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Optimization of aerated biodiesel production from selected waste cooking oils using a CuO/CaO catalyst derived from *kuhol (Sulcospira)* shells

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ABSTRACT

This study optimized biodiesel production from waste palm, vegetable, and coconut oils using a CuO/CaO catalyst derived from *kuhol (Sulcospira)* shells. Preheating and filtration improved oil quality, and low free fatty acid (FFA) levels (<2 wt%) allowed direct aeration-assisted transesterification. CuO/CaO particles significantly enhanced the transesterification process. A two-factorial, three-level design was employed to evaluate the relationship between varying operating conditions and biodiesel yield for different waste cooking oils. The properties of pure biodiesel (B100) and blended biodiesel (B5) were compared to the Philippine National Standards for coconut methyl ester. Results showed that the majority of properties for B100 and B5 conformed to the standards. The lower values of FFA content, acid value, saponification value, and moisture content indicate favorable properties for the highest biodiesel conversion yield achieved using CuO/CaO. Engine emission testing results for B100 and B5, reveal significantly lower emissions compared to commercial diesels. Additionally, emission results imply the potential of B100 as an efficient and sustainable additive to commercially available diesel.

Keywords: aeration, biodiesel, central-composite design, heterogeneous catalyst, transesterification, waste cooking oil

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1. Introduction

For several years, fuel production and consumption have been major contributors to greenhouse gas emissions, prompting extensive research on sustainable alternatives. In 2023, global energy-related carbon emissions rose by 1.1%, adding 410 Mt to reach a record 37.4 Gt, compared to a 1.3% rise (490 Mt) in 2022. Over 65% of the 2023 increase came from coal emissions [1]. The depletion of petroleum reserves and worsening environmental issues have driven the pursuit of renewable energy sources, with biodiesel emerging as a promising alternative. Biodiesel offers significant environmental and economic benefits, being non-toxic, biodegradable, and derived from locally available resources, which reduces pollution. This study focuses on optimizing biodiesel production using innovative approaches such as aeration-assisted transesterification with particles as catalysts. The higher brake thermal efficiency of biodiesel, approximately 26% and 23% compared to petroleum diesel [2], aligns with this research's objective to develop a cost-effective and sustainable catalyst for improved biodiesel yield and quality.

Biodiesel is typically produced through transesterification, a reversible reaction in which fatty acids, alcohol, and catalysts are combined as reactants [3]; where triglycerides—the main components of oils and fats—are converted into biodiesel and glycerol by reacting with alcohol, typically methanol or ethanol, in the presence of a catalyst. This process is crucial for transforming raw oils and fats into a sustainable and environment-friendly fuel source. Catalysts, which can be strong bases, acids, or solid materials, facilitate the cleavage of ester bonds in triglycerides, lowering activation energy and enhancing reaction efficiency. Methanol is commonly used due to its high reactivity, ensuring efficient production of fatty acid methyl esters (FAME), which constitute biodiesel. The by-product, glycerol, can be repurposed for various industries, such as cosmetics, food production, and oleochemicals. Without a catalyst, this reaction would require extreme conditions of temperature and pressure, rendering it economically and technically unfeasible.

Biodiesel can be produced in the presence of a catalyst by transesterification of vegetable oil or animal fat with alcohol. A low-cost heterogeneous catalyst has been extensively studied for biodiesel production. It was noted that various types of natural waste shells could be used to generate bio-based calcium oxide (CaO) with comparable chemical properties that significantly enhance transesterification activity. The oxygen anion present on its surface is responsible for the catalytic impact of CaO in the reaction. However, the stability of CaO-catalyzed transesterification is limited, and studies have demonstrated a decrease in catalytic reactivity when the catalyst is reused multiple times. This resulted in the utilization of mixed metal oxides (MMOs) for better transesterification reactivity during biodiesel production. The combination of multiple metal oxides in hetero-metal catalysts (e.g., CuO/CaO) provides synergistic effects that improve catalytic efficiency, such as better adsorption of reactants and enhanced electron transfer during transesterification.

Heterogeneously catalyzed biodiesel synthesis has gained preference due to its environmental benefits, lower water usage, and easier product separation. The use of heterogeneous catalysts like MMO [4] and CaO derived from snail or waste shells [5] enables effective recovery, regeneration, and reusability. The catalyst made from waste shells allows for the production of renewable catalysts while

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also recycling the waste created [6,7]. These catalysts facilitate reaction efficiency while reducing purification costs and minimizing waste, making them eco-friendly alternatives to homogeneous catalysts such as sulfuric acid. Additionally, their derivation from low-cost, renewable biowaste materials enhances their cost-effectiveness and sustainability. Other examples include CaO derived from snail shells, calcined dolomite (CaO-MgO), and sodium-loaded pumice.

Optimal reaction conditions are equally important in ensuring the success of transesterification. For methanol-based systems, reaction temperatures typically range from 60 °C to 70 °C, and a high alcohol-to-oil molar ratio, such as 6:1, drives the reaction toward completion. Sufficient reaction time and effective agitation are crucial to maximize the conversion of triglycerides into biodiesel. These factors, along with efficient heterogeneous catalysts, contribute to a more sustainable and economically viable biodiesel production process.

