**American Journal of Science, Engineering and Technology**
2023; 8(3): 173-183
http://www.sciencepublishinggroup.com/j/ajset
doi: 10.11648/j.ajset.20230803.18
ISSN: 2578-8345 (Print); ISSN: 2578-8353 (Online)

# Optimization Study of Methyl Ester (Biodiesel) Synthesis from Chicken Tallow Using Polyoxomolybdate Catalyst

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## To cite this article:

Ibrahim Garba Wawata, Abubakar Umar Birnin Yauri, Aliyu Muhammed, Babayemi Wasiu. Optimization Study of Methyl Ester (Biodiesel) Synthesis from Chicken Tallow Using Polyoxomolybdate Catalyst. *American Journal of Science, Engineering and Technology*. Vol. 8, No. 3, 2023, pp. 173-183. doi: 10.11648/j.ajset.20230803.18

**Received**: August 9, 2023; **Accepted**: August 25, 2023; **Published**: September 6, 2023

**Abstract:** Biodiesel, which consists of fatty acid alkyl esters, is currently accepted as a potential alternative to petro-diesel due to its low carbon footprint and environmental advantages. This study synthesized a polyoxomolybdate catalyst in an organic-aqueous phase at a pH of 2, using Ammonium Molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) salt. The catalyst underwent characterization through a UV-visible spectrophotometer method. The physicochemical properties of the chicken tallow were determined using standard methods from AOCS and other established techniques. The transesterification of chicken tallow utilizing polyoxomolybdate was optimized using a three-level, four-factorial Box-Behnken experimental Design with 27 runs of Response Surface Methodology (RSM). Furthermore, the produced biodiesel was characterized using FTIR, while the profiles of fatty acid methyl esters were determined using the Gas chromatography-mass spectrometry (GC-MS) technique. The fuel properties of the biodiesel were analyzed using ASTM methods. The spectroscopic studies of the catalyst unveiled the presence of predominantly ($Mo_2O_2^{2+}$) and $H_2MoO_4$ species. The chicken tallow reveals low acid and free fatty acid values, with a moderate degree of unsaturation (iodine value) and saponification value. The experimental results and surface response plot indicated an optimal biodiesel yield of 96.9% at 60°C for 60 minutes, using an oil-to-methanol ratio of 1: 6 with a catalyst loading of 1.2g. Additionally, the FTIR and GC-MS analyses demonstrate the successful conversion of chicken tallow into methyl ester, exhibiting favorable fuel properties that fall within the acceptable limits set by ASTM. The polyoxomolydate catalyst showcases exceptional activity, good reusability (up to 3 cycle run), and ease of separation from the product mixture.

**Keywords:** Polyoxomolybdates, Catalyst, Methyl Esters, Chicken Tallow, Transesterification, Biodiesel, Optimization

## 1. Introduction

The energy resources of fossils, which include coal, petroleum, and natural gas, continue to play a decisive role in the economies of most developing countries. Nevertheless, these energy sources are non-renewable and finite, primarily due to excessive dependence and utilization. Additionally, growing environmental concerns revolve around challenges such as elevated levels of carbon dioxide, greenhouse gases, polycyclic hydrocarbon (PAH), and nitrated compounds in the atmosphere.

Consequently, the escalating demand for energy and the increasing cost of petroleum, combined with the limited reserves of this resource, have spurred an urgent need to develop and employ modern technologies and efficient bioenergy conversion processes. These advancements aim to be competitive with fossil fuels while addressing the energy challenges of the new millennium [1-3].

Biodiesel (mono alkyl esters), is a potential substitute for petroleum diesel which is derived from biological origin. It is

currently attracting global interest as it reduces over-dependence on petroleum-based fuels and mitigates environmental pollution. Biodiesel is composed of mono-alkyl esters of long-chain fatty acids derived from renewable sources e.g. vegetable oils and animal fats [4].

Transesterification is a reaction between lower molecular weight alcohols and triglycerides. This reaction is a three-step or two-step reversible process resulting in the formation of fatty acids alkyl esters (Biodiesel), and glycerol. There are vast sources of raw materials for biodiesel production which include; animal fats, plant oils, microbial mass, and others. Currently, vegetable oils and animal fats are successfully being used in biodiesel synthesis. [5]

However, the major challenges associated with the use of vegetable oil and animal fats are due to the high cost and competitiveness in the food market. Consequently, non-edible oils and waste animal fats are thought to be cheaper and sustainable sources. In addition, animal fats have low pour points, flash points, elevated viscosity, and low cetane numbers [6].

To overcome the problems associated with using animal fats as a fuel source for biodiesel, various processes are employed such as; pyrolysis, preheating dilution, emulsification, and transesterification. Moreover, the transesterification process is proven to be ideal and widely used for the reduction of viscosity and improve volatility of animal-based biodiesel [7-9].

The choice of catalyst for the transesterification reaction depends on the quality of the feedstock. Acid catalysts are employed when synthesizing biodiesel from feedstock with a higher free fatty acid (FFA) value (> 3%), whereas alkaline catalysts are used for feedstock with a lower FFA value (< 3%). Acid catalysts present challenges such as soap formation in high FFA feedstock, high costs associated with waste treatment and disposal, and separation from products [10, 11]. Conversely, heterogeneous catalysts, despite their drawbacks of miscibility and sintering issues, are commonly used in biodiesel production due to their ease of separation compared to homogeneous catalysts [12].

Recently, the high product and demand for white meat due to health benefits have created enormous waste from slaughterhouses. The extracted chicken fat from chicken waste demonstrates great promise as a viable source for biodiesel production [13]. Most of these fats and tallows obtained from local butcher and chicken shops, were subjected to a straightforward purification process involving melting, filtering, and drying to eliminate impurities [14].

Chicken skins represent one of the sources of solid waste that is typically not utilized, thus contributing to environmental waste. According to the report, the oil was initially extracted from the waste chicken skins obtained from local poultry farms and subsequently underwent transesterification, leading to the formation of FAME (Fatty acid methyl esters) and glycerol. The findings of the experiment indicated that the calorific values of FAME produced from chicken skin fat closely resembled those of petroleum-derived diesel [15, 16].

