Optimum biodiesel production from waste vegetable oil using functionalized cockle shell and watermelon peels as catalyst

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CERTIFICATION

This is to certify that this research work was carried out by ONWUMA CHIMYENUM NKEMDINUM of the Department of Chemical Engineering at the University of Benin, Benin City, Edo State, Nigeria.

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DEDICATION

This Project is dedicated to Almighty God. Without Him, this project would not have been accomplished. Also, thanks to the Department of Chemical Engineering for providing us with the best opportunity to complete this research successfully.

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ABSTRACT

The components of bio-waste are particularly abundant in essential minerals like calcium and potassium, which are essential for the manufacture of effective biocatalysts for biodiesel. This study evaluated the potential of bio-based heterogeneous catalyst of fused cockle shells and watermelon peels for the transesterification of waste vegetable oil.

At 900°C and 500°C, the waste materials were dried, calcined, and carbonized, respectively. In order to evaluate the compositional, morphological, structural, and thermal features of both the catalyst and the precursor materials, they were both characterized. The Box-Behnken design was utilized to generate 29 experimental runs to examine the impact of operational parameters such catalyst loading, temperature, methanol-to-oil molar ratio, and reaction time. The presence of basic (calcium and potassium) and acidic oxides (silicon and nickel) demonstrated that the catalyst was bi-functional.

The catalyst's surface area (105.35 m^2/g) and pore volume (0.60 cm^3/g) obtained from the BET analysis contributed to a 91.77% biodiesel yield at 63.34 °C reaction temperature, 149.41 min reaction time, 1.05wt% catalyst loading, and a 14.45:1 methanol to oil ratio. The physicochemical parameters of the biodiesel produced were measured and determined to be acceptable according to the European National (EN) and American Society for Testing of Materials (ASTM) quality standards, demonstrating the product's suitability for use as fuel.

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND OF STUDY

Energy is a necessity for human survival on a fundamental level. Because of the ever-increasing global population, the transportation, industrial, and power generation sectors consume the majority of global energy (Avhad & Marchetti, 2015). Currently, traditional fossil fuels including diesel fuel, natural gas, gasoline and liquefied petroleum gas provide the majority of energy. These fossil fuels and oil reserves are being depleted at an alarming rate, and its utilization has been identified to be a significant contributor to the discharge of hazardous gases (Gaurav et al., 2017) . To fulfill present and future energy demands, curb imminent problems and ecological effects, researchers began to investigate alternative sources (Baskar & Aiswarya, 2016). For reducing the reliance on petroleum, biodiesel is a viable alternative among the various renewable energy sources. Rudolf Diesel, a German, created the diesel engine in 1890. Rudolf Diesel was the first to power a diesel engine with vegetable oil. The decline of vegetable fuels began following Diesel's death in 1913. Vegetable oils gained popularity after the 1970s oil crises, but their high viscosity meant that newer diesel engines couldn't run on them. In 1937, a Belgian; Charles Chavanne of the University of Brussels was granted patent on biodiesel when he proposed using acidic trans-esterified palm oil ethyl esters. However, it wasn't until 1988 that the word "biodiesel" was first used in a Chinese scientific study (André Cremonez et al., 2015; Ayadi et al., 2016). The use of biodiesel is a greener alternative to gasoline because it's nontoxic, biodegradable, carbon neutral, low-polluting, and environmentally beneficial (Nisar et al., 2017). Worldwide, biodiesel has remained a viable alternative to petroleum-based vehicle fuels and is currently considered a global fuel source (Baskar & Aiswarya, 2016). Biodiesel has recently gained prominence, as a renewable energy source, not just a fuel additive or extender (Boey et al., 2011). Biodiesel is an alternative fuel for internal combustion engines made up of monoalkyl esters and long-chain fatty acids derived from biomass. In biodiesel, the standard alkyl fatty acid chain extends from C_{14} - C_{22} esters of ethanol or methanol. Due to its chemical composition, biodiesel is an excellent substitute for regular diesel fuel (Nanda et al., 2018).

In comparison to petroleum-based fuel, biodiesel becomes more expensive. It turns out that about 70 - 75% of the cost of making biodiesel fuel comes from the feedstock used (Mohammadshirazi et al., 2014). This is because biodiesel is made from high-quality virgin oils like cottonseed, soybean (Istadi et al., 2015), olive, sunflower (Atabani et al., 2012b)and linseed. These oils cost a lot because they are expensive and high-quality. This has slowed the marketing of biodiesel. The utilization of low-grade feedstock like waste vegetable oil (WVO) and non-edible oils in biodiesel synthesis is becoming more prevalent as a result of increase in food costs and environmental concerns. These oils are renewable and widely available, making their usage as feedstock for biodiesel synthesis economically viable (Tshizanga et al., 2017). Biodiesel production has a significant financial impact, so the catalyst employed is an important consideration. In this regard, the use of inexpensive and highly efficient solid catalysts may be the best course of action to take (Mahmood Khan et al., 2020). In contrast to liquid catalysts, which must be separated, purified, and ecofriendly before they can be used, solid catalysts have recently gained a lot of study focus as they are resistant to corrosion, can be reused and can be saponified. Due to the benefits, they provide they have recently been the focus of a lot of study (Singh et al., 2020).

Using waste to provide feedstock and catalyst for the reaction is one way to reduce biodiesel production costs while also reducing pollution and improving global health. These materials also comprise components for heterogeneous catalyst synthesis. In order to produce biodiesel from heterogeneous catalysts, many researchers have used a variety of precursor materials. For example (Hadi et al., 2017), utilized waste cockle shell as a natural catalyst for biodiesel production. Using a catalyst concentration of 1.5 wt%, a yield of 93.20 percent was achieved (Etim et al., 2018) produced ash generating biodiesel from the peels of ripe plantain fruits as an environmentally friendly catalyst. They reported the biodiesel production utilizing plantain peels as a cheap feedstock.(Olatunji et al., 2021) and (Laskar et al., 2020)employed (unripe plantain peels and watermelon rind) and mango peels respectively as heterogeneous catalyst in their work.

Cockle shells are mostly found at sea shores and also obtained from the food industry. In most cases, these shells constitute waste which causes environmental problems (Nuamsrinuan et al., 2018). Cockle shell waste has been used as a calcium-based catalyst for the transesterification of rubber seeds oil with high levels of fatty acids (FFA) (Zamberi & Ani, 2016), as activated carbon for heterogeneous catalysts for making biodiesel, and as a source of calcium. Compared to inorganic catalysts, biomass waste-ash generated catalysts have several advantages: renewable resources, vast volumes, non-toxic products that may be reused, simple and safe manufacturing processes, and low water use. These wastes, includes animal bones, shells, and scales, fruit peels etc. are abundant and sustainable.

This research focuses on optimizing factors for biodiesel generation from waste vegetable oil utilizing a novel bi-functional heterogeneous catalyst.

1.2 STATEMENT OF PROBLEM

The over-dependence on petroleum fuel, as well as its rising demand, has put a strain on alternative energy sources. Due to the world's ever-increasing population, the world is on the verge of a worldwide energy crisis. This has led to limited resources and possibility of depletion. Inflation of petroleum products is also caused by a decrease in global fossil fuel supply. The growing populace is a case of concern especially in developing country as this leads to energy poverty.

A pressing concern in the modern world is the development of clean, renewable energy. This is associated with toxic side effects experienced by the environmental and health sector which arises from the consumption of fossil fuels. Fumes from burning fossil fuels generate a significant increase in greenhouse gas emissions leading to environmental contamination. Excessive emission of these injurious gases and air pollutants has posed serious problems.

Environmentally, the improper dispose of waste on land and water bodies is a threat to land use, aquatic species as well as human health. Concern has been growing over the deterioration of environmental and diminishing supply of petroleum conditions around the world. The issue of poor waste management has been a great issue of concern in developing countries. Used vegetable oil is routinely dumped into water bodies, as are waste shells formed from aquatic animals and agricultural produce dumped on lands, all of which fall under the category of improper waste management practices.

The use of homogeneous catalyst causes soap generation and waste water, affecting production yield and quality. Its transesterification approach is expensive due to the high cost of purification of methyl esters, corrosion, and energy consumption associated with the process. It would be quite intriguing to know how these factors account for biodiesel production and the extent of adverse effect proposed by homogenous catalyst.

1.3 AIM AND OBJECTIVES

The aim of this research is the optimization of biodiesel production from waste vegetable oil using a novel bi-functional catalyst prepared from the chemical modification of waste cockle shells and watermelon peels. The objectives for accomplishing this are as follows:

i. Catalyst preparation from cockle shell and water melon peels
ii. Synthesis and Characterization of the heterogeneous catalyst.
iii. Production of biodiesel from waste vegetable oil.
iv. Characterization of biodiesel production using standard procedure.
v. To ascertain the biodiesel production yield by measuring the catalytic activity of shell and watermelon peel catalyst generated.
vi. Optimization of process conditions using Response Surface Methodology (RSM).

1.4 SCOPE OF STUDY

This study is performed on a laboratory scale and chosen base stock for production of biodiesel in this work is from waste cooking vegetable oil. The waste oil was obtained from the University of Benin Canteen, pretreated and purified to obtain its physico-chemical properties using standard analytical procedures. Preparation of the bi-functional heterogeneous catalyst via simultaneous transesterification and esterification, characterization of the bi-functional catalyst produced from cockle shell and watermelon peels supported on nickel nitrate and by employing the box – behnken design of response surface methodology for the optimization of biodiesel yield. Properties of biodiesel to be produced at optimum conditions will be analyzed and compared to some standards for biodiesel properties.

1.5 RELEVANCE OF STUDY

Implementing biodiesel as a fuel source would assist in reducing the high vulnerability associated with reliance on fossil-derived fuels and maintaining the petroleum supply. This contributes to a reduction in greenhouse gas emissions, which lead to climate change by increasing renewable energy and non-toxic fuel production; thereby aiding reduction in demand of the damaging fossil fuel and lessen the impact on the global climate. Additionally, this contributes to the reduction of diesel's growing price by offering an opportunity for developing countries' domestic oil markets to strengthen.

Using a variety of waste feedstock to produce biodiesel could help minimize pollution and mobile carcinogens level. Such a sustainable strategy can enhance energy efficiency while simultaneously balancing economic and social development through environmental conservation.

The synthesis of biodiesel using heterogeneous catalysts from waste materials is an effective and environmentally beneficial option for petroleum-based diesel due to high activity, higher reusability and selectivity. For the purpose of a sustainable biodiesel production to achieve the goal of developing catalyst that is low in cost, simple to prepare, and environmentally friendly, more search has been oriented in the production of bi-functional heterogeneous catalyst.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

The search for bio-based petroleum derivatives has encouraged shortage of fossil fuels, high energy demand and environmental problems. The best substitute for these bio-based petroleum derivatives are fatty alkyl esters, also known as Biodiesel. Due to similarities such as; fuel properties and its physicochemical nature to petroleum-based oil, with few or no modifications it can be applied to compression ignition diesel engines. Apart from its eco-friendliness, qualities such as its renewable nature and a view towards reducing depleted productions has aided biodiesel to be considered as an alternative (Demirbas, 2009). This fatty alkyl ester of a long chain fatty acid 'biodiesel' is produced through transesterification of fats and oil derived from animals and plants in the presence of alcohol such as ethanol and methanol. Oil and fats cannot be utilized directly in engines and as such must be transformed into forms that solves the problems of poor atomization, limited volatility and high viscosity to advert the effect of carbon deposits. Exhaust gas developed by biodiesel combustion contains trace amounts of CO, no So_x, particulate matter and unburnt hydrocarbon when compared to conventional diesel fuel combustion products, these alongside its biodegradability and non-toxicity (Dunn & Knothe, 2001; Karmee & Chadha, 2005; Ma & Hanna, 1999; Ramadhas et al., 2005). Due to its many advantages, there is a growing demand for biodiesel and its synthesis process is needed to be speed up in order to meet this growing demand.

2.2 RENEWABLE ENERGY

2.2.1 Biofuels

Since prehistoric times, humans have used bioenergy and biofuels for domestic reasons. Biofuels are plant biomass and the refined products that are used to generate energy (light and heat). Since the early days of automotive industry, biodiesel have been utilized. For example, when pulverized coal was proven to be inadequate, Rudolph Diesel tested his first engine on peanut oil (Jeswani et al., 2020). Wood and other plant materials were burned to provide heat and light, which was used to cook meals, warm dwellings, cure clay objects and illuminate the night .Biofuels, such as fossil fuels, come in liquid, solid, and gaseous forms (Guo et al., 2015).

Based on the variety of fundamental criteria biofuels can be classified, such as, feedstock type, fuel technical specifications, conversion process, and application. Because of the numerous distinctions that can be made, several definitions for biofuel kinds are in use (Jeswani et al., 2020).The benefits of biofuels over petroleum fuels are; they are sustainable due to their biodegradable nature, they can be easily harvested from biomass, and more environmental friendly and their combustion is based on carbon dioxide (Gaurav et al., 2017)

According to the EASAC report 2012, “Biofuels are usually classified as the first, second and third generation of biofuel that primarily based on the origin of biofuels, whereas the fourth-generation biofuels drawn from man-made biological tools and is at infancy level of fundamental research”

First Generation biofuel

The majority of biofuels utilized are first generation biofuels. They are termed as the original biofuels. The majority of first-generation biofuels come from crop plants in the form of energy-containing compounds such as sugars, oils, and cellulose. The main advantages of first-generation feedstock include crop availability and a relatively simple conversion technique. The biggest disadvantage of using these feedstock's is its food-versus-fuel controversies i.e. risk of limitation in food supply chain (Nanda et al., 2018). First-generation biomass feedstocks can be converted to bioethanol or biodiesel via fermentation or trans-esterification, respectively. The most prevalent application is as a first-generation biofuel (Ben-Iwo et al., 2016)

Second Generation biofuel

Non-edible plant wastes such as wood, straw, grasses, and other non-edible plant residues make up the second-generation biomass. Unlike first-generation biomass (starch-based feedstocks), which may be used directly in bio-refineries to produce fuel, a series of pretreatment steps is required in the second generation to extract the fermentable sugars(Nanda et al., 2018). As a result, using second-generation biomass for biofuel production necessitates additional processing processes and operational costs.

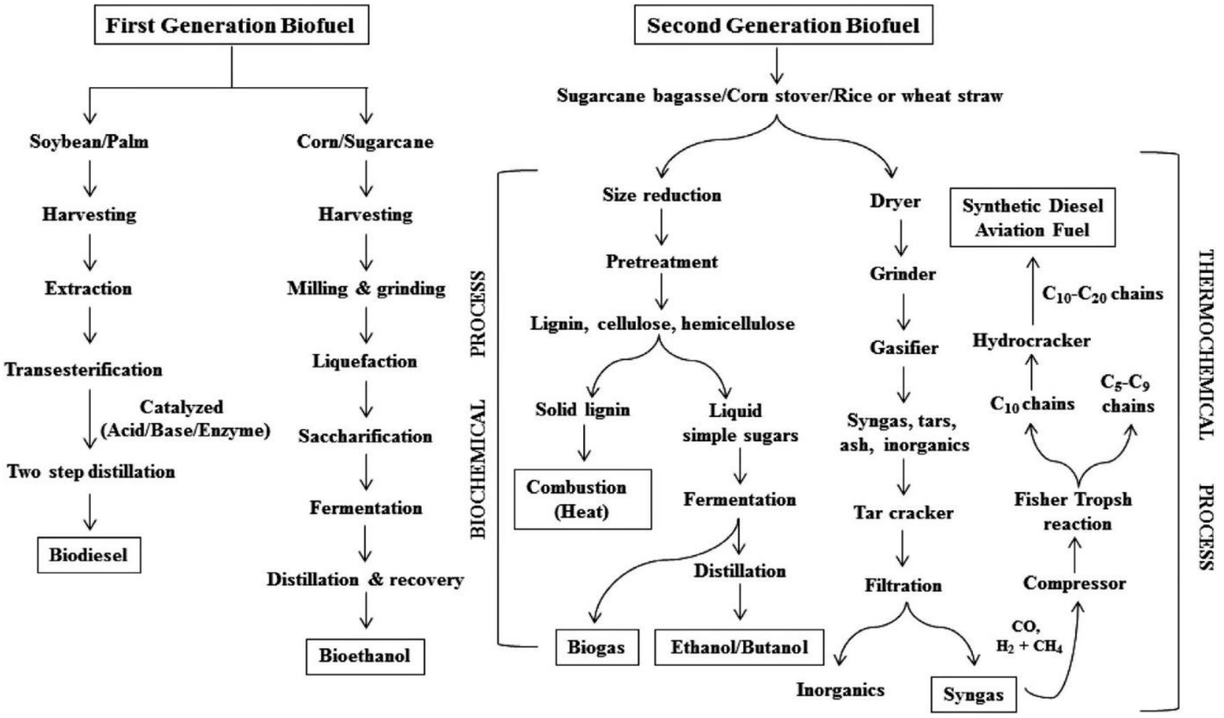


Figure 2. 1: Techniques used in the production process of first and second generation biofuels (Dutta, Daverey and Lin, 2014)

Third Generation Biofuel

Algae (microalgae and microalgae) biomass production is the basis for third-generation biofuels. High yield of algae can be generated using bioreactors. Hyacinth, caltrop diatoms, seaweed, duckweed, salvinia and kelp are examples of marine biomasses that could be used to make biofuels, particularly biodiesel.

Unlike first generation biofuel with food-versus-fuel controversies, the third generation biofuel escapes food competition and land use problems via the cultivation of microalgae on non-arable land, in saline, waste water or brackish water, and they develop exceedingly quickly. However, biofuel production through this means requires a lot of energy and is currently unprofitable (Jeswani et al., 2020).

Fourth Generation Biofuel

Biofuels generated through genetic engineering of plant/biomass such as algae is discussed under the fourth-generation biofuel term. It utilizes the microorganisms' capacity to convert CO_2 into fuel by photosynthesis (Alalwan et al., 2019). Genetic modification can be employed in lipid production and CO_2 capture as well as the development of sustainable, fast-growing biomass feedstock that require fewer fertilizers and pesticides (Ben-Iwo et al., 2016). Aside genetic modification, several fourth-generation innovations involve pathways, solar-to-fuel, upgrading, pyrolysis (temperature range of 400-600ºC), gasification, whose goal is to boost HC yield while also creating an artificial carbon sink to eliminate or diminish carbon emissions.

