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Biodiesel Synthesis from Waste Vegetable Oil Utilizing Eggshell Ash as an Innovative Heterogeneous Catalyst

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Abstract: The objective of this research is to explore the production of biodiesel using waste vegetable oil (WVO) as the primary feedstock and calcined eggshell ash as an environmentally sustainable catalyst. The WVO, characterized by a free fatty acid content of 2.86%, serves as the primary feedstock for biodiesel production through transesterification. The eggshell ash undergoes a rigorous process, including washing with distilled water to remove impurities, drying at 100°C for 24 h, crushing into fine particles, and final calcination in a muffle furnace at 900°C. Process optimization is achieved by varying key reaction parameters, including temperature, catalyst loading, and the methanol-oil molar ratio. The optimal conditions are identified at 65°C, utilizing a methanol-oil molar ratio of 6:1 and a 5 wt% catalyst loading. Under these optimized reaction conditions, a substantial biodiesel yield of 91.3% is obtained. The produced biodiesel meets the stringent quality requirements specified by the American Standard (ASTM D 6751) and European Standard (EN 14214) for biodiesel fuel, ensuring its suitability for various applications. This study demonstrates the potential of utilizing calcined eggshell ash as an eco-friendly catalyst for sustainable biodiesel production from WVO.

Keywords: biodiesel, heterogeneous catalyst, transesterification, biomass, eggshell

1. Introduction

There is growing concern regarding the use of diesel due to the adverse impacts associated with the escalating levels of greenhouse gases in the atmosphere [1]. This surge is a consequence of the substantial emission of carbon dioxide resulting from the incomplete combustion of diesel fuel in various vehicular applications [2]. Additionally, the release of pollutants, such as nitrogen oxides, stemming from the incomplete combustion of diesel fuel, significantly contributes to smog formation and can trigger severe respiratory complications [3].

The heightened energy demands of both industrialized nations and domestic sectors have intensified pollution challenges due to the

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widespread reliance on fossil fuels [4]. This underscores the imperative to create sustainable energy sources that leave a smaller environmental impact compared to traditional fossil fuels like diesel [5].

Biodiesel from renewable resources such as vegetable oils and animal fats is an excellent replacement for conventional, petroleum-based diesel due to their biodegradability, non-toxicity, and lower emission profiles when compared to traditional diesel fuel [6, 7]. Biodiesel offers a sustainable and renewable alternative to traditional diesel fuel, sharing properties similar to its petroleum-derived counterpart [8]. It is characterized by a chemical structure primarily composed of alkyl esters, originating from materials such as fats from animals and oils sourced from vegetables [9]. Feedstock for biodiesel production is obtained from agricultural commodities like palm oil, soybeans, sunflower seeds, animal fats, and vegetable oils. Moreover, biodiesel synthesis can involve biological organisms such as algae and cyanobacteria, further enhancing its potential as an adaptable and eco-friendly energy source [10].

These diverse sources serve as the raw materials for biodiesel production, also known as biofuel [6]. The biodiesel production process involves a chemical transformation of the molecular compositions of its feedstock using alcohol and catalysts. Chemically [11–13], biodiesel produced through this method is classified as fatty acid methyl ester (FAME) [14]. The adoption of biodiesel as a sustainable energy alternative holds great promise due to its renewability and its ability to generate fewer environmentally harmful exhaust emissions compared to traditional petroleum-based diesel fuels, aligning with the pursuit of sustainable energy solutions [15].

Biodiesel can be synthesized through a chemical reaction known as transesterification, which typically employs short-chain alcohols [9]. Various alternative techniques are available to facilitate this process, including supercritical processes and ultrasonic methods [16]. Transesterification serves as the primary method for separating glycerin from vegetable oils or animal fats. This chemical conversion results in the production of methyl esters, the desired biodiesel product, while glycerin is commonly repurposed for soap production and various other applications.

The transesterification process involves the interaction of oil and alcohol in the presence of a catalyst, ultimately yielding biodiesel with glycerol as a by-product. The quality of the final product depends on several factors, including the type and quantity of the catalyst, the nature of the oil feedstock, the alcohol-to-oil ratio, the presence of free fatty acids (FFAs), and water content in the oil [17]. Operational parameters like agitation speed and temperature also play a crucial role in determining the quality of the product [18].

Considering that vegetable oils currently dominate the feedstock landscape in commercial biodiesel production, this research primarily focuses on biodiesel synthesis utilizing vegetable oils as the primary source. In addition to its role as an alternative fuel, biodiesel is well-regarded for its capacity to enhance lubricity when blended with petroleum diesel [19]. Biodiesel exhibits complete miscibility with petroleum diesel at all ratios, and the mere addition of 1 vol.% biodiesel significantly improves the lubricating properties of the blend [20]. The numerous advantages of biodiesel, especially its favorable environmental attributes, have prompted governments worldwide to encourage its adoption through tax incentives and regulatory mandates [21]. Biodiesel can be produced both on a small scale and in large-scale facilities [22]. Notably, Singapore is now home to the largest biodiesel production plant globally, boasting an annual production capacity of 800,000 tons, owned and operated by Neste Oil, as detailed in the Renewable Energy Policy Network, REN21 [23].

Traditionally, first-generation biodiesel feedstock has predominantly relied on edible oils, as detailed by Reddy et al. [24]. However, the prevailing trend is veering away from these sources due to concerns related to competition with food resources and environmental issues linked to waste disposal [25]. Instead, there is a growing emphasis on the utilization of non-edible oils and waste vegetable oil (WVO) as promising feedstock options, considering them as low-grade resources for biodiesel production, as underscored by Topi [8]. These oils, chosen as biodiesel feedstock, have garnered significant attention due to their renewability and ready availability, as highlighted in Pikula et al. [26]. Biodiesel derived from low-grade vegetable oils such as WVO and non-edible oils like jatropha, karanja, and mahua, which contain elevated levels of FFAs, presents superior economic viability compared to petroleum-based counterparts [27]. This transition leads to cost reduction and a subsequent decrease in greenhouse gas emissions, as elucidated by Ogunkunle and Ahmed [28]. While the literature extensively covers biodiesel production using WVO, it is pertinent to acknowledge significant drawbacks, particularly concerning the presence of impurities and the substantial abundance of FFAs in this feedstock.

Biodiesel production commonly relies on catalysts, which can be either acids or bases, available in both homogeneous and heterogeneous forms [29]. Each type possesses distinct advantages and disadvantages due to their unique properties. Notably, base catalysts exhibit higher reaction rates in biodiesel production compared to acid catalysts, with their optimal activity occurring at temperatures near the boiling point of methanol, approximately 65°C, as indicated by Jayakumar et al. [30].

