67
15	P	Phosphorus	30.80	25.99
26	Fe	Iron	3.43	5.23
14	Si	Silicon	3.92	3.00
12	Mg	Magnesium	2.37	1.57
13	Al	Aluminium	1.87	1.38
16	S	Sulfur	0.20	0.18

4.1.5 **Elemental Composition of Catalyst**

The results of elemental composition of catalyst were conducted using X-ray fluorescent (XRF). From table 4.5, the results obtained revealed the presence of silicon oxide (SiO_2) concentration at 50.4% and Aluminium oxide (Al_2O_3) concentration at 41.436%. other compounds were at trace amounts. XRF results also revealed the compostion of elements presents in the catalyst and they are summarized in table . oxygen was revealed to be the most predominant element at concentration 49.079% followed by the presence of aluminium and silicon at conc. 21.931% and 23.559% respectively.

Table 4.5 compound layer composition of catalyst

Component	**Conc. (wt%)**
Silicon oxide	50.4
Aluminium oxide	41.436
Titanium oxide	4.760
Other trace amounts	3.394

Table 4.6 element compostion of the sample

Element	**Conc. (wt%)**
Oxygen	49.079
Silicon	23.559
aluminium	21.931
Titanium	2.854
Other trace amounts	2.541

4.1.6 **Crystallinity of the Catalyst**

The crystallinity of the compounds present in the clay sample was determined with an X-ray diffractometer. The results obtained from (Figure 4.3) revealed a crystalline arrangement for the compound present in the catalyst (Rizwanul Fattah et al., 2020). The results obtained in (figure 4.5), It reveals that the calcined sample used contains high of amount of Calcium Zinc Hydrogen Phosphate (47%) and fluorapatite (33%) and trace amounts of osumilite (13.8%) and quartz (6.5%).

