

Integrating Waste Valorization and Green Energy: Biodiesel Production Using Microwave-Derived Chitosan Catalyst from Raw Tilapia (*Oreochromis Niloticus*) Scales

Tristan Roy Panaligan^{1*}, Andrea Marie Alam¹, Jean Margaret Berroya¹, and Princess Lynelle Carysse Torres¹

¹Mapúa Institute of Technology at Laguna, Mapúa Malayan Colleges Laguna, Cabuyao, Laguna, Philippines, 4025

Abstract. This study presents an integrated approach to biodiesel production using waste vegetable oil (WVO) and chitosan derived from raw tilapia (*Oreochromis niloticus*) scales, synthesized via microwave-assisted methods. The chitosan acted as a heterogeneous catalyst during the transesterification of pre-treated WVO. Key process parameters included esterification and transesterification stages, with acid value and volume changes monitored throughout. Characterization of the resulting biodiesel was conducted in accordance with the Philippine National Standard PNS/DOE QS 002:2015, focusing on total sulfur content, water and sediments, and Fatty Acid Methyl Ester (FAME) content. The final product exhibited compliant sulfur and water levels, though the FAME content remained below specification, attributed to limited glycerol separation time. Despite this, the process achieved a 64% conversion and reduced the acid value from 2.11 to 0.262 mg KOH/g, indicating high potential for further optimization. This research supports sustainable fuel development while promoting circular utilization of agrowaste in developing economies.

1 Introduction

The global rise in carbon dioxide (CO₂) emissions has contributed to an approximate 1 °C increase in global temperatures since the industrial era, with countries like the Philippines ranking as the 69th most polluted globally in 2022 [1]. A major contributor to greenhouse gas emissions, the transportation sector is expected to surpass coal-fired power plants in CO₂ emissions by 2040 at an annual growth rate of 5.8% [2]. The pressing need to cut CO₂ emissions has made the hunt for alternative renewable energy sources a top priority for countries like the Philippines that rely largely on fossil fuels. Made from plant or animal fats, biodiesel is a sustainable substitute for traditional diesel because it is non-toxic, biodegradable, and emits fewer exhaust pollutants, making it a perfect fit for the transportation industry [3].

* Corresponding author: trlpanaligan@mcl.edu.ph

In alignment with the Philippine government's Republic Act No. 9367 (Biofuels Act of 2006), this study highlights the abundant yet underexploited potential of waste vegetable oil (WVO) as a renewable, low-cost feedstock for biodiesel production. Even within the European Union—despite its progressive stance on waste management—substantial collection inefficiencies remain. It is estimated that the EU generates approximately 4 million tonnes of waste cooking oil (WCO) annually, based on a per capita production of 8 liters for a population of around 500 million. However, current collection efforts capture only about one-fourth of this potential volume, highlighting a significant gap between generation and recovery [4]. Additionally, Pakistan generated approximately 468,842 tonnes of WVO in 2023, reinforcing the relevance of national-scale valorization frameworks [5].

Despite global availability, the Philippines has yet to fully realize the potential of its own WVO stream. While comprehensive national data remain scarce, foreign industry trends and domestic policy statements suggest significant uncollected volumes from food establishments and households.

Beyond underutilization, improper WVO disposal presents a growing environmental concern. As highlighted in recent studies, the absence of structured WVO management contributes to serious pollution issues. For example, Hamdi et al. [6] reported that poor handling practices in restaurants, hotels, and food-processing industries—particularly those using retort technology—can lead to odor problems and oil film formation on water surfaces, thereby increasing biological oxygen demand and degrading aquatic ecosystems.

Given that WVO typically contains high levels of free fatty acids—ranging from 5% to 20%—pretreatment is essential to minimize soap formation and improve biodiesel yield [7]. Utilizing WVO not only reduces reliance on fossil fuels but also addresses environmental concerns associated with improper disposal, which can lead to pollution and public health risks [8], [9].

This study responds to these challenges by employing chitosan synthesized from tilapia fish scales as a biodegradable, heterogeneous catalyst—a novel approach that enhances sustainability. The chitosan was prepared via microwave-assisted demineralization, deproteinization, and deacetylation, as previously established in our earlier work [10], which enabled a more rapid and eco-efficient synthesis process. The same microwave technique was also applied to the transesterification step. Despite a limited 9-hour separation period for biodiesel and glycerol—shorter than typical reaction durations—the process demonstrated favorable energy performance and practical viability.