Previous research has highlighted the effectiveness of heterogeneous catalysts, particularly base catalysts, in biodiesel production from oils with elevated levels of FFAs [23, 31, 32]. This effectiveness arises from their ability to absorb water present in WVO, preventing the formation of soap resulting from FFAs [31]. Moreover, heterogeneous catalysts offer the convenience of easy removal from the reaction mixture for potential reuse [30]. However, it is important to note that these catalysts face significant mass transfer limitations, leading to the formation of three phases alongside oil and alcohol, as reported by Boey et al. [33]. To achieve optimal biodiesel yields, higher temperatures and extended reaction times are often necessary, as highlighted by Sakthivel et al. [34].

Recent investigations have explored an innovative approach to biodiesel production, involving the use of ash derived from waste eggshells as heterogeneous catalysts, as outlined by Yaşar [35]. Heterogeneous base catalysts made from alkaline earth metal oxides have been studied for their potential in biodiesel production. These studies have demonstrated the viability of CaO extracted from waste material ash as a promising heterogeneous catalyst. This novel approach not only aligns with eco-friendly principles but also offers economic benefits.

This study aims to investigate the production of biodiesel using WVO with a significant FFA content. Furthermore, it aims to assess the feasibility of utilizing a heterogeneous catalyst obtained from eggshell ash in the transesterification process. The study will encompass the examination of various factors and operational

conditions, including temperature variations, the alcohol-to-oil molar ratio, catalyst loading, and the evaluation of the physical and chemical properties of both the oil and biodiesel.

2. Materials and Methods

2.1. Materials

The materials are as follows: WVO, locally sourced eggshells, methanol, sulphuric acid (H_2SO_4), benzene, chloroform, Wijs solution, sodium thiosulfate ($Na_2S_2O_3$), starch solution, potassium iodide (KI), viscometer, etc.

2.2. WVO analysis

While WVO can be subject to analytical techniques such as thin layer chromatography and gas chromatography (GC), the present practical implementation involved manual analysis of both the WVO and the resulting biodiesel. Initial physical treatment procedures, including oil heating and sieving, were executed to eliminate solid particles and food debris. A 100-micron mesh sieve was used to filter out solid particles from the waste cooking oil according to a process described by El-Far et al. [36], and it was revealed that the total suspended solids in the filtered oil were reduced by 98.6%. This indicates that a sieve with a fine mesh can effectively remove most of the solid impurities from the oil, thereby optimizing the reaction conditions. Subsequently, the WVO underwent comprehensive characterization encompassing acid value, percentage of free fatty acid (%FFA) content, density, specific gravity, viscosity, kinematic viscosity, iodine value, and moisture content assessments.

2.3. Acid value

The acid value of the WVO was assessed through a titration method [37]. This value serves to quantify the quantity of FFA present in the oil sample [38]. The acid value is determined by titrating a known concentration of potassium hydroxide (KOH) with a sample of the oil [39]. Manual titration necessitates the use of a color indicator, such as phenolphthalein, and organic solvents, such as toluene/benzene or isopropyl alcohol, to dissolve the oil sample and achieve a clear end point.

During the practical procedure, a 0.05 M KOH solution was introduced into the burette, while 10 ml of benzene and 10 ml of ethanol were separately measured in two measuring cylinders. A 1 g sample of the oil was measured and placed in a conical flask. Subsequently, 10 ml of benzene and 10 ml of ethanol were mixed with the oil sample and stirred until a homogenous mixture was obtained. Three drops of phenolphthalein were added to the mixture, which were then titrated with the 0.05 M KOH solution until neutralization occurred. The titre value obtained was utilized to calculate the acid value using the following formula as seen in Equation (1):

$$\text{Acid value} = \frac{(\text{Titre value} - \text{Blank value}) \times \text{molecular weight, KOH} \times \text{conc. KOH}}{\text{mass of oil}} \tag{1}$$

2.4. %FFA content

The percentage of FFA present in the oil was determined during the practical procedure through a comprehensive calculation approach rather than a stepwise one [32]. It is well-established in the literature that maintaining the %FFA content below 1% (of the oil) is crucial [32]. This ensures that glycerol production is minimized during the transesterification reaction, thereby promoting a higher biodiesel yield [23, 31]. The %FFA content was derived from the acid value of the oil that was tested, using the following formula as seen in Equation (2):

$$\%\text{FFA content} = \frac{\text{Acid value}}{2} \tag{2}$$

2.5. Density and specific gravity

The density of the oil was determined using a density bottle. Initially, the temperature of the oil was recorded according to Dey et al. [37]. Subsequently, the mass of the empty density bottle (50 ml) with its cork was recorded, as well as the mass of the density bottle filled with the oil sample and its cork. The density was calculated using the following formula as seen in Equation (3):

$$\text{Density} = \frac{\text{mass of density bottle (with oil sample)} - \text{mass of empty density bottle}}{\text{volume of oil sample}} \tag{3}$$

The density of water varies at different temperature. Hence, the specific gravity of the oil was given as follows as seen in Equation (4):

$$\text{Specific gravity at a given temp} = \frac{\text{density of oil at given temp}}{\text{density of water at given temp}} \tag{4}$$

2.6. Viscosity and kinematic viscosity

The viscosity of the oil was determined using a viscometer at the same temperature and a specified volume of the oil [40]. The kinematic viscosity was calculated using the following formula as seen in Equation (5):

$$\text{Kinematic viscosity } (\upsilon) = \frac{\text{viscosity } (\mu)}{\text{density } (\rho)} \tag{5}$$

2.7. Iodine value

The iodine value of an oil or fat is a metric that quantifies the amount of iodine, in grams, absorbed by 100 g of the oil or fat during analysis with Wijs solution. This parameter is indicative of the level of unsaturation within the fat, primarily denoting the quantity of double bonds present [41].

To determine the iodine value of the oil sample, a series of preparations were made, including Wijs solution, starch solution, potassium iodide, and chloroform solution. Subsequently, 0.5 g of the oil sample was placed in a conical flask labeled “oil sample,” and another conical flask labeled “blank” was prepared. Both conical flasks received 10 ml of chloroform and 10 ml of Wijs solution, which were thoroughly mixed. The flasks were then covered with foil paper and left undisturbed for approximately 30–60 min. After this incubation period, 10 ml of potassium iodide (KI) was added to both conical flasks.

A 0.1 M solution of sodium thiosulphate ($Na_2S_2O_3$) was prepared and placed in a burette. Three drops of a starch solution with a known concentration were added to both mixtures. Subsequently, both mixtures were titrated with the 0.1 M $Na_2S_2O_3$ solution until neutralization was achieved. The titre values obtained from these titrations were then used to calculate the iodine value using the formula below as seen in Equation (6):

$$\text{Iodine value} = \frac{12.69 \times (\text{Titre value of blank} - \text{Titre value of oil sample}) \times \text{Conc } N_{a2}S_2O_3}{\text{mass of oil}} \quad (6)$$

2.8. %Moisture content

Moisture content, also referred to as water content, represents the amount of water present in a given oil sample. Various methods can be employed to determine the moisture content of oils, with the oven drying method being utilized in this practical study.