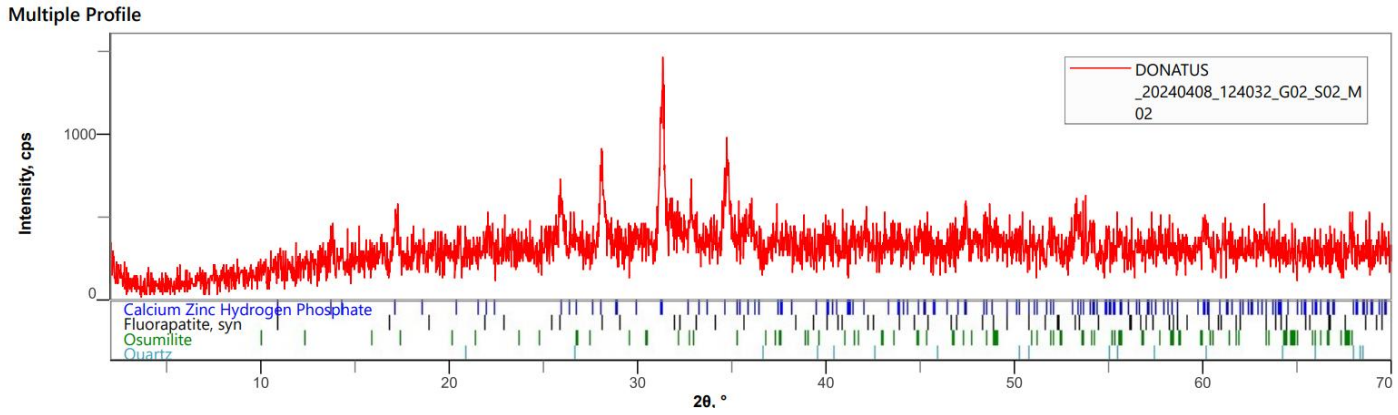


Figure 4.3 X-ray difractogram of calcined sample

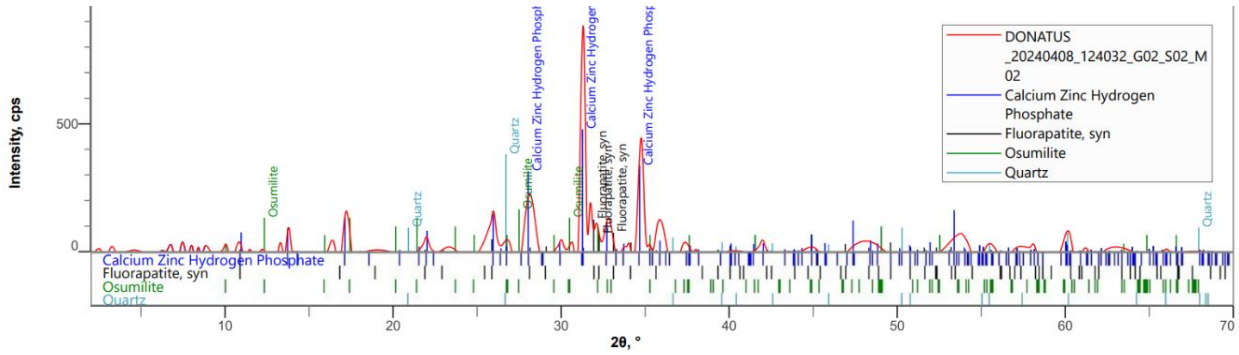


Figure 4.4 XRD chromatogram of sample

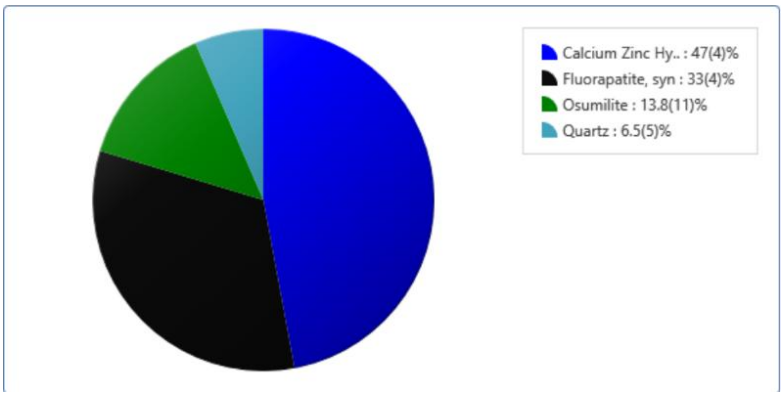


Figure 4.5 XRD pie chart of calcined sample

4.2 REACTION SURFACES METHODS: A STATISTICAL ANALYZATION

Variance analysis is one statistical technique that is frequently used to evaluate the significance and applicability of the quadratic regression model. It helps determine how each variable affects the result and interacts with the others. Response surface methods and a central composite design with four parameters (methanol to oil ratio, catalyst loading, reaction temperature, and reaction time) were used in the tests (Supraja et al., 2020), which are shown in Table 4.7.

Table 4.7 Experimental Results of RSM BBD Design for Biodiesel Yield

Run	**A:Temperature** *°C*	**B:Time** *Mins*	**C:Catalyst Loading** *wt%*	**D:Methanol to oil ratio** *mol/mol*	**Yield** *%*
1	55	60	3	6	61.5
2	55	75	3	12	82.3
3	70	60	3	12	66.2
4	40	75	3	6	58.4

5	70	75	3	6	57.1
6	55	60	3	18	74.7
7	55	75	1	6	71.9
8	55	75	1	18	80
9	55	60	5	12	69.5
10	55	90	3	18	90.1
11	40	90	3	12	75.6
12	40	75	3	18	66.2
13	55	75	3	12	81.5
14	55	75	3	12	80.5
15	55	90	5	12	77.9
16	40	75	5	12	65.3
17	70	90	3	12	76.2
18	**55**	**90**	**1**	**12**	**93.2**
19	55	75	3	12	80.5
20	40	75	1	12	71.3
21	55	60	1	12	76.4
22	55	75	5	18	75.8
23	70	75	1	12	76
24	55	75	5	6	59.6
25	55	90	3	6	72.1
26	55	75	3	12	79.6
27	40	60	3	12	62.7

28	70	75	5	12	66.1
29	70	75	3	18	75.6

From table 4.7, The yield that was obtained varied from 57.1% to 93.2%. Over the course of 29 manual trials, independent factors such as reaction temperature, duration, catalyst concentration, and methanol-to-oil ratio were changed. These data points were effectively fitted into a quadratic polynomial model. Equation (4.1) derived from the variance analysis serves as a tool to predict biodiesel yield at any specified combination of independent parameters.

$$\mathbf{Yield = +80.84 + 1.47A + 6.17B - 4.55C + 6.82D + 2.67AD - 2.10BC + 2.02CD -9.98A^2 - 1.69C^2 - 6.69D^2} \quad \ldots (4.1)$$

In the given equation, denoting temperature as A, time as B, catalyst concentration as C, and methanol to oil molar ratioas D, negative coefficients signify detrimental impacts on yield, whereas positive coefficients indicate beneficial effects. The disparity between experimental and predicted yields exhibited minimal errors. Equation 4.1, which uses coded variables A, B, C, and D, makes it easier to anticipate response outcomes when these components are present in certain combinations. These variables are encoded as +1 for high levels and -1 for low levels, enabling a comparative assessment of their respective influences via coefficient analysis. Within Equation 4.1, factors A, B, D, AD, and CD positively impact biodiesel yield enhancement. However, the reaction is negatively impacted by components C, BC, A2, C2, and D2, which lowers the yield of biodiesel.

A graphical representation, depicted in Figure 4.5, illustrates the proximity of these variables, affirming their correlation. The fact that data points in both plots are close to the diagonal line

indicates a high level of agreement between expected and observed responses, confirming the model's ability to estimate biodiesel yield effectively.