The increasing problem of food waste has also opened avenues for sustainable biofuels. Waste cooking oils (WCOs), a by-product of cooking processes, primarily from frying at high temperatures, and is composed of used vegetable oils or animal fats mixed with food residues, free fatty acids (FFAs), and water, generated in restaurants, fast-food chains, and catering establishments represent a significant feedstock for biodiesel production. These oils are rich in FFA, making them a valuable yet challenging resource. In the Philippines, where a typical city consumes approximately 35,000 L of cooking oil per month from households and commercial establishments, the resulting WCO presents both a challenge and an opportunity. While some WCO is recycled and reused for cooking, its contamination with impurities and residues raises concerns about its safety for human consumption. Proper management and pretreatment, including filtration, degumming, and acid esterification, are essential to improve WCO quality and ensure successful transesterification. Repurposing WCO for biodiesel production offers a sustainable solution, reducing environmental pollution while converting waste into a renewable energy source, for a heavy cooking oil-consuming countries like the Philippines.

The choice of catalyst is critical in determining the efficiency and sustainability of the transesterification process. This study employs CuO/CaO particles derived from *kuhol (Sulcospira)* shells as a heterogeneous catalyst. These particles exhibit a high surface area and provide basic sites that promote the formation of methoxide ions, which attack the carbonyl group of triglycerides, driving their conversion into biodiesel and glycerol. Unlike homogeneous catalysts, which dissolve in the reaction medium, heterogeneous catalysts remain in a separate phase from the reactants, offering significant advantages in biodiesel production—easier catalyst recovery and regenerability, enhancing the overall efficiency and cost-effectiveness of the process.

The selected WCOs—vegetable oil, palm oil, and coconut oil were fed to the direct aeration-assisted transesterification reactor with methanol and catalysts particles. The transesterification system required bubbling of WCO to enhance its reaction with methanol. Production of crude biodiesel took place and was followed by washing to remove glycerin. After the washing stage, neat biodiesel was collected. The physicochemical properties of the biodiesel were analyzed using gas chromatography, and blended biodiesel (B5) was compared to industry standards, including the Philippine National Standard (PNS) for coconut methyl ester (CME).

In light of recent innovations and discoveries, the utilization of waste materials as components of biofuels will be a major development on a global scale. Accordingly, this study aimed to optimize biodiesel production from selected WCOs through an existing aeration-assisted transesterification reactor, employing a heterogeneous catalyst and comparing the properties of the produced biodiesel to industry standards. Furthermore, the impact of the process and the physicochemical properties of raw materials were determined. Through the use of these components in biodiesel production, various economic and ecological issues were addressed including solid and food waste management.

2. Materials and methods

2.1. Materials

The materials used in this study are WCOs (vegetable, palm, and coconut oils) waste *kuhol* shells, copper (II) chloride dihydrate, and sodium hydroxide pellets.

2.2. Preparation and pre-treatment of WCOs

The production of biodiesel in this study utilized specific WCOs as the main raw material (Figure 1). These oils were sourced from selected food establishments known for generating substantial quantities of WCOs, ensuring a sufficient supply for the process. Approximately 220 L each of vegetable oil, palm oil, and coconut oil were allocated by the operation matrix, including the duplication. The initial stage of the pre-treatment of the WCOs samples involved pre-heating. In this pretreatment process, the oil was loaded into the main reactor tank and was pre-heated at 55-60 °C. Afterwards, the collected oil samples were filtered using a filter cloth placed on the mesh located in the existing prototype's oil storage tank. Upon preparing the setup, the oil feedstock was carefully dispensed from containers, and the lever-type handle of the equipment was pulled to push the volume of oil through the filtration system. Since WCOs often contain impurities that could significantly affect the operation, a purification step was implemented. This process utilized a basic filtration system comprising a strainer, filter cloth, and heater to ensure that no unnecessary food particles, fats, or contaminants, regardless of size, will be included in the optimization process. In addition, the esterification process was conducted based on the characterized FFA content of the oil samples.