To determine the moisture content, 3 g of the oil sample was accurately measured in a small beaker. Subsequently, the beaker with the oil sample was placed in an oven and subjected to drying for a duration of 5–6 h. After the drying process, the beaker containing the oil was removed from the oven, and its new mass was recorded. This new mass was lower than the initial mass due to the removal of water from the oil during the drying process.

The moisture content was then calculated using the following formula as seen in Equation (7):

$$\%\text{Moisture content} = \frac{\text{initial mass of oil} - \text{final mass of oil}}{\text{initial mass of oil}} \times 100 \quad (7)$$

2.9. Catalyst preparation

To prepare the base catalyst from eggshell, a series of pre-treatment processes were carried out to ensure the eggshell was free of impurities as seen in Figure 1. The collected eggshells underwent a thorough washing using deionized water to remove the dried albumen layer and any attached dirt. Subsequently, the eggshells were cleaned and dried in an oven at 100°C for a period of 24 h to eliminate any residual moisture. Following this, the eggshells were finely chopped into small pieces and subjected to calcination at 900°C for a duration of 6 h. This process, known as calcination, is employed to convert calcium carbonate ($CaCO_3$), which is the main component of eggshells, into calcium oxide (CaO) [42].

The calcination process at these elevated temperatures serves to reduce the particle size, thereby increasing the surface area of the material. Furthermore, it leads to a reduction in the carbon content within the substance.

2.10. Esterification reaction

Esterification, a sub-category of the transesterification process, serves as a pre-treatment step with the primary objective of reducing the FFA content in WVO [43]. In this study, 200 g of WVO was introduced into a conical flask, while separate beakers contained 1.2 wt% sulfuric acid catalyst and 24 wt% methanol. The oil was placed on a magnetic stirrer, heated, and stirred until its temperature reached 60°C. Subsequently, the sulfuric acid and methanol were gently mixed and added to the heated and stirred oil. The reaction continued for approximately 1 h, resulting in the formation of alkyl esters and water as products.

2.11. Transesterification reaction

The transesterification reaction experiment closely mirrored the esterification process, albeit with the utilization of calcined eggshell ash, CaO, as the catalyst. Methanol served as the primary solvent, leading to the production of FAME. In a conical flask containing 200 g of WVO, methanol and CaO were introduced. The reaction was facilitated by a magnetic stirrer, which simultaneously heated and stirred the mixture.

The study aimed to optimize several key parameters, including temperature (ranging from 55° to 75°C), catalyst loading (ranging from 1 to 5 wt% of oil), and alcohol-to-oil ratio (ranging from 6:1 to 10:1) while keeping two variables constant per run. The mass of alcohol needed for the alcohol-to-oil ratio optimization was calculated based on the specified ratios as seen in Equation (8):

For example, for alcohol-to-oil ratio of *P*:*Q*.

$$\frac{\text{mass of oil}}{\text{molecular weight of WVO}} \times P = \frac{\text{mass of alcohol}}{\text{molecular weight of alcohol}} \times Q \quad (8)$$

2.12. Experimental procedure

To investigate the influence of temperature, catalyst loading, and alcohol-to-oil molar ratio on biodiesel yield, a total of 15 separate experimental runs were conducted. Methyl ester synthesis took place in 500 ml conical flasks, each containing 200 g of WVO.

Figure 1
Egg shell ($CaCO_3$) converted to CaO $CaCO_3 \rightarrow CaO + CO_2$ (highly endothermic in nature, +183 KJ/mol)

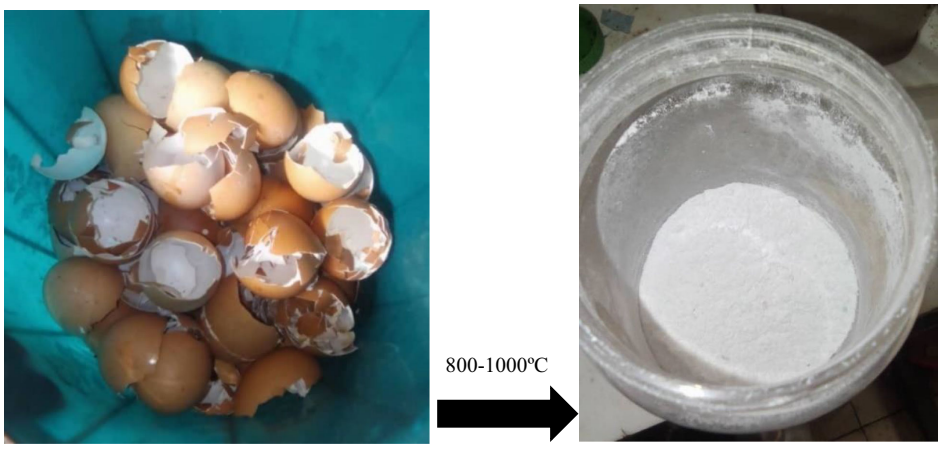


Figure 2
(a) Washing biodiesel and (b) washed and dried biodiesel



These experimental runs were designed to vary three key factors: temperature, alcohol-to-oil ratio, and catalyst loading. Specifically, five different levels were explored for each of these parameters.

The first set of runs, labeled by temperature, encompassed temperatures of 55, 60, 65, 70, and 75°C while keeping alcohol-to-oil ratio and catalyst loading constant at 6:1 and 5 wt%, respectively. For each run, 200 g of WVO was heated to the specified temperature in a 500 ml conical flask. Subsequently, a mixture comprising 10 g of CaO suspended in 43.44 g of methanol was introduced, and the resulting suspension was stirred for 1 h. This procedure was repeated for each of the five runs within this group.

The second set of runs, labeled by catalyst loading, kept temperature of 60°C and an alcohol-to-oil ratio of 6:1 constant while varying catalyst loadings, a catalyst loading of 1, 2, 3, 4, and 5 wt% were employed, with each run using 200 g of oil sample.

The third set of runs, labeled by alcohol-to-oil ratio, kept a temperature of 60°C and a catalyst loading of 5 wt% constant while varying alcohol-to-oil molar ratios. The alcohol-to-oil molar ratios explored were 6:1, 7:1, 8:1, 9:1, and 10:1. The process remained consistent, with 200 g of oil sample being heated to 60° C, followed by the introduction of a mixture containing 10 g of CaO suspended in methanol at the specified molar ratio.

After each experimental run, the mixtures were allowed to cool and settle in separate beakers until phase separation occurred. The bottom layers of the systems consisted of glycerine and residual CaO, while the top layers comprised a mixture of methyl esters, unreacted methanol, and intermediates. These top layers were decanted, and the biodiesel was subsequently washed and dried. Any residual FAME combined with CaO was separated using a centrifuge machine to obtain the pure biodiesel. Finally, the yield of FAME produced in all 15 runs was calculated.