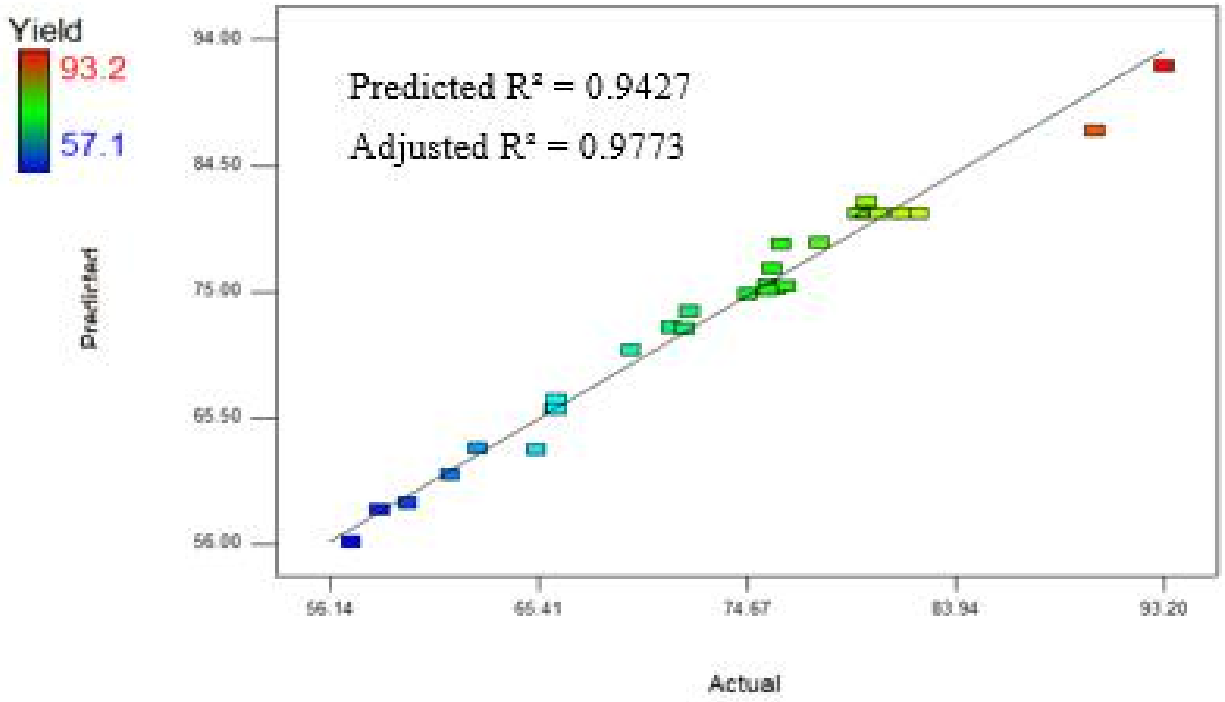


Figure 4.6 Predicted yield versus actual biodiesel yield.

Detailed insights into biodiesel yield concerning the genuine factors are provided in Table 4.7, elucidating the relationship derived from the definitive equation originating from Equation 4.2.

Table 4.8 Final Formula Considering Real Factors

Yield	=
-117.08984	
+4.62131	× Temperature

+0.62167	× Time
+3.49037	× Catalyst Loading
+3.45753	× Ratio of Methanol to Oil
+0.029722	× Temperature × Ratio of Methanol to Oil
-0.070000	× Time × Catalyst Loading
+0.16875	× Catalyst Loading ×Methanol to Oil ratio
-0.044360	× Temperature^2
-0.42340	× Catalyst Loading^2
-0.18593	Methanol to Oil ratio^2

The equation, when expressed in terms of actual factors and their corresponding units, makes it possible to predict responses at particular factor values. It is important to remember that this equation isn't the best for determining the relative importance of different components because the intercept doesn't match the design space centre and the coefficient adjustments line up with factor units. Table 4.3 provides a concise overview of the biodiesel yield model.

Table 4.9 Synopsis of Model Data for Biodiesel Production

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	6.30	0.5752	0.5044	0.3998	1345.83	
2FI	6.98	0.6084	0.3908	-0.0028	2248.50	
Quadratic	**1.35**	**0.9886**	**0.9773**	**0.9427**	**128.49**	**Suggested**
Cubic	1.28	0.9956	0.9797	0.6482	788.80	Aliased

This reveals that the proposed quadratic model exhibits the most elevated R^2 value, reaching 0.9886, surpassing all other models except for the aliased cubic model. Emphasizing the model summary statistics, the emphasis lies on optimizing R^2 and predicted R^2 values. A greater R^2 signifies a robust model, reflecting accurate response prediction. Here, the R^2 value stands at 0.9886, signifying a remarkable 98.86% explanation of response variability.

As shown in Table 4.10, the **ANOVA Quadratic Model Analysis of Variance** demonstrates the relevance of the model terms by displaying the probability value (P) and Fisher's test (F-test).

P-values assess the likelihood of errors, providing insights into the overall and individual term significance within the model. A P-value below 0.0500 indicates significant model terms(Yatish et al., 2016). In this instance, the model's overall significance is confirmed at a 95% confidence level by the model's F-value of 106.82 and P-value of <0.0001. The values of the individual parameters define the overall P-value of the model equation. The relevance of the model is further supported by its Model F-value of 106.82, as shown in Table 4.10.