By valorizing both waste vegetable oil and fish-processing by-products, this work addresses critical environmental and energy issues while contributing to the United Nations Sustainable Development Goals (SDGs) 7 and 13.

2 Methodology

2.1 Chitosan Preparation as Heterogeneous Catalyst

Chitosan used in this study was synthesized from raw tilapia (*Oreochromis niloticus*) fish scales via microwave-assisted demineralization, deproteinization, and deacetylation, following the optimized procedure established in our previous work [10]. The prepared chitosan was subsequently employed as a heterogeneous catalyst in the transesterification of waste vegetable oil for biodiesel production.

2.2 Preparation of WVO for Biodiesel Production

WVO was collected from a local restaurant in Muntinlupa, Philippines. The preparation procedure was adapted from Sahar et al. [2] with necessary modifications. Initially, the WVO was filtered using a 200-mesh sieve to eliminate coarse particulates and solid impurities. Following filtration, the oil was heated to 105 °C and maintained at boiling for 30 minutes to remove residual moisture. Once moisture removal was completed, the oil was allowed to cool to room temperature in preparation for the subsequent citric acid degumming process.

2.3 Citric Acid Degumming

Citric acid degumming was utilized to remove phospholipids and other polar impurities from the filtered oil, a critical step in improving biodiesel quality. Following the procedure described by El Knidri et al. [11] with slight modifications, 200 mL of the pre-treated oil was mixed with 6 mL of 30% (v/v) citric acid solution and heated to 70 °C under continuous stirring for 20 minutes. The mixture was subsequently cooled to 40 °C, at which point 2 mL of distilled water was added to facilitate phase separation. The emulsion was then centrifuged at 4000 rpm for 45 minutes, allowing the separation of the degummed oil from the gum residue.

2.4 Esterification

In order to reduce the amount of free fatty acids (FFAs) in the oil and improve the effectiveness of the transesterification procedure that followed, the esterification phase was used to transform the FFAs into methyl esters. This pretreatment is essential for avoiding soap production, which can have a negative impact on the yield and purification of biodiesel. Following the methodology outlined by Supraja et al. [12], with appropriate modifications, 40 mL of degummed waste vegetable oil was combined with 240 mL of methanol and 0.4 mL of sulfuric acid in a 500 mL round-bottom flask. The mixture was subjected to microwave irradiation for 1 minute, then transferred into a separatory funnel and allowed to settle under gravity for 45 minutes. This process produced two layers: the upper ester-rich phase and a lower aqueous layer. The esterified oil was carefully decanted, washed with warm distilled water to remove residual acid and methanol, and subsequently dried using sodium sulfate to ensure removal of moisture and impurities.

2.5 Transesterification

Transesterification was conducted to convert pretreated waste vegetable oil into biodiesel using chitosan as a heterogeneous catalyst. In a 500 mL round-bottom flask, 40 mL of pre-treated waste vegetable oil was combined with 240 mL of methanol and 0.4 g of chitosan derived from tilapia scales. The reaction mixture was subjected to microwave irradiation for 30 minutes with a ramping time of 4 minutes, following the procedure described by Babel et al. [7].

Upon completion of the reaction, the mixture was transferred to a separatory funnel and allowed to stand undisturbed to facilitate gravity separation of the two phases. The bottom glycerol-rich aqueous layer was drained, leaving the ester-rich oil layer. The ester oil was then washed with warm distilled water at approximately 55°C and gently agitated. After standing for 9 hours, the two layers were again separated, and the aqueous phase was removed, as described by Arachchige et al. [13].

To remove residual water, a dry washing step was performed by adding 4 to 5 g of sodium sulfate to the ester layer. The mixture was left to stand until the sodium sulfate clumped with

moisture and impurities. The biodiesel product was then filtered to remove the desiccant and yield a purified biodiesel sample, consistent with the method outlined by Demir and Soyhan [14].

2.6 Biodiesel Quality Analysis

To evaluate the effectiveness of the conversion process, acid value determination and biodiesel volume monitoring were conducted at two key stages: after esterification and after transesterification. The acid value, expressed in mg KOH/g, quantifies the amount of potassium hydroxide needed to neutralize the free fatty acids in a given gram of substance, providing a benchmark for assessing fuel quality and its long-term storage stability [15]. It serves as an intermediary for FFA content, which has a direct impact on the transesterification reaction's efficiency and soap formation potential. Successful FFA neutralization is indicated by a significant drop in acid value, which improves the quality of biodiesel and process dependability in general. Standard titrimetric techniques were used to quantify the acid values, and biodiesel quantities were noted at the conclusion of each step to track the development of the yield.