2.13. Biodiesel purification

Following the attainment of the optimal yield, crude biodiesel underwent a purification process involving washing with 28% (by volume of the feedstock) of distilled warm water as seen in Figure 2. This procedure, as described by Sisa and Masak (2018), aimed to eliminate impurities and enhance the quality of the biodiesel product. Given that both glycerol and methanol possess high solubility in water, the crude biodiesel readily mixed with the warm distilled water. An agitation was applied at 250 rpm speed using a magnetic stirrer to prevent the formation of emulsions during this phase. The process was iterated until the wash water turned colorless, signifying the thorough removal of impurities.

Subsequently, the biodiesel underwent a drying process, accomplished by applying heat until it attained clarity, as per the methodology outlined by Moradi and Ghanadi [15]. This purification procedure was implemented to ensure compliance with international standard specifications established by the American Society for Testing and Materials (ASTM D 6571) and the European Standard EN 14214. It aimed to eliminate contaminants such as residual methanol, glycerol, catalyst residues, glycerides, and FFAs, all of which have the potential to compromise the quality of biodiesel and impact engine performance, as highlighted in the study by Osorio-Gonz et al.

The yield is calculated as follows: (Equation (9)):

$$\text{Yield } (\%) = \frac{\text{Weight of Biodiesel}}{\text{Weight of Oil}} \times 100 \tag{9}$$

2.14. Biodiesel characterization

Following the purification process, biodiesel underwent a comprehensive characterization to assess its adherence to essential standards, particularly the ASTM specifications and the European Standard EN 14214, in preparation for testing on a diesel engine. The characterization encompassed an array of key properties, including acid value, %FFA content, density, specific gravity, viscosity, kinematic viscosity, flash point, cloud point, pour point, and carbon residue. This rigorous assessment aimed to confirm the suitability of the biodiesel for subsequent engine testing, ensuring compliance with established quality benchmarks.

3. Results and Discussion

3.1. Characterization of WVO

The analysis of WVO involved both pre- and post-esterification assessments, with a focus on various properties critical for biodiesel production as seen in Table 1. Prior to esterification, manual analytical techniques were employed without resorting to GC experiments, relying solely on laboratory equipment. The obtained results are presented in Table 1. The acid value of WVO was determined through titration, yielding a value of 24.4. Subsequently, the %FFA content was calculated, amounting to 12.2%. Literature suggests that elevated FFA levels can diminish catalyst efficacy and reduce biodiesel yield, hence it is recommended that the FFA content in WVO should ideally not surpass 1–3 wt% [44].

Table 1
Waste vegetable oil characterization

Properties	Value (before esterification)	Value (after esterification)
FFA content (%)	12.2	2.81
Density (g/ml)	0.928	0.9
Specific gravity	0.93	0.904
Viscosity (*cP*)	65.4	60.4
Kinematic viscosity (mm^2/s)	69.5	67.1
Iodine value ($g^{-10-2}g^{-1}$)	25.38	33
Moisture content (wt%)	2	1

To address the high %FFA content, an esterification reaction was conducted to reduce it. Following esterification, the titration process was repeated, resulting in an acid value of 5.61, corresponding to a %FFA of 2.81%. Additionally, the density and specific gravity, viscosity and kinematic viscosity, iodine value, and % moisture content were determined both before and after the esterification process. The density and specific gravity of the oil (before esterification) at 28.8°C were 0.928 g/ml and 0.93, respectively, whereas after esterification at the same temperature, these properties measured 0.9 g/ml and 0.904, respectively. The viscosity of the oil before esterification was 64.5 cP, reducing to 60.4 cP after esterification. Correspondingly, the kinematic viscosities were calculated as 69.5 and 67.1 mm^2/s before and after esterification, respectively. The iodine values of the oil before and after esterification were 25.38 and 33 $g/10^2$ g^{-1}, respectively. Finally, the % moisture content of the oil was analyzed, resulting in values of 2% before esterification and 1% after esterification.

3.2. Parameters optimization in biodiesel production

Parameters optimized in the biodiesel production were based on the effect of catalyst loading, temperature, and the methanol-oil molar ratio with respect to biodiesel yield.

3.3. Effect of catalyst loading on biodiesel yield

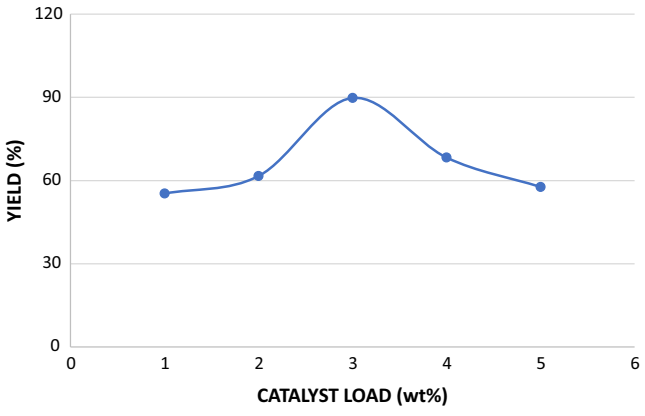
Maintaining all other variables constant, different catalyst loadings were introduced into each sample at levels of 1, 2, 3, 4, and 5 wt% during the transesterification process. The corresponding biodiesel yields were 55.3, 61.6, 89.8, 68.3, and 57.7%, respectively. It was observed that lower catalyst loadings (1–3 wt%) resulted in relatively lower yields (ranging from 55.3 to 61.6%). These lower catalyst concentrations proved insufficient to drive the transesterification reaction to completion for methyl ester formation. The highest biodiesel yield of 89.8% was achieved at the optimal catalyst loading of 3 wt%. Beyond this range (4–5 wt%), a decline in biodiesel yield was evident.

The reaction rates increased proportionally as the reactants occupied more catalytic sites, reaching a saturation point. The transesterification reaction's progress strongly relies on the catalyst's weight, which subsequently influences the yield, as emphasized by Sreenivas et al. (2011). A sufficient increase in catalyst concentration leads to a greater number of active sites, thereby enhancing methyl ester production. As seen in Table 2 and Figure 3, an excessive catalyst loading results in elevated slurry viscosity, leading to suboptimal reaction mixtures, in line with the findings of Salaheldeen et al. [11] and Moradi and Ghanadi [45].

Table 2
Biodiesel yield at different catalyst loading

Runs	Methanol-oil	Temp. (°C)	Catalyst load (wt%)	Yield (%)
1	6:1	60	1	55.3
2	6:1	60	2	61.6
3	6:1	60	3	89.8
4	6:1	60	4	68.3
5	6:1	60	5	57.7

Figure 3
Effect of catalyst loading on biodiesel yield



The graph below shows the increase and decrease in biodiesel yield as the catalyst loading increases from 1 to 5 wt%.