Table 4.10 ANOVA Quadratic Model ANALYSIS OF VARIANCE

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	2204.97	10	220.50	106.82	< 0.0001	Significant
A-Temperature	26.11	1	26.11	12.65	0.0023	
B-Time	457.57	1	457.57	221.66	< 0.0001	
C-Catalyst Loading	248.43	1	248.43	120.35	< 0.0001	

D-Metanol to Oil ratio	557.60	1	557.60	270.12	< 0.0001	
AD	28.62	1	28.62	13.87	0.0016	
BC	17.64	1	17.64	8.55	0.0091	
CD	16.40	1	16.40	7.95	0.0114	
A^2	670.18	1	670.18	324.66	< 0.0001	
C^2	19.30	1	19.30	9.35	0.0068	
D^2	301.41	1	301.41	146.01	< 0.0001	
Residual	37.16	18	2.06			
Lack of Fit	32.83	14	2.34	2.17	0.2371	not significant
Pure Error	4.33	4	1.08			
Cor Total	2242.13	28				

The independent variables A, B, C, and D had a large impact on the response; tiny p-values imply significance. The least important element was discovered to be reaction temperature ($p = 0.0023$), whilst the most critical elements were determined to be time, the weight of the catalyst percentage, and methanol to oil molar ratio ($p < 0.0001$). Significant interaction terms included combinations of temperature and methanol to oil ratio, time and catalyst weight, and methanol to

oil ratio and catalyst weight (AD, BC, CD). The quadratic terms A2, C2, and D2 were similarly significant (p values<0.1000, 0.0068, and <0.1000, respectively). The p-value for the lack of fit parameter was 0.2371, showing a satisfactory fit between the experimental data and the quadratic model. The 2.17 Lack of Fit F-value indicates insignificance in relation to pure error, and noise has a 27.70% possibility of producing a high F-value of this magnitude. There are enough experiments to explore the effects of factors on the response when there is a minor lack of fit (Hu et al., 2022).

A measure of the degree of variability between observed and predicted values is the coefficient of determination (R2). Strong fits are shown by elevated R-squared values, which imply the least amount of difference between the observed and projected values (Putra et al., 2018). As indicated in Table 4.5, the R2 value in this case is 0.9834, showing a very strong fit between the model and the experimental data. This shows that the model equation (Yahya et al., 2020) accounts for 98.34% of the experimental data, leaving only 1.66% of the variability unexplained for

Table 4.11ANOVA statistical parameters for the quadratic model

Std. Dev.	1.44
Mean	73.23
C.V. %	1.96
PRESS	104.02
R-Squared	0.9834
Adj R-Squared	0.9742
Pred R-Squared	0.9536
Adeq Precision	40.484

The adjusted coefficient of determination (adj R^2) corrects for small discrepancies between experimental and predicted models. A difference of less than 0.3 between adj R^2 and predicted R^2 indicates model significance. Here, adj R^2 is 0.9742, and predicted R^2 is 0.9536, meeting the criterion for significance. The coefficient of variation (CV) reflects data accuracy, with lower values indicating higher accuracy (Dharma et al., 2016). In this study, CV is 1.96%, suggesting reasonable model accuracy. Adequate precision, a measure of signal-to-noise ratio in the analysis of variance, should exceed 4; the model's value of 40.484 indicates sufficient precision(Yahya et al., 2020).

4.3 THE EFFECT OF PROCESS PARAMETERS ON THE YIELD OF BIODIESEL

4.3.1 The Impact Of Temperature And Reaction Ratio Between Methanol And Oil On The Yield Of Biodiesel

According to the study, temperature and the methanol to oil ratio had a significant impact on fame yield ($p = 0.0016$). Fig. 4.2 shows these effects under constant circumstances (3% catalyst weight and 75 min reaction duration). Increasing temperature enhances biodiesel yield until reaching its peak at 55 °C. This enhancement is attributed to increased activation energy required for reaction completion, reducing diffusion resistance across methanol, oil, and catalyst layers. This facilitates rapid transesterification (Foroutan et al., 2020).At temperatures exceeding the optimal 55°C, the yield progressively diminishes. This drop is explained by the high temperature above methanol's boiling point. Methanol therefore turns into a gas and escapes the reaction vessel. As a result, the ratio of methanol to oil decreases, which lowers yield (Dhawane et al.,

2016).Esters degraded at high temperatures, producing other chemicals and lowering the amount of biodiesel produced.