Widyan and Al-shyouck (2002) reported biodiesel production from chicken fat with an FFA content of 0.57% and recorded a biodiesel yield of 86% [17]. Shrammt et al reported the use of oil obtained from chicken skin in the production of biodiesel via the transesterification process. The fuel properties of the biodiesel obtained are found to compare favorably with those of petroleum-derived diesel [16].

An acid catalyst ($H_2SO_4$) was reportedly employed in biodiesel production using chicken fat with a high Free Fatty Acid (FFA) value of 4.16% in a two-step process. Initially, an esterification step employing an acid catalyst ($H_2SO_4$) was conducted, followed by a subsequent step using an alkaline-based catalyst. The use of a 1 wt% catalyst and a molar ratio of 1: 6 at 60°C for 120 minutes resulted in a higher methyl esters yield of 93.4%. The Chicken fat methyl esters displayed favorable fuel properties, meeting the standards outlined in the American Society for Testing and Materials (ASTM) guidelines [18].

However, Olutoye et al. reported biodiesel synthesis from chicken fat waste using a $ZnO/SiO_2$ heterogeneous catalyst. The process was conducted via a two-step process. The first step esterification process was carried out using sulphuric acid at a temperature of 60°C for 1 hour to reduce the FFA, before the second step of transesterification. The transesterification process carried out using a $ZnO/SiO_2$ heterogeneous catalyst was conducted using a three-level, four-factorial Box Behnken experimental design (BBD). The findings reveal; a biodiesel yield within the range of 56 – 88%. The quality of the biodiesel is in line with the ASTM standard limit for diesel fuel [19].

Despite renewed interest and studies on the use of Polyoxomolybdates as a catalyst, very little literature exists on the use of Polyoxomolybdates catalyst for the transesterification of chicken tallow to Biodiesel. This work, therefore, seeks to bridge this gap by systematically investigating the potential of Polyoxomolybdates catalysts for biodiesel production using chicken tallow.

# 2. Experimental

### *2.1. Sample Collection*

Chicken tallow was obtained from Labana farm in Aliero town, Kebbi state Nigeria. The tallow was boiled in water at 100°C then separated from the mixture using a separating funnel. The chicken tallow was dried, then kept in a glass bottle and stored in a cold dry place for further use.

All the reagents used in this study were obtained from reputable sources. Ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$), Sodium Sulphate ($Na_2SO_4$), Nitric acid ($HNO_3$), and Ethanol ($C_2H_5OH$) were procured from Sigma Aldrich, while Methanol ($CH_3OH$) was obtained from Loba Chemie. Potassium hydroxide (KOH) and Hydrochloric Acid (HCl) were purchased from Merck, and Silica gel and Wij's iodine solution were obtained from Fischer Scientific. It is worth noting that these reagents are either analytical or laboratory-grade.

The determination of Free Fatty Acid value, Acid value, Saponification, and Iodine value was conducted using AOCS standard methods and methods reported by Warra et al with slight modification [20].

### *2.2. Catalyst Synthesis*

The synthesis of the polyoxomolybdate catalyst was carried out using the method reported by Wawata [21] with slight modifications. The method description is as follows: An accurate amount of ammonium heptamolybdate salt (0.5 – 1.7 g) was dissolved in 4 ml of deionized water. The solution was then mixed with 30 ml of methanol while stirring in a 50 ml beaker. The mixture formed a white colloidal solution, which turned into a clear yellow solution upon adding 2-3 drops of dilute nitric acid solution. However, the pH of the solution was adjusted by gradually adding ammonia solution.

### *2.3. Characterization of Catalyst*

*UV – visible Spectrophotometry*

The catalyst synthesized was characterized using Genesys 10S UV – visible spectrophotometer (Thermo Scientific UK) with the following operation parameter; light source; dual beam, slit width – 1.0 nm, scan wavelength 190 – 800 nm, sample interval 0.1 nm, at a medium scan speed, running on VISION Lite software. This is to ascertain the nature of the polyoxomolybdate species.

### *2.4. Design of Experiment*

This study employed a Box-Behnken design (BBD) of response surface methodology, consisting of a three-level, four-factorial arrangement, to examine the transesterification of Chicken tallow methyl ester. The study aimed to identify the optimal values for process parameters, including reaction Temperature (A), Catalyst loading (B), Time (C), and Oil to Methanol ratio (D). The choice of the design is based on its good combination, few runs, and excellent outcome.

The reaction parameters were altered based on the experimental design, utilizing the response surface methodology (RSM) with the Minitab 18 software version. The details are outlined in Table 1.

***Table 1.*** *Independent Variables: Actual and Encoded Factors along with their Respective Levels for Response Surface Design.*

| Factors | Factor Code | Lower (-1) | Mid (0) | High (+1) |
|---|---|---|---|---|
| Temperature (°C) | A | 30 | 60 | 90 |
| Catalyst Loading (g) | B | 0.7 | 1.2 | 1.7 |
| Time (min) | C | 30 | 60 | 90 |
| Oil to Methanol Ratio | D | 1: 3 | 1: 6 | 1: 9 |

#### *2.4.1. Catalytic Testing*

Transesterification of Chicken tallow with methanol was conducted using a three-necked round bottom flask fitted to a condenser under constant stirring with a magnetic stirrer. The oil to methanol ratio of 5: 30 ml (1: 6) was used with 1.2 g of the catalyst at 60ºC for an hour. The resulting mixture was placed in a separating funnel and allowed to stand for 5 hours, forming two distinct layers. The upper layer, which contained an excess of methyl esters in methanol, was separated from the lower layers containing catalysts in glycerol. The catalyst was recovered from the glycerol phase by centrifuging at a speed of 1500 rpm for 30 min. The remaining unreacted methanol was removed from methyl esters by simple distillation at 80°C. The methyl esters were dried using Silica gel and the percentage yield of the methyl esters was calculated using the formula;

$$Biodiesel\ Yield\ (\%) = \frac{Weight\ of\ Methyl\ Esters\ (g)}{Weight\ of\ Chicken\ tallow\ (g)}\ X\ 100 \quad (1)$$

#### *2.4.2. Reusability Test*

The Optimum parameter was used for the reusability test. The catalyst recovered from the initial reaction was washed with methanol to remove glycerol and then reused for the second and third runs, and the CTME was calculated using Equation 1 above. The fuel properties of the methyl esters (Biodiesel) were determined following the ASTM standard methods [22].