3.4. Effect of temperature on biodiesel yield

While keeping all other variables constant, the reaction temperatures for each sample were set at 55, 60, 65, 70, and 75°C, yielding biodiesel production rates of 63, 74, 91.3, 61.4, and 45.2%, respectively, during the transesterification process. Temperature exerts a significant influence on reaction mass

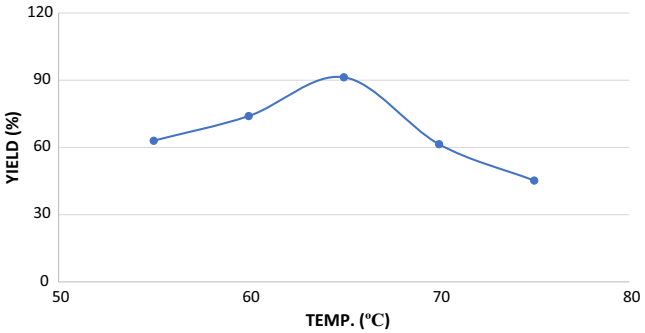
transfer, as noted in prior studies Dias et al., 2013; Osorio-gonz et al., [46]. The optimal temperature, determined to be 65°C, yielded the highest biodiesel production rate at 91.3%.

In the current investigation, elevating the reaction temperature to 65°C resulted in an increased reaction rate due to the augmented energy input and reduced mass transfer resistance. However, surpassing 65°C led to reduced production. This reduction occurred because temperatures exceeding the boiling point of methanol (65°C) caused continuous vaporization of methanol [47, 48], resulting in its transition into the gas phase within the system. Consequently, this led to a reduction in methanol concentration within the reaction medium as seen in Table 3 and Figure 4 (Armendáriz et al., 2015).

Table 3
Biodiesel yield at different temperatures

Runs	Methanol-oil	Temp. (°C)	Catalyst load (wt%)	Yield (%)
1	6:1	55	5	63
2	6:1	60	5	74
3	6:1	65	5	91.3
4	6:1	70	5	61.4
5	6:1	75	5	45.2

Figure 4
Effect of temperature on biodiesel yield



The graph below shows the increase and decrease in biodiesel yield as temperature increases from 55 to 75°C.

3.5. Effect of methanol-oil on biodiesel yield

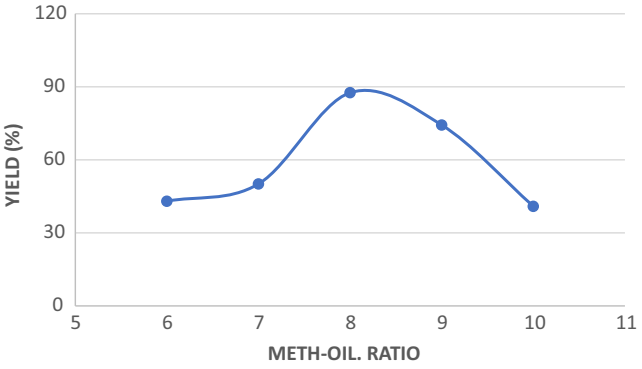
In each sample undergoing the transesterification process, the methanol-oil ratios were varied while keeping other parameters constant. The ratios tested were 6:1, 7:1, 8:1, 9:1, and 10:1, resulting in biodiesel yields of 43, 50.1, 87.6, 74.3, and 40.9%, respectively. The highest biodiesel yield was achieved at a methanol-oil molar ratio of 8:1.

Analysis depicted in Table 4 and Figure 5 illustrates that increasing the molar ratio beyond the optimum point (8:1) adversely impacted the biodiesel yield. The yield exhibited a significant drop to 74.3% at a methanol-oil ratio of 9:1 and further plummeted to 40.9% at a ratio of 10:1. This decline is attributed to the dilution effect of excessive methanol and the interference between the high methanol/oil molar ratio and the catalyst (Ce, 2010; [49]. As a result, there was an increased solubility and

Table 4
Biodiesel yield at different oil-methanol ratios

Runs	Methanol-oil	Temp. (°C)	Catalyst load (%)	Yield (%)
1	6:1	60	10	43
2	7:1	60	10	50.1
3	8:1	60	10	87.6
4	9:1	60	10	74.3
5	10:1	60	10	40.9

Figure 5
Effect of methanol-oil on biodiesel yield



reduced separation of glycerin and methyl ester. The excessive methanol load deactivated the catalyst, promoting the reverse reaction of the transesterification process [50, 51].

Transesterification processes involving vegetable oil and WVO have been conducted using alcohol-to-oil molar ratios spanning from 3:1 to 40:1 [11]. Typically, the most frequently employed molar ratios, averaging across various oil types, fall within the range of 6:1 to 25:1 in biodiesel production when utilizing eggshell ash (CaO) as a heterogeneous catalyst [43, 52]. The degree of biodiesel conversion is directly influenced by the alcohol-to-oil molar ratio, and the optimal ratio may vary depending on the quality and type of oil employed [45].

Figure 5 below shows the increase and decrease in biodiesel yield of methanol-oil ratio.

3.6. Biodiesel characterization

The biodiesel, with the optimum yield (91.3%) from the optimization process, was washed and dried and was characterized thereafter. Like the WVO, the produced biodiesel was characterized with respect to its acid value, %FFA, density and specific gravity, viscosity and kinematic viscosity, flash point, cloud point, pour point, and % carbon residue, all in comparison to the ASTM D 6751 standard and Europe Standard EN 14214 as seen in Table 5. The acid value was calculated through titration to be 2.13, with %FFA being 1.07%. At 28.8°C temperature of biodiesel, the values of density and specific gravity were calculated to be 0.876 g/ml and 0.88, respectively; the viscosity and kinematic viscosity of biodiesel were 5.02 cP and 5.73 mm2/s, respectively. The flash point temperature was gotten to be 115°C, the cloud point and pour point temperatures were also gotten to be 3.2 and 0.6°C respectively, and lastly, the % carbon residue of the biodiesel was calculated to be 0.042 wt%.