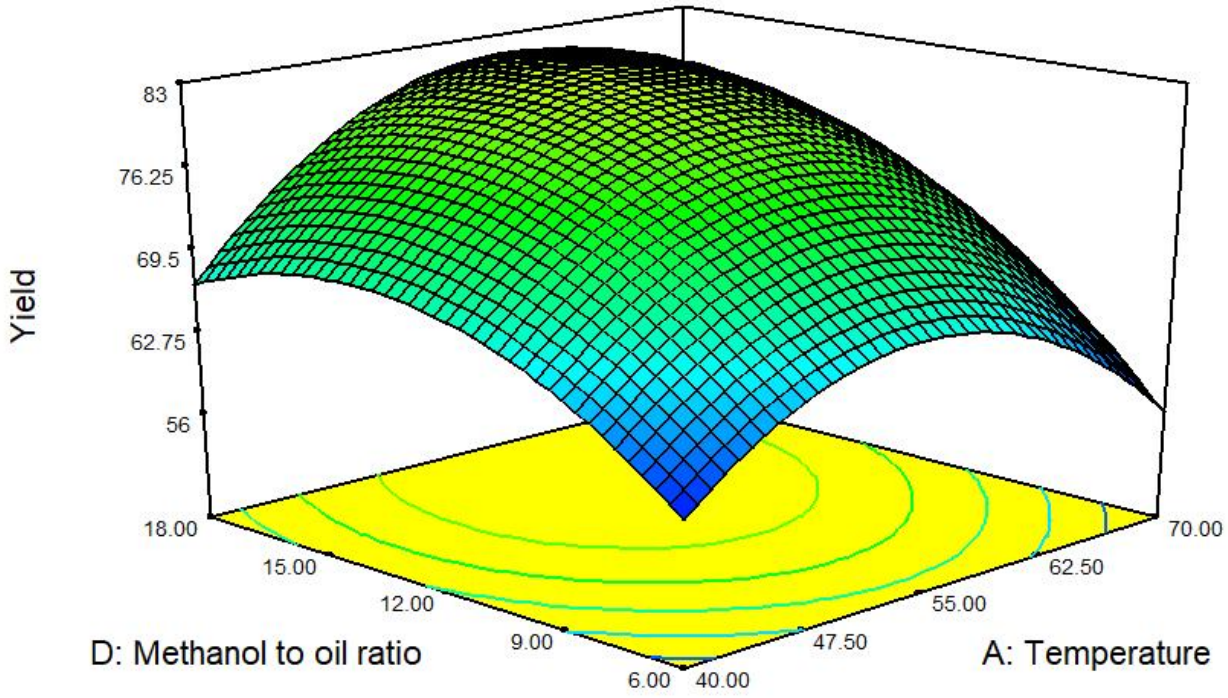


Figure 4.7 3D surface plots illustrating how reaction temperature and methanol/oil ratios affect the output of biodiesel

4.3.2 Impact of the Catalyst to Oil Weight Ratio and the Methanol to Oil Ratio on Biodiesel

As seen in Fig. 4.3, the 3D response surface analysis shows the combined effect of the methanol-to-oil ratio and the catalyst-to-oil weight ratio. The yield of biodiesel is significantly increased by raising the catalyst concentration from 1% to 3% while keeping the same reaction time and temperature of 80 minutes and 60°C, respectively. (Maradin, 2021) explains that this improvement can be attributed to the higher number of active sites, which accelerates response

times. Having said that, methyl ester synthesis decreases if the 3% catalyst threshold is crossed. This decrease is associated with higher mass transfer resistance brought on by too much catalyst, which makes reactant mixing more challenging (Ghurri et al., 2012). Another possibility is that an excess of catalyst makes the glycerine more viscous, which eventually lowers the ester yield. Alternatively, the ester yield increased significantly and eventually achieved its maximum value when the methanol-to-oil molar ratio was raised to 12:1. According to Le Chatelier's principle, this rise in methanol quantity propels the reaction towards completion. However, the yield dramatically dropped after the ratio of 12:1. Dilution effects, in which extra methanol becomes unneeded and dilutes the glycerol, were the reason for this drop. Because of this dilution, the product is harder to separate, which slows down the methyl esters' production and eventually reduces yield.

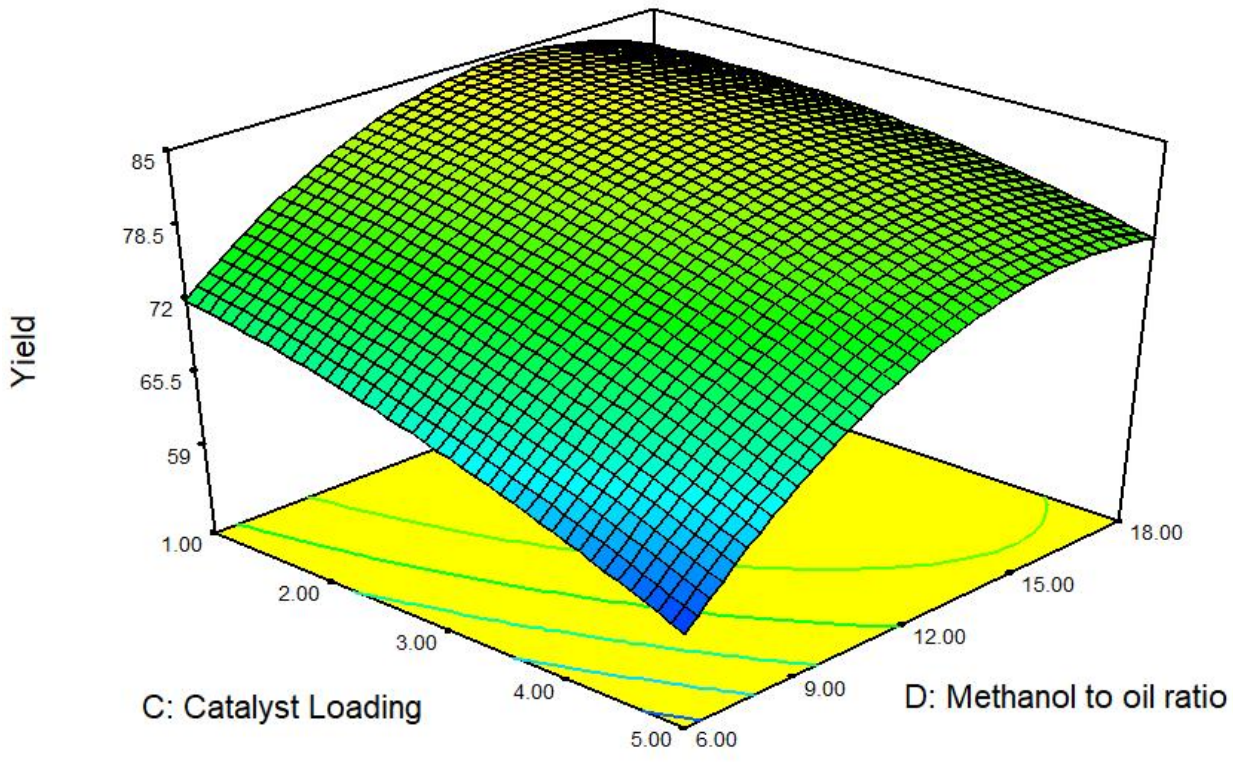


Figure 4.8 3D surface plots illustrating how catalyst and methanol/oil affect the output of biodiesel