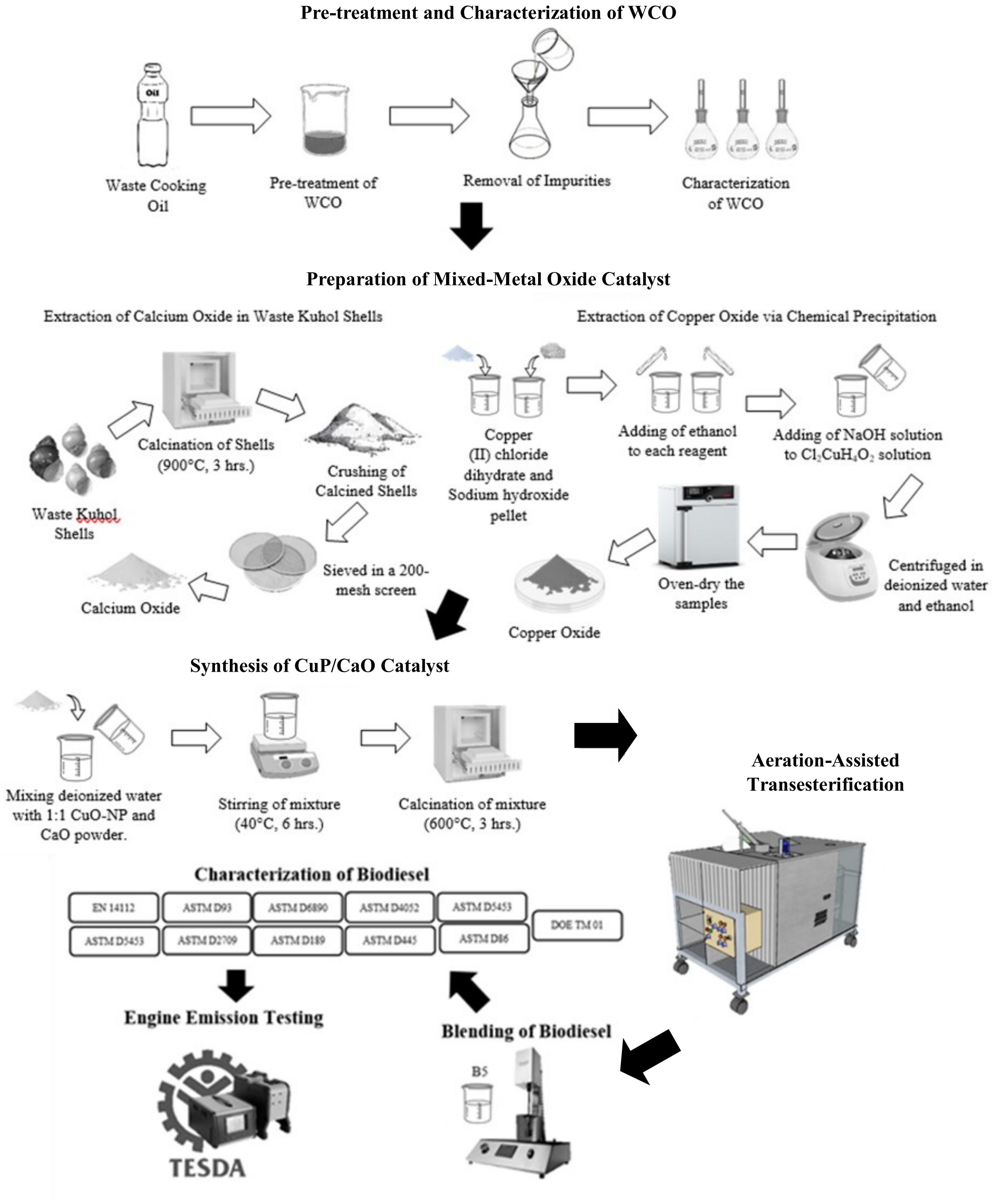

Figure 1. Schematic diagram of methodology.

2.2 Preparation of catalyst

About 5 kg of *kuhol* shells, as the source of the CaO catalyst, were gathered in sacks and containers directly from the wet market and various restaurants in Batangas and then cleaned with running water. There is a separate extraction for the copper oxide, which was done through a different chemical process using various reagents, such as copper(II) chloride dihydrate, sodium hydroxide pellets, ethanol, and deionized water.

The waste *kuhol* shells from seafood restaurants and fields in Lucena City, Quezon Province were treated through several chemical processes to produce CaO catalyst. The shells were washed to remove any impurities, and sun-dried. Then, it was dried again using a cabinet dryer at 80 °C for 2 h. After drying, the waste shells were statically calcined in a muffle furnace at approximately 900 °C for 3 h. The calcined shells were crushed and sieved in a 200-mesh screen until white $CaCO_3$ powder was obtained. Before being used, all calcined and crushed samples were stored in glass bottles to avoid reactions with CO_2 and water vapo. Then, the $CaCO_3$ was refined using the sol-gel method.

During the sol-gel method, a 200 mL HCI (concentrated) and 200 mL NaOH (concentrated) was added to 20 g of $CaCO_3$ via hydrolysis using a two-neck distillation flask and a condenser. The gel that was produced in this setup was aged overnight at ambient temperature and was filtered and washed with distilled water several times to obtain clear gel. The gel was vacuum-dried then calcined at 900 °C for 1 h. During the sol-gel and calcination processes, the $CaCO_3$ turned to CaO and CO_2.

For CuO synthesis, 50 g of $CuCI_2$•$2H_2O$ and 30 g of NaOH pellets were dissolved in ethanol separately. At room temperature, dropwise addition of NaOH solution to $CuCI_2$•$2H_2O$ solution was carried out with steady stirring. As the reaction progressed, the hue of the solution changed from green to bluish-green, then black. CuO was the dark precipitate. These particles were washed with deionized water and ethanol three to four times using centrifugation at 4000 rpm for 10 min. to remove impurities. Finally, the CuO nanoparticles (NPs) were scraped from the centrifuge vials then dried in a multipurpose oven.

In various biodiesel processes, mixed-metal oxides are effectively used as catalysts, typically at a 1:1 molar ratio [4]. CuO/CaO catalyst was made by mixing 50 ml deionized or distilled water with 1:1 CuO-NP and CaO powder. Due to their identical catalytic properties that can be exploited in biodiesel production, metal oxide prefers to mix at an equal concentration. The mixture was agitated for 5 h at 40 °C, then passed to a vacuum filter and dried in a universal oven to remove any water content. Then, the catalyst was calcined for 3 h at 600 °C to get rid of any adsorbed moisture. Afterward, the calcined CuO-CaO catalyst was ground and sieved in a 200-mesh screen to become NPs. The CuO-CaO catalysts were stored in sealed glass containers.