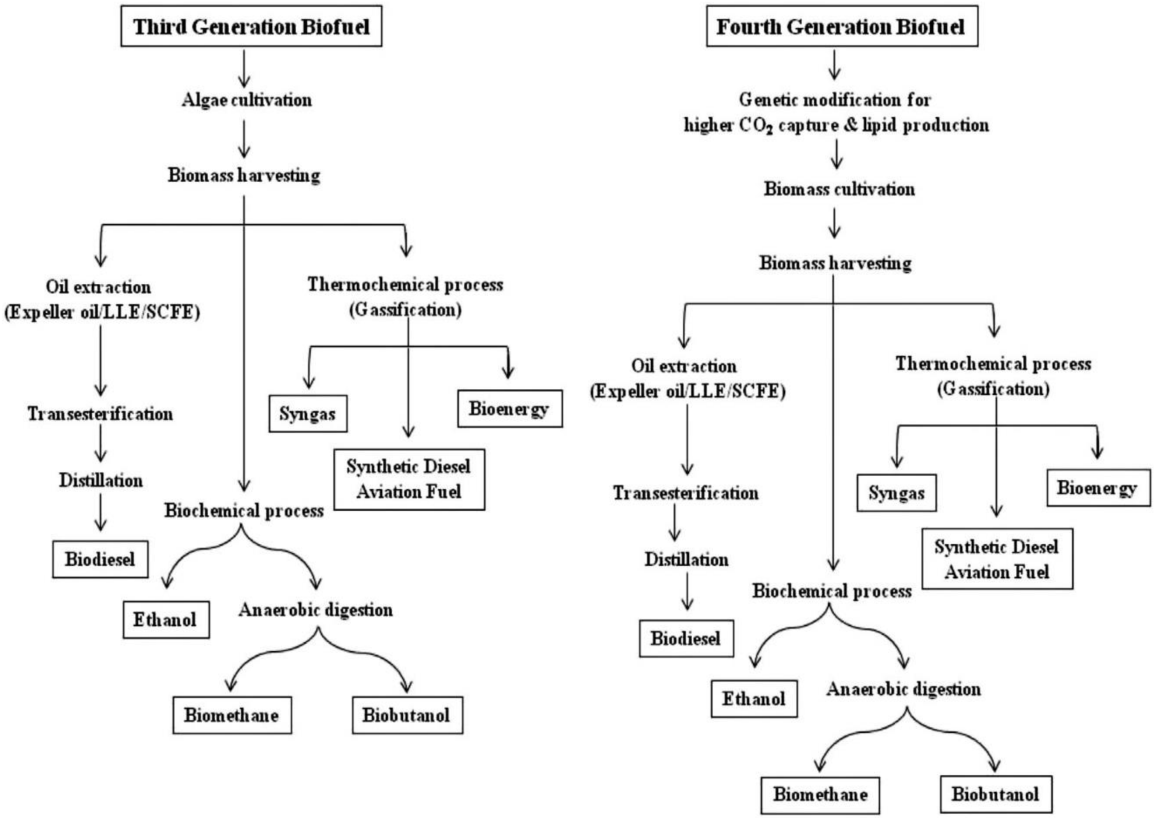


Figure 2. 2: Techniques used in the production process of third and fourth generation biofuels (Dutta, Daverey and Lin, 2014)

2.3 BIODIESEL

Biodiesel is a renewable fuel derived from the transesterification process that has superior qualities over petro-diesel, such as viscosity and lower density (Aghbashlo et al., 2021). It is used as an alternative fuel for a variety of reasons, including a focus on reducing greenhouse gas (GHG) emissions, procuring a more viable alternate fuel source to fulfill current energy demand, having a lesser impact on global climate and to ensure the utilization of renewable energy. Biodiesel has a number of advantages over diesel fuel, including renewability, high flash point, environmental friendliness, nontoxicity and biodegradability (Singh et al., 2020).

The production of biodiesel can be obtained from a variety of feedstock such as animal fats, algal oils, microbial, vegetable oil (i.e. those obtained from plants) such as cotton seed oil, neem oil, etc., waste oil (Kaur & Ali, 2011). Considering a major obstacle "high cost" for biodiesel production commercialization, with a potential to significantly reduce its production cost, waste cooking oil (WCO) is identified as a promising feedstock (Math et al., 2010) .

The composition of the parent feedstock determines the biodiesel's composition. Biodiesel can be utilized in the transportation industry as it possesses properties similar to petroleum diesel as well as lower emissions hence, is used as an alternative to diesel fuel. With rate expansion in usage biodiesel could reduce the movable carcinogens and pollutants.

2.3.1 Properties and Qualities of Biodiesel

Improvements on biodiesel quality are being made to determine finished product quality, feedstock criteria for consumer confidence, biodiesel storage and commercialization.

Therefore, Standardization of biodiesel quality is required in the production of biodiesel at various scale plants with various origins, qualities, and properties in order to ensure excellent engine performance. Biodiesel properties and qualities must meet international biodiesel standard specifications (Mishra & Goswami, 2018). The usage of pure fuel (B100) or blends with petroleum diesel in various concentrations are some of the uses of biodiesel. ASTM D-6751 AND EN 14214 (Europe) are the most globally renowned standards for B100 (USA), and are nearly similar with differences in parameters.

Characterization to ascertain the properties or quality of biodiesel are carried out through it's physical and chemical properties. They include; flash point (C), caloric value (MJ/kg),CN, viscosity (mm2/s),cloud and pour points (C), density (kg/m3), acid value (mg KOH/g-oil),distillation range, ash content (percent), carbon residue, phosphorus (mg/kg), Sulphur content, oxidation stability and glycerin presence (percent m/m) are some of these. The type of raw material (also known as feedstock) and the fatty acid composition determines the chemical and physical properties of biodiesel (Atabani et al., 2012).

Some of the listed properties are further explained as follows;

1. **Kinematic viscosity**

   The viscosity of the fuel is an important parameter in determining its flow capability. In the atomization and penetration of fuel spray, viscosity plays a crucial role (Singh et al., 2019).This also has an impact on fuel injection equipment operation, operating at low temperatures when an increase in viscosity leads to a decrease in the fuel's fluidity.

In comparison to fossil fuel, biodiesel has higher chemical structure and molecular mass therefore having a higher viscosity. According to some studies, high viscosity causes less precise fuel injector operation and poorer atomization of the fuel spray. The easier it is to pump and atomize biodiesel with a lower viscosity and achieve finer droplets, the lower the viscosity of the biodiesel. The kinematic viscosity of biodiesel fuel ranges from 3.5mm^2/s to 5mm^2/s, according to EN standards, 1.9mm^2/s to 6mm^2/s, according to ASTM standards and 2.5mm^2/s to 6mm^2/s according to Indian standards(Armendáriz et al., 2015; Nurdin et al., 2015; Sánchez et al., 2015)

2. Acid number

The presence of free fatty acids in a fuel sample is determined by acid number (AN).AN is measured in mg KOH/g. Thus an increase in free fatty acid content causes a corresponding increase acid value, causing corrosion in the engine's fuel delivery channel (Atabani et al., 2012). According to international standards, permissible value of AN is 0.5mg KOH/g. The standards used to determine the acid number (AN) for biodiesel fuel are EN 104, 14, ASTM D664 and P1.

3. Boiling point

An equality of surrounding pressure and vapor pressure signifies boiling point of a simple element. The bond that exists between the elements' molecules is determined by boiling point. With the aid of ASTM-D7398 standard (100- 615°C) the range of boiling point is determined using gas chromatography (Singh et al., 2019).

4. Density

The test techniques ASTM D1298, ISO 3675/P32 and EN ISO 3675/12185 provide a wide range of options for measuring biodiesel density. Density should be measured at 15 or 20 degrees Celsius in accordance with this standard (Atabani et al., 2012). To determine the amount of fuel an injection system delivers, an improved fuel characteristics known as density is utilized (Sakthivel et al., 2018). The density of biodiesel fuel is influenced by a variety of factors, which includes feedstock type, biodiesel production process and methyl ester profile.

5. Flashpoint (FP)

The temperature at which fuel ignites due to exposure of fuel to a spark or flame is known as its flash point. Biodiesel fuels outperform petro diesel in terms of travel and storage safety. The flash point (FP) of biodiesel is higher than 150°C, whereas standard diesel has an FP of approximately 55–65°C. The standards used to specify the flashpoint of biodiesel are ASTM D93, P2 and EN ISO 3679. Flash point varies inversely with the fuel's volatility.

6. Cetane number (CN)

The ignition properties or ability of fuel to self-ignite soon after injection indicates its cetane number. It has a significant effect on ignition delay phase of fuel. The ignition delay is referred to as the difference in time between discharge of fuel into the cylinder or combustion chamber and the start of ignition. After the delivery of fuel into the combustion chamber, it has the capacity to self-ignite. This indicates a high cetane number (CN) value, which is always associated with better fuel quality. The CN of biodiesel according to ASTM D613 is 47, 51 for ISO 5156 and EN ISO 5165 respectively (Atabani et al., 2013).

7. Cloud point

Cloud Point is the most commonly used criterion for determining low-temperature fuel controls. After the cooling of fuel, the cloud point is the temperature at which wax crystals first appear. Biodiesel is produced from variety of feedstock and depending on the fatty acid content of these feedstock, cloud point varies (Singh et al., 2020)

An important feature of biodiesel is its low temperature. Biodiesel's low-temperature is important because the partial or complete solidification of the fuel can lead to blockage of filters and fuel lines which tend to result to difficulty starting and driving, engine damage due to insufficient lubrication and fuel starvation (Atabani et al., 2012).

8. Oxidation stability

Oxidation stability is used to ascertain the level of biodiesel oxidation and reaction with air (Bhuiya et al., 2016). Unsaturated fatty acid chains and a double bond present in the parent molecule causes oxidation, occurring due to a reaction of oxygen with air when exposed(Atabani et al., 2012). The potential reactivity with air, need for antioxidants and the degree of oxidation, can all be determined by oxidation stability. Biodiesel fuels are more susceptible to oxidative degradation due to their chemical composition than fossil diesel fuels. Calculation of oxidation stability of fuel is obtained by the biodiesel storage conditions, storage period and FAME compositional characteristics.

9. Pour point

The characteristic feature of a liquid fuel by which it loses its flow behaviour at minimum temperature is known as pour point (PP). For cold flow process, pour point is an important parameter because the fuel is only suitable for operation above the pour point value (Sakthivel et al., 2018). The pour point of biodiesel fuel is typically lower than those of biodiesel fuels. ASTM D97 methodology is used to determine the value of PP for biodiesel fuel.

10. Cold filter plugging point (CFPP)

Plugging in the test filter occurs due to fuel components that have begun to coagulate or crystallize, the temperature at which this occurs is known as cold filter plugging point (CFPP). CFPP is an important criterion for assessing a fuel's cold flow operability and it reflects how well it performs in cold weather. ASTM D6371 is used to measure CFPP. For biodiesel and diesel, the CFPP has a better correlation and defines the fuel's filterability limit than the cloud point.

Table 2. 1: Properties of biodiesel from all vegetable oil (UNE-EN 14214)

Property	Units	Test	Limit
Ester Content	% (w/w)	EN 14103	98.5 min
Flash point (closed cup)	℃	D 93	93.0 min
Water and sediment	ppm	D 2709	500 max
Density, 15℃	kg/m^3	ASTM D6751	860 - 900
Kinematic viscosity, 40℃	mm^2/s	D 445	1.9 - 6.0
Sulfur Content	ppm	EN 20846	10 max
Cetane Number	–	D 613	47
Acid Number	mg KOH/g	D 664	0.05 max
Oxidation Stability	hours	EN 14112	3 min
Boiling Point	℃	ASTM PS121	182 - 338
Flashpoint	℃	ASTM PS121	100 - 170
Pour point	℃	ASTM PS121	-15 to 10

2.3.2. Advantages and Disadvantages of Biodiesel

Advantages

1. Easy to use: Does not require any fueling equipment or vehicle adjustments

2. Biodiesel is a fuel with excellent combustion characteristics due to its oxygen content (10 - 11) percent (Mishra & Goswami, 2018).
3. Biodiesel is an ideal fuel for heavily polluted cities and urban areas because of its property characteristics such as non-toxicity, renewability, reduction in tailpipe emissions, sustainable, availability and high combustion efficiency (Hassan & Kalam, 2013)
4. Due to its higher octane number, it has shown better performance in vehicles when compared to gasoline (Alalwan et al., 2019)
5. In terms of flash point, biodegradability, aromatic and sulfur content, biodiesel outperforms diesel fuel (Alalwan et al., 2019) .
6. Production of biodiesel is carried out locally with easily sourced feedstock making it more cost efficient than diesel.
7. Biodiesel is a useful fuel because of its proven power generation, cost efficiency and performance.
8. Biodiesel has a higher Cetane Number (60–65 depending on the vegetable oil) than petroleum diesel, which reduces ignition delay and prolongs engine life,

Disadvantages

1. Increase in fuel consumption (2 – 10) percent as a result of lower energy content.
2. Clogging can occur as result of accumulation of biodiesel dirt in fuel filters (Mahmudul et al., 2017).
3. Comparatively, biodiesel requires more injector pressure due to its low volatility and higher viscosity (11–18 times that of petroleum diesel) (Atabani et al., 2012; Mishra & Goswami, 2018).

4. It produces higher NO_x levels ranging from 10- 14 percent than diesel during combustion as a result of its high oxygen content.
5. Cost of fuel increases drastically if the transesterification process is not economical as a result necessitate costly acid catalysts or fatty acid separation of these oils.
6. Large scale production of biodiesel are made from edible oils used as automotive fuels. This has a capacity to generate global food demand and supply imbalance (Mishra & Goswami, 2018).
7. In comparison to diesel, biodiesel has higher nitrogen emission, pour point and cloud point.

2.4. METHODS OF BIODIESEL PRODUCTION

Biodiesel production has been documented across generations. This comprises of first generation biofuels that are produced from edible oils, second generation from non-edible oil and third generation (algae) which macro and micro species (Baskar & Aiswarya, 2016). Oils from plant feedstock, animal fats, waste oils and microalgae, animal fats, and waste oils are utilized in the manufacturing of biodiesel. Biodiesel output from oil crops is mostly determined by the crop species. Oils from plant feedstock, animal fats, waste oils and microalgae, animal fats, and waste oils are utilized in the manufacturing of biodiesel. Biodiesel output from oil crops is mostly determined by the crop species.

There are two primary processes in the manufacture of biodiesel. The first step involves extraction of oil from algae biomass or seed, proceeded by conversion to biodiesel utilizing many key processes such as pyrolysis, dilution, transesterification and micro-emulsification (Singh et al., 2020a).

2.4.1. Oil Refining

During the process of oil refining, components such as phosphatides, colorants, free fatty acids and tocopherols are removed as they have an impact on subsequent processing procedures as well as the oil's storage life. The refining process is influenced by the type of feedstock resources available and physicochemical qualities of oil. The first stage of refining is degumming, during which phosphatides are eliminated. Phosphatides must be removed since they encourage accumulation of water and makes oil muddy. Phosphatides removal can be carried out in two ways: acid and water degumming (Singh et al., 2020).

The next step in the refining process is de-acidification. For first-generation edible oils this process is essential because it prevents the formation of rancid flavors from free fatty acids (FFA).. Phenol, oxidized fatty substances, heavy metals and phosphatides are also removed using this method. Because these components have a direct impact on the transesterification process and storage life, they must be eliminated not only for edible oil but also for fuel development. De-acidification methods include de-acidification and removal of pigments and odors using a variety of solvents such as propane, ethanol, and furfural, distillation and alkali neutralization.

Bleaching is the next refining step, it is a process by which colorants are removed. This process extends the storage time. Adsorbents such as silica gel, activated carbon, and bleaching earth are employed in bleaching process (Singh et al., 2020).

In carrying out oil refining, odiferous components such as aldehydes and ketones are removed. This process is known as deodorization.

Final stage of refinement is, dehydration during which the water content is removed. Water content removal is done at low pressure using distillation process.

2.4.2. Refined Oil to Fuel Techniques

The production of biodiesel involves the usage of various feedstock as well as various technologies (Ambat et al., 2018).Several methods for this production are being researched. Pyrolysis or thermal cracking, dilution, catalytic distillation, reactive distillation technologies, micro emulsion, supercritical fluid procedures, and transesterification are some of the processes used.

There are four strategies that are most advantageous for producing biodiesel from various generation oil feedstock among these techniques.

2.4.2.1. Pyrolysis

Pyrolysis, also known as thermal cracking, is the process of applying heat to convert organic materials to fuel in the absence of oxygen. Fuels produced this way have reduced viscosity, a tolerable quantity of sulfur and a reduced ignition delay (as evidenced by a higher cetane number) (Ambat et al., 2018). Changes in the chemical structure of the compound occur during pyrolysis, such as breaking down of chemical bonds to tiny molecules (Rezania et al., 2019).This process produces biodiesel with sufficient amounts of water and sulfur, but insufficient amounts of residual carbon and ash. Main disadvantage of this process is high cost of maintenance.

2.4.2.2. Dilution

Blending or dilution is the simplest and oldest process. It is a process which involves a decrease in the amount of solute in a solution by increasing the amount of solvent or oil dilution, solvents such as diesel fuel and diesel fuel can be utilized. Viscosity and oil density reduction are the aftermath of this technique. Although the dilution process is simple, it does have certain drawbacks, such as incomplete combustion, carbon buildup in engine cylinders. A 10% vegetable oil/conventional fuel mixture was able to achieve a higher efficiency in a pre-combustion chamber engine (Ambat et al., 2018).

2.4.2.3. Micro-emulsion

Micro-emulsions are colloidal dispersions of isotropic fluid made from a single or multiple amphiphiles and two non-miscible liquids. As demonstrated using ethanol in soybean oil, this technique uses both ionic non-ionic aqueous solutions to achieve maximal viscosity (Ambat et al., 2018). Micro-emulsion is based on the generation of micro-emulsions with colloidal microstructures utilizing various alcoholic solvents such as ethanol, hexanol, methanol, butanol and 1-butanol to achieve the needed viscosity for commercially produced diesel (Mishra & Goswami, 2018).

2.4.2.4. Transesterification

Transesterification is a process which produces biodiesel (mono alkali ester) and glycerol by reacting triglycerides in the vegetable with alcohol (Kumar, 2020). Similar qualities are seen in the biodiesel produced using this process to diesel fuel, this process is economical for commercial production (Singh et al., 2020). Figure 2.3 depicts the biodiesel synthesis transesterification reaction. Triglycerides are esters of three free fatty acids and glycerol found in animal and vegetable oil.

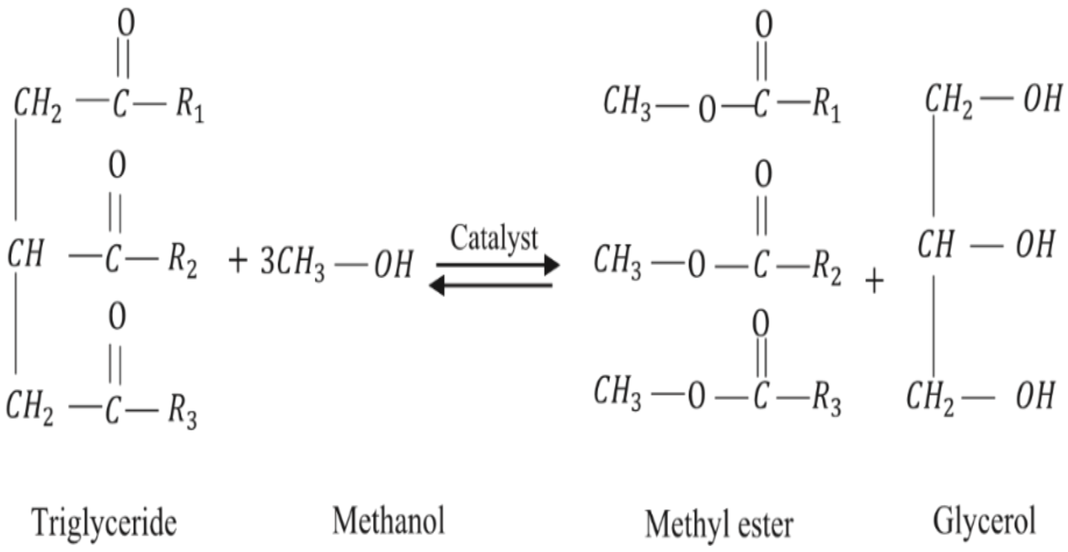


Figure 2. 3: Transesterification process for biodiesel production (Rezania et al., 2019)

2.5. TRANSESTERIFICATION

For the generation of biodiesel, transesterification is a common and widely utilized technique. With the aid of a catalyst, this process entails the conversion of fats and oils with alcohol (often ethanol or methanol) (Ambat et al., 2018). Due to the reaction of free fatty acid with alcohol, transesterification is also known as alcoholysis (Singh et al., 2020). Numerous forms of catalyst such as heterogeneous, homogeneous, and enzyme catalysts, can be utilized. In conjunction with ultrasound-assisted membrane technology, transesterification process can be used. Separation of end products obtained from transesterification process is carried out: biodiesel rises to the top, whereas glycerol sinks dues to its heavy weight. To avoid a reverse process, the separation procedure should be completed quickly (Mahmudul et al., 2017).