The characterization of biodiesel derived from WVO is essential to ensure compliance with fuel quality standards and environmental regulations. In accordance with the Philippine National Standard for Biofuels – Coconut Methyl Ester B100 (PNS/DOE QS 002:2015), this study focused on three critical parameters: total sulfur content, water and sediment, and FAME (Fatty Acid Methyl Ester) content. These metrics serve as key indicators of biodiesel quality and engine compatibility. Total sulfur content is regulated to mitigate harmful SO_x emissions and extend engine life, while the water and sediment test ensures fuel cleanliness and stability, reducing risks of corrosion and microbial contamination. FAME content, set at a minimum of 96.5% mass by the standard, is vital for verifying the completeness of the transesterification process and ensuring combustion efficiency. All characterization tests in this study were conducted at Intertek Testing Services Philippines, Inc., located in Makati City, Metro Manila, a Department of Energy (DOE)-accredited laboratory for fuel quality analysis in the Philippines.

2.7 Results and Discussion

Figure 1 presents both the acid value reduction and the corresponding biodiesel yield achieved through the microwave-assisted process. The acid value, serving as an indicator of free fatty acid content, was initially measured at 2.11 mg KOH/g in the untreated waste vegetable oil. This was effectively reduced to 0.422 mg KOH/g after acid-catalyzed esterification and further decreased to 0.262 mg KOH/g following transesterification, successfully meeting the Philippine National Standard (PNS) biodiesel specification limit of 0.50 mg KOH/g.

For instance, existing literatuers achieved an acid value reduction from 4.81 to below 0.5 mg KOH/g using microwave-enhanced transesterification in two minutes [16],[17]. Alongside the acid value data, the same figure shows the biodiesel product volumes: from an initial 1.75 L of WVO, the volumes after esterification and transesterification were recorded at 570 mL and 480 mL, respectively, indicating a final biodiesel yield of approximately 27.4%.

Table 1 summarizes the analytical results of the produced biodiesel as evaluated by Intertek Testing Services Philippines, Inc. The sample exhibited a total sulfur content of 0.0007% and a water and sediment content of 0.01%, both of which are well within the acceptable limits set by the Philippine National Standard PNS/DOE QS 002:2015. However, the measured FAME content was 64.8%, which falls below the minimum required value of

96.5%. This lower FAME content corresponds to a biodiesel yield of 64% and may be attributed to the limited separation time of only 9 hours for biodiesel and glycerol layers, a deviation from the conventional 24-hour settling period reported in prior studies [13].

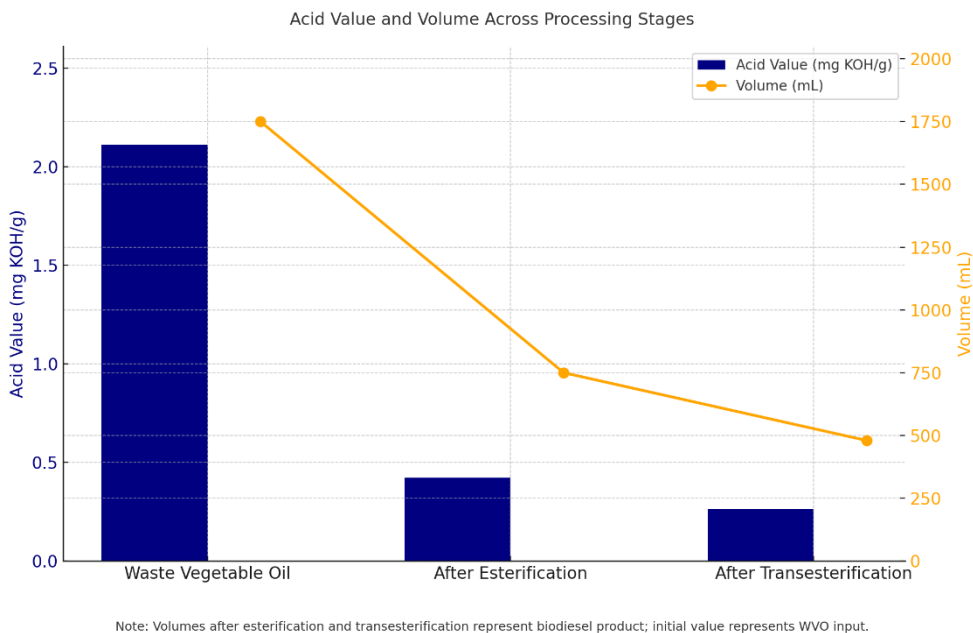


Fig. 1. Acid Value Reduction and Biodiesel Yield at Different Stages of Processing Using Microwave-Assisted Conversion of Waste Vegetable Oil.