2.2. Characterization of WCOs

Improper disposal of WCOs, stemming from various establishments and households, is a significant contributor to water pollution. Excessive and uncontrolled disposal poses environmental risks, making biodiesel production from WCOs a promising solution to this issue. To achieve this, the physicochemical properties of three selected WCOs were characterized following their purification. Analytical techniques were used to determine key properties, including density, viscosity, FFA content, acid value, saponification value, and moisture content. Density was measured using a pycnometer bottle, with oils heated, and weighed before and after filling with a 50 mL oil sample. Viscosity was assessed using a Brookfield viscometer at 25 °C and a constant speed of 100 rpm for 1 min. FFA levels were determined using the AOCS Method Ca 5a-40, involving titration of a neutralized ethanol-oil solution. Acid value was calculated through titration with KOH until a light pink color appeared. Saponification value was obtained by saponifying the oil sample, followed by titration with HCI. Moisture content was measured by drying the oil samples in a vacuum oven at 30 °C and calculating the percentage weight loss.

2.3. Transesterification process

Transesterification was done using an aeration-assisted system, consisting of four stages: preheating, synthesis, washing, and polishing. Aeration was employed to enhance the contact between the WCOs and catalyst, resulting in enhanced reaction efficiency. In the preheating stage, the oil samples were heated at a 55-60 °C in the aeration-assisted reactor, allowing immediate catalytic reaction. While doing this, the methanol and the CuO/CaO catalyst at three concentrations (1, 1.5, 2 wt%) were prepared for the synthesis stage.

The synthesis began by adding a concentration of methanol to the oil samples at a constant methanol-oil molar ratio of 6:1 [8] at a flow rate of about 1.5 L/min. Then, the CuO/CaO catalyst, with an average particle size of 98.59 nm, was added to the methanol-oil mixture with a concentration of 1, 1.5, and 2 wt%. This step was crucial, as the catalyst significantly enhanced the reaction rate and biodiesel yield. The aeration system was then turned on to assist in speeding up the reaction by producing a large interfacial area by dispersing bubbles of the gas into the liquid and creating more reaction sites. In doing this, it was ensured that the aeration (reaction) took place for numerous runs under the exact operating conditions provided at the matrix. Similar to the other parameters, the aeration was set to three different conditions at 2, 2.5, and 3 h, respectively, at a constant reaction temperature of 60°C [8].

After completing this stage, the aeration system was turned off and all the glycerol was allowed to settle. The glycerol was then drained out from the reactor and once completely done, water was pumped into the reaction mixture for washing. During this stage, all the unreacted catalysts were washed out and recovered. Each washing process was carried out for 30 min and was repeated three times. After this process, the heater and aerator were switched off. Lastly, the polishing stage allows the elimination of impurities through the reactor drain valve. This was performed at 105 °C. The heater and aerator were switched on again for the removal of the remaining water and moisture. The process was then repeated following the conditions provided in the matrix for each type of WCOs. Moreover, the percentage yield of the biodiesel for each run was calculated using the equation:

$$\%\,Biodiesel\ Yield\ = \frac{Volume\ of\ Biodiesel\ Produced}{Volume\ of\ Waste\ Cooking\ Oil\ Used} \times 100 \qquad (1)$$

2.4. Blending of biodiesel

Biodiesel produced from the highest-yielding run was mixed with petrodiesel at a volume/volume (v/v) basis to yield blended biodiesel. In blending, 5% of the produced biodiesel and 95% of the petrodiesel were placed in a 1 L beaker and thoroughly mixed using an agitator. The initial CME blend was set to 1%, according to the Biofuels Act of 2006, and was increased to 2% in 2017. However, the benefits of a 5% biodiesel blend (B5) have been highlighted numerous times, including cleaner air, increased mileage and savings for vehicles, public health through clean air, and poverty alleviation among coconut producers. This study compared the PNS for B5 and pure (B100) biodiesels produced from selected WCOs. In addition, it examined their performance and efficiency in engine applications.

2.5. Characterization of biodiesel

To determine the efficiency and quality of the produced biodiesel, its characterization was conducted using different analytical methods in accordance with the PNS for CME, along with the Department of Energy (DOE). Each necessary property was characterized using its corresponding PNS testing method. The methods include ASTM D4052, ASTM D445, ASTM D2709, ASTM D189, ASTM D6890, ASTM D5453, ASTM D6584, DOE TM 01, ASTM D86, EN 14112, and ASTM D93. All testing procedures were conducted at the DOE - Energy Research and Testing Laboratory to ensure adherence to established standards and protocols.

2.6. Engine emission testing

In determining the efficiency of the B100 and B5 biodiesels, various engine emission tests and analyses were performed. Vehicle emissions testing determined whether or not a vehicle emits pollutants and how much it emits. The engine parameters and emission findings were examined using a variety of high-dynamic engine trials and analysis procedures in several facilities or laboratories.

Moreover, laboratory tests for the produced B5 and B100 biodiesels were conducted in the Technical Education and Skills Development Authority – Regional Training Center CALABARZON located at P. Herrera St., Batangas City. The tests were performed to evaluate whether the B100 and B5 emit hazardous compounds, such as aromatic hydrocarbons, carbon monoxide, carbon, dioxide, and oxides of nitrogen. Biodiesel characterization is significant to help evaluate quality and compliance with standards, and troubleshoot problems caused by biodiesel blending, trace metals, and other fuel quality challenges.