4.3.3 Impact of Catalyst Loading and Reaction Time on Biodiesel Yield

Based on the 3D surface model, Figure 4.4 shows the relationship between the catalyst loading (wt%), reaction time (mins), and biodiesel output. The three-dimensional figure illustrates how, even with a significant decrease in catalyst loading, biodiesel output grew steadily with reaction time. A catalyst loading of one and a reaction duration of ninety minutes were utilized to produce the finest biodiesel..

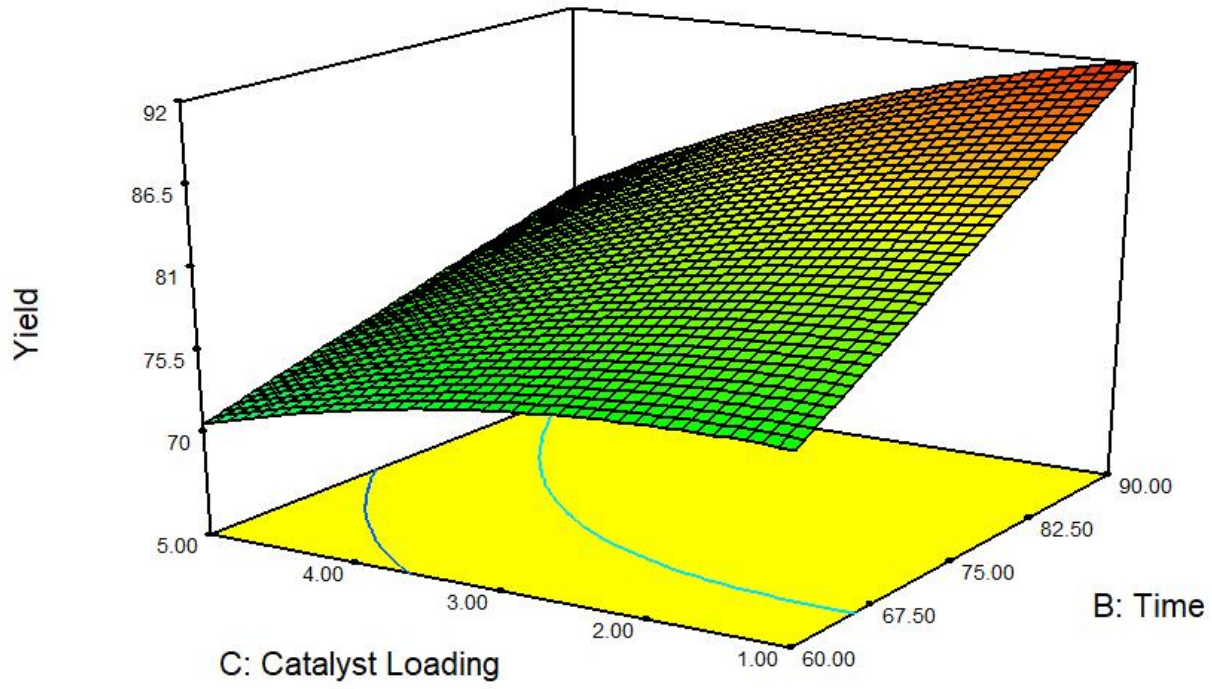


Figure 4.9 3D surface plots illustrating how catalyst loading and time affect the output of biodiesel.

4.3.4. Impact of Oil to Methanol Ratio and Reaction Time

Figure 4.5, which is based on the 3D surface model, illustrates the relationship between the methanol/oil ratio (mol/mol), the reaction duration (min), and the production of biodiesel. The 3D graphic indicates that a longer reaction time led to higher biodiesel production, which in turn caused the methanol to oil ratio to rise to its maximum value of 12:1 before rapidly declining. The optimal amount of biodiesel was created with a 12:1 methanol to oil ratio and an incubation period of 90 minutes.