Additionally, earlier findings such as those by Babel et al. [8] demonstrated higher conversion efficiencies under more optimized transesterification conditions. These results suggest that further refinement of post-reaction handling and process conditions is necessary to enhance yield and meet the standard specification for biodiesel quality.

Table 1. Biodiesel Characterization Results Based on Philippine National Standards (PNS/DOE QS 002:2015)

TEST CONDUCTED	METHOD	UNIT	SPECIFICATION	RESULT
Total sulfur content	ASTM D2622	% mass	0.001 (max)	0.0007
Water and Sediments	ASTM D2709	% vol	0.05 (max)	0.01
FAME Content	EN14078 mod	% vol	96.5 (min)	64.8

3 Conclusion and Recommendations

This study demonstrated a viable, low cost, and environmentally responsible approach to biodiesel production through the valorization of two locally abundant waste streams: waste vegetable oil and tilapia fish scales. By employing microwave assisted synthesis and reaction technologies, the research achieved substantial reductions in acid value and produced biodiesel with acceptable sulfur and water sediment levels in accordance with PNS/DOE QS 002:2015. Although the measured FAME content did not meet the minimum specification, the observed biodiesel yield and acid value profile validate the technical promise of this dual

waste valorization framework. The innovative aspect of the work is the incorporation of waste-derived chitosan as a heterogeneous catalyst, which simplifies the procedure and makes it faster and more sustainable than traditional protocols. These results demonstrate the method's potential scalability for decentralized biofuel projects, especially in areas with limited access to extended reaction infrastructure and conventional catalysts. To further increase FAME content and overall conversion efficiency, process improvement should be given the highest priority moving forward, especially with regard to reaction duration, separation methods, and catalyst reuse. This initiative addresses local environmental management issues while connecting with global sustainability goals and making a significant contribution to the continuing conversation on renewable energy innovation and circular economy practices.

References

1. IQAir, Philippines Air Quality Index (AQI) and Air Pollution information, Aug. 2022
2. S. Sahar, et al., *Sustainable Cities Soc.* 41, 220 (2018)
3. Zulqarnain, et al., *Sustainability* 13, 788 (2021)
4. J. Ibáñez, S. Martel Martín, S. Baldino, C. Prandi, and A. Mannu, *Processes* 8, 798 (2020)
5. F. Musharavati, K. Sajid, I. Anwer, A.-S. Nizami, M.H. Javed, A. Ahmad, and M. Naqvi, *Sustainability* 15, 16550 (2023)
6. N.A. Hamdi, A. Sulaiman, M.H. Harun, N.F. Mohd Noor, A.S. Ahmad, *IOP Conf. Ser.: Earth Environ. Sci.* 1091, 012054 (2022)
7. A. Mannu, et al., *Waste Manag.* 96, 1 (2019)
8. S. Babel, S. Arayawate, E. Faedsura, H. Sudrajat, in *Utilization and Management of Bioresources*, S. Ghosh (Ed.), Springer, Singapore (2018)
9. A. Kharina, S. Searle, A. D. Rachmadini, A. Kurniawan, A. Prionggo, *Int. Council Clean Transport* (2018)
10. T.R. Panaligan, J. Aquino, A.M. Alam, J.M. Berroya, P.L.C. Torres, *Environ. Sci. Eng.* (2025)
11. H. El Knidri, et al., *Process Saf. Environ. Prot.* 104, 395 (2016)
12. K.V. Supraja, B. Behera, B. Paramasivan, *Environ. Sci. Pollut. Res. Int.* 22 (2015)
13. U.S. Arachchige, et al., *Nat. Environ. Pollut. Technol.* 20, 1973 (2021)
14. V.G. Demir, H.S. Soyhan, *Eur. J. Eng. Nat. Sci.* 2, 137 (2017)
15. P. Onu, C. Mbohwa, in *Agricultural Waste Diversity and Sustainability Issues*, P. Onu, C. Mbohwa (Eds.), Academic Press, 97 (2021)
16. M.-C. Hsiao, P.-H. Liao, N.V. Lan, S.-S. Hou, *Energies* 14, 437 (2021)
17. X. Hu, B. Zhang, Q. Wang, Y. Liu, *Energies* 16, 1741 (2023)