Methanol and ethanol are commonly employed in the transesterification process. Methanolysis occurs when methanol is used to react with free fatty acids during the transesterification process. Application of heat is carried out on a combination of oil (80–90%) and methanol (10–20%), and also a very little amount of catalyst, during the methanolysis process. Due to less solubility of methanol in oil, adequate mixing is required. After the process, the biodiesel produced is fatty acid methyl ester (FAME) (Verma & Sharma, 2016). Properties such as high reactivity, affordability makes methanol more favourable for transesterification process than other alcohols. Reaction of free fatty acid with ethanol produces a transesterification process known as ethanolysis. Ethanol is less harmful, improves the cetane number and heat content of the fuel when compared to other alcohols. Disadvantages of ethanolysis include difficulty in separating the ester from the glycerol and higher energy requirements for the reaction (Hajjari et al., 2017).

The fatty acid ethyl ester biodiesel produced by the ethanolysis process is called biodiesel (FAEE).

The following are some of the process parameters that influence biodiesel yield:

i. FFA content
ii. Catalyst type and its concentration
iii. Reaction time
iv. Molar ratio of alcohol to oil
v. Reaction temperature

2.6. CATALYST

For chemical reactions, catalysts are the industry's workhorses. Catalytic processes produce around 85–90% of the chemical industry's output. A catalyst is a substance which speeds up the rate at which a chemical reaction approaches equilibrium while being unaffected by the reaction. This activity is accomplished by the creation of bonds with reactive molecules which reacts to produce a product, this thereby leaves it unmodified for the next reaction by dissociating from the catalyst. In reality, the catalytic reaction can be described as a cyclic event in which the catalyst takes part and then returns to its original state at the end of the cycle (Kakaei et al., 2019). By creating a less difficult path for molecules, the catalyst increases the kinetics of the reaction toward thermodynamic completion.

2.6.1. Properties of a catalyst

1. Catalyst has no effect on the equilibrium constant and equilibrium state composition, because it affects the forward and reverse rate of the reaction equally.
2. Catalysts accelerates reaction without being consumed by it or appearing in the net reaction equation.
3. It takes place through a reaction mechanism that involves small activation energy. Thus, brings about an interaction between the reacting components and the catalyst.
4. The equilibrium constant, and consequently the equilibrium composition, are unaffected by catalysts.
5. Alternative reaction routes are provided by catalysts.

2.6.2. Catalysis in Biodiesel Production

Catalyst of various categories are employed in transesterification reaction for the production of biodiesel. They include heterogeneous, homogeneous or enzyme catalyst (Ambat et al., 2018). A catalyst accelerates the rate of reaction. An increase in the rate of reaction, leads to a corresponding increase in product yield (Baskar & Aiswarya, 2016).The catalyst to be employed is dependent on the fatty acid content of the oil (Verma & Sharma, 2016).

Presence of large amount of free fatty acid content in the oil results in low biodiesel yield efficiency and soap development which is detrimental to biodiesel production.

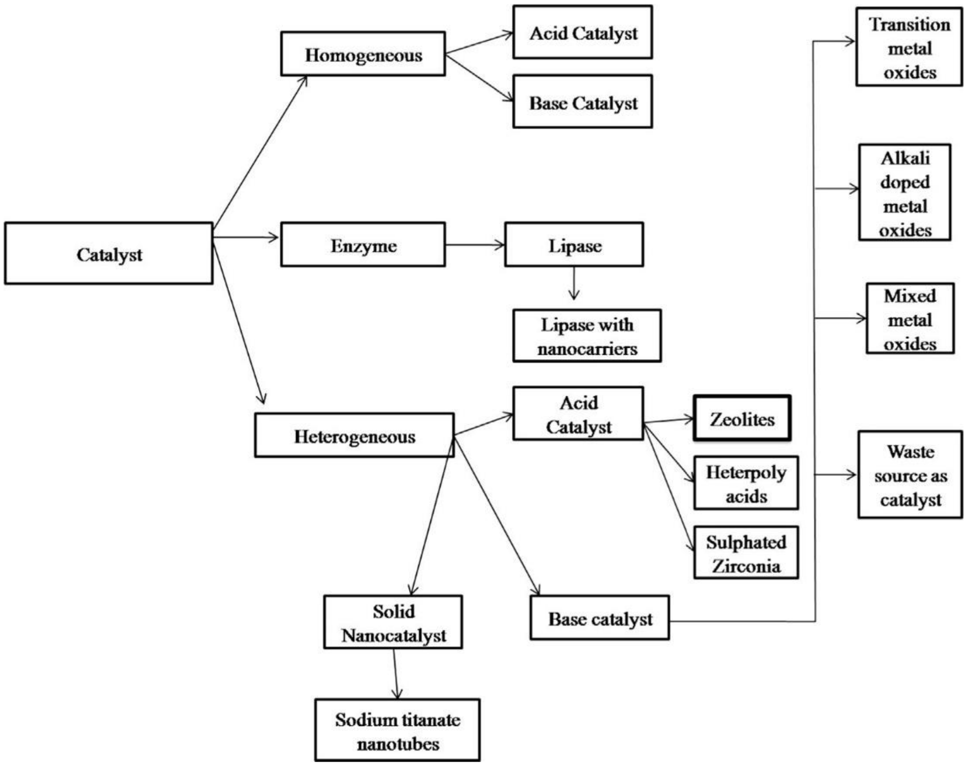


Figure 2. 4: Trends showing various catalyst in biodiesel production

2.6.2.1. Homogeneous base-catalyzed reaction

Homogeneous catalysts are the most frequently utilized catalysts for biodiesel synthesis because their lower reaction time and are easy to use. Its mechanism is based on the attack of a nucleophile on the carbonyl group.

It has been discovered that alkaline catalysts are 4000 times faster than acid catalyst (Baskar & Aiswarya, 2016).Potassium hydroxide, sodium hydroxide (NaOH), sodium methoxide (CH_3ONa), and are the most frequently used alkali catalysts. KOH takes a longer time to dissolve in methanol, therefore NaOH is often recommended. For the preparation of biodiesel commercially, alkaline based catalyst is more preferred. For a reaction at 65°C, with a methanol to oil ratio of 6:1, alkaline catalysts such as KOH and NaOH were used. 85.9 percent and 91.67 percent, respectively, were the biodiesel yields. In this type of catalyzed reactions, alcohol reacts with the base forming nucleophilic alkoxide. This is a critical step in the formation of alkyl esters because this attacks the triglyceride's electrophilic group and generates a tetrahedral intermediate. To facilitate transesterification, a base catalyst removes a proton from the alcohol, undergoes structural reorganization returns it back to the esters or generates a new ester altogether in the catalytic cycle (Ambat et al., 2018).Figure 2.4 shows a step-by-step analysis of the reaction.

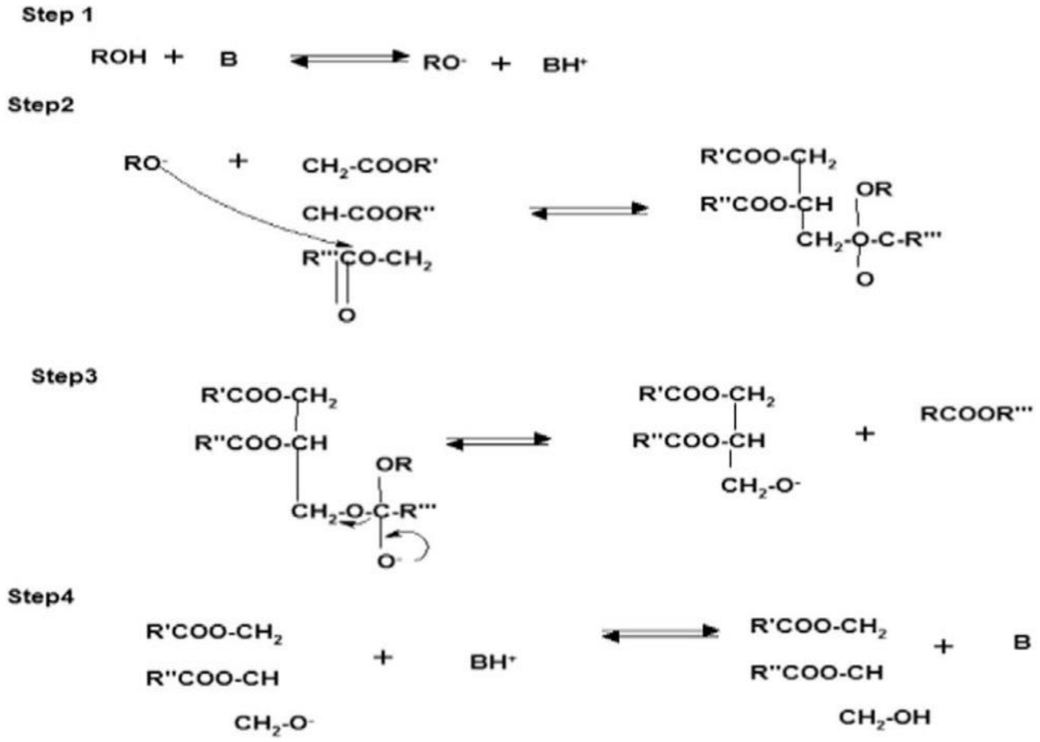


Figure 2. 5: Reaction kinetics of base-catalyzed homogenous reaction

2.6.2.2. Homogenous acid-catalyzed transesterification

Various acids are utilized as catalysts in transesterification, most commonly used include; organic, sulfonic acid, sulfuric acid, ferric sulphate and hydrochloric acid (Syakirah Talha & Sulaiman, 2016).Acid catalyzed processes are often carried out at low-to-moderate temperatures and pressures, high acid catalyst concentrations and high alcohol-to-oil molar ratios (Mishra & Goswami, 2018). High level of conversion efficiency is attained and to obtain a high yield, acid-catalyzed reaction require high alcohol-to-oil ratio (Callegari et al., 2020). A high biodiesel yield can be achieved by using bronsted acids such as sulfuric and sulfonic acids for transesterification. The methyl/ethyl ester is formed through displacement of alcohol and protonation of an ion. Reaction of fatty acid and a homogeneous base in biodiesel synthesis causes soap formation which is undesirable since it complicates separation and purification, and also reduce the ultimate ester yield. As a result, acid catalyzed simultaneous esterification and transesterification of feedstocks that contain an even higher percentage of free fatty acid or acid-catalyzed free fatty acid esterification could be considered (Avhad & Marchetti, 2015). Disadvantages with the acid catalysis include; water formation (caused by the presence of a polar carboxylic group in the feedstock), corrosion, low product yield. Figure 2.7 depicts the mechanism of the acid-catalyzed process.

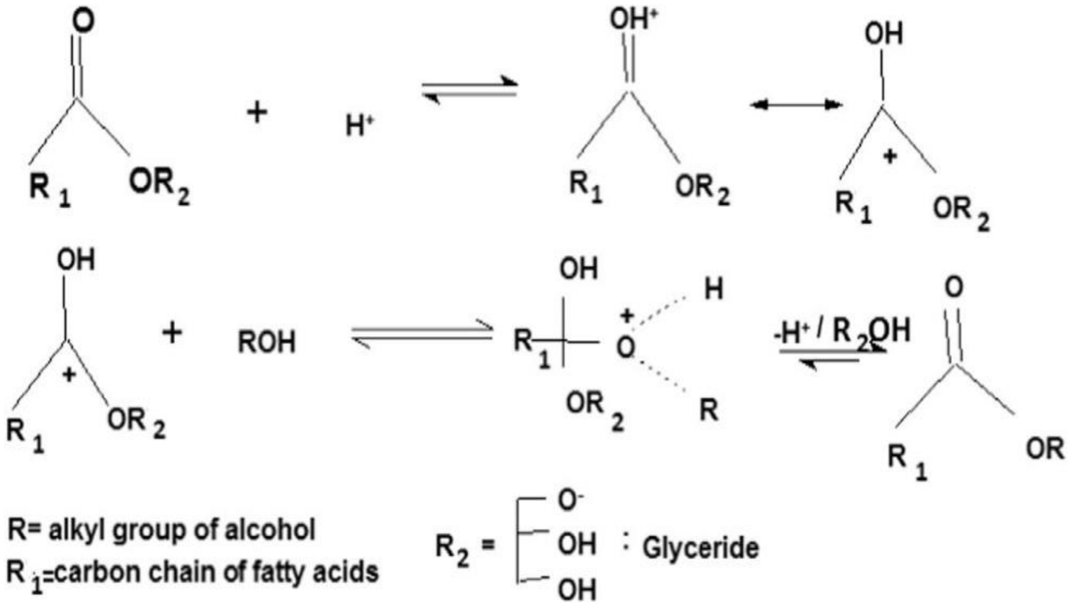


Figure 2. 6: Homogenous acid-catalyzed reaction mechanisms

Three steps are required for the reversible reaction to take place; the formation of tetrahedral intermediates, breakdown of unstable tetrahedral intermediates via an ionic exchange reaction with alcohol into monogylceride and diglyceride ions, formation of glycerol and esters as byproducts of proton loss along with the recovery of the catalyst.

A major drawback in using homogeneous catalyst is; because they are used up in the reaction mixture, they are not capable of being regenerated; resulting in difficulty in the separation process, which typically results in equipment corrosion, environmental problems originated from generation of significant amounts of toxic waste water as a by-product and increased production cost (Etim et al., 2020).

2.6.2.3 Heterogeneous base-catalyzed transesterification

Heterogeneously catalyzed transesterification makes use of acid or base catalysts in the preparation of biodiesel. Advantages of heterogeneous catalyst over homogeneous include; recyclability, reusability and non-corrosive properties (Etim et al., 2020). In this form of reaction separation of products is easy because they are not dissolved or consumed in the reaction. Biodiesel production has been aided by the use of strontium oxide (SrO), calcium oxide (CaO), alkali and alkaline earth metal supported oxides, magnesium oxide (MgO), mixed metal oxides, anionic resins, hydrotalcites, among other catalysts (Avhad & Marchetti, 2015a).Because of its high basicity, long catalytic life, low solubility, increased activity and ease of handling, calcium oxide has been extensively studied as a heterogeneous catalyst. Calcium-based catalysts can be made at minimal cost using various natural and waste materials. CaO catalysts can then be employed in the manufacture of biodiesel from these calcium species once they have been thermally processed. Catalyzing the transesterification reaction between palm oil and methanol using waste capiz shells at 900°C for 120min yielded CaO catalyst. (Avhad & Marchetti, 2015b) reported the biodiesel yields of 92.83 percent were recorded after 360 minutes of methanolysis at 60ºC utilizing an 8:1 alcohol-to-oil molar ratio and 3 wt. percent catalyst.

A number of research have found that calcination temperature has a significant impact on heterogeneous catalysts' catalytic activity and reusability. Using a high-temperature calcination range of 700 °C–900 °C, (Kandaramath Hari & Yaakob, 2017) found out that zirconia's average crystallite size reduced as the calcination temperature increased, as well as the porosity of the catalyst.. The sodium zirconate solid catalyst was applied for biodiesel synthesis from jatropha oil. In addition, it can account for reusability of up to five cycles. Formation of three phases with oil and alcohol which limits mass transfer and reduces reaction rate is a major disadvantage of heterogeneous catalyst (Baskar & Aiswarya, 2016).Using solvents which improves oil-solvent miscibility such as tetrahydrofuran, n-hexane and ethanol aims to alleviate these limitations. Heterogeneous catalysts have a large surface area and pores, allowing for active interaction between the reactant and the oil.

2.6.2.4 Heterogeneous acid-catalyzed transesterification

Heterogeneous acid catalyst possess the ability to conduct both esterification and transesterification simultaneously. In addition, they enable a simplified catalyst separation procedure from product, the removal of the biodiesel washing phase, corrosion problems reduction and possibility of reuse regeneration of catalyst (Syakirah Talha & Sulaiman, 2016).

Sulphonated zirconia (SZ), tungsten oxides, sulphonated saccharides, organosulphoric functionalized mesoporous silica and Nafionl resins are examples of solid acid catalysts often employed in esterification and transesterification reaction works (Syakirah Talha & Sulaiman, 2016). Certain properties such as tolerance to free fatty acid and water concentration in feedstocks makes biodiesel production from heterogeneous acid catalyst more advantageous than base catalyst. To avoid diffusional difficulties, the ideal heterogeneous acid catalyst must have hydrophobicity, a moderate acid strength, porosity, large number of obtainable active sites.

2.6.2.5. Enzyme (Biocatalyst) catalyzed transesterifications

The advantages of using enzyme catalyst for biodiesel production cannot be over-emphasized. These include; mild reaction condition, catalyst regeneration, absence of by-products and insensitivity to high free fatty acid oil (Syakirah Talha & Sulaiman, 2016). In comparison to the chemical process, biodiesel production through enzyme catalysis has shown tremendous promise to be an environmentally friendly. As a result of problems associated with other catalysts, lipase has gained popularity such as glycerol separation during the process. Lipase is an excellent catalyst for transesterification because of its ease of isolation, reusability and requires mild conditions. Low-energy enzymatic transesterification can effectively utilize feedstocks with a high free fatty acid content. A major disadvantage of enzymes catalyst is their inability to complete a reaction under standard in spite of their high fatty acid level tolerance conditions (Baskar & Aiswarya, 2016). Babassu oil produced the highest biodiesel output of 96.0 percent as reported by (Simões et al., 2015). Immobilized lipase on SiO2 carried out the transesterification reaction. Novozym-435 is an example of immobilized (enzyme catalyst) ,commodified and widely used for biodiesel synthesis. This is because of its higher reaction rate and its accessibility all over the world.

This method of trans-esterifying waste cooking oil is successful due to the insensitivity of enzymatic reactions to free fatty acids and water concentration in the feedstock (Math et al., 2010).

2.6.2.6. Waste-derived heterogeneous catalysts

Biodiesel can be produced from a variety of low-grade feedstocks using cost efficient and environmentally friendly catalysts invented, converted, and used in recent years. Recent investigations have led to the discovery of agricultural wastes and residues as an excellent source of green solid catalyst and catalytic supports. Potash, a byproduct of the combustion of waste agricultural biomass has been found to have significant potential as a source of alkali that might be utilized as an alternative to NaOH and KOH. The high catalytic potential of these waste ashes has been connected to the existence of large metal oxide content, particularly potassium and other metals such as magnesium, calcium, and sodium, which are essential sources of alkali production. Many studies have investigated inorganically produced potash as a high-catalytic-activity active base, but production is both toxic and unrenewable. Agricultural waste materials and animal waste containing biogenic waste-derived catalysts are safe and reliable in contrast to inorganic or metal-derived heterogeneous catalysts. Washing, drying, burning, grinding, and calcination are all part of the overall preparation process (Etim et al., 2020). Examples of waste-derived agricultural waste include; cockle shell, egg shell, banana peel, watermelon pod, discarded fish bone, coconut husk ash etc. (Etim et al., 2018) in his study used ripe plantain peels as an agro-base catalyst; the peels were washed three times with distilled water, chopped into pieces, oven dried for 24 hours at 80 °C, and then burned to generate ash. The ash was ground and sieved before being calcined for 4 hours at 700 degrees Celsius. Different ranges of calcination temperature (200 °C–1000 °C) were studied using eggshell as heterogeneous catalyst for the production of biodiesel from soybeans by (Tshizanga et al., 2017) and from observation, samples with a calcination temperature below 600 °C contained water and organics; at 700°C/2h calcination temperature contained $CaCO_3$, but samples calcined for 2h from 800 °C to 1000 °C for 2 h the elimination of CO_2 results in the creation of CaO, which provides the greatest catalytic performance and yield possible.