Table 5
Biodiesel analysis in comparison to ASTM D 6751 and EN 14214

Analysis	FAME values	ASTM D 6751	EN 14214
FFA content (%)	1.07	–	–
Density at 30°C (kg/m^3)	876	–	860–900
Specific gravity	0.88	–	–
Viscosity (*cP*)	5.02	–	–
Kinematic viscosity at 40°C (mm^2/s)	5.73	1.9–6.0	3.5–5.0
Flash point (°C)	115	<130	<120
Cloud point (°C)	-3.2	–	–
Pour point (°C)	0.6	–	–
Carbon residue (wt%)	0.042	0.05	–

3.7. Discussion

This study aligns with existing literature, which underscores the significance of reaction temperature, methanol-oil molar ratio, and catalyst concentration as primary factors influencing the conversion efficiency and rate of the transesterification process [53]. The findings recorded by Rodrigues [10] indicated that all three variables had a discernible impact on the methyl ester yield and a noteworthy yield of 91% was achieved under an optimal temperature range of 65 ± 5°C, a methanol to oil molar ratio of 22.5:1, a reaction duration of 5 h and 30 min, and a catalyst loading of 3.5 wt%. Another research by Banerjee et al. [54] showed the effectiveness of eggshell in the transesterification process of biodiesel utilizing waste cooking oil, in the research a high methyl ester yield of 94% was recorded. Yaşar [35] noted a very high biodiesel yield of 96.81% after concluding research conducted on utilizing eggshell as a low-cost catalyst in the production of biodiesel.

At the end of our research, it can be seen that our result aligned accurately with existing literature. Our research findings demonstrated that, in the presence of a calcined catalyst, WVO containing 2.86% FFA can yield a high percentage of biodiesel (91.3%), which aligns with previous study done by Yuan et al. [23]. This showed the effectiveness of reducing the high %FFA through esterification process.

ASTM D6751 was used to characterize the purified biodiesel. ASTM defines the parameters that pure biodiesel (B100) must meet before it can be used as a standalone fuel or blended with diesel fuel.

The density of a biodiesel determines how much biodiesel can be produced from a given amount of feedstock and how much energy can be obtained from burning a given volume of biodiesel, the produced biodiesel was shown to have a density of 876 kg/m^3, which conformed to the standard set by ASTM D 6751 AND EN14214 of 860–900 kg/m^3.

In particular, the kinematic viscosity was measured at 40°C. The kinematic viscosity of waste cooking oil biodiesel was measured to be 5.73°C. Several authors have reported varying kinematic viscosities at 40°C for biobased diesel. Palm oil and palm kernel Tri-Methyl-Polyol TMP esters have been reported to have a cSt value of 39.7 [55], sesame oil TMP esters have been reported to have a cSt value of 35.43 [56], and 10-undecenoic acid TMP esters have been reported to have a cSt value of 11.2–36.1 [57]. Furthermore, the qualities of the waste cooking oil biodiesel matched the ASTM D 6751 standard specification requirements for biodiesel.

In very cold conditions, the fluidity of a biodiesel at low temperatures is crucial. When evaluating flow qualities at low temperatures, the pour point and cloud point, or the temperature at which a lubricant stop flowing or the point at which crystals begin to form; which in turn can cause the biodiesel to gel and flow slower than it should, is crucial. Choosing a biodiesel among many alternatives with similar features may become the deciding element. The temperature at which biodiesel begin to flow, known as their "pour point," is the slightest detectable change in temperature. The produced pour point and cloud point were recorded to be −3 and 3.2°C, which was in accordance with previous studies. Hazrat et al. [58] reported soybean biodiesel to have a pour point of −3°C and a cloud point of 3°C, while rapeseed biodiesel to have a pour point of −9°C and a cloud point of −4°C, and Folayan et al. [59] also reported the pour point and cloud point values for biodiesel samples derived from soybean and canola, which showed soybean biodiesel to have a pour point of −3°C and a cloud point of 1°C, while canola biodiesel exhibited a pour point of −12°C and a cloud point of −7°C.

4. Conclusion

This study aims to synthesis biodiesel from WVO utilizing eggshell ash as an innovative heterogeneous catalyst. The following conclusions have been drawn:

1. The characterization of the WVO showed it contained a high % FFA, which, when used, produced a saponification reaction. Hence, for it to be considered a viable feedstock for the production of biodiesel, it must be esterified to reduce the %FFA.
2. From result gotten, the ideal values for the variables for the production of biodiesel from vegetable oil utilizing eggshell ash were a methanol-oil molar ratio of 6:1, a catalyst loading of 5 wt%, and a reaction temperature of 65°C, resulting in an optimal biodiesel yield of 91.3%. This outcome suggests that the catalyst was employed in an adequate quantity relative to the oil, promoting methyl ester formation.
3. Comparative analysis of the physicochemical parameters of the resultant biodiesel met ASTM D 6751 biodiesel requirements, which proved that without engine modifications, this biodiesel is an acceptable replacement for petroleum-based lubricants in automobiles. Hence, the optimized biodiesel production from waste cooking oil utilizing eggshell as catalyst could be applied in a biodiesel pilot plant.

Ethical Statement

This study does not contain any studies with human or animal subjects performed by any of the authors.

Conflicts of Interest

The authors declare that they have no conflicts of interest to this work.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study

Author Contribution Statement

Favour Okechi Ifeanyi-Nze: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration. **Charles Olumakinde Omiyale:** Conceptualization, Validation, Writing – review & editing.

Innocent Ugochukwu Okonkwo: Formal analysis, Investigation. **Chinemerem Jerry Chukwu:** Methodology, Visualization. **Chidimma Maryjane Nwankwor:** Writing – original draft. **Adebola Olatunde Onabanjo:** Data curation. **Sarah Onyabakpa Adoga:** Project administration. **Johnson Obasi Chukwu:** Supervision. **Kenechukwu Fortunate Chukwurah:** Writing – review & editing, Project administration. **Marcus Ebikemiyen:** Investigation. **Godstime Uduak Okon:** Resources. **Olaoluwa John Adeleke:** Data curation. **Kazeem Arowosaye Tajudeen:** Validation.

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APPENDICES

Appendix A: Oil characterization calculations

(Before esterification of Oil)
At oil temperature of 28.8°C;

1. Acid value and %FFA content;

$$\text{Acid value} = \frac{(\text{Titre value} - \text{Blank value}) \text{ x molecular weight, KOH x conc. KOH}}{\text{Mass of Oil}}$$

Mass of oil
Where;
Titre value = 8.8 ml
Blank value = 0.1 ml
MW KOH = 56.1 g/mol
conc. KOH = 0.05 M
mass of oil = 1 g

$$\therefore \text{Acid value} = \frac{(8.8 - 0.1) \text{ x } 56.1 \text{ x } 0.05}{1} = = 24.4 \text{ mg KOH/g oil}$$

$$\%\text{FFA content} = \frac{\text{Acid value}}{2} = \frac{24,4}{2} = 12.2\%$$

2. Density and specific gravity of oil;

$$\text{Density of oil, } \rho = \frac{\text{mass}}{\text{volume}} = \frac{m_1 - m_2}{v}$$

where;

m_1 = mass of oil-filled 25ml density bottle = 45.42 g
m_2 = mass of empty 25ml density bottle = 18.50 g
v = volume of oil in density bottle = 29 ml

$$\therefore \text{Density, } \rho = \frac{45.42 - 18.50}{29} = 0.928 \text{g/ml}$$

$$\text{Specific Gravity of oil} = \frac{\text{Density of oil @ 28.8°C}}{\text{density of water @ 28.8°C}}$$

Where density of water @ 28.8°C is 0.995

$$\therefore\therefore \text{S.G. of oil} = \frac{0.928}{0.995} = 0.93$$

3. Viscosity and kinematic viscosity;

Viscosity, μ, of oil as read from the viscometer = 64. 5 mPa.s = 64.5 cP
where cP is the centipoise.

$$\text{Kinematic viscosity } (\upsilon) = \frac{\text{Viscosity } (\mu)}{\text{Density of oil } (\rho)} = \frac{64.5}{0.928} == 69.5cSt = 69.5mm2/s$$

where *cSt* is the centistoke.