2.7. Design of experiment

The central composite design, consisting of two factors with three levels, was utilized and employed for the optimization of biodiesel production. This method was applied to reduce the number of experiments required to obtain the optimal conditions for maximum biodiesel yield. Using this design, the required and necessary number of trials and their conditions were determined and finalized. The factors considered for the optimization process for each WCO at constant methanol-oil molar ratio and temperature are: (i) catalyst concentration and (ii) reaction time (Table 1). The ranges of the catalyst concentration (1, 1.5, 2 wt%), and reaction time (2, 2.5, 3 h) applied for each WCO were based on the preliminary experiments and fell within the desirable conditions identified through the optimization studies. For statistical analysis, the Design-Expert software (DES) package was used, and the transesterification response plots and equation of regression were determined using analysis of variance (ANOVA). Moreover, the DES was utilized to analyze and determine the ideal conditions and parameters for the biodiesel production process.

Table 1. Parameters for optimization of biodiesel production

Controlled parameter	Unit	Level 1	Level 2	Level 3
Catalyst Concentration	wt%	1	1.5	2
Reaction Time	h	2	2.5	3

3. Results and discussion

The physicochemical properties of the pre-treated WCOs, such as palm, vegetable, and coconut oil, were determined and calculated. The determined properties include the density, viscosity, FFA content, acid value, saponification value, and moisture content of the WCOs (Table 2). The values were subjected to statistical treatment to determine significance of the feedstock for biodiesel production.

Table 2. Physicochemical properties of pre-treated WCOs

Physicochemical property	Palm oil	Vegetable oil	Coconut oil
Density at 25°C, g/mL	0.9013	0.9004	0.9073
Viscosity at 25°C, mPa·s	8.9703	8.2812	8.4835
FFA Content, %	0.3873	0.6455	0.3550
Acid Value, mg KOH/g	0.7707	1.2845	0.7065
Saponification Value, mg KOH/g	0.5471	0.8207	0.4103
Moisture Content, %w/w	0.0020	0.0040	0.0020

3.1. Influence of operating conditions to biodiesel production from WCOs

To optimize biodiesel production, the effects of catalyst concentration and reaction time on biodiesel yield were studied. Using a central composite design (CCD), consisting of two factors with three levels, the biodiesel yields for the three WCOs were assessed under 27 experimental runs. The average yield for the two trials of each run was obtained and the effects of catalyst concentration and reaction time were also determined.

Table 3 presents the biodiesel yield for each varying condition set. It shows the results of the biodiesel conversion process for each WCO.

Table 3. Biodiesel yield from WCO at varying operating conditions

Type of oil	Run	CuO/CaO Catalyst concentration (%)	Reaction time (h)	Trial 1 % yield (v/v)	Trial 2 % yield (v/v)	Average % yield (v/v)
Palm	1	1	2	68.25	70.85	69.55
	2	1.5	2	78	85.5	81.75
	3	2	2	86.75	91.75	89.25
	4	1	2.5	75.75	76.25	76
	5	1.5	2.5	87	88	87.5
	6	2	2.5	88.5	89.5	89
	7	1	3	85.5	84.5	85
	8	1.5	3	83.5	85	84.25
	9	2	3	95.25	93.75	94.5
Vegetable	10	1	2	49.5	51	50.25
	11	1.5	2	72.15	66.85	69.5
	12	2	2	74.65	72.45	73.55
	13	1	2.5	62	60.5	61.25
	14	1.5	2.5	70.45	72.65	71.55
	15	2	2.5	75.8	83.9	79.85
	16	1	3	68.45	70.65	69.55
	17	1.5	3	75	77	76
	18	2	3	80	82.5	81.25
Coconut	19	1	2	82.75	80.5	81.625
	20	1.5	2	85.5	85	85.25
	21	2	2	90.5	90	90.25
	22	1	2.5	78	75.5	76.75
	23	1.5	2.5	86	87	86.5
	24	2	2.5	86.75	88	87.375
	25	1	3	85.5	86.25	85.875
	26	1.5	3	94	91.75	92.875
	27	2	3	97	95	96

Coconut oil at 2% catalyst concentration and 3 h of reaction time achieved the highest yield (96%). This is better than [9], which reported a 90% yield using a similar catalyst but under different conditions, highlighting the originality of this study's approach. The high yields achieved in this study, particularly for coconut oil, are comparable to and exceed those reported in prior research. For instance, [10] achieved a 97.76% yield using a NaOH catalyst under microwave-assisted transesterification, whereas this study utilized CuO/CaO catalysts derived from waste *kuhol* shells, demonstrating the feasibility of eco-friendly and cost-effective catalysts.

The ANOVA results for biodiesel production from palm, vegetable, and coconut oils are summarized in Table 4. It showed p-values of 0.0003, 0.0010, and 0.0216, respectively, indicating that all models were statistically significant ($p < 0.05$). The model for palm and vegetable oils follows a linear fit, while coconut oil follows a quadratic fit. For palm and vegetable oils, the concentration (A) and time (B) were significant model terms, with p-values less than 0.1000. Among these, catalyst concentration had the greatest influence, as indicated by its higher F-value and lower p-value. The linear model F-values were 41.49 for palm oil, and 26.89 for vegetable oil, both were significant, with very low probabilities of occurring by chance. The quadratic model F-value for coconut oil was 16.52, also significant, with a 2.16% chance of occurring due to noise.