## 3. Results and Discussion

### *3.1. Physicochemical Properties of the Chicken Tallow*

***Table 2.*** *Physicochemical Properties of Chicken Tallow.*

| Properties | Values |
|---|---|
| Appearance | Golden yellow |
| Free fatty acid (%) | 0.67 ± 0.05 |
| Acid value (mgKOH/g) | 0.70 ± 0.06 |
| Iodine value ($gI_2$/100g) | 142.1 ± 0.20 |
| Saponification value (mgKOH/g) | 208.3 ± 0.06 |
| Density ($g/cm^3$) | 0.8870 ± 0.002 |

* The values in Table 1 above are the mean and standard deviation of the triplicate analysis

The quality of CT oil and its potential applications can be determined by examining the physicochemical properties presented in Table 2. The table shows that CT has a clear golden-yellow appearance and specific values for Free Fatty Acid, Acid value, Iodine value, Saponification value, and Density. These values are reported as 0.67 ± 0.05, 0.70 ± 0.06, 142.1 ± 0.20, 208.3 ± 0.06, and 0.8870 ± 0.002, respectively.

#### *3.1.1. Free Fatty Acid and Acid Value*

Free Fatty Acid (FFA) and Acid value are crucial factors in the transesterification process of glycerides with alcohol using a catalyst [23]. Oil with acid and free fatty acid values exceeding 5% are unsuitable for base-catalyzed transesterification reactions [24]. High FFA content (>1% w/w) in oils leads to the formation of soap and makes product separation challenging. Table 2 shows that CT has FFA and acid values of 0.67 ± 0.05 mg KOH/g and 0.70 ± 0.06 mg KOH/g, respectively. These values are lower than 2.805 – 2.68 mg KOH/g and 5.33 – 5.61% reported for Chicken oil [21, 25], but close to 0.55 mg KOH/ reported by Mata et al [26]. These findings suggest that the quality,

freshness, and pretreatment method of CT may contribute to these lower values. The choice of catalyst depends on the FFA level, with basic and acid catalysts suitable for oils with less than 1% FFA, while oils with FFA higher than 1% are best catalyzed by acid-based catalysts. With an FFA value of 0.70 ± 0.06, CT is suitable for both acid and base-catalyzed transesterifications.

### *3.1.2. Iodine Value*

The iodine value reflects the unsaturation of fats and oils, with higher values indicating higher unsaturation [27]. Table 2 shows an iodine value of 142.1 ± 0.20 $gI_2$/100 g for CT, which is greater than 55.64 and 42.58 $gI_2$/100 g reported by [19, 25]. This finding aligns with the fatty acid profiles observed in the GC-MS chromatogram of the Fatty acid methyl profile of Chicken tallow in Figure 7.

### *3.1.3. Saponification Value*

The saponification value of 208.3 ± 0.06 reported for CT in Table 2 is higher compared to val109.4 and 103.785 reported by [19, 25] respectively. A high saponification value indicates that the oil consists of normal triglycerides, which are essential in the production of biodiesel.

### *3.1.4. Density*

Density refers to the mass per unit volume of a material and is typically lower than that of water for vegetable oils. In the case of CT, the density of 0.8870 ± 0.002 g/$cm^3$ (Table 2) agrees with 0.867g/$cm^3$ reported by Bhatti et al [29] and is lower than the value reported by Odetoye et al. [25]. Generally, the density of oils decreases with molecular weight and increases with the unsaturation level of the oil [29].

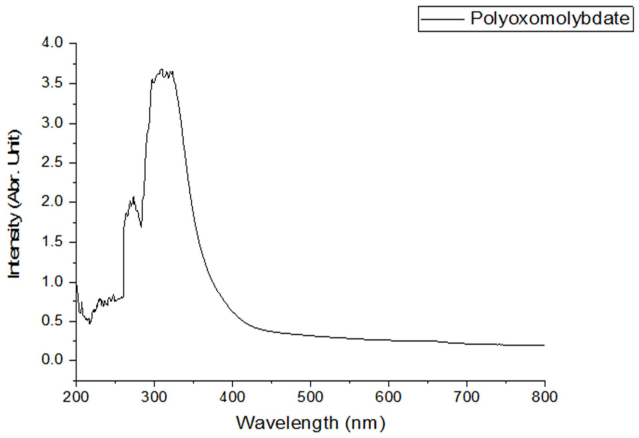



***Figure 1.*** *UV – Visible spectra of polyoxomolybdates species in methanol at pH 2.*

The UV-visible spectra presented in Figure 1 above exhibit prominent absorption peaks at 313 nm and 270 nm for polyoxomolybdate species. The absorption band at 270 nm is associated with the charge transfer transition of Mo=O, while the band at 313 nm is attributed to the charge transfer transition of Mo-O-Mo. The absorption peak at 313 nm is likely indicative of the presence of octahedral polymeric Mo complexes species ($Mo_2O_2^{2+}$), whereas the shoulder peak at 270 nm suggests the presence of tetrahedrally coordinated monomeric or dimeric Mo species ($HMoO_4^-$), as reported by [30, 31]. Moreover, the broadening of the peaks within the 306-400 nm and 310-400 nm regions suggests the formation of complex polymeric Mo species, as documented by Fournier [32].