4. Iodine value;

$$\text{Iodine value, I} = \frac{\text{Iodine value Constant} * (\text{Titre value of blank} - \text{Titre value of oil sample}) * \text{ conc. } N_{a2}S_2O_3}{\text{Mass of Oil}}$$

where;
Iodine value constant = 12.69
Titre value of blank = 16
Titre value of oil sample = 6

Conc. $Na_2S_2O_3 = 0.1$ M
Mass of oil sample = 0.5 g

$$I = \frac{12.69*(16-6)*0.1}{0.5} = 25.38 g^{-10-2} g^{-1}$$

5. % Moisture content;

$$\%\ \text{Moisture content} = \frac{\text{Initial mass of oil} - \text{Final mass of oil}}{\text{Mass of Oil}} * 100\% = \frac{m_1 - m_2}{M_0} * 100\%$$

where;
Initial mass of oil (m_1) = mass of 50 ml conical flask containing oil = 35.87 g
Final mass of oil (m_2) = mass o 50 ml conical flask containing heated oil = 35.81 g
Mass of oil = 3 g

$$\therefore \%\ \text{Moisture content} = \frac{35.87 - 35.81}{3} * 100\% = 2\ \text{w}\%$$

Oil Analysis before the esterification reaction

Oil analysis	Value
Acid value (mg KOH/g oil)	24.4
FFA content (%)	12.2
Density (g/ml)	0.928
Specific gravity	0.93
Viscosity (*cP*)	64.5
Kinematic viscosity (mm^2/s)	69.5
Iodine value ($g^{-10-2}g^{-1}$)	25.38
%Moisture content (w%)	2

(After esterification of Oil)
At Oil temperature of 28.8°C;

1. Acid value and %FFA content;

$$\text{Acid value} = \frac{(\text{Titre value} - \text{Blank value})\ \text{x molecular weight, KOH x conc. KOH}}{\text{Mass of Oil}}$$

where;
Titre value = 2.1 ml
Blank value = 0.1 ml
MW KOH = 56.1 g/mol
conc. KOH = 0.05 M
mass of oil = 1 g

$$\therefore \text{Acid value} = \frac{(2.1 - 0.1)\ \text{x}\ 56.1\ \text{x}\ 0.05}{1} == 5.61\ \text{mg KOH/g oil}$$

$$\%\text{FFA content} = \frac{\text{Acid value}}{2} = \frac{5.61}{2} = 2.81\%$$

2. Density and specific gravity of oil;

$$\text{Density of oil, } \rho = \frac{\text{mass}}{\text{volume}} = \frac{m_1 - m_2}{v}$$

where
m_1 = mass of oil-filled 25 ml density bottle = 44.60 g
m_2 = mass of empty 25 ml density bottle = 18.50 g

v = volume of oil in density bottle = 29 ml

$$\therefore \text{Density, } \rho = \frac{44.60 - 18.50}{29} = 0.9\text{g/ml}$$

$$\text{Specific Gravity of oil } = \frac{\text{Density of oil @ 28.8°C}}{\text{density of water @ 28.8°C}}$$

Where density of water @ 28.8°C is 0.995

$$\therefore \text{S.G. of oil} = \frac{0.9}{0.995} = 0.904$$

3. Viscosity and kinematic viscosity:

Viscosity, μ, of oil as read from the viscometer = 60. 4 mPa.s = 60.4 cP
where cP is the centipoise.

$$\text{Kinematic viscosity } (\upsilon) = \frac{\text{Viscosity } (\mu)}{\text{Density of oil } (\rho)} = \frac{60.4}{0.9} == 67.1cSt = 67.1mm2/s$$

where *cSt* is the centistoke.

4. Iodine value;

$$\text{Iodine value, I} = \frac{\text{Iodine Value Constant} * (\text{Titre value of blank} - \text{Titre value of oil sample}) * \text{conc. } N_{a2}S_2O_3}{\text{Mass of Oil}}$$

where;
Iodine value constant = 12.69
Titre value of blank = 16
Titre value of oil sample = 3
Conc. $Na_2S_2O_3$ = 0.1 M
Mass of oil sample = 0.5 g

$$\text{I} = \frac{12.69*(16-3)*0.1}{0.5} = 33g^{-10-2}g^{-1}$$

5. % Moisture content:

$$\%\text{ Moisture content} = \frac{\text{Initial mass of oil} - \text{Final mass of oil}}{\text{Mass of Oil}} * 100\% = \frac{m_1 - m_2}{M_0} * 100\%$$

where;
Initial mass of oil (m_1) = mass of 50 ml conical flask containing oil = 33.65 g
Final mass of oil (m_2) = mass o 50 ml conical flask containing heated oil = 33.62 g
Mass of oil = 3 g

$$\therefore \%\text{ Moisture content} = \frac{33.65 - 33.62}{3} * 100\% = 1\text{w}\%$$

Oil Analysis after the esterification reaction

Oil analysis	Value
Acid value (mg KOH/g oil)	5.61
FFA content (%)	2.81
Density (g/ml)	0.9
Specific gravity	0.904
Viscosity (cP)	60.4
Kinematic viscosity (mm^2/s)	67.1
Iodine value ($g^{-10-2}g^{-1}$)	33
Moisture content (wt%)	1