This thesis is focused on generating CaO from waste cockle shell, watermelon pod as catalyst doped with nickel to produce biodiesel from waste vegetable oil.

2.6.2.7. Cockle shell and calcium oxide

In terms of commercialization, the catalytic potential of calcium oxide (CaO) is enormous. Catalytic transesterification processes have been reported to use laboratory-grade CaO, according to a number of studies. CaO research has recently been widened due to recent findings that waste material can be used as a source of CaO. Found to be a substantial source for CaO were cockle shells, because it includes at least 95% calcium carbonate, it is the ideal alternative ($CaCO_3$) (Hadi et al., 2017). The mineral is widely employed in a variety of applications because of its different polymorph qualities, notably used for biodiesel generation as a heterogeneous catalyst, as an active ingredient in agricultural lime, for heavy metal ion removal as a biosorption material and for bone healing as a biomaterial.

Biodiesel yields of over 97% were achieved in three hours using the optimal conditions of 4.9 weight percent catalyst (activated at 900oC for two hours) and a MeOH/oil mass ratio of 0.54:1. In the study by Boey et al waste cockle shells (Anadara granosa) was used as a heterogeneous catalyst (CaO) .This catalyst was found to be very active in catalyzing transesterification. According to optimal conditions (4.9 wt. percent catalyst and 0.54:1 Me OH/oil mass ratio), the catalyst could be reused at least three times (Sanjay, 2013).

(Zamberi & Ani, 2016) investigated the use of waste cockle shells for biodiesel generation from transesterification of rubber seed oil (FFA). The waste cockle was calcined 0for 4 hours at 900ºC to transform $CaCO_3$ to CaO species. It was found that a catalyst percentage of around 9 wt. %, a ratio of 16:1 methanol/oil and a reaction period of about 3 hours resulted in the best yield.

2.6.3. Bi-functional Catalysts

The use of a bi-functional heterogeneous catalyst in catalysis is a recent innovation. As a result, amphoteric catalysts, which possess acidic and basic sites and can act as either at the same time, can be produced. Physiochemical features are added to biomass-produced catalysts in this process. Esterification and transesterification process can be carried out simultaneously by a bi-functional heterogeneous catalyst in the same reaction. Bi-functional catalyst is a cost-effective method for reducing the number of reaction steps and circumstances commonly found in two-step processes with high FFA triglycerides. These methods can be used to transform non-edible virgin oils, such as those of low grade, directly (Etim et al., 2020).

2.6.3.1. Methods of preparing bi-functional catalyst

Wet Impregnation Method

In this modification, the goal is to boost the catalytic activity of agricultural waste-derived solid catalysts generated from agricultural waste-derived solid catalysts in order to increase yield while also improving the quality and purity of the finished product (Omojola Awogbemi , Daramy Vandi Von Kallon, 2021). For efficient oil-to-biodiesel conversion from modified biomass catalyst, wet impregnation method is the simplest approach (Etim et al., 2020). This method is carried out by combining the catalyst and supporting chemicals using a stirrer to generate a slurry. A dry cake is formed through oven drying of the slurry at a desired amount of time and an appropriate temperature. After that, the dried cake is crushed, sieved, and calcined at a high temperature (Omojola Awogbemi, Daramy Vandi Von Kallon, 2021).

In order to increase the catalytic activity, chemical characteristics, biodiesel output, and reusability of waste-derived catalysts, wet impregnation was adopted by (Nisar et al., 2017). For the transesterification of Jatropha oil into FAME, waste animal bone was treated with KOH. Drying, crushing, and calcining the bone powder at 900°C produced a fine powder. At 200rpm, KOH solution was added to the calcined powder, and the mixture was agitated to generate a slurry.

Sol gel method

For ultra-homogeneous structures, the sol gel method is the most appropriate technology and has been widely employed for the manufacture of ceramics, glasses and composite catalyst. Due to its cheaper costs and easier control of working conditions, the sol-gel process has demonstrated promising results in terms of covering big and complex geometric structures with a uniform coating. Because of the nano-crystalline characteristics of the coating, this approach has the capability of altering the physiochemical properties of the products (Yaqoob et al., 2019).

Co-precipitation method

In the co-precipitation method of catalyst modification, catalyst precursors are dissolved in distilled water and mixed at high speeds (Omojola Awogbemi , Daramy Vandi Von Kallon, 2021). Precipitating agents, usually alkaline in nature, such as potassium hydroxide (KOH), potassium carbonate (K2CO3), sodium hydroxide (NaOH), and ammonium hydroxide (NH4OH) are added to this combination and allowed to precipitate with continual stirring for 3 hours while maintaining the pH of the solution at 10. Drying at 110 °C overnight, the dried sample would next be calcined at the proper temperature in the furnace (Mansir et al., 2018).

(Yusuff et al., 2019) employed this technique in their research to develop mixed oxides catalysts for the production of biodiesel using waste frying oil as feedstock. Nickel nitrate, cobalt nitrate, and anthill powder were mixed with fine powder made from waste chicken eggshell, then dissolved in deionized water at 80 °C for 5 h. In order to regulate the pH, Na_2CO_3 was dissolved into the resulting slurry and aged in a fume hood .Once the slurry had coagulated, it was then filtered. After dehydration at 110°C for 12 hours, the residue was calcined at 1000°C for 4 hours. High stability, a biodiesel production of 90.23 percent, and the capacity to be reused in four cycles were all identified in the created catalyst.

Physical mixing methods

Physical mixing is accomplished by combining and crushing pure metal oxides in an agate mortar. In a beaker, the oxides are normally combined with distilled water and swirled continuously for five hours. For this purpose, the slurry would be calcined to the desired temperature in a furnace (Mansir et al., 2018).

2.7 Response surface Methodology (RSM)

Response surface methodology, sometimes known as RSM, is a flexible mathematical tool employed for parametric modeling and design. (Danmaliki et al., 2017a). It's a method of empirical modeling in which one or more responses (dependent variables) are correlated to a set of independent variables (Samuel et al.,2020).

For data collection and identification of significant factors and relationships influencing process response, the RSM utilises the design of experiment (DoE) concept. The RSM is distinctive in that it allows for the interpretation of communication between experimental variables within the analyzed ranges. The model iterates until either an ideal process is found or the available experimental resource limit is reached. By optimizing the causality model as the objective function, RSM obtains optimal factor settings (Hadiyat et al., 2022).

Maximizing output of a target material by optimization of operational parameters is possible with the use of statistical methods like RSM. When several variables influence yield, output, or percent elimination of a certain process, this method proves invaluable. Among the many varieties of symmetrical experimental design are the three-level factorial design, the Box–Behnken design, central composite design (CCD) and the Doehlert design (Danmaliki et al., 2017).

In the RSM, it has been assumed that the unknown relationship between the response variables and the input variables would follow the polynomial model of the form;

$$Y = f(x)\,\beta + \varepsilon \qquad (2.1)$$

Where $x = (X_1, X_2, X_3 \ldots X_k)$, $f(x)$ is a vector function of p elements that consists of powers and cross products of powers of $= X_1, X_2, X_3 \ldots, X.\beta$ is a vector of p unknown constant coefficients called parameters while ε is a random experimental error. All the square terms, linear terms and linear by linear interaction in the quadratic second order response model can be used to approximatively characterize a process with X_i independent variables and the relationship between response Y and the variables as represented by;

$$Y = \beta_o + \sum_{i=1}^{k} \boldsymbol{\beta}_i \boldsymbol{X}_i + \sum_{i=1}^{k} \boldsymbol{\beta}_{ii} \boldsymbol{X}_{ii}^2 + \sum_{i<j} \sum \boldsymbol{\beta}_{ij}\ \boldsymbol{X}_i \boldsymbol{X}_j + \varepsilon \qquad (2.2)$$

Where β_o is the constant, β_i is the slope or linear effect of the input factor X_i, β_{ij} the linear by linear interaction effect between the input factor X_i and X_j, β_{ii} is the quadratic effect of input ε is random error.

The Taguchi tool with its orthogonal array of design options is another technique with similarities to the Response surface.

2.8 Review of Previous work done

Sunflower oil, rapeseed, palm oil, and soya bean are the most commonly used edible oils in commercial production. (Sulaiman et al, 2017) utilized palm oil in the process of biodiesel production using ultrasound-assisted two-stage optimization procedure. Maximum biodiesel yield was 95.2% for RSM-based optimization and 95.1% for ANN/GA-based optimization. To obtain a maximum yield of 94.30% (w/w) of FAMEs from palm oil, a novel catalyst was created using calcium carbonate from fishbone treated with aluminum nitrate as a solid oxide catalyst. The optimal yield conditions were a calcination time of 6.11 hours, a catalyst loading of 4.02% (w/w) and, a fishbone calcium oxide concentration of 34.49% (w/w).

(Sajjadi et al., 2017) reported biodiesel production from palm oil utilizing an ultrasound-assisted two-stage optimization process. Both RSM and ANN-GA based optimization resulted in maximum biodiesel yields of 95.2% and 95.1%, respectively. Despite the high yield achieved, one problem that is associated with palm oil is the creation of alkali-catalyzed biodiesel. This is due to the fact that palm oil contains a large quantity of saturated fatty acids.

Commercial production has often made use of edible oils such palm oil, rapeseed oil, soyabean oil, and sunflower oil, soybean oil. However, the cost of these oils is higher than that of diesel fuel. Biodiesel from edible sources is too expensive to commercialize. An overuse of edible crops will cause a food shortage in developing nations. Hence Waste cooking oils (vegetable or frying oil) and animal fats can be used to make low-cost biodiesel (Marwaha et al., 2018). (Lou et al., 2008) transesterified waste cooking oil at 80 °C, using a 30:1 methanol-to-oil molar ratio, 10wt% catalyst, and 8 h reaction time attaining a yield of 92%.

Although oils and fats can be trans-esterified with a homogeneous catalyst at moderate temperatures and atmospheric pressure, but this approach has significant limitations notably that the catalyst is often not recycled and must be removed from the product streams (biodiesel and alcohol/glycerol). Soap is produced as a byproduct when a catalyst combines with contaminants in oil, most notably free fatty acids (Mardhiah et al., 2017). Heterogeneous catalysts, which are simple to isolate from the end product and reuse, have recently attracted a lot of interest as a superior option. Since heterogeneous catalysts offer a cheaper route to biodiesel production, they are increasingly being used in this industry. The cost of making biodiesel could be lowered by the use of heterogeneous catalysts that are manufactured from waste products (Thangaraj et al., 2019).

(Correia et al., 2014) in his work compared the transesterification performance of two waste shells. Eggshell and crab shell were calcined for 2 hours at 900 °C to decompose organic materials and convert to CaO. Under 3 wt% catalyst loading, 9:1 methanol-to-oil ratio, and 3 h reaction period, eggshell produced 97.75% FAME. At reaction conditions of, 3 wt% catalyst load, 6:1 methanol-oil ratio, and 4 h reaction period, crab shell yielded 83.1% FAME.

(Yusuff et al., 2019) utilized anthill and eggshell to develop a mixed metal oxide catalyst that was then doped with nickel and cobalt to increase its activity. Similarly, (Etim et al., 2021) derived a renewable catalyst from fused chicken eggshell and pawpaw peels and reported a maximum yield of 91.20%. Despite the fact that heterogeneous catalysts based on calcium are more efficient, economical, and advantageous to the biodiesel production process, side reactions are possible in conjunction with the methanolysis process examples include the catalytic neutralization of free fatty acids and the saponification of glyceride and methyl ester, prolonged reaction times and catalyst efficiency decline due to active phase leaching into the reaction mixture.

Various strategies have been developed by researchers to combat this problem. For instance, (Lee et al., 2015)used $CaO-La_2O_3$ mixed oxide catalyst in biodiesel production from Jatropha Oil and obtained a yield of 98.76%. In spite of these results, it has been reported that metal oxide-based catalysts have a low surface area, limiting mass transfer and reusability (Tan et al., 2015). Some authors have combined biomass and calcium-based materials to create more active catalyst in order to overcome this challenge.

Optimizing biodiesel production by developing a composite heterogeneous catalyst from waste cockle shells and watermelon peels is the focus of this study, which aims to advance research toward a more cost-effective, ecologically friendly biodiesel production process using waste vegetable oil. To the best of my knowledge, biodiesel production using fused cockle shell and watermelon peel for the development of heterogeneous catalysts have not been investigated, thus the need for this research.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 APPARATUS USED

Table 3. 1: Equipment used in the study

APPARATUS/EQUIPMENT	MAKE	FUNCTIONS/USES
Facemask	Eco guard 3-ply disposable nose mask	Face masks are used to cover the mouth and nose area. They also prevent splashes or sprays from reaching the user's mouth and nose.
Measuring cylinder	Pyrex (250ml)	For volumetric measurement of liquids, solutions or chemicals
Beaker	Pyrex (250ml)	It's a versatile piece of equipment that can be used to contain a chemical reaction, hold

		samples or measure liquids.
Conical flask	Pyrex (250ml)	Utilized for heating, boiling and measuring chemical liquid samples. Used also for sample storage on a short-term basis.
Dropper	3.0ml rubber droppers	Used for holding and transferring phenolphthalein droplet into titration solution
Filter Paper	Whatman No.1	Used to separate ash water mixture and provides pathways for liquid particles
Laboratory Funnel	Petri Labs	Used to channel fluids or powders into laboratory containers with a narrow neck or orifice as well as to keep the filter paper in place filtration.

Thermometer	THD Liners	For measuring temperature of methanol, oil and mixture samples during experiment
Separating funnel	Pyrex	For separating the mixture (biodiesel and glycerol) into distinct layers
Burette	Pyrex	Used in qualitative chemical analysis to measure the volume of oil and biodiesel produced
Muffle Furnace	Uniscope's Surgifriend Medicals, England	Used for heating, recovery, and cooling of catalyst (cockle shell and watermelon peels) samples at high temperatures in self-contained, energy-efficient cabinets.
Magnetic stirrer	MS300	Used to stir/mix solutions; utilized in impregnation

		and transesterification reactions.
Vacuum desiccator	Garg	As an air tight container to protect dry samples of catalyst from contact with air.
Reagent bottles	Pyrex	Used to store chemicals (methanol, hydrochloric acid etc.) in liquid or powder form and are stored in shelves or cabinets
Volumetric Flask	Hirschmann	Used to prepare standard solutions and dilutions with high precision.
Laboratory scale	Hirschmann(250ml)	It is utilized to establish a sample's mass or weight.

3.1.2 Reagents

Table 3. 2: Reagents employed

REAGENTS	SOURCE	USES
Waste Vegetable oil	University of Benin Canteen	Feedstock for the production of biodiesel
Cockle Shell	Borokiri town market Port harcourt	Used in the production of biodiesel as a catalyst providing basic properties
Watermelon Peels	Campus vendor	Catalyst for the synthesis of biodiesel providing basic properties
Methanol	Campus vendor	Feedstock for biodiesel production
Phenolphthalein	Campus vendor	In the acid-base titration and other WVO sample tests, this is used as an indicator.
Potassium hydroxide	Campus vendor	Determination of acid value
Benzene	Campus vendor	Determination of acid value
Acetic acid	Campus vendor	To obtain peroxide value
Absolute Ethanol	Campus vendor	To ascertain acid value

Hydrochloric acid	Campus vendor	Used to evaluate saponification value
Sodium thiosulphate	Campus vendor	Used to ascertain acid value
Chloroform	Campus vendor	Used to determine iodine value
Nickel Nitrate	Campus vendor	Used as a doping agent during wet impregnation.

3.2 METHODS

3.2.1 Oil Characterization

3.2.2.1 Acid value test

The acid value is the milligrams of potassium hydroxide (KOH) needed to neutralize one gram of fatty acid methyl ester. The free fatty acid concentration in a new fuel sample can be determined using this method (Mishra & Goswami, 2018). According to ASTM D664, an acid test is conducted to determine the oil's acid value. Using a laboratory scale, 1.0g of waste vegetable oil was measured. This was placed into a conical flask and was dissolved in 10milliliters of benzene, then 10ml of ethanol was added; the flask sample was heated subsequently phenolphthalein was added, and the solution was titrated with 0.1 N potassium hydroxide as reported by (Ismail & Ali, 2015). After titrating the mixture with KOH the acid value was calculated using;

Acid value = $\frac{V \times N \times 56.1}{W}$ (3.1)

Where V= Volume of KOH titrant (ml)

N= Normality of KOH titrant (mol/1000ml)

W= Sample mass in g

3.2.2.2 Saponification value test

Saponification test as carried out by (Azeem et al., 2016).

The average molecular weight of biodiesel can be accurately determined using the SV method. In a conical flask, 1g of oil or biodiesel sample was combined with 25ml of 0.5M ethanoic potassium hydroxide to determine the saponification value. A condenser attached to a water bath gently heats the flask for around 1 hour. After cooling, the mixture of the reaction was titrated was using two drops of phenolphthalein in a 0.5M hydrochloric acid solution until the color changed from pink to colorless. In a similar manner, a blank (distilled water) experiment was carried out in which the similar volume of oil-free potassium hydroxide solution was treated. The saponification values was thus calculated using this equation;

Saponification value = $\frac{(V_1 - V_2) \times N \times 56.1}{W}$ (3.2)

Where, V_1= Volume of titrant of HCL solution for blank (ml)

V_2= Volume of titrant of HCL solution for oil (ml)

56.1= Molecular weight of KOH (mg/mol)

W= Weight of oil/biodiesel (g)

3.2.1.3 Iodine Value

Determination of iodine value on waste vegetable oil as reported by (Azeem et al., 2016; Onukwuli et al., 2017). The iodine content of 1g of waste vegetable oil was tested by weighing it into a conical flask and dissolving it in 10ml of chloroform (CCL4).