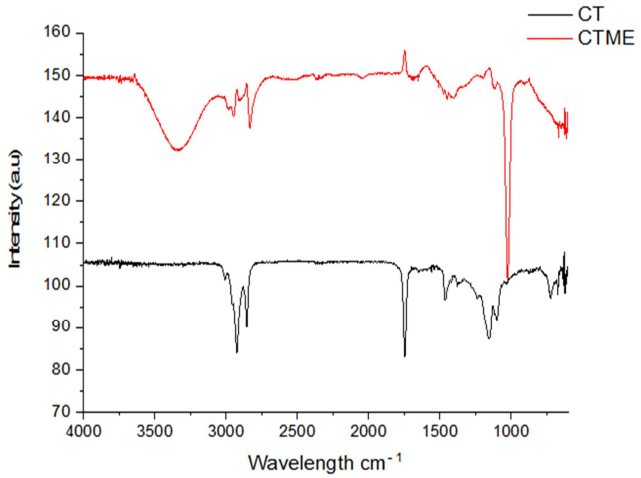



***Figure 2.*** *FTIR spectra of Chicken Tallow (CT) and Chicken Tallow Methyl Esters (CTME).*

The FTIR spectra in Figure 3 reveal various functional groups and vibrational frequencies for both Chicken tallow (CT) and Chicken tallow methyl esters (CTME). The CT spectra depict peaks between 3009 - 2847 $cm^{-1}$ which are assigned to symmetric and asymmetric stretching vibrational mode of $CH_3$ in an ester (-CO-O-$CH_3$), the peak at 1464 $cm^{-1}$ is assigned to $CH_3$ symmetric deformational vibration. In addition, a sharp and strong peak at 1746 $cm^{-1}$ is attributed to the (C=O) carbonyl group in the ester, and the peaks between 1229 - 1098 $cm^{-1}$ are attributed to the stretching vibration of the (- C- O-) ester group. The lower vibrational peaks at 715 $cm^{-1}$ and 675 $cm^{-1}$ are assigned to $CH_2$ rocking vibration on the chicken tallow. The broad band at 3335 $cm^{-1}$ in the CTME is assigned to OH- stretching vibration, with bands at 2927 and 2827 $cm^{-1}$ assigned to $CH_2$ and $CH_3$ stretching vibration. The bands at 1677 $cm^{-1}$ and 1403 $cm^{-1}$ are assigned to C=O stretching and bending vibration respectively. In addition, bands at 1196 $cm^{-1}$, 1116 $cm^{-1}$, and 1028 $cm^{-1}$ are assigned to C – O – C symmetric stretching, O – $CH_2$ – C asymmetric stretching, and $CH_3$ stretching vibration. a are in agreement with those reported by [33, 34]. The lower band at 712 $cm^{-1}$ and 724 $cm^{-1}$ on CTME and CT are assigned to $CH_2$ rocking respectively. The broad OH stretching vibration is prominent on CTME but absent on CT. This could be due to excess methanol, a reactant in transesterification reaction. The strong sharp band at 1028 $cm^{-1}$ is attributed to $CH_3$ stretching vibration in esters in Biodiesel, which is absent on CT. However, the increase in intensity in 1028 $cm^{-1}$ on CTME could be due to the formation of methyl esters (Biodiesel). The presence of oxygen functional groups in Biodiesel gives them an edge over Diesel fuel, with better combustion properties. This reveals its advantages over petroleum diesel as fuel.

***Table 3.*** *Fuel properties of Chicken tallow methyl esters (CTME).*

| Property | Results | ASTM limit |
|---|---|---|
| Cloud point (°C) | -19 | |
| Pour point (°C) | -45 | -15 – 16 |
| Flashpoint (°C) | 175 | 130 Min |
| Kinematic Viscosity ($mm^2/s$) | 2.70 | 1.9 – 6.0 |
| Cetane number | 55 | 47 Min |
| Density ($g/cm^3$) | 0.86 | |

### *3.2. Fuel Properties of the Biodiesel Produced*

The properties of the fuel are key indicators of the quality of most biodiesel. The values in Table 3 above represent various fuel properties such as the cloud point, pour point, flash point, kinematic viscosity, cetane number, and density, which are -19°C, -45°C, 175°C, 2.7 mm/s, 55, and 0.86g/cm$^3$, respectively. These values illustrate the fuel properties of the Chicken tallow methyl esters (Biodiesel) that were produced.

#### *3.2.1. Cloud Point and Cloud Point of CTME*

The pour point of – 19°C reported for CTME is in close conformity with -12°C reported by Hariprasath et al, but higher than 11°C reported by Seffati et al [35] for Chicken oil methyl esters. In addition, a cloud point of - 45°C for CTME is extremely low when compared with the – 15 – 16°C ASTM standard limit for biodiesel. However, the lower pour and cloud points affect the flow of biodiesel in pipes of the engine fuel system during cold weather. This could be attributed to the unsaturated fatty acid methyl esters observed in the GS-MS Chromatogram of Fatty acid methyl esters profile of Chicken tallow in Figure 7.

#### *3.2.2. Flash Point*

The flash point of 175°C reported in Table 3 for CTME is in close agreement with 171.1°C, and 179°C reported by Santosa [36] and Seffati et al [35] for biodiesel obtained from chicken oil or tallow respectively. The CMTE Flash point is with the ASTM limit of 130°C Minimum limit. The higher flash point of 175°C indicates that fuel is safe for handling, storage, and transportation even under mild conditions of temperature [37, 38].

#### *3.2.3. Kinematic Viscosity*

Kinematic viscosity refers to the resistance of a liquid to flow under the influence of gravity. It is a crucial property that represents the flow characteristics of a fuel. This property plays a significant role in guiding fuel atomization, combustion, and fuel distribution. The kinematic viscosity of CTME is found to be 2.7 mm/s as recorded in Table 3, this value is lower than the 4.94 mm/s reported by Santosa [36], but within the ASTM standard range (1.9-6.0). The Kinematic viscosity of the CTME suggests the presence of unsaturated methyl fatty acid esters with short to moderate chain lengths. These unsaturated methyl esters are likely to result in fewer deposits when utilized in combustion engines.

#### *3.2.4. Cetane Number*

The CTME exhibits a Cetane number of 55, as shown in Table 3. This value surpasses the 35 reported by Hariprasath et al., yet it remains within the ASTM minimum limit of 47 specified for biodiesel. The Cetane number serves as a measure of a fuel's ignition performance [39], and is a fuel quality parameter associated with ignition delay time and combustion quality. In general, higher cetane numbers indicate shorter ignition delays and a greater tendency for the oil to ignite [40]. The cetane number is typically observed to increase with longer carbon chain lengths and branching [41].

#### *3.2.5. Density*

The density of 0.86 g/cm$^3$ for CTME as shown in Table 3, conforms with 0.887 g/cm$^3$ and 0.883 g/cm$^3$ reported by Seffarati et al and Santosa respectively for Chicken oil methyl esters. [35, 36]. This value is lower than 0.9 g/cm$^3$ for most fats and tallows, making CTME lighter with good atomization properties when used as fuel in Diesel engines.