Appendix B: Percentage Yield calculations from Biodiesel Optimization

$$\text{Yield } (\%) = \frac{Weight_{Biodiesel}}{Weight_{oil}} * 100\%$$

1. **Effect of catalyst loading on biodiesel yield**
   (At constant methanol-oil ratio and temperature)
   At 1 wt% (2 g CaO);

$$\text{Yield } (\%) = \frac{110.6}{200} * 100\% = 55.3\%$$

At 2 wt% (4 g CaO);

$$\text{Yield } (\%) = \frac{123.2}{200} * 100\% = 61.6\%$$

At 3 wt% (6 g CaO);

$$\text{Yield } (\%) = \frac{179.6}{200} * 100\% = 89.8\%$$

At 4 wt% (8 g CaO);

$$\text{Yield } (\%) = \frac{136.6}{200} * 100\% = 68.3\%$$

At 5 wt% (10 g CaO);

$$\text{Yield } (\%) = \frac{115.4}{200} * 100\% = 57.7\%$$

2. **Effect of temperature on biodiesel yield;**
   (At constant methanol-oil ratio and catalyst loading)
   At 55°C;

$$\text{Yield } (\%) = \frac{126}{200} * 100\% = 63\%$$

At 60°C;

$$\text{Yield } (\%) = \frac{148}{200} * 100\% = 74\%$$

At 65°C;

$$\text{Yield } (\%) = \frac{182.6}{200} * 100\% = 91.3\%$$

At 70°C;

$$\text{Yield } (\%) = \frac{122.8}{200} * 100\% = 61.4\%$$

At 75°C;

$$\text{Yield } (\%) = \frac{90.4}{200} * 100\% = 45.2\%$$

3. **Effect of methanol-oil molar ratio on biodiesel yield;**
   (At constant temperature and catalyst loading)

At 6:1 methanol-oil ratio;

$$\text{Yield } (\%) = \frac{86}{200} * 100\% = 43\%$$

At 7:1 methanol-oil ratio;

$$\text{Yield } (\%) = \frac{100.2}{200} * 100\% = 50.1\%$$

At 8:1 methanol-oil ratio;

$$\text{Yield } (\%) = \frac{175.2}{200} * 100\% = 87.6\%$$

At 9:1 methanol-oil ratio;

$$\text{Yield } (\%) = \frac{148.6}{200} * 100\% = 74.3\%$$

At 10:1 methanol-oil ratio;

$$\text{Yield } (\%) = \frac{81.8}{200} * 100\% = 40.9\%$$

Yield of the various optimization parameters

Optimization parameters	% Yield
Catalyst loading	
1 wt%	55.3
2 wt%	61.6
3 wt%	89.8
4 wt%	68.3
5 wt%	57.7
Temperature	
55°C	63
60°C	74
65°C	91.3
70°C	61.4
75°C	45.2
Methanol-oil molar ratio	
6:1	43
7:1	50.1
8:1	87.6
9:1	74.3
10:1	40.9

Appendix C: Determination of the Mass of Methanol for the Methanol-oil Ratio Optimization

Recall that for a P: Q methanol-oil ratio;

$$\frac{\text{mass of oil}}{\text{molecular weight of WVO}} \times \text{P} = \frac{\text{mass of alcohol}}{\text{molecular weight of alcohol}} \times \text{Q}$$

where;

Mass of oil = 200 g

Mass of methanol = x g

Molecular weight of WVO = 885 g/mol (assumed)

Molecular weight of methanol = 32.04 g/mol

$$\therefore \text{Mass of methanol, } xg = \frac{200P*32.04}{885Q}$$

At 6:1 methanol-oil ratio;

$$xg = \frac{200*6*32.04}{885*1} = 43.44 \text{ g}$$

At 7:1 methanol-oil ratio;

$$xg = \frac{200*7*32.04}{885*1} = 50.68 \text{ g}$$

At 8:1 methanol-oil ratio;

$$xg = \frac{200*8*32.04}{885*1} = 57.92 \text{ g}$$

At 9:1 methanol-oil ratio;

$$xg = \frac{200*9*32.04}{885*1} = 65.17 \text{ g}$$

At 10:1 methanol-oil ratio;

$$xg = \frac{200*10*32.04}{885*1} = 72.41 \text{ g}$$

Appendix D: Biodiesel Characterization Calculations

At biodiesel temperature of 28.8°C;

1. Acid value and %FFA content;

$$\text{Acid value} = \frac{(\text{Titre value} - \text{Blank value}) \text{ x molecular weight, KOH x conc. KOH}}{\text{Mass of Oil}}$$

where;
Titre value = 0.86 ml
Blank value = 0.1 ml
MW KOH = 56.1 g/mol
conc. KOH = 0.05 M
mass of biodiesel = 1 g

$$\therefore \text{Acid value} = \frac{(0.86 - 0.1) \text{ x } 56.1 \text{ x } 0.05}{1} = = 2.13 \text{ mg KOH/g oil}$$

$$\%\text{FFA content} = \frac{\text{Acid value}}{2} = \frac{2.13}{2} = 1.07\%$$

2. Density and specific gravity of biodiesel;

$$\text{Density of oil, } \rho = \frac{\text{mass}}{\text{volume}} = \frac{m_1 - m_2}{v}$$

where;
m_1 = mass of biodiesel-filled 25 ml density bottle = 43.89 g
m_2 = mass of empty 25 ml density bottle = 18.50 g
v = volume of biodiesel in density bottle = 29 ml

$$\therefore \text{Density, } \rho = \frac{43.89 - 18.50}{29} = 0.876 \text{g/ml}$$

$$\text{Specific Gravity of oil } = \frac{\text{Density of oil @ 28.8°C}}{\text{density of water @ 28.8°C}}$$

where density of water @ 28.8°C is 0.995

$$\therefore \text{S.G. of oil} = \frac{0.876}{0.995} = 0.88$$

3. **Viscosity and kinematic viscosity:**
   Viscosity, μ, of biodiesel as read from the viscometer = 5. 02 mPa.s = 5.02 cP
   where *cP* is the centipoise.

$$\text{Kinematic viscosity } (\upsilon) = \frac{\text{Viscosity } (\mu)}{\text{Density of oil } (\rho)} = \frac{5.02}{0.876} == \ 5.73cSt \ = \ 5.73mm2/s$$

   where *cSt* is the centistoke.

4. **Flash point temperature, T_f** = 115°C
5. **Cloud point temperature, T_{cp}** = 3.2°C, Pour point temperature, T_{pp} = 0.6°C
6. **% Carbon residue;**:

$$\%\ \text{Carbon residue} = \frac{\text{Initial mass of biodiesel } - \text{ Final mass of biodiesel}}{\text{Mass of biodiesel}} * 100\% = \frac{m_1 - m_2}{M_0} * 100\%$$

where;
Initial mass of biodiesel (m_1) = mass of biodiesel + mass of crucible = 47.38 g
Final mass of biodiesel (m_2) = mass of carbon residue formed upon heating in crucible + mass of crucible = 47.37916 g
Mass of biodiesel in crucible = 2 g

$$\therefore \%\ \text{Carbon residue} = \frac{47.38 \ - \ 47.37916}{2} * 100\% = 0.042\ \text{w}\%$$

Biodiesel analysis and values

Biodiesel analysis	Value
Acid value (mg KOH/g oil)	2.13
FFA content (%)	1.07
Density (g/ml)	0.876
Specific gravity	0.88
Viscosity (*cP*)	5.02
Kinematic viscosity (mm^2/s)	5.73
Flash point (°C)	115
Cloud point (°C)	3.2
Pour point (°C)	0.6
% Carbon residue (w%)	0.042