25mL of Wj's (iodine monochloride acetic acid) reagent was added, and the mixture was left in the dark for 30 minutes to avoid contact with sunlight. Potassium iodide (20ml, 10%) was added at the end of the time period, to which 100 ml of distilled water was added, and the surplus iodine was titrated with sodium thiosulfate (0.1N) until the yellow color of the solution had almost vanished, Following the addition of a few drops of starch to serve as an indicator, the titration process was carried out until all traces of the blue color were gone. The identical conditions were used for the blank test. The amount of iodine in 100g of oil is expressed in grams of I_2.

$$\text{Iodine Value } (gI_2/100\text{g oil}) = \frac{12.69 \times M(V_1 - V_2)}{W} \tag{3.3}$$

Where;

V_1= Volume of Na_2SO_3 for blank

V_2= Volume of Na_2SO_3 for oil

N= Molality/strength of Na_2SO_3

W= Weight in gram of oil sample

3.2.1.4 Peroxide Value

As described by (Ismail & Ali, 2015), 1 g of WVO was poured into a conical flask containing 1 mL saturated potassium iodide and 12 mL of a solvent mixture (3 vol glacial acetic acid: 2 vol chloroform). Iodine is liberated by adding distilled water (12 ml) to the chloroform layer. In the presence of a 1 percent starch solution as an indicator, sodium thiosulfate solution (0.1N) was gradually titrated until the blue grey color in the upper layer of the aqueous layer was completely eliminated. At the same time and under the same conditions, a blank determination is performed (Onukwuli et al., 2017). Calculated peroxide values were expressed using the formula;

$$\text{Peroxide value (milli equivalents/100g sample)} = \frac{1000 \times N \times (V_1 - V_2)}{W} \qquad (3.4)$$

Where, N =Normality of $Na_2S_2O_3$

V_1= Volume of $Na_2S_2O_3$ for blank (ml)

V_2= Volume of $Na_2S_2O_3$ for oil used (ml)

W= weight of oil

3.2.1.5 Determination of Free Fatty Acid

1g of WVO was dissolved in a 25ml neutral liquid in a conical flask (equal volume of absolute ethanol and diethyl ether). 0.1M potassium hydroxide solution was titrated into the oil solution to determine the end point, and three drops of phenolphthalein served as an indicator for this. An oleic acid-based expression is the method used to determine how much free fatty acid a sample contains. (Onukwuli et al., 2017).

$$\text{FFA (\%)} = \frac{V \times 0.0282 \times 100}{W} \qquad (3.5)$$

3.2.1.6 Specific Gravity

The empty capacity of a 50ml specific gravity bottle (volumetric cylinder) was weighed. Having thoroughly drained and cleaned the bottle, it was then filled with WVO and the weight of the mixture was measured, the bottle was then reweighed after being filled with water. Keeping the temperature constant, the experiment was run as soon as feasible (Onukwuli et al., 2017). This relationship was used to calculate the specific gravity of an oil sample,

$$\text{Specific gravity, S.G} = \frac{\text{Weight of sample}}{\text{Weight of equal volume of water}} \tag{3.6}$$

3.2.1.7 Kinematic viscosity

The viscosity of a material is the most essential factor in establishing its capacity to flow (Mishra & Goswami, 2018). The Ostwald viscometer was cleaned with acetone prior to drying to remove any grease or contaminants. In order to determine the kinematic viscosity of the WVO (200ml) between two marked points (lower and upper meniscus) at a constant temperature of 40 °C using a vertically mounted Ostwald viscometer in a viscometer tube, the time of flow was measured and the viscosity was calculated by multiplying the time of flow (Sani et al., 2018). The Kinematic viscosity was determined using this relation;

$$\mu = (k)t \tag{3.7}$$

where μ= Viscosity (cst)

K= Ostwald viscometer constant

t= time at which fluid flows through capillary (s)

3.2.1.8 Density

The density of the WVO was determined using a volumetric density bottle. The density of the bottle was initially determined and recorded, followed by the weight of the WVO in conjunction with the density bottle. A change in weight is detected, and the value of the change is recorded. In order to estimate the weight/mass of the oil, the difference in weight of both samples is calculated, from which the density of the oil is measured by mass-to-volume ratio (Ismail & Ali, 2015).

$$\text{Density} = \frac{\text{Mass of oil (g)}}{\text{Volume of oil (cm}^3\text{)}} \qquad (3.8)$$

3.2.2 Catalyst Preparation

According to the approach given by (Hadi et al., 2017) with a few modifications, the Cao catalyst was produced. The cockle shells were picked from Borokiri Town Market in Port Harcourt and given a thorough hot water wash to help remove proteins and lipids, followed by a wash in distilled water to remove dust and debris left before being sun dried for about 3 days. A powdered form of the cockle shell was obtained by crushing the shells in a laboratory mill and sieving them through a sieve tray with a size of 300µm. Calcination of the powdered cockle shell was then carried out in a muffle furnace for four hours at a temperature of 900°C. To avoid air contact, the calcined cockle shell was removed after cooling and immediately placed in a desiccator.

The acquired watermelon peels was prepared in same method, the watermelon peels was separated from unwanted debris and dirt by washing thoroughly with distilled water, chopped into small pieces, and sun-dried for 4 days. A powdered form of the watermelon peels was obtained by crushing the peels in a laboratory mill and sieving them through a sieve tray with a size of 300µm. For three hours at 500℃ in a muffle furnace, powdered watermelon peels were carbonized before being cooled in a desiccator. The calcined watermelon peel ash samples that were produced were kept in a desiccator until they could be used for further testing.

3.2.2.1 Preparation of bi-functional catalyst from calcined cockle shell and watermelon peels with Nickel-nitrate

Wet impregnation method was used to prepare the nickel-doped composite catalyst from carbonized watermelon peels and calcined cockle shell, as reported by (Yusuff et al., 2019).` Mixed in proportions of 70% (calcined cockle shell), 17% (carbonized watermelon peels), and 13% (nickel nitrate) in 400 ml of deionized water, where they were stirred vigorously for 2 hours at 80℃ with a magnetic stirrer. The resulting slurry was then oven dried for 1 hour and subsequently calcined for 4 hours at 900℃. The resulting catalyst was allowed to cool in a desiccator and then stored in an airtight container for subsequent use.

3.2.2.3 Biodiesel Production

The procedure for producing biodiesel from WVO by transesterification was described by (Kara et al., 2021) with a few modifications.

For each run of transesterification reaction, conical flasks containing 1g of Waste Vegetable oil (WVO) were heated to their respective run temperatures as specified by table 3.3 using magnetic stirrers. Based on experimental design, the heated oil was mixed with a corresponding amount of methanol and allowed to cool for 5 minutes. After that, the mixture of heterogeneous catalysts was added to the reactor, and the reaction was allowed to run for the allotted time.

After completion, the reactions mixture was cooled and decanted (for phase separation), allowing separation of glycerol via gravity. The layers (glycerol, methyl ester, and catalyst) were further separated. In a separating funnel, the remaining liquid separated overnight. The upper layer, which contained unreacted methanol and biodiesel, was then separated from the lower layer, which contained glycerol and some residual solid catalyst (Ngadi et al., 2017). To eliminate excess methanol, glycerol, and catalyst from the recovered biodiesel, it was washed thrice with warm distilled water. Further drying was performed to remove any remaining moisture from the biodiesel. Afterwards, it was placed in a bottle and kept for characterization purposes.

The yield obtained was calculated using the following formula, which can be found in equation;

$$\text{Percentage of biodiesel yield} = \frac{\text{weight of biodiesel produced}}{\text{weight of oil}} \times 100 \qquad (3.9)$$

3.2.3 Characterization of catalyst and precursor

For the purpose of evaluating the characteristics of the newly synthesized catalyst (cockle shell and watermelon peels) as well as its precursors, various characterization tests were run on the samples and analyzed as follows**;**

i) The morphology and elemental composition of the samples were determined using the Scanning Electron Microscopy which utilizes an energy dispersive X-ray detector (SEM)-EDX technique.

ii) An X-ray diffractometer (XRD) with Cu Kα radiation with a wavelength of 0.15406 n was used to investigate the catalysts' crystalline phase.

iii) The Brunauer-Emmett-Teller (BET) analysis was used to determine the surface area and pore volume using the Brunauer, Emmett and Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis.

iv) Fourier Transform Infrared Spectroscopy (FTIR) analysis was utilized to determine the bond structure and interactions in the calcined catalyst at a resolution of 4cm^{-1} measured between 400 and 4000 cm^{-1} with Nicolet iS10 FT-IR Spectrometer.

3.3 Design of Experiment (DOE)

Design Expert Software was employed in this study to conduct experimental runs and optimization of reaction conditions. The range of these input variables was determined by preliminary experimentation and prior research (Balajii & Niju, 2019).The Box-Benhken tool in the STATISTICA 10 software was employed for experimental design using the following ranges of experimental values as shown in the table

Table 3. 3: Process Parameters and their Lower, Middle and Upper Limits

Process parameters		**Levels**		
		-1	**0**	1
Reaction time, min	**X_1**	60	105	150
Reaction Temperature, ºC	**X_2**	40	65	80

Methanol-to-oil molar ratio, X	X_3	3:1	9:1	15
Catalyst Concentration, wt%	X_4	1	3	5

3.3.1 Analysis of model fit

The analysis of variance (ANOVA) is used to assess the model's goodness of fit and the key process variables that influence the production of biodiesel. Based on the selected model parameter such as F value, lack of fit, p value etc., ANOVA results estimate the statistical significance (Mäkelä, 2017) and fit of a model, which can be tested by comparing variations in the model's explanations and in the model's residuals (Veljković et al., 2019).

3.3.1.1 F values

The F-test has the advantage of assessing numerous coefficients simultaneously. To estimate the F-value, the ANOVA separates two estimated variances: one based on the variability in group mean values, the other on variability within groups.

3.3.1.2 P value

The P-test can be used to establish the significance of model coefficients. A factor is considered significant if its p-value is less than 0.05. If the study requires extreme precision, lower p-values may be specified at a p-value significance threshold (Witek-

Krowiak et al., 2014). The lower the value of p, the more the variables interact and the more important those variables become in the model (Yatish et al., 2016).

3.3.1.3 Coefficient of determination (R^2)

The coefficient of determination (R^2) is defined as the ratio of sum of squares due to regression to total sum of squares, and is interpreted as the fraction of data variability explained by the ANOVA (Anuar et al., 2013). It is employed to assess the fitted model's general prediction capabilities (Yolmeh & Jafari, 2017). The coefficient of determination can explain how much of the original data varies. The adjusted R^2 value adjusts the R^2 value for the model's term count and sample size. In order to be valid, the R-squared and related adjusted values must both be close to one. A value of 1.0 reflects the ideal condition, in which the chosen model can explain 100% of the variation in observed values. If the fitted model's R^2 values are appropriate, it means that it accurately describes the process's behavior and can be utilized for optimization. The closer to 1.0 the predicted R-squared value is, the better (Ghorbannezhad et al., 2016).

3.3.1.4 Lack of Fit

Inadequacy of the model causes variations known as lack of fit (Anuar et al., 2013). For the quadratic regression model, the lack of fit is also calculated. Lack of fit in a quadratic regression model suggests that the model is insufficient to characterize a relationship between the independent factors and the dependent variable (Dharma et al., 2016).

3.3.1.5 Predicted Residual Sum of Squares (PRESS)

PRESS is the predicted residual sum of squares, i.e., the sum of squared differences between observed and predicted responses

3.3.1.6 Adequate Precision

"Adequate Precision" is a signal-to-noise ratio metric with a value greater than 4 indicating that it is adequate (Anis & Haydar, 2019).

3.3.2 Optimization of response

RSM's primary goal is to find the optimal control variable settings that result in the maximum (or minimum) response over a specific region of interest, R. Because the value of the optimum is determined with the help of a 'good' fitting model, having a model that adequately represents the mean response is essential for inclusion in optimal criteria (Khuri & Mukhopadhyay, 2010).Optimal biodiesel production was the focus of this research.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Physiochemical Properties of Waste Cooking Vegetable Oil

According to ASTM standard, the physicochemical properties of Waste cooking vegetable oil were examined as described in chapter three.

Table 4. 1: Physicochemical Properties of Waste Cooking Oil

Properties	Values
Acid value (mg KOH/g)	7.5
% FFA	3.75
Viscosity (mPa.s)	23
Peroxide value(meq/kg)	12.3
Saponification value (mg KOH/g)	210.4
Iodine value (mg I_2/100g)	64.31
pH	6.01

4.2 Characterization of Prepared Catalyst

4.2.1 SEM-EDX analysis

The morphological characteristics of the precursor materials and the produced catalyst are depicted in the SEM images provided in Fig 4.2. The watermelon peel has a highly irregular porous structure and a heterogeneous fiber-bundled appearance due to its significant structural alteration. The observed spongy nature is a result of the calcination-induced sintering of tiny mineral aggregates and flocculated particles, and is therefore indicative of activation and catalysis-accessible surface area (Betiku et al., 2016).

Fig. 4.2b illustrates the rough surface, uneven and compactly formed particles collected into mass, and overall bulky appearance of cockle shells. A non-uniform structure of the particle size distribution is seen in Fig. 4.2c for produced fused catalysts, which typically consists of the development of smaller aggregates of varied morphologies. Ash samples of used banana peels have been observed to have similar morphological findings (Betiku et al., 2016) , and also watermelon rind (Fakayode et al., 2020). Identical pore micro properties were noted by (Zamberi & Ani, 2016) for cockle shell-based heterogeneous catalysts, (Dampang et al., 2021) observed identical characteristics while producing Cao using waste seashells as the source of $CaCO_3$.C lusters of Ni-Cao particles may occur during preparation and calcination of metal impregnated catalysts, which could account for the irregular morphology. During the production of the catalyst, (Etim et al., 2021b)noticed a nonuniform surface and particle size distribution, comparable to that shown in fig 4.2c, and they characterized it as the outcome of the two waste materials' particle size structures combining during the catalyst synthesis.

Edx analysis, as given in table 4.2, determined the elemental composition of the catalyst samples and shows the presence of elements such as Na, k, S, O, Ca, Si, Fe, Ni etc. The composite catalyst's alkaline (calcium, potassium) and acidic (silicon, nickel) constituents indicate bifunctionality. This implies the catalyst can catalyze esterification and transesterification simultaneously. In (Nath et al., 2020) investigation of heterogenous catalyst developed from *Sesamum indicum* plant, the inclusion of calcium, potassium, and silicon boosted the catalyst's activity.(Etim et al., 2018) observed a similar observation for ripe plantain peels, as well as s for calcined eggshell and pawpaw peels composite catalyst (2021).

Table 4. 2: EDX analysis of cockle shell, watermelon peels and composite catalyst.

Element Name	**Element symbol**	**Weight percent**		
		Cockle shell	**Watermelon peels**	**Composite Catalyst**
Nickel	Ni	0	0	5.3
Calcium	Ca	59	2.75	4.3
Phosphorus	P	3	3.68	1.23
Nitrogen	N	3	6.3	0.43
Sulfur	S	4.5	2.04	1.3
Carbon	C	8.5	65.28	25.4
Potassium	K	0	10.12	5.2
Silicon	Si	10	0.2	23
Oxygen	O	10	9.2	33.51
Iron	Fe	2	0	0
Sodium	Na	0	0.43	0.33

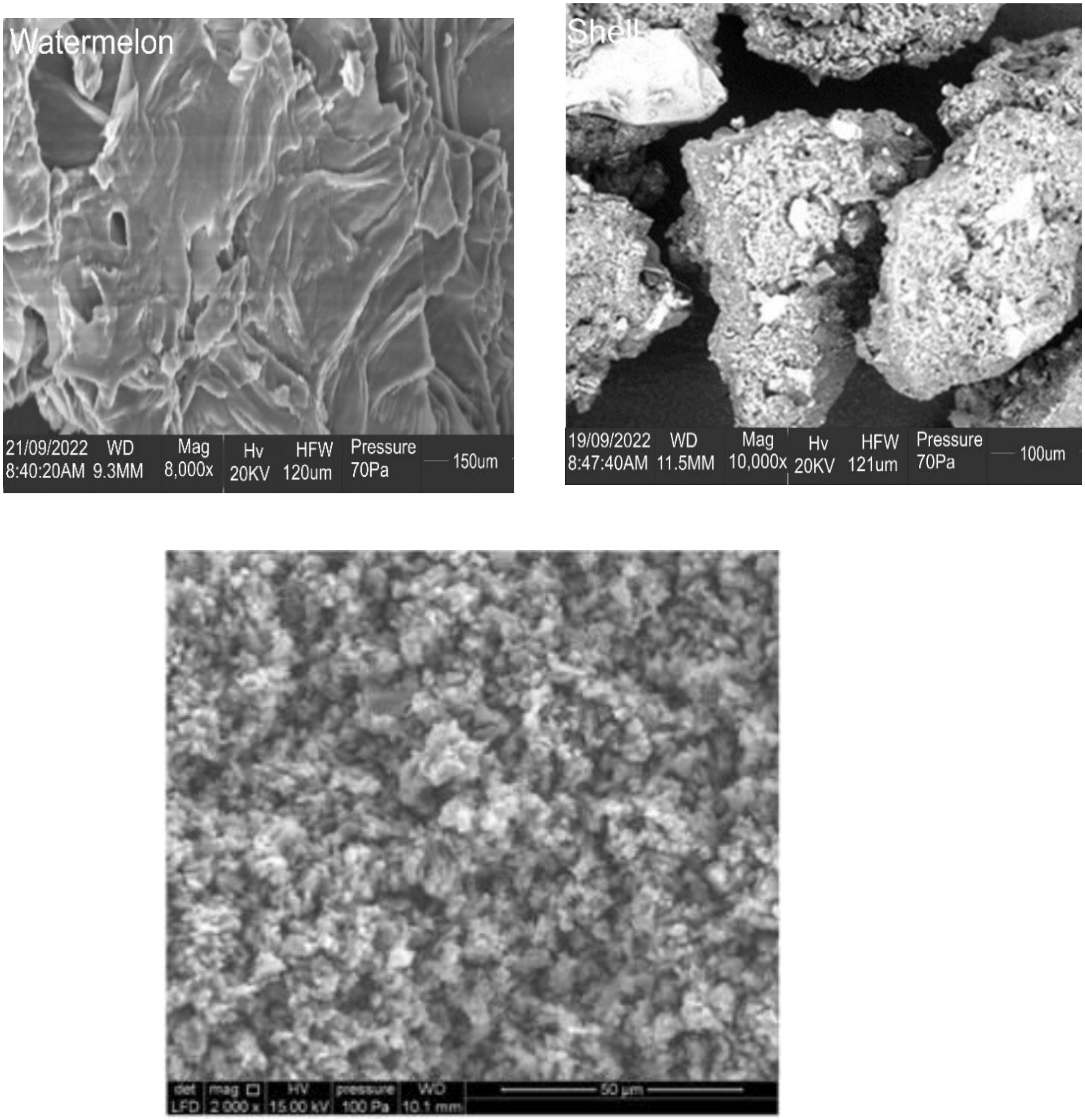
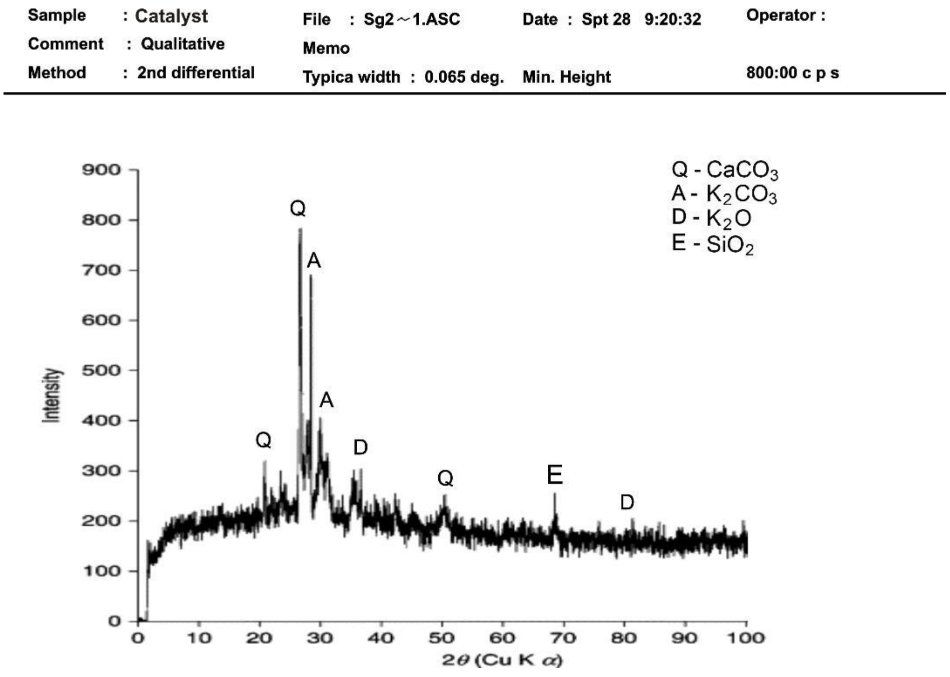


Figure 4. 1: SEM analysis – a (watermelon peels), b (cockle shell) , c (composite catalyst) (a) x150 (b) x100 (c) x50

4.2.2 XRD analysis

Intensity peaks at 22°, 25°, 29°, 30°, 32°, 36°, and 49°, 68° in the XRD spectra of the composite catalyst indicate the cubic Cao phase formed from cockle shells.(Reddy et al., 2017) and (Zamberi & Ani, 2016) generated catalysts with similar peaks, indicating that Cao was the predominate oxide. Similar to the finding reported in the work of (Gohain et al., 2017), who characterized the catalyst derived from Musa balbisiana peel, these XRD spectra showed weakly-intensified peaks at 2 values of 37.0°, 43.0°, and 62.5°, representing the presence of K_2CO_3, and the presence of k_20, represented by the peaks at 2ϴ values of 26.71°.