Table 4. ANOVA table for transesterification of palm, vegetable, and coconut oils

Source	Sum of squares	df	Mean square	F-value	p-value	Remarks
Model						
Palm	457.53	2	228.77	41.49	0.0003	Significant
Vegetable	666.63	5	333.31	26.89	0.0010	Significant
Coconut	255.44	5	51.09	16.52	0.0216	Significant
A-Concentration						
Palm	405.08	1	405.08	73.47	0.0001	
Vegetable	479.36	1	479.36	38.67	0.0008	
Coconut	143.82	1	143.82	46.50	0.0065	
B-Time						
Palm	52.45	1	52.45	9.51	0.0215	
Vegetable	187.27	1	187.27	15.11	0.0081	
Coconut	51.77	1	51.77	16.74	0.0264	
AB						
Coconut	0.5625	1	0.5625	0.1819	0.6985	
A^2						
Coconut	7.19	1	7.19	2.32	0.2248	
B^2						
Coconut	52.11	1	52.11	16.85	0.0262	
Residual						
Palm	33.08	6	5.51			
Vegetable	74.38	6	12.40			
Coconut	9.28	3	3.09			
Cor Total						
Palm	490.61	8				
Vegetable	741.01	8				
	26	1.5	3	94	91.75	92.875
	27	2	3	97	95	96

3.2. Influence of transesterification process variables

In this study, parameters A and B were considered for the evaluation of transesterification of WCOs into biodiesel using a CCD. A constant methanol-to-oil ratio of 6:1 and a fixed temperature of 65 °C were employed in the experiments.

Figures 2, 3, and 4 show the relationships between catalyst concentration and reaction time. The plot demonstrates how variables A and B affect the yield in v/v%. The contour plots show that optimal biodiesel yields were obtained at 2% A and 3-h B across all oil types, with coconut oil yielding the highest biodiesel at 96%.

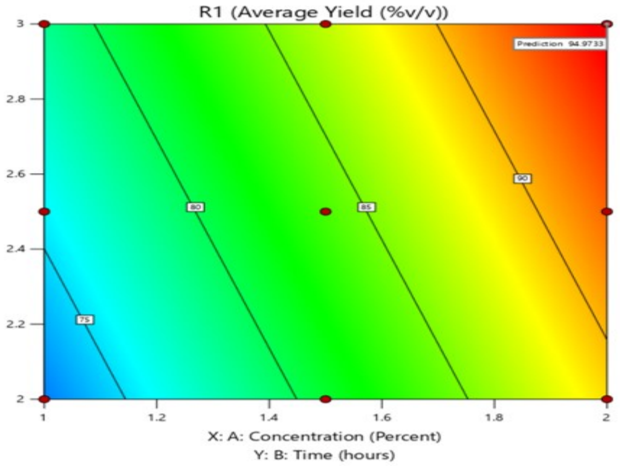

Figure 2. Interaction effects of operating variables on palm oil.

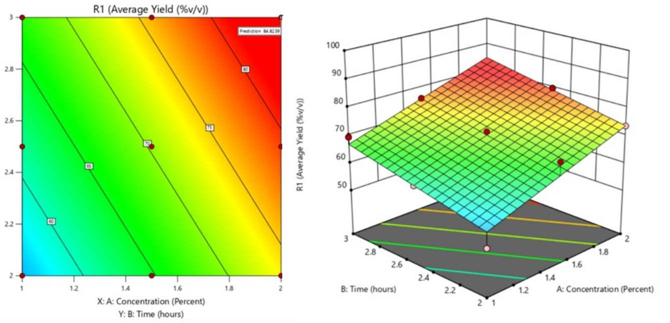

Figure 3. Interaction effects of operating variables on vegetable oil.

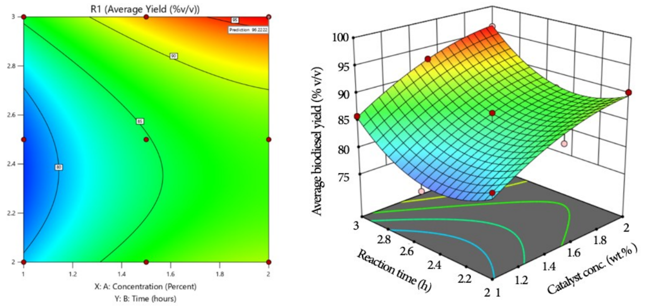

Figure 4. Interaction effects of operating variables on coconut oil.

B influences the effectiveness of the transesterification process. It was varied between 2 h, 2.5 h, and 3 h. Results show an increase in yield with increasing B. Based on the results gathered, the highest biodiesel yields from the WCOs were achieved at B = 3 h. The results are comparable to those of [11] and [4], which revealed a similar trend in yield while varying B.

A was highly influential for the CME yield. Smaller particle size increases the exposure of basic active sites, resulting in improved catalytic activity. A high CME yield of 96% v/v was observed at 2% A. For instance, higher A improved yield up to an optimal point but resulted in diminishing returns and side reactions when exceeded. Similarly, longer B enhanced conversion but plateaued, as the reaction reached completion. These findings align with a previous study [12], which emphasizes the critical role of controlled reaction conditions in optimizing biodiesel yield. Also, soap and gel may form when A increases beyond the optimum level, preventing ester layer separation [13].