***Table 4.*** *Experimental Design results from the Box-Behnken RSM design for optimizing chicken tallow.*

| S/N | Temperature | Catalyst | Time | Ratio | Yield (%) |
|---|---|---|---|---|---|
| 1 | 30 | 1.2 | 60 | 9 | 79 |
| 2 | 30 | 1.2 | 30 | 6 | 65.4 |
| 3 | 60 | 0.7 | 60 | 3 | 38.7 |
| 4 | 30 | 1.2 | 90 | 6 | 86 |
| 5 | 60 | 1.2 | 30 | 9 | 59.3 |
| 6 | 90 | 1.7 | 60 | 6 | 72 |
| 7 | 90 | 1.2 | 60 | 9 | 90 |
| 8 | 90 | 0.7 | 60 | 6 | 34.4 |
| 9 | 60 | 1.2 | 60 | 6 | 96.9 |
| 10 | 60 | 1.2 | 90 | 3 | 43.3 |
| 11 | 60 | 1.7 | 30 | 6 | 48.3 |
| 12 | 60 | 1.2 | 30 | 3 | 72 |
| 13 | 60 | 0.7 | 30 | 6 | 34.3 |
| 14 | 60 | 0.7 | 90 | 6 | 35 |
| 15 | 30 | 0.7 | 60 | 6 | 30 |
| 16 | 90 | 1.2 | 30 | 6 | 86.9 |
| 17 | 60 | 1.2 | 90 | 9 | 90 |
| 18 | 90 | 1.2 | 60 | 3 | 65 |
| 19 | 60 | 0.7 | 60 | 9 | 37 |
| 20 | 30 | 1.2 | 60 | 3 | 48 |
| 21 | 60 | 1.2 | 60 | 6 | 95 |

| S/N | Temperature | Catalyst | Time | Ratio | Yield (%) |
|---|---|---|---|---|---|
| 22 | 30 | 1.7 | 60 | 6 | 70 |
| 23 | 60 | 1.7 | 60 | 9 | 61.5 |
| 24 | 60 | 1.7 | 60 | 3 | 55 |
| 25 | 60 | 1.2 | 60 | 6 | 95 |
| 26 | 90 | 1.2 | 90 | 6 | 88 |
| 27 | 60 | 1.7 | 90 | 6 | 72 |

***Table 5.*** *Analysis of Variance (ANOVA).*

| Source | DF | Seq SS | Contribution | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|---|---|
| Model | 9 | 11454.0 | 91.29% | 11454.0 | 1272.66 | 19.80 | 0.000 |
| Linear | 4 | 3612.5 | 28.79% | 3612.5 | 903.11 | 14.05 | 0.000 |
| A | 1 | 279.4 | 2.23% | 279.4 | 279.37 | 4.35 | 0.052 |
| B | 1 | 2391.4 | 19.06% | 2391.4 | 2391.36 | 37.21 | 0.000 |
| C | 1 | 192.8 | 1.54% | 192.8 | 192.80 | 3.00 | 0.101 |
| D | 1 | 748.9 | 5.97% | 748.9 | 748.92 | 11.65 | 0.003 |
| Square | 4 | 6959.4 | 55.47% | 6959.4 | 1739.85 | 27.07 | 0.000 |
| $A^2$ | 1 | 214.5 | 1.71% | 250.9 | 250.86 | 3.90 | 0.065 |
| $B^2$ | 1 | 5126.1 | 40.86% | 6597.3 | 6597.27 | 102.64 | 0.000 |
| $C^2$ | 1 | 193.9 | 1.55% | 661.1 | 661.07 | 10.29 | 0.005 |
| $D^2$ | 1 | 1425.0 | 11.36% | 1425.0 | 1424.99 | 22.17 | 0.000 |
| 2-Way Interaction | 1 | 882.1 | 7.03% | 882.1 | 882.09 | 13.72 | 0.002 |
| CD | 1 | 882.1 | 7.03% | 882.1 | 882.09 | 13.72 | 0.002 |
| Error | 17 | 1092.7 | 8.71% | 1092.7 | 64.27 | | |
| Lack-of-Fit | 15 | 1090.3 | 8.69% | 1090.3 | 72.68 | 60.40 | |
| Pure Error | 2 | 2.4 | 0.02% | 2.4 | 1.20 | | |
| Total | 26 | 12546.6 | 100.00% | | | | |

Temperature, B – Catalyst amount, C- Time. D- Methanol to oil ratio

The $R^2$ depicts that the model reveals a 91.29% variation in the yield (%) of biodiesel is explained by the model. Furthermore, R-sq (Adj) 86.68% variation in the Biodiesel yield (%) is explained by the only significant terms in the model.

*Analysis of variance (ANOVA)*

The ANOVA results in Table 5 are analyzed at a significance level of $\alpha = 0.05$. If the obtained p-value is less than $\alpha = 0.05$, the terms are found to be significant or else non-significant. However, the catalyst is found to be the most significant factor that affects the yield of biodiesel yield, while the oil: methanol ratio indicates less significance to biodiesel yield. In addition, the Temperature and Time are not significant to biodiesel yield.

The F-value of 19.80 for the model indicates the model is statistically significant at a 95% confidence limit.

*Regression equation*

Thus, a good agreement exists between the experimental and predicted FAME yields for the quadratic model in Equation 2 below;

$$\text{Yield} = -252.2 + 1.075\,A + 365.9\,B + 0.628\,C + 14.53\,D - 0.00762\,A^2 - 140.7\,B^2 - 0.01237\,C^2 - 1.816\,D^2 + 0.1650\,CD \quad (2)$$