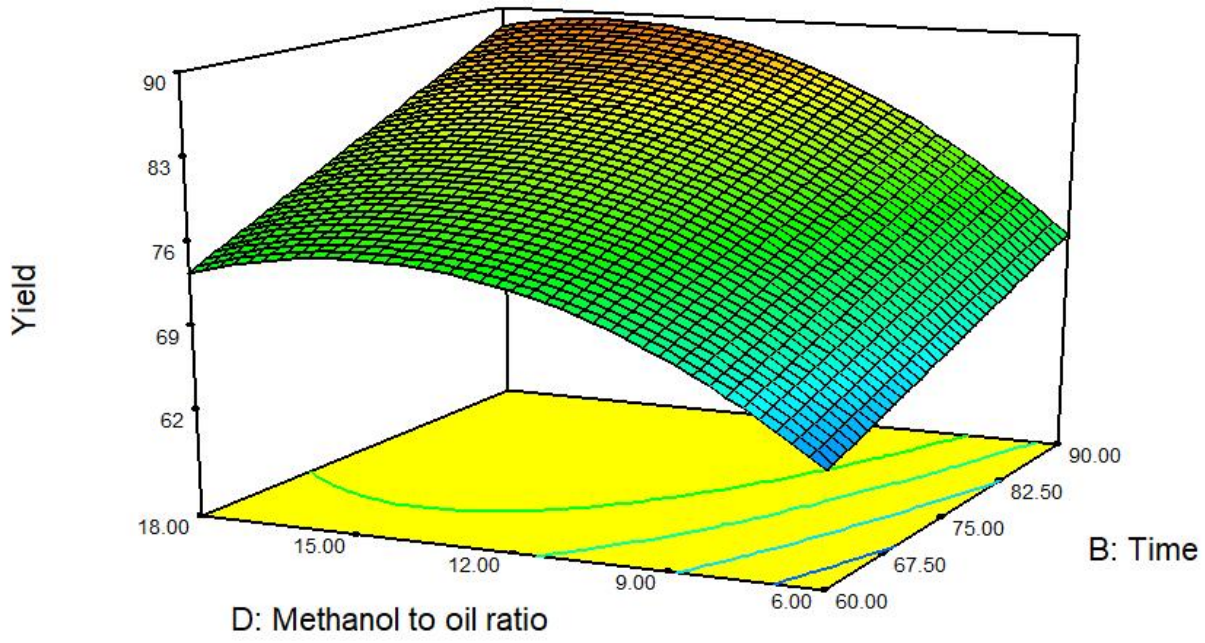


Figure 4.10 3D surface plots illustrating how reaction time and methanol/oil ratios affect the output of biodiesel

4.4 MODEL VALIDATION

The goal was to maximise yield by utilising the numerical optimisation capability of the Design Expert programme. The ideal circumstances for highest yield were found by numerically optimising additional parameters, as Fig. 4.6 illustrates. The model indicated that the following

parameters led to the greatest yield of 93.2%: a reaction temperature of 70^0C, a methanol-to-oil ratio of 18:1, a reaction time of 90 minutes, and a catalyst concentration of 5%. Subsequent manual experimentation with three replications validated these conditions, yielding a 93.2% yield, closely aligning with the predicted value. The desirability score of 0.9536 suggests the high reliability of the model for future applications(Seffati et al., 2020).