For 2ϴ values of 21.39, 25.78, and 72.78, the spectra indicated the presence of SiO2 in the catalyst. Catalysts for biodiesel synthesis using calcined wood ash and M. balbisiana underground stem were also discovered to contain SiO_2 (Sharma et al., 2012),(Sarma et al., 2014).



Sample : Catalyst
Comment : Qualitative
Method : 2nd differential
File : Sg2～1.ASC
Memo
Typica width : 0.065 deg.
Date : Spt 28 9:20:32
Min. Height
Operator :
800:00 c p s

Figure 4. 2: XRD ANALYSIS

4.2.3 BET analysis

The catalytic activity of any given solid base heterogeneous catalyst is highly dependent on its surface area, porosity, and mineral content. The BET method (surface area) and the BJH desorption summary (pore volume and pore size) were utilized to characterize the composite catalyst in order to determine the effectiveness of the calcination procedure. Based on the results of the BET analysis, it was determined that the composite catalyst possess a surface area of 105.350 m^2/g. Additionally, the pore volume and pore size were determined as 0.60cm^3/g, 30.32A respectively. In comparison to other solid catalyst reported (Reddy et al., 2017b)(surface area = 85.27m^2/g, pore volume = 0.423cc/g), (Tan et al., 2015)(surface area = for chicken eggshells (54.6 m^2/g) and ostrich eggshells

($71.0m^2/g$), pore volume = 0.0218 cm^3 g-^{1}, 0.0148 cm^3 g^{-1} respectively), (Betiku et al., 2016b)(surface area = (4.442 m^2/g, pore volume = $0.020cm^3/g$), the synthesized catalyst displayed a high surface area and this can be attributed to the process of reduction in size and sieving that was carried out. These results therefore show that the catalyst's external surface possesses the active site. Due to the larger pore size, it can improve diffusion problems, resulting in better flow channels. In the reaction mixture, this could expedite the rate of interaction between the material and the alcohol, thereby accelerating the reaction.

4.2.4 FTIR analysis

The spectroscopic technique of Fourier transform infrared spectroscopy was employed to determine the bond vibrations in the sample. Significant peaks were seen in watermelon peels at $4010cm^{-1}$,$3500cm^{-1}$,$3000cm^{-1}$,$1850cm^{-1}$,$1500cm^{-1}$. Watermelon peels' FT-IR spectra are depicted in Fig. 4.3 The weak bands observed in fig at 3200−3500cm^{-1} are assigned to the strong H−OH stretch or Si−OH, while bands at 1650, 1455.78, 1251, and 1159 cm^{-1} are assigned to carbonate C−O stretching and bending vibrations, which suggest the presence of carbonate. According to the observations of (Sulaiman & Ruslan, 2017), the vibration of hydroxyl groups and C0, respectively, was responsible for the formation of peaks at 3570 - 3420 cm-1 and 1640 - 873 cm-1. The 900 -cm^{-1} peak is also influenced by symmetric and asymmetric stretching vibration bands in Si-O-Si.

Cockle shell catalyst FTIR spectra (Fig 4.4) shows two CaCO3 peaks at 711 cm^{-1} and 846-880 cm^{-1} which is attributed to carbonate ion ($Co_3^{2-)}$ stretching vibration. At $3638cm^{-1}$, a distinct OH stretching band related to water physisorbed on Cao's surface also begins to show. Observing peaks at $3641cm^{-1}$ when heterogeneous catalysts are synthesized from anadaragranosa shell, (Linggawati, 2016) work supports our findings. Similar observations were made by (Dampang et al., 2021), who attributed peaks at 3400 cm^{-1} to the presence of OH group in Ca $(OH)_2$.

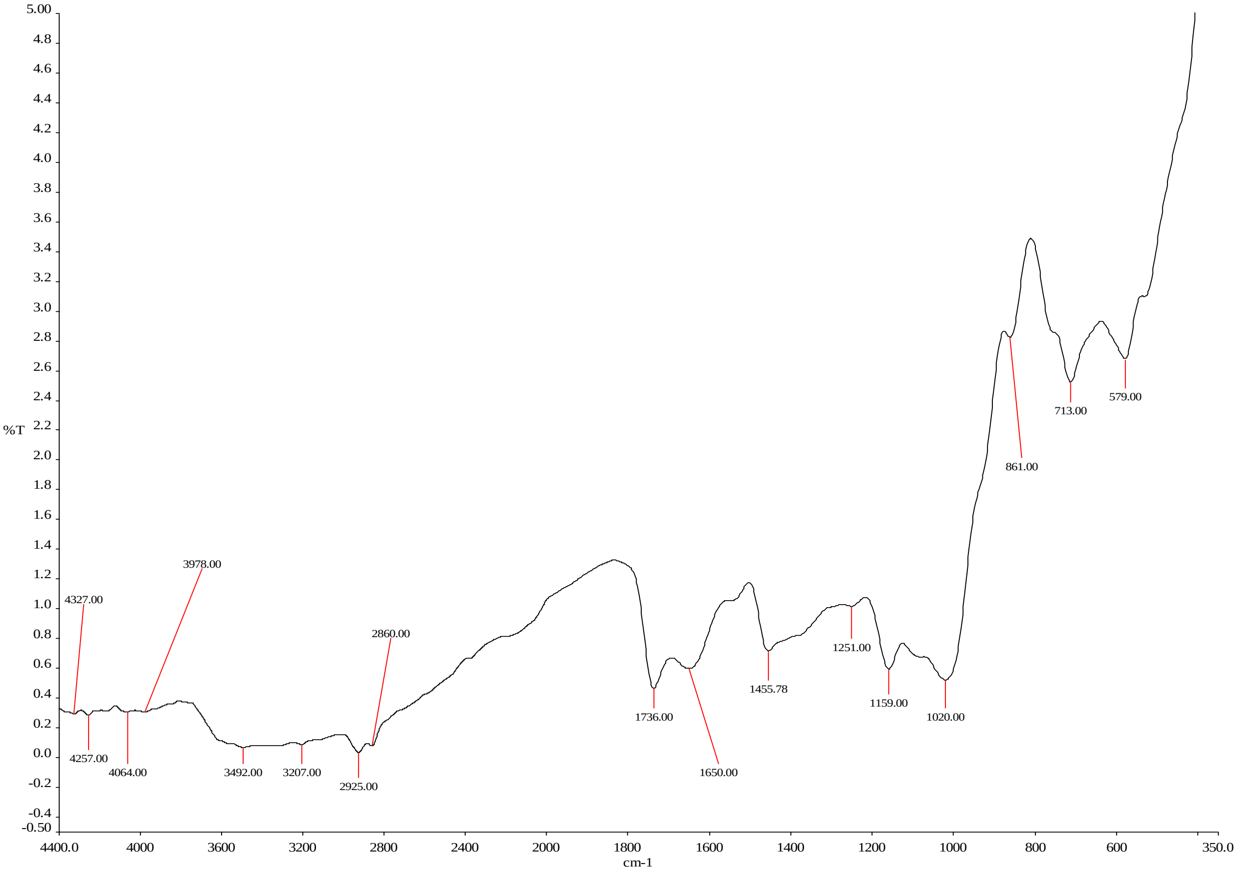


Figure 4. 3: FTIR spectra for watermelon peels

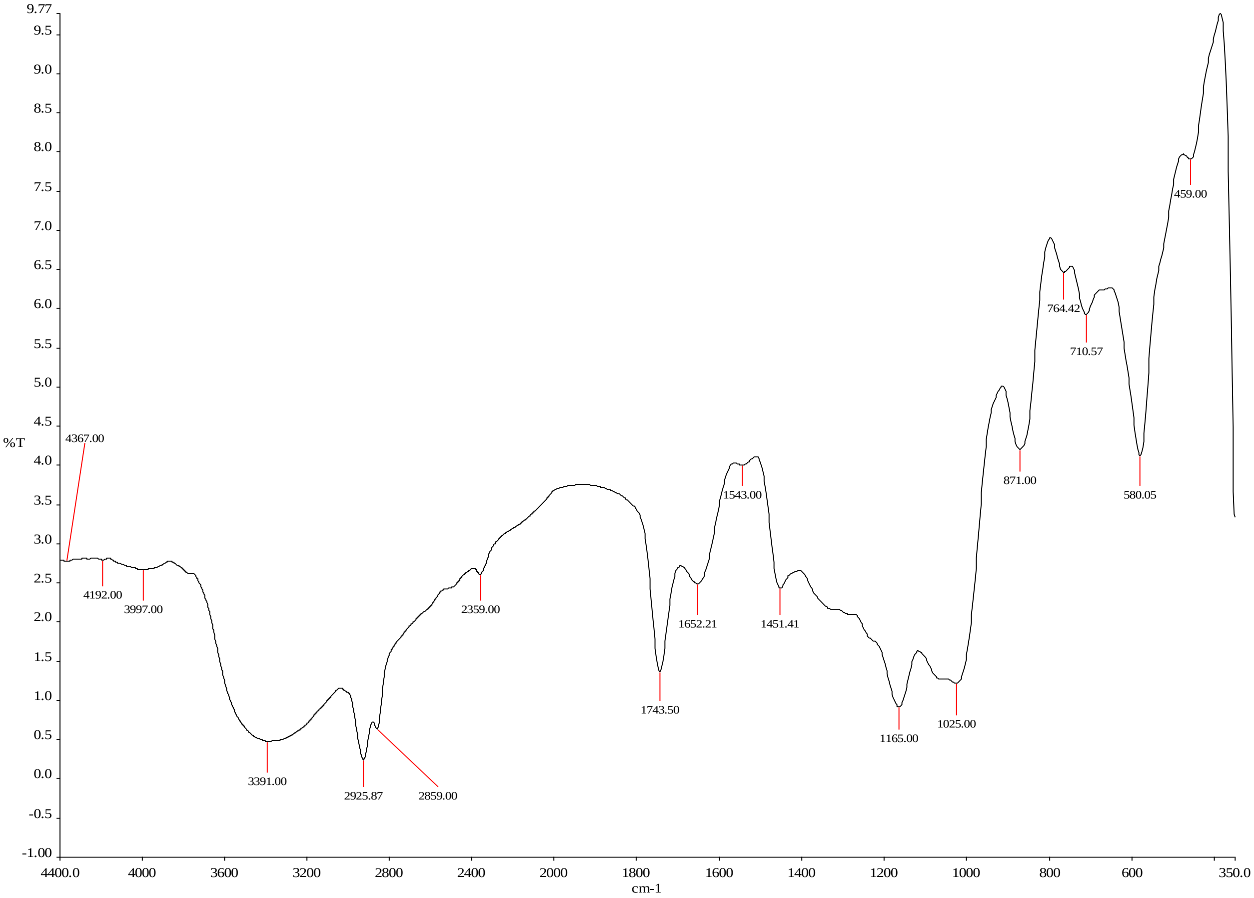


Figure 4. 4: FTIR spectra for cockle shell

4.3 Statistical Analysis from Response Surface Methodology (RSM)

For statistical evaluation and process optimization of experimental data, the Box Benkhen design was utilized.

Table 4. 3: Model Summary Statistics

Source	**Sequential p-value**	**Lack of Fit p-value**	**Adjusted R^2**	**Predicted R^2**	
Linear	0.1325	0.0012	0.121	-0.1546	
2FI	0.2747	0.0013	0.1976	-0.5937	
Quadratic	**< 0.0001**	**0.1299**	**0.9345**	**0.8261**	**Suggested**
Cubic	0.9378	0.023	0.8913	-1.8501	**Aliased**

The experimental data in Table were used to verify the statistical design via a fit to the quadratic regression model (Equation (2.2)). The response variable is the methyl ester yield, which varies as a function of the four specified parameters (reaction time, molar ratio, reaction temperature, and catalyst dosage). Using a mathematical equation established, this dependency defines the link between response output (yield) and input parameters.

4.3.1 Physicochemical Properties of Biodiesel

The biodiesel from waste cockle shell and watermelon peels is darkish brown in colour with a pungent smoky smell. Table 4.4 shows some of the physical properties of biodiesel.

The acid value for biodiesel (0.39 mg KOH/g) is within the ASTM D675-12 standard range(0.50max) and much lower than those for waste vegetable oil. In excessively high acid value is undesirable as it means the fuel is strongly acidic, which would corrode engine parts.

The density of biodiesel obtained was 0.836. To allow for optimal air-to-fuel ratios for complete combustion, the density value must be kept within tolerable ranges. Particulate matter emissions and incomplete combustion are possible results of high-density biodiesel use.

The calorific value is a measure of the amount of heat energy contained in a fuel produced by a chemical reaction in the engine's combustion chamber. The biodiesel had a calorific value of 38.2Mj/kg. Higher calorific power translates into more fuel energy.

Cetane number obtained is 48.7(< 51) EN14214 standards. The biodiesel's cetane number tells us whether or not it will spontaneously ignite when injected into the engine. It's important to note that a higher cetane number implies good combustion, which in turn increases the efficiency of the engine motor.

Fuel flammability is quantified by the flash point, which is inversely proportional to volatility In the absence of a flame or spark, it depicts the lowest temperature at which the fuel can ignite spontaneously. High flash point increases handling and storage safety. he samples' flashpoints are within ASTM D93 limits (min 130℃). This means the biodiesel sample can be safely handled.

The less viscous biodiesel is, the simpler it is to pump it into an engine for atomization.

The amount of moisture present in biodiesel has an effect that promotes an increase in acidity, which then leads to the formation of soap. Hence a low moisture content is desirable. The moisture content which was attained was 1.5%. The moisture content was very low.

The biodiesel's pour point as well as its cloud point were both ascertained at -1.7℃ and 1.6℃. The lowest temperature at which fuel can flow is known as the pour point (pp) whereas the temperature at which wax first becomes apparent after cooling the fuel is known as the cloud point (cp).

The rancidity level and the degree to which fuel has been oxidized can typically be ascertained by measuring the peroxide value. Peroxide value (2.53meq/kg) is within biodiesel tolerance limits.

Biodiesel's Saponification value was 196.7mg KOH/g. A small amount of saponification reduces pump and injector friction. However, excessive amounts can have a negative impact on fuel properties and reduce the amount of biodiesel produced during the transesterification process.

The oil's iodine value dropped from 64.31 ($g/I_2 100g$) to 54.21 ($g/I_2 100g$) after transesterification, well below the 120 ($g/I_2 100g$) threshold for biodiesel. Saturation levels in fuel are quantified in terms of iodine. Extremely high levels of unsaturation can cause the fuel to polymerize as the free molecules combine with oxygen or excessive carbon buildup in the engine's combustion chamber following combustion.

According to the specifications, biodiesel has a pH of 6.73. The acidity or alkalinity of the oil/biodiesel can be quantified by its pH value. Both the waste vegetable oil and the biodiesel are acidic.

Table 4. 4: Physiochemical properties of Biodiesel

Properties	**Values**
Acid value (mg KOH/g)	0.39
Density (g/m^3)	0.836
Calorific value (Mj/kg)	38.2
Cetane Number	48.7
Flashpoint (°C)	145.8
Viscosity (mPa.s)	6.17
Moisture content (%)	0.015
Pour point (°C)	-1.7
Cloud point (°C)	1.6
Peroxide value(meq/kg)	2.53
Saponification value (mg KOH/g)	196.7
Iodine value (mg I_2/100g)	53.2
pH	6.73

4.3.2 Waste Vegetable Oil (WVO) Biodiesel Yield Analysis

The table below shows that the WVO methyl ester yield ranged from 60% to 90%. At 105minutes of reaction time, 40°C temperature, a 3:1 methanol/oil molar ratio, and a 3wt% catalyst loading, the minimum WCO methyl ester yield of 60.9% was achieved. After optimizing of reaction time, temperature, methanol/oil molar ratio, and catalyst loading, the highest yield (90.78%) was achieved at 60°C, 15:1, and 3wt%.

Table 4. 5: Experimental Design Data of the Response Variable with Actual And Predicted Yield Values

Run order	A: Reaction time (mins)	B: Reaction Temperature (°C)	C: Methanol-oil ratio	D: Catalyst concentration (wt%)	Actual Value	Predicted Value
1	150	60	9	5	81.62	82.05
2	105	40	3	3	60.91	61.86
3	150	40	9	3	68.23	69.36
4	150	60	3	3	86.22	85.12
5	105	60	9	3	76.09	74.69
6	105	60	9	3	75.59	74.69
7	105	60	15	1	82.54	84.23
8	150	80	9	3	81.76	82.77

9	105	60	3	5	74.45	74.26
10	105	40	15	3	78.12	80.07
11	105	80	3	3	84.46	84.13
12	60	80	9	3	75.09	75.47
13	60	60	3	3	83.26	82.38
14	150	60	15	3	90.78	88.53
15	105	80	9	5	70.26	70.44
16	105	60	9	3	73.54	74.69
17	105	80	9	1	85.28	83.37
18	60	40	9	3	72.06	72.56
19	105	40	9	1	71.45	68.14
20	105	60	3	1	87.26	88.81
21	105	60	15	5	87.09	87.05
22	105	80	15	3	73.45	74.12
23	60	60	9	5	78.42	79.26
24	150	60	9	1	86.39	87.17
25	105	40	9	5	70.56	69.34

26	60	60	15	3	89.21	87.18
27	105	60	9	3	74.61	74.69
28	60	60	9	1	84.67	85.86
29	105	60	9	3	73.62	74.69

According to the aforementioned data, the empirical model that shows the link between the process variable and the % biodiesel yield in terms of coded components utilizing multiple regression analysis, is as follows:

$Y_1 = 74.69 + 1.02A + 4.08B + 2.05C - 2.93D + 2.63AB - 0.3475AC + 0.37AD - 7.05BC - 3.53BD + 4.34\ CD + 5.55A^2 - 5.21B^2 - 5.526C^2 + 3.34D^2$

Where;

Y_1 is WCO biodiesel yield, A is Reaction time, B is Temperature, C is methanol-to-oil molar ratio, D is catalyst dosage (wt%).