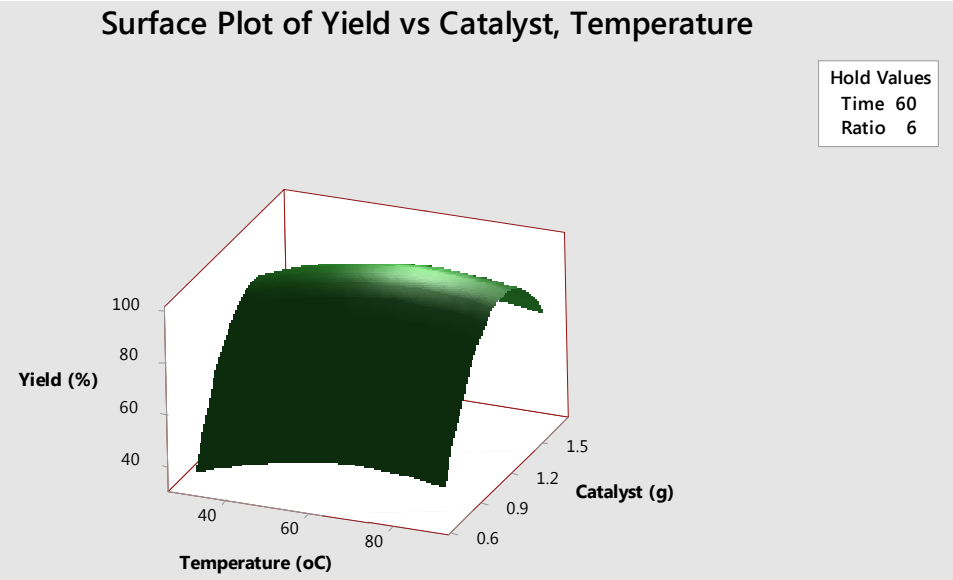



***Figure 3.*** *3D Response surface plot; effect of Temperature and Catalyst on CTME Yield.*

An increase in the catalyst amount results in a reduction in the yield of the CTME due to increasing mass transfer resistance of the reactant and the catalyst leading to an increase in the viscosity of the reaction mixture [42]. Furthermore, an increase in temperature affects the rate constant which increases methyl ester yield (moving the reaction forwards). Since esterification and transesterification are highly endothermic and reversible reactions based on the Arrhenius law. However, an increase in temperature above 80°C results in a decline in methyl ester yield due to the thermal decomposition of the carbon chain in ester molecules. Similarly, the effect was reported for Chicken methyl ester by Santosa [36].

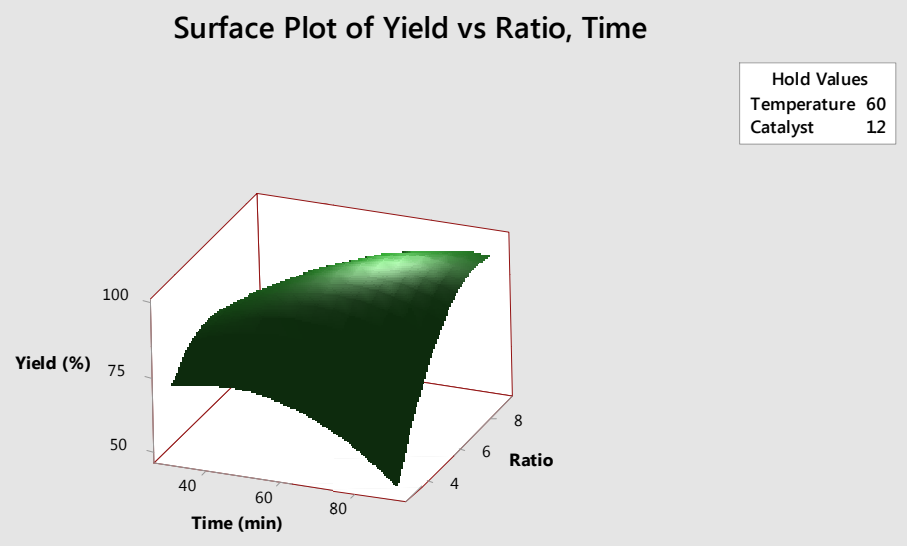
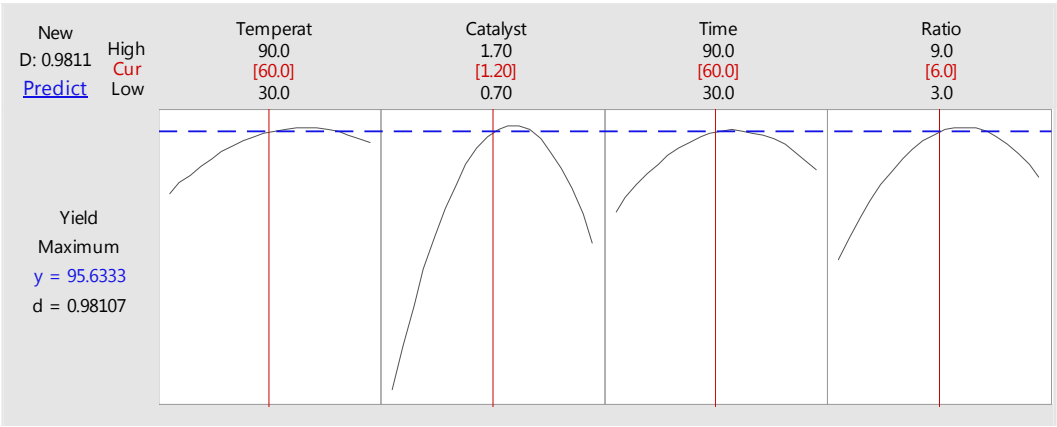



***Figure 4.*** *3D Response surface plot; effect of Time and Methanol Ratio on CTME Yield.*

Maximum yield of CTME (96.9%) was achieved using 1.2 g of catalyst with an oil: methanol ratio of 1: 6, at 60°C, and for a duration of 60 min. However, an increase in methanol ratio up to 1: 8 could increase CTME yield pushing the forward reaction of transesterification into completion. However, a further increase in the methanol ratio could result in lowering catalyst concentration as such reducing CTME yield. Ecinar reported that excess alcohol (glycerol and methanol); reaction products triggered the backward reaction, resulting in the conversion of methyl ester into a starting product. [43] In addition, an increase in the during of the reaction above 60 min could reduce CTME yield due to the reverse reaction effect.




(D - composite desirability, y = predicted response, d = desirability)

***Figure 5.*** *Response optimization plot of the four independent reaction parameters.*

The optimization of the reaction parameter in Figure 5 reveals that 95.63% yield of CTME is achieved at 60°C, with a catalyst loading of 1.2 g using an oil: ratio of 1: 6 for a period of 60 min.

This predicted value is slightly lower than the 96.9% obtained from the experimental data in Table 4. The plot in Figure 5 reveals that catalyst loading has a significant influence on the yield of CTME. In addition, the oil: methanol ratio depicts a considerable effect, while Time and Temperature reveal a less significant effect on CTME yield.