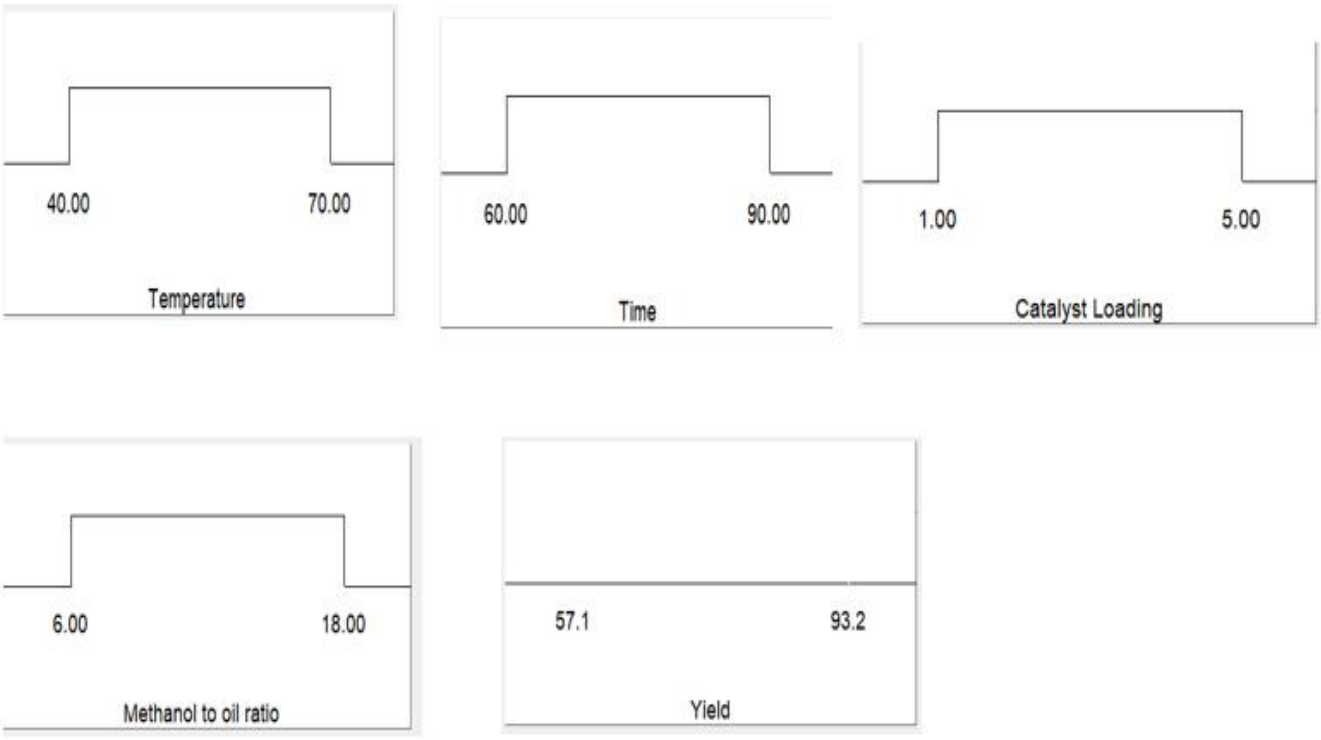


Figure 4.11 Optimum Model Validation on Biodiesel Yield

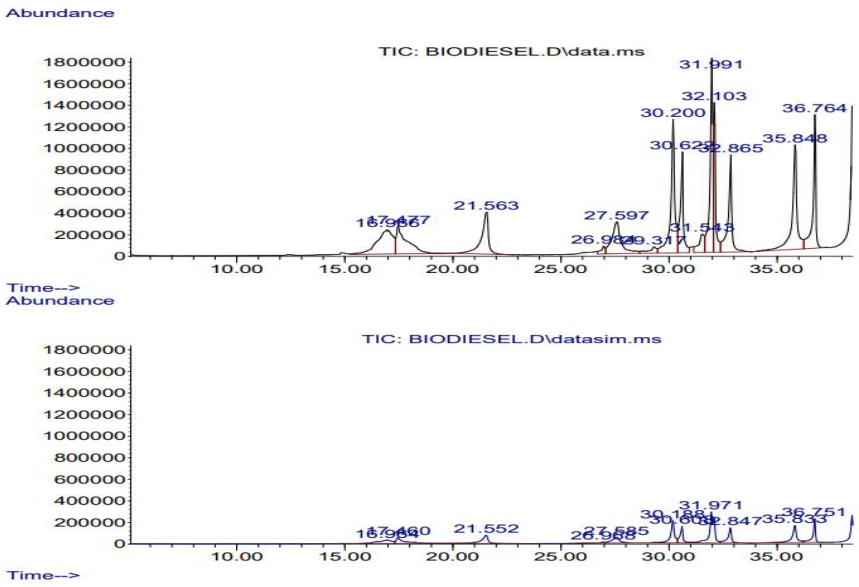


Figure 4.12 GC-MS spectrum of the biodiesel obtained from waste cooking oil using a calcined calcium phosphate scum as catalyst.

Table 4.12 Fatty acid methyl esters obtained via GC-MS analysis

Compound name	Concentration (%)	Retention time
1,4-Bis(trimethylsilyl)benzene	8.81	16.966
Linoleic acid ethyl ester	6.92	17.477
Oleic Acid	6.90	21.563
9-Octadecenoic acid (Z)-, 2,3-dihy droxypropyl ester	9.985	31.5325
6-Octadecenoic acid, (Z)-	7.03	30.622
Z-4-Nonadecen-1-ol acetate	11.86	31.991
9-Octadecenoic acid, (E)-	7.46	32.103
n-Propyl 11-octadecenoate	11.47	35.848
cis-9-Tetradecenoic acid, heptyl ester	8.56	36.764

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The study successfully achieved its aim of optimizing the production of biodiesel from waste cooking oil using response surface method technique. Using the synthesized catalyst, Response Surface Methodology (RSM) was employed to maximize the transesterification of left over oil under specific operating conditions. The following conclusions were drawing from the WCO's characterization, bio – diesel, impact of variables.

i. The characterization of the waste cooking oil was carried out successfully.
ii. The heterogeneous catalyst was prepared successfully from calcium phosphate scum
iii. The optimization of biodiesel production from waste cooking oil catalysed by heterogenous catalyst via Response Surface Method
iv. The physiocchemical properties of WCO that were found under optimal conditions met the biodiesel standards set by ASTM D6 751 and EN 16214 after the WCO was characterized
v. The investigation of the variables showed that the catalyst concentration, time, and methanol-to-oil ratio had the greatest significant effects on the reaction.
vi. The production and characterization of the biodiesel was successful carried out, it was discovered that the calcium phosphate scum from the sugar refining industries was shown to be a highly efficient and reasonably priced substitute supply of calcium oxide for the creation of heterogenous catalyst used in the biodiesel manufacturing process.

5.2 RECOMMENDATION

In conclusion, it was shown that calcium phosphate scum from the sugar refining industries offers a highly efficient and reasonably priced substitute source of heterogeneous calcium oxide catalyst for biodiesel generation.

The following suggestions are recommended for future experimental work:

(i). Exploring additional doping agents is advisable for enhancing the Calcium Phosphate Scum for biodiesel production.

(ii). Exploring different calcination temperatures and durations for catalyst synthesis is essential to ascertain optimal production parameters.

(iii). Future experimental investigations to ascertain the efficacy of calcium oxide heterogeneous catalyst for biodiesel generation can employ other oils, particularly waste oils.

(iv). Further investigation is warranted to minimize methanol consumption in the biodiesel manufacturing procedure.

(v). Conducting emission assessments is imperative when utilizing the produced biodiesel in diesel engines.

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