3.3. Comparative characterization of B100 and B5

According to the standard set by the DOE, the biodiesel properties of CME include a density range of 0.85–0.90 kg/L and a maximum kinematic viscosity of 6.0 mm²/s. Water content must not exceed 0.05% by volume, and carbon residue is capped at 0.30% (mol/mol). Sulfur content is limited to a maximum of 10 ppm, while free glycerin and total glycerin are restricted to 0.02% (w/w) and 0.24% (w/w), respectively. FAME content must be at a minimum of 96.5%. The distillation temperature should not exceed 360°C, oxidation stability requires a minimum of 10 h, and the flash point is set at a minimum of 100 °C.

Table 5 shows the properties of B100 produced from the highest-yielding optimal conditions. It presents that the majority of the properties conform to the national standards, and the non-conforming properties possess only a small difference from the provided limits. The obtained data for density indicates that the produced B100 almost conforms to the allowable limits, ensuring the best air-to-fuel ratios for full combustion. In light of the result for kinematic viscosity, the data obtained conforms to the set limit at 3.01 mm^2/s. The measured water content and carbon residue of the produced B100 didn't conform to the set limits, indicating that the fuel is decomposing and forming carbonaceous material.

Table 5. Properties of B100 compared to the PNS for CME

Property	Method	Measured value	DOE-PNS standard
Density, kg/L	ASTM D4052	0.9303	0.85-0.90
Kinematic viscosity, mm^2/s	ASTM D445	3.01	6.0 max.
Water content, % v/v	ASTM E203	0.162	0.05 max.
Carbon residue, % w/w	ASTM D4530	0.54	0.3 max.
Calculated cetane index	ASTM D4737-Proc B	21.8	-
Sulfur content, ppm	ASTM D7039	3.7	10 max.
Free glycerin, % w/w	EN 14105 modified	0.01	0.02 max.
Total glycerin, % w/w	EN 14105 modified	0.1	0.24 max
FAME content, % w/w	PNS/DOE TM 01	96.55	96.5 min.
Distillation Temperature, ˚C	ASTM D86	296.5	360 max.
Oxidation stability, h	EN 14112	21.6	10 min.
Flash point, ˚C	ASTM D93-Proc. A	139.0	100 min.

The measured water content of the produced B100 didn't also conform to the set limits of the national standards at 0.162% (v/v). It is a fact that in comparison to petroleum diesel, biodiesel is more tolerant to moisture, indicating its undesirable characteristic to hold water. However, a higher percentage of moisture may result in issues including water accumulation and microbiological growth in fuel tanks and other transportation-related equipment, leading to corrosion [14]. Hence, there is a need for significant water content reduction to preserve the effectiveness of the condensation system installed in the reactor. A machine modification concerning this matter is necessary [8].

Another property that did not conform to the set limits is carbon residue. The obtained data on this parameter is beyond the 0.3 maximum value which indicates that the fuel is decomposing into carbonaceous material, which can clog diesel fuel injection nozzles and obstruct flow (Table 5) [15].

Since no testing equipment for cetane number is available locally, calculated cetane indices were provided [16]. The sulfur content of fuels also significantly affects engine efficiency and emissions. Moreover, the free and total glycerin content of the B100 sample both conform to the standards, as well as the FAME content at 96.55% (w/w). Additionally, the product's compliance with the distillation temperature allows it to have room for a higher purification from all the unreacted oil components, sulfur, and metal-catalyst content [17]. In terms of oxidation stability, the conformity of the B100 sample indicates that it is resistant to any chemical changes that might occur during the long storage of the biodiesel. Lastly, the obtained high flash point of 139 ˚C indicates the B100's low fire hazard when exposed to high-temperature heat sources [18].

Presented in Table 6 are the results for the available property testing in the produced B5. Among the 12 properties obtained from the produced B100, only eight of them are available in the blended set-up. And among these eight, only one, which is carbon residue, did not conform to the set national standards. This is primarily due to the huge amount of carbon content in the added commercial diesel which signifies a higher fuel emission compared to the produced B100 [19]. On the other hand, the rest of the properties comply with the limits which suggest that the produced B100 can be a beneficial additive to commercially-available diesel fuels.

Table 6. Properties of produced B5 compared to the PNS

Properties	Method	Measured Value	DOE-PNS B5
Density, kg/L	ASTM D4052	0.8472	0.82-0.86
Kinematic Viscosity, mm^2/s	ASTM D445	3.663	2.0-4.5
Water Content, % v/v	ASTM E203	0.018	≤ 0.1
Carbon Residue, % w/w	ASTM D4530	0.34	≤ 0.15
Calculated Cetane Index	ASTM D4737-Proc B	53.1	≥ 50
Sulfur Content, ppm	ASTM D7039	0.0035	≤ 0.005
Distillation Temperature, ˚C	ASTM D86	355.2	≤ 370
Flash Point, ˚C	ASTM D93-Proc. A	65	≥ 55

3.4. Statistical analysis of the lab test results for biodiesels

The differences between the parameters of the generated B100 and the PNS for CME are presented in Table 7. All the null hypotheses for the properties are accepted, indicating that there is no significant difference in the properties of pure biodiesel produced from the highest-yielding run among the three WCOs compared to the national standards.