Based on the experimental measurements in Table 4, an optimum condition: Temperature, Catalyst amount, oil: methanol

ratio, and Time of 60 C, 1.2 g, 1: 6, and 60 min respectively biodiesel yield of 96.9% was obtained, while 95.6% was predicted by the model. This indicates a close relationship between the predicted and experimental. This finding is in agreement with the optimization study of biodiesel from *Prosopis julifera* seed reported by Hundie and Akuma [44].

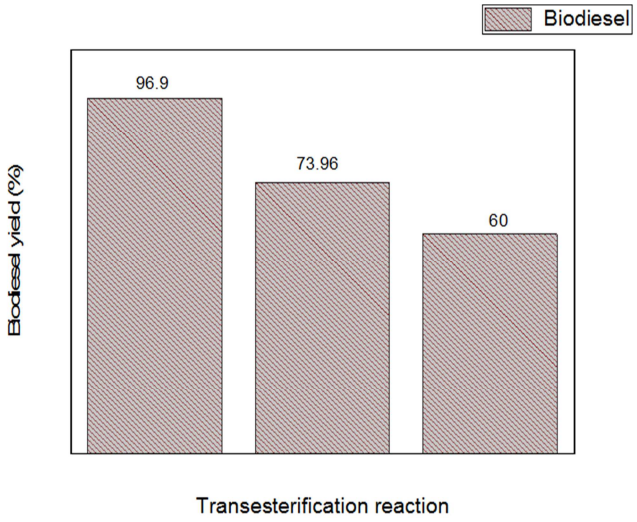



***Figure 6.*** *Reusability test of Polyoxomolybdate Catalyst in transesterification of Chicken Tallow.*

*Reusability of the Polyoxomolybdate catalyst*

The reusability and durability test was conducted using a Polyoxomolybdate catalyst under optimum conditions (methanol to oil ratio of 6: 1, catalyst weight of 1.2 g, temperature of 60°C, and time of 60 min). After each experimental run, the catalyst was separated by centrifuging for 30 minutes at 4000 rpm, washed with n-hexane and methanol, and finally dried in the oven at 70°C for 2 hours. The recovered catalyst was successfully utilized three times in the trans-esterification reaction without experiencing a significant reduction in its activity. The decline in methyl esters yield can be attributed to the adsorption of water molecules, which replace H atoms in the polyoxomolybdate structure, as well as other impurities on the catalyst surface. Figure 6 depicts the yield of three sequences of cycles of 96.9%, 73.96%, and 60%. respectively. The catalyst surface is covered by larger oil molecules, resulting in a reduction of active sites and a subsequent decrease in the FAME yield. We observe a complete loss in catalyst activity at the fourth run under the optimum conditions, which could be attributed to a loss in the active site for transesterification reaction or collapse of the Polyoxomolybdate keggin structure due to strong adsorption of water molecules and impurities on active sites. Similar effects were reported for phosphomolybdic acid on graphene oxide catalysts [42].

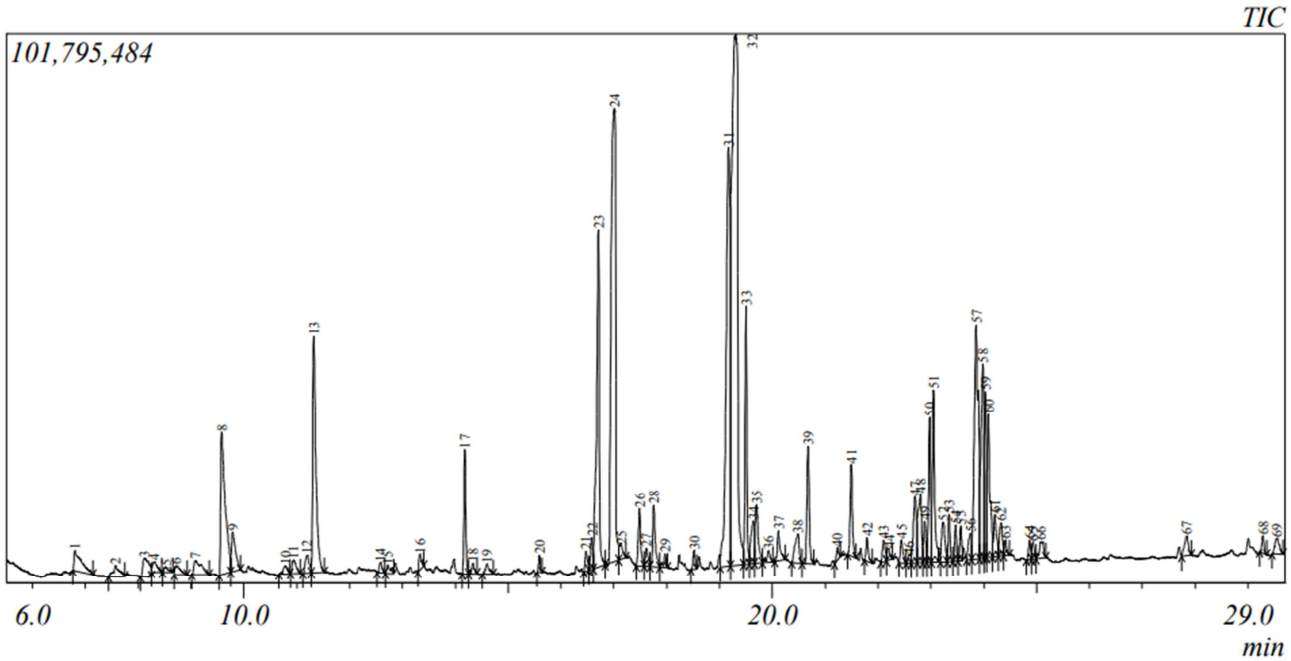



***Figure 7.*** *GC – MS chromatogram Fatty acid methyl ester profile of Chicken tallow.*

Figure 7 above reveals 69 peaks from the chromatogram of the transesterified chicken tallow, with the prominent peaks attributed to methyl esters. These fatty acids methyl esters include Nonanoic acid, 9-oxo-methyl ester (Azelaaldehydic acid methyl ester), Nonanoic acid, dimethyl ester (Azelaic acid dimethyl ester), tridecanoic acid, 12-methyl – methyl ester (Methyl isomyristeate), 9-Hexadecenoic acid methyl ester (Z) (Methyl Palmitoleate), Pentadecenoic acid, 14-methyl, methyl ester, 9,12 – Octadecadienoic acid (Z,Z) methyl ester (Linoleic acid methyl ester), 9-Octadecenoic acid methyl ester (E)(Elaidic acid or oleic acid methyl ester), Octadecenoic acid methyl ester (Stearic acid methyl esters), Methyl (11R, 12R, 13S) – (Z) – 12,13 – epoxy – 11- - methoxy -9- octadecanoate, Octadecanoic acid, 9 – oxo, methyl ester (Methyl 9 – oxostearate), Octadecanoic acid 9,10- dihydroxyl methyl ester (Methyl 9,10 – dihydroxyl stearate), and Glutaric