4.3.3 Analysis of Variance (ANOVA)

Response Surface Methodology was used to examine the interaction effect of temperature, catalyst concentration, reaction time, and methanol-oil ration on waste vegetable oil transesterification process. The transesterification process was modeled and optimized using the BBD with three factors and three levels. Twenty-nine experimental runs with a single response were produced. ANOVA was used to determine the model's significance, and the results are shown in table 4.6. The F-value helps determine the significance of the parameters' regression coefficient. The model is statistically significant with an F-value of

29.53 and a P-value of < 0.0001. An F-value this high could only have occurred due to noise if the probability was 0.01%. All model terms were statistically significant, with the exception of the single term for the effect of reaction time, the term for the interaction between the methanol-oil ratio and time, and the terms for the interaction between catalyst and reaction time.

Among other aspects, the biodiesel yield was most affected by the reaction temperature that resulted in a larger coefficient.

Table 4.6 gives some statistical details about the model deducted

Table 4. 6: ANOVA for quadratic model

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	1436.63	14	102.62	29.53	< 0.0001	significant
A-Reaction time	12.59	1	12.59	3.62	0.0778	
B-Reaction temperature	199.84	1	199.84	57.51	< 0.0001	
C-Methanol-to-oil molar ratio	50.55	1	50.55	14.55	0.0019	
D-Catalyst concentration	103.19	1	103.19	29.7	< 0.0001	
AB	27.56	1	27.56	7.93	0.0137	

AC	0.483	1	0.483	0.139	0.7149	
AD	0.5476	1	0.5476	0.1576	0.6974	
BC	199.09	1	199.09	57.29	< 0.0001	
BD	49.91	1	49.91	14.36	0.002	
CD	75.34	1	75.34	21.68	0.0004	
A^2	200.13	1	200.13	57.59	< 0.0001	
B^2	175.76	1	175.76	50.58	< 0.0001	
C^2	200.49	1	200.49	57.69	< 0.0001	
D^2	72.34	1	72.34	20.82	0.0004	
Residual	48.65	14	3.48			
Lack of Fit	43.41	10	4.34	3.31	0.1299	not significant
Pure Error	5.24	4	1.31			
Cor Total	1485.28	28				

4.3.5 Fit Statistics

Table 4. 7: Fit Statistics

Std. Dev.	1.86
Mean	78.52
C.V. %	2.37
R^2	0.9672
Adjusted R^2	0.9345
Predicted R^2	0.8261
Adeq Precision	20.1039

The coefficient of determination (R^2) establishes the quadratic model's precision, and the e estimated R^2 for the selected model was found to be 0.9672 demonstrating the model's capacity to depict a variability of 90.78% and verifying its reliability in generating the predicted values. The difference in values between predicted R^2 (0.8261) and adjusted R^2 (0.9345) is less than 0.2, implying that they were in reasonable agreement. The reliability of the experiments was demonstrated by a coefficient of variation (CV) value of 2.37% (Table 4.7). Since CV measures deviation as a percentage of the mean, a low value is preferred. In order to determine the signal-to-noise ratio of the chosen model, the value of adequate precision must be greater than 4 and the equivalent value was determined to be 20.10, indicating an adequate signal to noise ratio. Consequently, it is desirable for the chosen model to establish the relationship between the operational parameters and the response. The model's fitness was good as indicated by the Lack of fit F-value (3.31). Fig

4.7 represents the relationship between the actual experimental results and the predicted values. Within the intended range, the model and experimental results fitted reasonably.

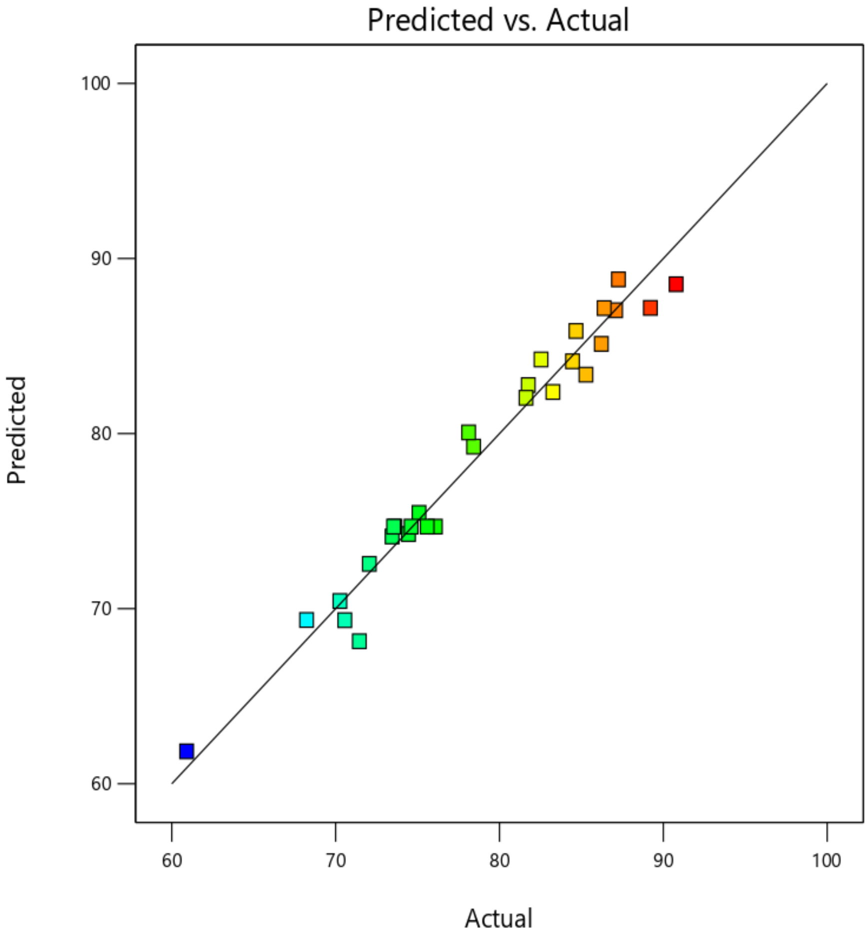


Figure 4. 5: Actual vs Predicted yield of biodiesel

4.4 Optimization of variables Affecting Biodiesel yield

4.4.1 Effect of Catalyst concentration and Methanol-oil-molar ratio on biodiesel yiel

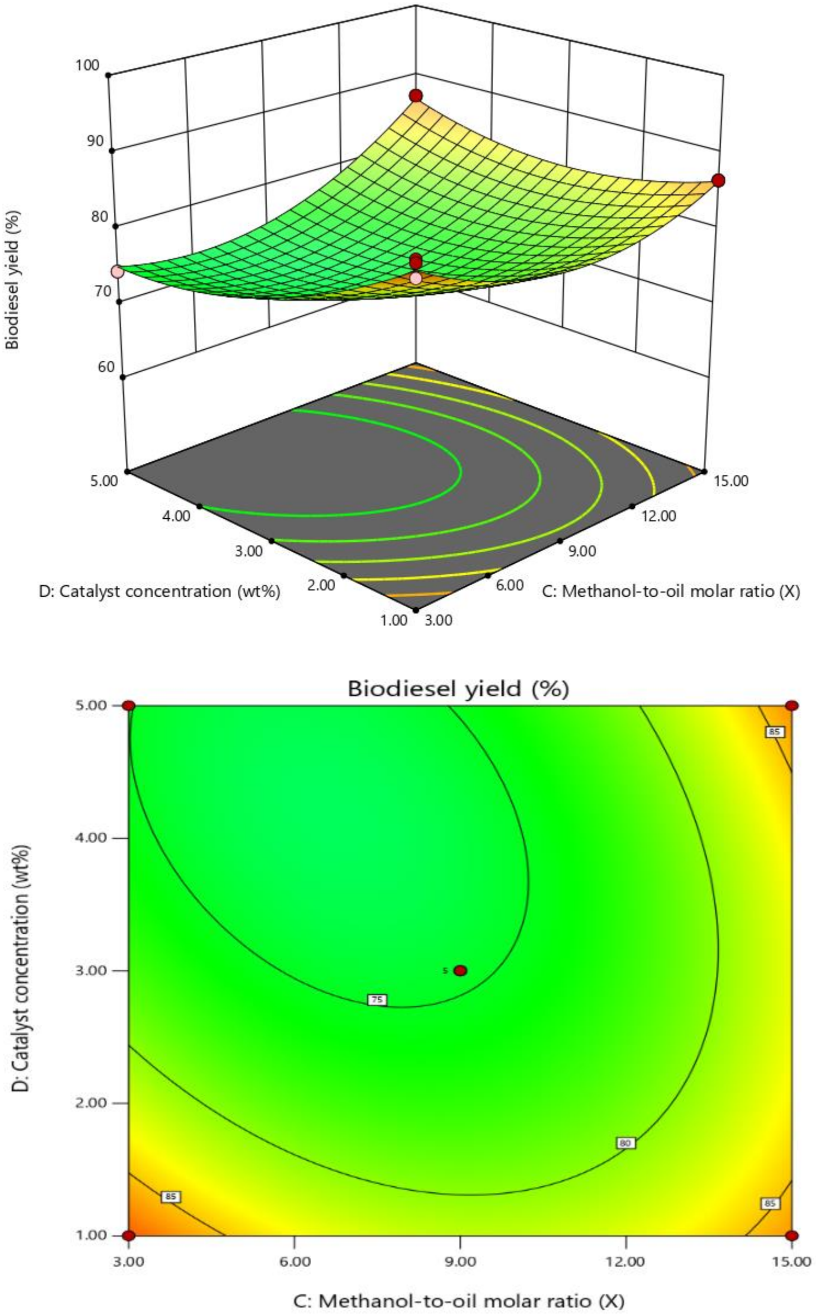


Figure 4. 6: 3D Representation and contour plots showing the effect of catalyst concentration and Methanol-oil ratio on Waste Vegetable oil biodiesel yield

Figure 4.7 shows the effect of methanol-oil molar ratio and catalyst concentration on biodiesel yield. From the figure, an increase in catalyst concentration leads to an increase in biodiesel yield. It is observed that the yield increases as the catalyst concentrations increase at a high alcohol to oil molar ratio. The rate of increasing biodiesel yield changes slowly as the concentration of the catalyst gradually decreases at the other alcohol molar ratio. The biodiesel yield was low at low catalyst concentration (1-2wt%) and lower methanol contents (3-6), this can be attributable to the presence of few active sites and an inadequate amount of methanol necessary for the process to convert the triglycerides to methyl esters. Similarly, (Balajii & Niju, 2019b) observed same trend when *Musa acuminata* pendicule was utilized for biodiesel production.

4.4.2 Effect of Catalyst Concentration and Reaction time on biodiesel yield

Figure 4.8 depicts the response for the interacting factors of catalyst concentration and reaction time. Increasing the catalyst concentration and reaction time were observed to increase biodiesel yield. However, with the addition of an excessive amount of catalyst, the yield first increases and then decreases. This may be due to the viscosity of the reactant-catalyst mixture, which creates problems with mixing and hence inadequate reaction. Similar trends were reported by (M. Agarwal et al., 2012) for the transesterification of waste cooking oil to study the catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel production.

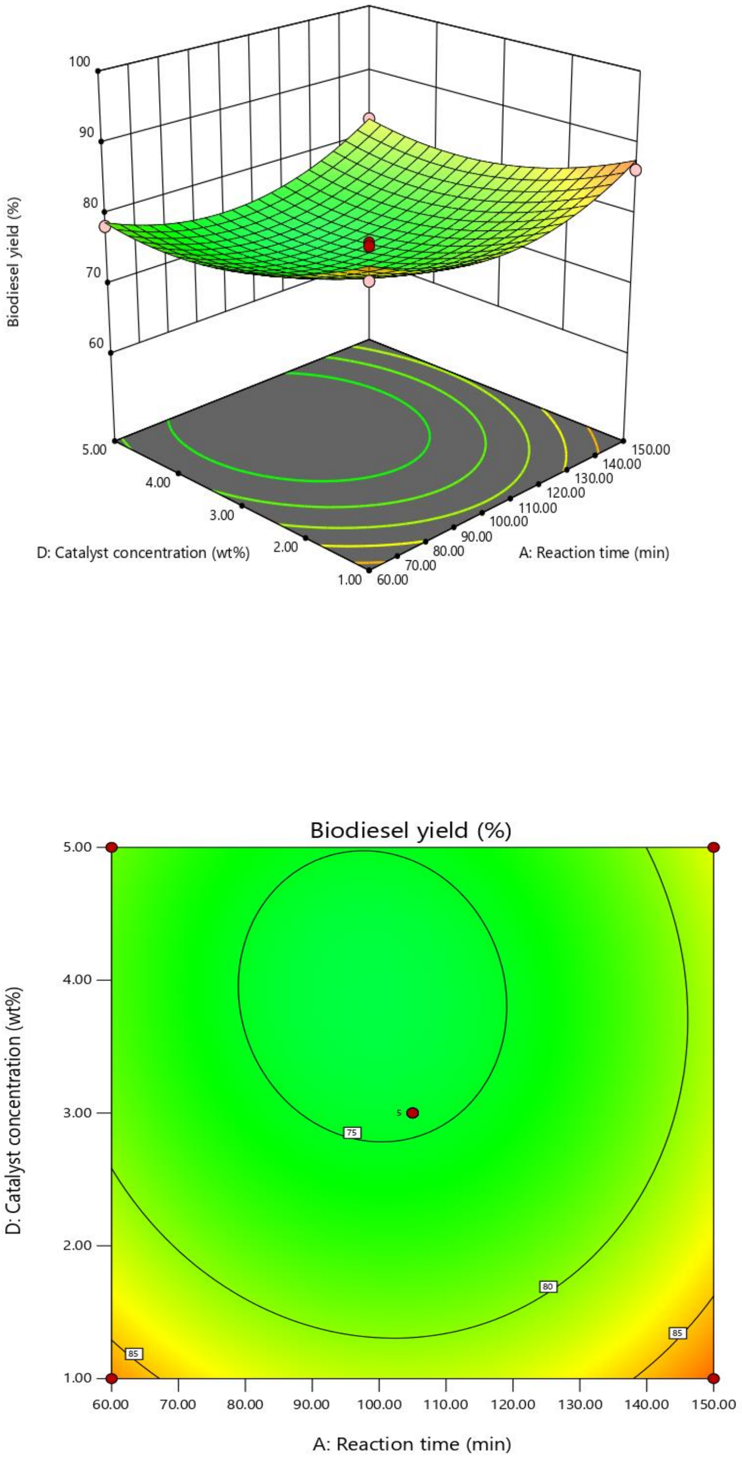


Figure 4. 7: 3D Representation and contour plots showing the effect of catalyst concentration and reaction time on Waste Vegetable oil biodiesel yield

4.4.3 Effect of Reaction temperature and Reaction time on biodiesel yield

Figure 4.9 shows the surface plot of the WVO yield as a function of reaction temperature and reaction time while the methanol-to-oil ratio and catalyst concentration was kept constant. The amount of biodiesel produced increases as both the temperature and the reaction time increase. The surface plot shows that the maximum biodiesel yield was attained at the highest reaction temperature within the range of 50-70℃ and reaction time within the range of 100 – 130min. On increasing the temperature from 55 to 72℃ there was a tremendous increase in biodiesel yield at a corresponding value of 75.09% while at a reaction time within the range of 60- 110℃ there was an increase in yield but subsequent decrease at 110 to 150 ℃. In order to overcome the diffusion resistance of the catalyst, alcohol, and oil feedstock mixture, a higher temperature is preferred, since this will lead to a greater number of collisions between the reactant molecules (Makgaba et al., 2018). In this study, biodiesel production was maximized at 63.34(91.8%). This result was consistent to those of (Etim et al., 2021)who reported a temperature of 65 °C to obtain a maximum biodiesel yield of 91.2% from linseed oil using waste eggshell and pawpaw peel catalyst.

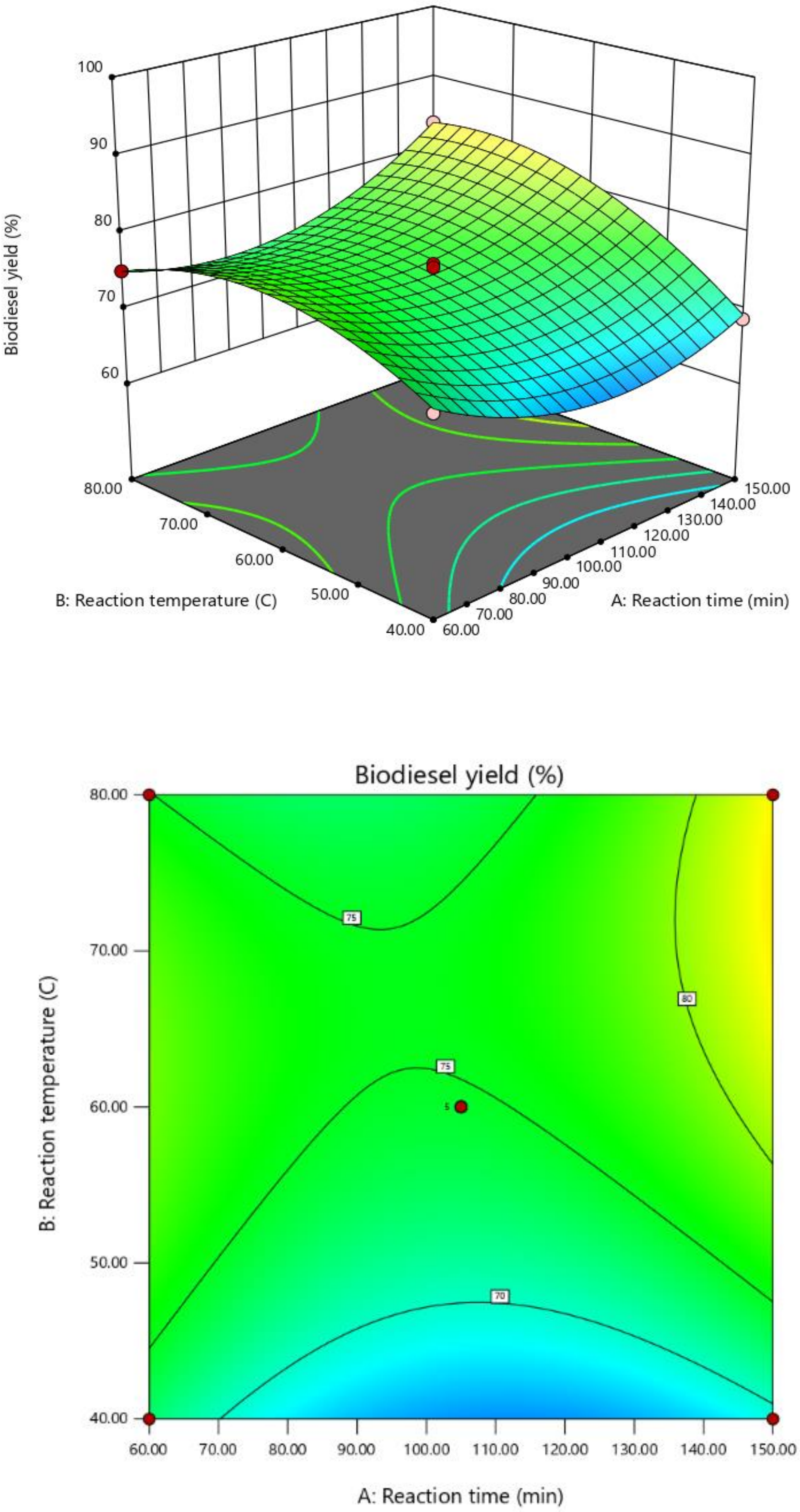


Figure 4. 8: 3D Representation and contour plots showing the effect of Reaction temperature and reaction time on Waste Vegetable oil biodiesel yield

4.4.4 Effect of Methanol-oil-ratio and Reaction time on Biodiesel yield

Figure 4.10 depicts the relationship of time and methanol-oil ratio on biodiesel yield. Biodiesel yield steadily increases with time at low methanol-oil concentrations, while it decreases with time at high alcohol concentrations. Within the first 60–70 minutes of the process, the biodiesel production initially increases with the ratio of methanol to oil concentration, but subsequently begins to decrease. Due to the fact that the transesterification reaction is reversible by its very nature, suggests that the drop in biodiesel production that was observed could be related to the likely loss of fatty acids as the reaction continues for a longer period of time (Makgaba et al., 2018). Similar trend was observed by (Yin et al., 2012) for the transesterification of sunflower oil. They attributed the decrease in yield with methanol-oil ratio rise to the prolonging of reaction time during transesterification reaction.