Table 7. Differences between the properties of produced B100 and PNS for CME

Properties	p-value	Computed t-values	Decision on Ho	Verbal interpretation
Density, kg/L	0.4667	0.0945	Accept	Not significant
Kinematic Viscosity, mm^2/s	0.3679	-0.3873	Accept	Not significant
Water Content, % v/v	0.0748	2.2860	Accept	Not significant
Carbon Residue, % w/w	0.4290	0.2269	Accept	Not significant
Calculated Cetane Index	-	-	-	-
Sulfur Content, ppm	0.2959	-0.6322	Accept	Not significant
Free Glycerin, % w/w	0.4187	-0.2610	Accept	Not significant
Total glycerin, % w/w	0.1062	2.8856	Accept	Not significant
FAME Content, % w/w	0.4998	-0.00054	Accept	Not significant
Distillation Temperature, ˚C	0.4448	-0.1753	Accept	Not significant
Oxidation Stability, h	0.2350	1.0987	Accept	Not significant
Flash Point, ˚C	0.5	0	Accept	Not significant

Table 8 presents the differences between the properties of the produced B5 with the PNS for CME, showing that the sulfur content and water content were deemed to be significant. Both parameters met the standards, but the measured values are lower than the given maximum standards; hence, their null hypothesis are rejected, showing a significant difference compared to PNS. On the other hand, it was determined that the properties classified as "not significant" clearly fall within the statistical range of values provided by the PNS for CME; hence, their corresponding null hypotheses are accepted, showing no significant difference in comparison with the national standards.

Table 8. Differences between the properties of produced B5 with the PNS for CME

Properties	p-value	Computed t-values	Decision on Ho	Verbal interpretation
Density, kg/L	0.4883	0.0331	Accept	Not significant
Carbon Residue, % w/w	0.1545	1.3518	Accept	Not significant
Distillation Temperature, ˚C	0.4873	-0.03997	Accept	Not significant
Flash Point, ˚C	0.4428	0.1818	Accept	Not significant
Sulfur Content, ppm	3.07246E-05	127.5621	Reject	Significant
Kinematic Viscosity, mm^2/s	0.3393	-0.5525	Accept	Not significant
Water Content, % v/v	0.00038	35.8460	Reject	Significant

3.5. Engine emission testing of the produced B100 and B5

The efficiency of the produced B100 and B5 samples was analyzed using engine emission testing. Presented in Table 9 are the results of the emission testing of produced biodiesel samples in comparison with a commercial diesel.

Table 9. Engine emission test results for produced biodiesels

	Commercial diesel	B5	B100
Hydrocarbon	21 ppm	17 ppm	15ppm
CO_2	2.2%	1.4%	1.1%
CO	0.06%	0.03%	0.02%

Source: TESDA - Region IVA

Through the testing method, the concentrations of hydrocarbons (HCs) and CO_2, with the latter as the major component of fuel atmospheric emissions were recorded. The results (Table 9) indicate that among the three samples, commercial diesel possesses the most harmful fuel emission that could contribute to air pollution. On the contrary B5 showed improved emissions, with HC at 17 ppm, CO_2 at 1.4%, and CO at 0.03%. The lower emissions of B100 and B5 underscore their potential for mitigating air pollution, specifically reducing greenhouse gas emissions. Additionally, B100 exhibitted the lowest emission, signifying its environmental compatibility for carbon emission reduction [20].

These outcomes reinforce biodiesel's environmental compatibility and its role in promoting cleaner energy alternatives. The reductions in CO and HCs are particularly noteworthy, as they directly contribute to improving air quality. Furthermore, the use of biodiesel as a fuel additive (B5) offers a practical approach to integrating renewable fuels into existing diesel engines without requiring significant modifications.

The findings underscore the socio-economic and environmental benefits of utilizing waste materials for biodiesel production. By repurposing WCO and *kuhol* shells, this study contributes to reducing environmental pollution and dependence on fossil fuels. The use of heterogeneous catalysts enhances process sustainability due to their reusability, as evidenced by successful recycling for up to eight cycles with yields above 50%.

The produced biodiesel aligns well with the PNS for CME, with most properties conforming except for minor deviations in density and moisture content. This demonstrates the potential of scaling up production for commercial viability. Moreover, the reduction in harmful emissions, such as hydrocarbons and carbon monoxide, further emphasizes the environmental advantage of biodiesel over traditional diesel fuels.

4. Conclusions

This study highlights the potential of WCO as a sustainable feedstock for biodiesel production, with waste coconut oil identified as the most optimal type. Under the conditions of 2% CuO/CaO concentration and a 3-h reaction time, an impressive biodiesel yield of 96% v/v was achieved, demonstrating the critical impact of these parameters on conversion efficiency. The properties of the produced biodiesels, B100 and B5, largely met the PNS for CME. Furthermore, emission testing revealed that biodiesel derived from WCO significantly outperforms commercial diesel in reducing harmful emissions, reinforcing its environmental advantages.

To enhance biodiesel production and quality, WCO property testing should be conducted in accredited laboratories for accurate characterization and initial treatment. Alternative cost-effective catalysts, such as mixed-metal oxides or calcium oxide from other sources, should be explored. Process improvements, including optimizing condensation systems and recovery methods for catalysts, can address water content issues and reduce material loss. Expanding the scope of biodiesel property testing and incorporating advanced performance evaluations, like combustion gas analysis, will ensure a more comprehensive assessment and align with national standards. These steps aim to improve efficiency, sustainability, and the broader adoption of WCO-derived biodiesel.

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