acid, 2,6 – dimethoxy phenyl pentadecyl ester. The fatty acid methyl esters profile of Chicken tallow in Figure 7 and Table 6 depict 91.01% methyl esters with 8.99% belonging to aldehyde, fatty acid, ketones, diene, and longer chain alcohol.

Moreover, the presence of oleic acid methyl ester, palmitic acid methyl ester, linoleic acid methyl ester, and stearic acid methyl ester at peak 32, 23, 31, and 33 respectively in greater amounts as observed in the GC-MS chromatogram in Figure 7. This finding is in agreement with fatty acid profiles for chicken fat reported by [45]. The presence of epoxides in the methyl esters could result from the partial oxidation of the unsaturated bond in the fatty acid chain. This could be attributed to the oxidative instability of the chicken tallow as observed by [46, 47]. However, lower chain fatty acid ester such as; Nonanoic acid, 9-oxo-methyl ester, Nonanoic acid, dimethyl ester, tridecanoic acid, and 12-methyl – methyl ester was recorded, with higher chain and branch fatty acid methyl esters like Methyl (11R, 12R, 13S) – (Z) – 12,13 – epoxy – 11- - methoxy -9- octadecanoate, Octadecanoic acid, 9 – oxo, methyl ester, Octadecanoic acid 9,10- dihydroxyl methyl ester, and Glutaric acid, 2,6 – dimethoxy phenyl pentadecyl ester. Hence, the presence of oxygen molecules in the CTME makes it an oxygenated fuel that will enhance complete combustion when used in diesel engines.

***Table 6.*** *Fatty acid methyl ester Profile of Chicken tallow.*

| Peak No. | R. Time (min) | Area% | Formula | MW (g/mol) | Name |
|---|---|---|---|---|---|
| 8 | 9.579 | 3.70 | $C_{10}H_{18}O_3$ | 186 | Nonanoic acid 9-oxo- methyl ester |
| 9 | 9.786 | 0.94 | $C_{10}H_{11}O_4$ | 202 | Octanedioic acid dimethyl ester |
| 13 | 11.323 | 4.32 | $C_{11}H_{20}O_4$ | 216 | Nonanedioic acid dimethyl ester |
| 17 | 14.179 | 1.32 | $C_{15}H_{30}O_2$ | 242 | Tridecanoic acid 12-methyl- methyl ester |
| 23 | 16.709 | 5.38 | $C_{17}H_{32}O_2$ | 268 | 9-Hexadecenoic acid methyl ester (Z)- |
| 24 | 17.009 | 11.63 | $C_{17}H_{34}O_2$ | 270 | Pentadecanoic acid 14-methyl- methyl ester |
| 31 | 19.170 | 9.43 | $C_{19}H_{34}O_2$ | 294 | 12-Octadecadienoic acid (Z, Z)-, methyl ester |
| 32 | 19.307 | 18.76 | $C_{19}H_{36}O_2$ | 296 | 9-Octadecenoic acid methyl ester (E)- |
| 33 | 19.503 | 2.61 | $C_{19}H_{38}O_2$ | 298 | Methyl stearate |
| 39 | 20.677 | 1.61 | $C_{20}H_{36}O_4$ | 340 | Methyl (11R,12R,13S)-(Z)-12,13-epoxy-11-methoxy-9-octadecenoate |
| 41 | 21.494 | 1.18 | $C_{19}H_{36}O_3$ | 312 | Octadecanoic acid 9-oxo- methyl ester |
| 50 | 22.978 | 1.81 | $C_{19}H_{38}O_4$ | 303 | Octadecanoic acid 9,10-dihydroxy- methyl ester |
| 51 | 23.050 | 2.30 | $C_{19}H_{38}O_4$ | 330 | Octadecanoic acid 9,10-dihydroxy- methyl ester (R* R*)- |
| 57 | 23.854 | 5.38 | $C_{20}H_{36}O_4$ | 340 | Methyl (11R,12R,13S)-(Z)-12,13-epoxy-11-methoxy-9-octadecenoate |

# 4. Conclusion

In conclusion, this study focused on utilizing a polyoxomolybdate catalyst to optimize the transesterification of chicken tallow into biodiesel. The UV-visible characterization of the catalyst showed the presence of predominantly ($Mo_2O_2^{2+}$) and $H_2MoO_4$ species at pH 2. The physicochemical properties of the chicken tallow were analyzed using standard methods, indicating low acid and free fatty acid values, moderate unsaturation (iodine value), and saponification value.

The Box-Behnken experimental design with 27 runs resulted in an optimized biodiesel yield of 96.9% at 60°C for 60 minutes, using an oil-to-methanol ratio of 1: 6 and a catalyst loading of 1.2 g. The characterization of the produced biodiesel through FTIR and Gas chromatography-mass spectrometry (GC-MS) demonstrated the successful conversion of chicken tallow into fatty acid methyl esters with favorable fuel properties that meet the acceptable limits set by ASTM.

Furthermore, the polyoxomolydate catalyst displayed exceptional activity, good reusability (up to 3 cycle runs), and ease of separation from the product mixture. Overall, this study highlights the potential of biodiesel derived from chicken tallow using a polyoxomolydate catalyst as an environmentally friendly alternative to petro-diesel, contributing to its low carbon footprint and environmental advantages.

# Acknowledgements

The authors wish to acknowledge the Tertiary Education Trust Fund (TETfund) Nigeria for sponsoring this research work under the 2017-2018 (Merged) TETFund Research Project (RP) Intervention, Ref No. TETFUND/ DESS/UNI/ALIERO?2018/RP/VOL. I.

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