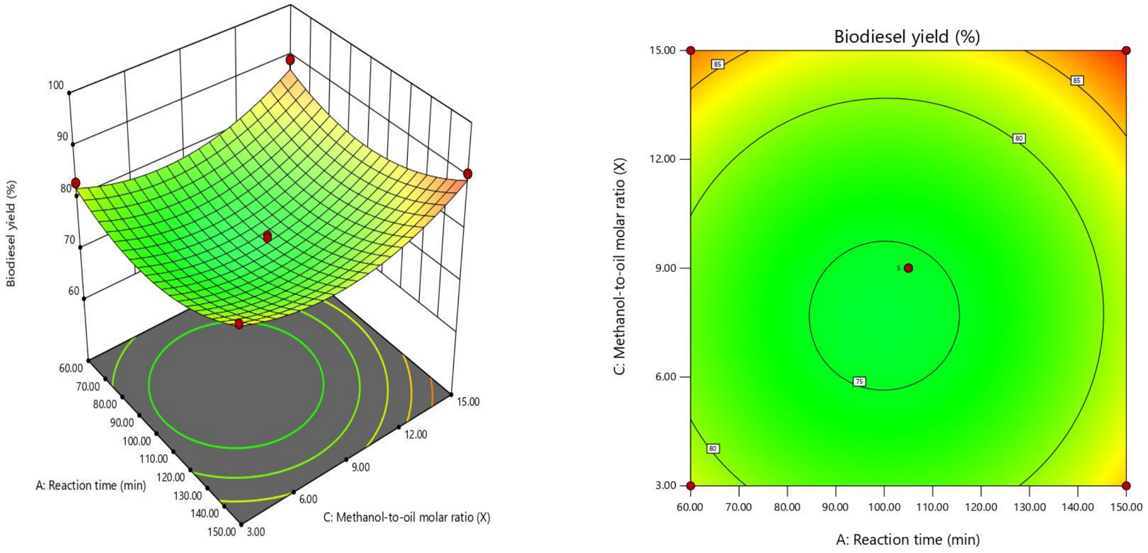


Figure 4. 9: 3D Representation and contour plots showing the effect of Reaction time and Methanol-oil ratio on Waste Vegetable oil biodiesel yield

4.4.5 Effect of Methanol-oil-ratio and Reaction Temperature on Biodiesel

Figure 4.11 demonstrates the interaction between the methanol-oil molar ratio and reaction temperature with relation to the biodiesel yield at constant catalyst loading and reaction time. It can be dedcued from the plot that the biodiesel yield increases with increase in temperature towards 50.00ºC up to 9 mol/mol ratio and thereafter significantly decreases with both a drop in temperature and methanol-oil ratio content. The contour plot reveals that more than 82.85% of yield was produced between 3-9 mol alcohol and 50-60℃ temperature.

With an increase in temperature (70-80°C) comes a gradual decrease of the rate at which biodiesel production increases. This may be because methanol is vaporized at high temperatures, and the formation of methanol vapor bubbles lowers biodiesel output. However, at higher methanol-oil concentrations, yield decreases. This may be due to the high solubility of methanol in glycerol, and an increase in glycerol solubility leads to a difficulty in separation of ester from water layer (A. K. Agarwal, 2007; Degfie et al., 2019). Similar results were observed by (Tshizanga et al., 2017) for the optimisation of biodiesel production from waste vegetable oil and eggshell ash.

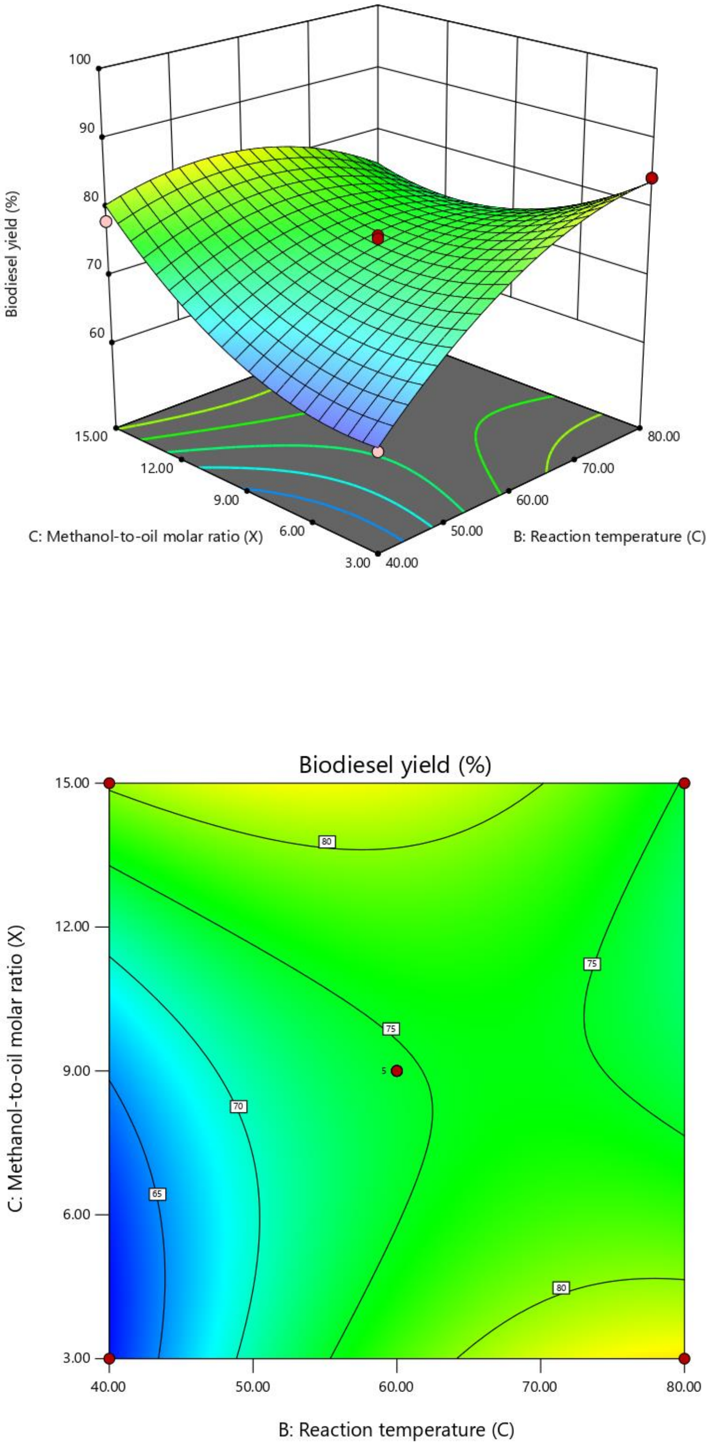


Figure 4. 10: 3D Representation and contour plots showing the effect of Methanol-oil ratio and Reaction Temperature on Waste Vegetable oil biodiesel yield

4.4.6 Effect of Catalyst concentration and Reaction temperature on biodiesel yield

Figure 4.12 displays the influence of temperature and catalyst concentration on biodiesel yield. At a low level of catalyst concentration, the results demonstrate that an increase in temperature results in an increase in yield. This might be as a result of the transesterification reaction being expedited by more energy input, which increased the molecules' collision (Hoque et al., 2011). The rate of biodiesel yield increases as the temperature increases at intial point, achieving its maximal yield at intermediate catalyst concentrations, and subsequently decreases at high catalyst concentration. This is the due to a negative temperature-concentration interaction as well as a negative quadratic concentration coefficient, likely resulting from soap formation side reactions. Similar results were obtained by (Gupta et al., 2016) for the optimization of biodiesel production from mixture of edible and nonedible vegetable oil.

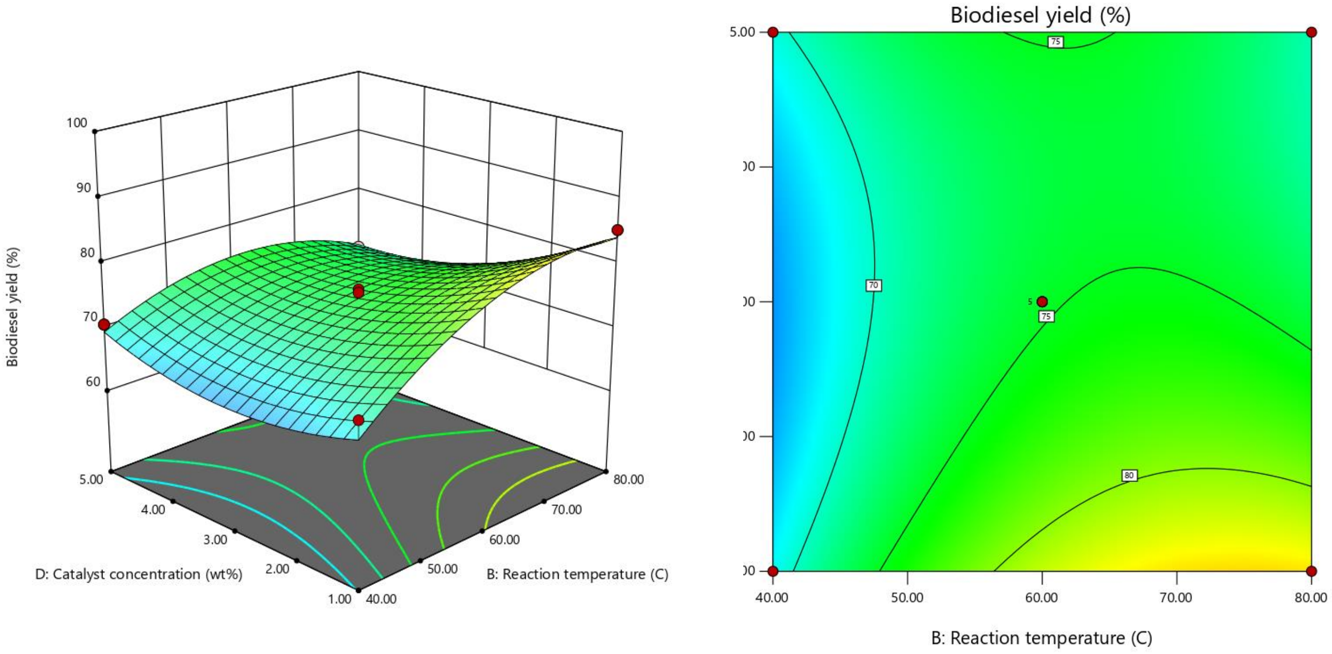


Figure 4. 11: 3D Representation and contour plots showing the Catalyst Concentration and Reaction Temperature on Waste Vegetable oil biodiesel yield

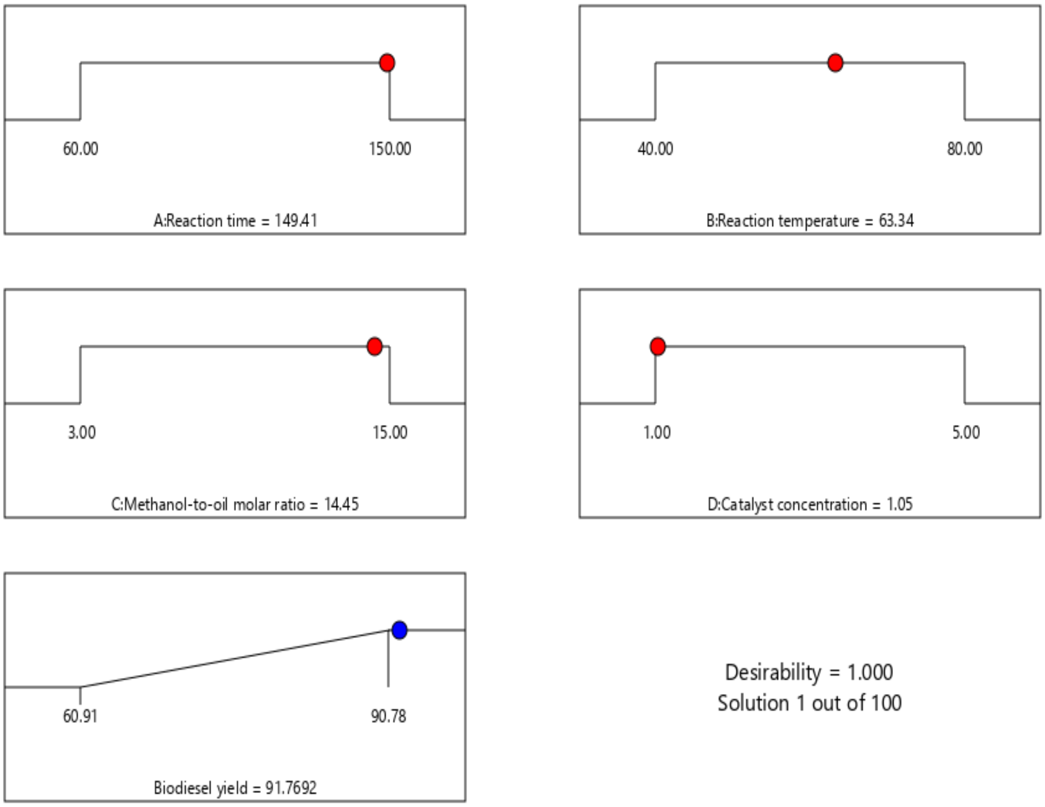


Figure 4. 12: Showing the Optimum biodiesel yield Parameters

A numerical optimization approach based on desire functions was utilized to maximize the response (% biodiesel yield) from the WVO transesterification reaction. The goal of optimization is to identify the ideal conditions that maximize or minimize the process' response variable. Calcined fusion of cockleshells and watermelon peels promoted a transesterification reaction in which the best condition for biodiesel production was identified at a temperature of 63.34℃, catalyst concentration of 1.05 wt%, reaction time of 149.41 min and methanol / oil molar ratio of 14.45:1 with the predicted biodiesel yield of 91.77 wt%. The reliability of this condition was further confirmed by performing three other experiments, and a weighted average biodiesel yield of 91.92 wt% was determined for the procedure. As can be seen, the predicted yield and the actual yield from the experiment are in agreement. The optimized biodiesel production parameters are in some level of agreement those of prior studies (Table 4.14)

Table 4. 8: Comparison of biodiesel production conditions with previous studies

Feedstock	**Catalyst source**	**Methanol to oil ratio**	**Catalyst loading (wt%)**	**Reaction time (min)**	**Reaction temperature (°C)**	**Biodiesel yield (%)**	**Reference**
Linseed oil	Calcined eggshell and pawpaw peels	14.9:1	3.78	80	65	91.2	(Etim et al., 2021c)
Waste cooking oil	Ostrich eggshell	12:01	1.5	120	65	96	(Tan et al., 2015b)
Waste Vegetable oil	Egg shell	22.5:1	3	330	65	91	(Tshizanga et al., 2017b)
Waste cooking oil	Waste Cockle shell	8.5:1	3.5	44	—	94.4	(Boey et al., 2011)
Waste cooking oil	waste Malleus malleus shells	11.85:1	7.5	86.25	65	93.81	(Niju et al., 2020)
Waste cooking oil	Cockle shell and watermelon peels	14.45:1	1.05	149.41	63.34	91.77	Present study

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Biodiesel is an efficient substitute for conventional diesel, and it may be utilized without any modifications to the engine. This research examined the development and potential of a bi-component bio-waste heterogeneous catalyst obtained from the fusion of calcined cockle shells and watermelon peels for the transesterification of waste vegetable oil (WVO). From the study, the following findings can be drawn:

1. Cockle shell and watermelon peels has been characterized and it has demonstrated that it is capable of functioning as a sustainable feedstock for biodiesel production.
2. The synthesized catalyst's analysis revealed that calcium (4.3) and K (5.2) were the catalysts' major active element, responsible for its high catalytic function.
3. The qualities of biodiesel produced were determined to be compliant with biodiesel standards (ASTM D 6751, EN 14214), which indicates that it is suitable for use in the powering of internal combustion engines.
4. Modeling and optimization of the transesterification process was accomplished by RSM. To evaluate the interaction effects between the process variables of reaction time, catalyst concentration, methanol-to-oil ratio, and temperature the BBD based on three levels and three parameters was employed.
5. The most influential variable that played a significant role in determining the final yield was temperature, followed by the concentration of the catalyst and methanol-oil ratio.

6. At optimal process parameters of reaction duration of 149min, temperature of 63.34°C, methanol-to-oil ratio of 14.45, and catalyst concentration of 1.05 wt%, the optimal biodiesel yield of 91.77 was attained.

5.2 RECOMMENDATIONS

The following recommendations are made on the basis of the findings of this study conducted on the optimization of waste cockle shells and watermelon peels for the production of biodiesel:

1. Due to the extensive research on the variety of catalysts for oil-to-biodiesel synthesis, a study on the synthesis of catalyst with tailored surface morphology, which has balanced active sites of acidic and basic nature can be carried out.
2. Heterogeneous catalysts have several advantages, they nevertheless take a long time to complete the reaction needed for biodiesel production. Hence the reaction time, as well as catalyst recyclability both need to be improved in future studies.
3. Future research can be carried out to identify the uncertainties around the economic and environmental effects of biodiesel and develop techniques for handling them.
4. Further investigation should be conducted into the reusability of catalysts as well as their reactivation and regeneration.

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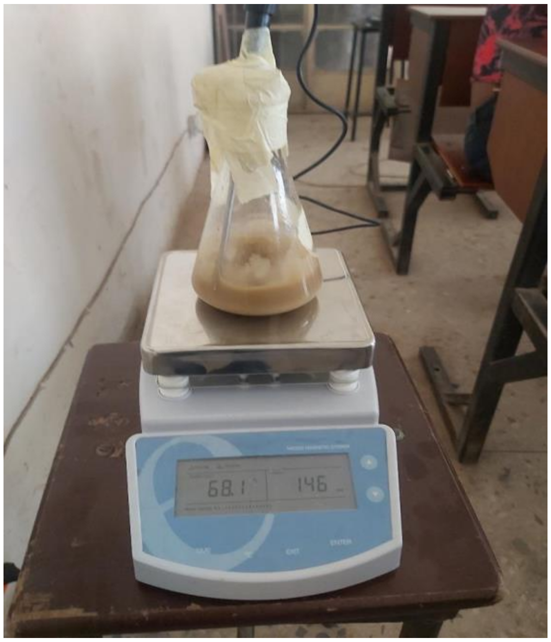
APPENDIX

Calcined cockle shell, Carbonized watermelon peels, and Nickel nitrate solution

Wet Impregnation of catalyst and nickel nitrate precursor



Simultaneous Esterification and Transesterification reaction using a Bi-functional catalyst

Reaction product left to settle into two distinct phases after reaction

vo

COCKLE SHELL

BIODIESEL PRODUCED