



Process Optimization, Environmental and Economic Assessment of TiO₂ Nanocatalyst-assisted Gmelina-Mucuna Oil-blends

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ABSTRACT

This study investigated the production, optimization, environmental performance, and techno-economic viability of biodiesel derived from a novel non-edible blended feedstock of *Gmelina arborea* and *Mucuna pruriens* oils using a TiO₂ nanocatalyst. Transesterification was optimized using Response Surface Methodology under a Central Composite Design, considering catalyst concentration, methanol-to-oil ratio (MOR), temperature, reaction time, and agitation speed as process variables. An optimal biodiesel yield of 96% was achieved at 1.2 wt% catalyst loading, 8:1 MOR, 55°C, 500 rpm agitation, and 70 minutes reaction time. The produced Gmelina-Mucuna oil meets key ASTM quality standards. Kinematic viscosity (ASTM D445), acid value (ASTM D664), and flash point (ASTM D93) were within acceptable limits. The measured density of oil was 0.946 g/mL, consistent with ASTM D1298 reference ranges for vegetable oils. Engine emission analysis of biodiesel-diesel blends (B10-B100) showed substantial reductions in carbon monoxide (35-45%) and lower smoke opacity compared to conventional diesel. Slight increases in CO₂ emissions for some blends were observed. However, the biodiesel blends indicated improved oxidation and more complete combustion due to the oxygenated structure of biodiesel. Techno-economic evaluation revealed an adjusted laboratory production cost of approximately ₦400/L after methanol recovery and removal of non-recurring expenses. At industrial scale, total production cost (CAPEX + OPEX) decreased from ₦980.5/L at 0.5 million L/year to ₦695.9/L at 7 million L/year, demonstrating strong economies of scale. Overall, TiO₂-catalyzed Gmelina-Mucuna biodiesel is technically feasible, environmentally beneficial, and economically promising.

Keywords: Biodiesel; Optimization; Gmelina-Mucuna; TiO₂ catalyst; Techno-economic assessment.

1. INTRODUCTION

The global reliance on fossil-derived diesel continues to pose significant challenges to energy security, environmental degradation, and greenhouse gas emissions (Yesilyurt, 2020). In developing economies such as Nigeria, these challenges are further compounded by rising fuel demand, limited refining capacity, and increasing pressure to diversify the national energy mix using locally available renewable resources. Biodiesel has emerged as a promising alternative fuel for compression ignition (CI) engines due to its biodegradability, renewability, and favorable emission characteristics (Ağbulut *et al.* 2019; Del *et al.* 2016). Chemically, biodiesel consists of monoalkyl esters of long-chain fatty acids produced through the transesterification of triglyceride-rich feedstocks, typically derived from vegetable oils or animal fats (Nahuelcura *et al.* 2024; Rezanian *et al.* 2020). Biodiesel is considered a low net-carbon fuel because the CO₂ released during combustion is partially offset by the CO₂ absorbed during the growth phase of the feedstock biomass (Samuel *et al.* 2023; Effiom *et al.* 2023;

Nkanang *et al.* 2024). Previous studies have explored biodiesel production from single non-edible oils and blended feedstocks using both homogeneous and heterogeneous catalysts. High biodiesel yields have been reported for Gmelina seed oil and other unconventional lipid sources. However, many of these investigations focused primarily on yield optimization, with limited consideration of environmental performance. In addition, the continued reliance on homogeneous catalysts poses challenges in catalyst recovery, wastewater generation, and operational sustainability. The study by (Sani and Gaya, 2019) achieved a biodiesel yield of about 96.8% from Gmelina seed oil using an MgO-ZnO catalyst, while (Ude *et al.* 2020) improved Gmelina oil biodiesel production using potassium hydroxide as the catalyst. However, these studies did not investigate the blending of biodiesel with other underutilized feedstocks. Additionally, (Singh *et al.* 2019) and (Nabgan *et al.* 2022) reported high biodiesel yields of approximately 98.4% and 97.2%, respectively, from microalgae and dairy scum. However, their studies primarily focused on feedstock valorization. Furthermore, the assessments by (Husaini *et al.* 2024; Brahma *et al.* 2022; Kumar *et al.*

2021) highlighted the potential for sustainability of oil-blend approaches. Still, they revealed a lack of systematic studies on non-edible tropical seed oils. Other studies, such as (Fadhil *et al.* 2017) and (Rezania *et al.* 2020), investigated blends of waste fish and castor oils, and evaluated fuel combinations produced *via* different processing routes. Despite the availability of abundant non-edible oil-bearing plants in tropical regions, systematic studies on blended tropical seed oils remain limited. The continued reliance on first-generation biodiesel feedstocks such as soybean, palm, and rapeseed has raised persistent sustainability concerns due to competition with food supply and agricultural land, thereby intensifying the “food-versus-fuel” debate. These challenges have shifted research focus toward second-generation biodiesel feedstocks, particularly non-edible oil-bearing crops that can be cultivated on marginal lands without threatening food security. Recent assessments of biodiesel development in Africa emphasize that non-edible feedstocks represent a practical and sustainable pathway for expanding biofuel production while minimizing food competition and enhancing rural economic opportunities (Kumar *et al.* 2021). In Nigeria, the abundance of underutilized tropical oilseeds provides a strategic opportunity to develop locally sourced biodiesel value chains. Among these, *Gmelina arborea* and *Mucuna pruriens* are particularly promising due to their non-edible nature, adaptability to tropical climates, and demonstrated oil yield potential. Previous experimental investigations have confirmed the suitability of *Gmelina arborea* seed oil for biodiesel production, reporting favorable physicochemical properties and high conversion efficiency (Sani and Gaya, 2019). Similarly, studies on tropical non-edible oil crops highlight the agronomic and environmental advantages of integrating such feedstocks into sustainable biofuel systems (Brahma *et al.* 2022). Collectively, these factors justify the selection of a blended *Gmelina*-*Mucuna* feedstock as a sustainable and locally relevant alternative to edible oil-based biodiesel production. Previous investigations on non-edible biodiesel feedstocks have primarily emphasized yield optimization and catalyst development, with comparatively limited attention to comprehensive environmental performance validation under real engine operating conditions. This gap underscores the importance of integrating emission analysis into biodiesel process evaluation. In particular, the combined utilization of *Mucuna pruriens* and *Gmelina arborea* oils has not been adequately investigated, despite their complementary agronomic and physicochemical characteristics. This study examines the production of biodiesel from a blended *Gmelina*-*Mucuna* oil feedstock using a TiO_2 heterogeneous nanocatalyst. The specific objectives are streamlined and to include oil extraction and characterization, TiO_2 -catalyzed biodiesel synthesis, Response Surface Methodology (RSM)-based process optimization, emission analysis, and techno-economic

assessment. However, the techno-economic feasibility of the process is examined to support potential scale-up.

2. MATERIALS AND METHODS

The materials and equipment employed for biodiesel production and subsequent characterization in this study comprised the following. Feedstocks and reagents: *Gmelina arborea* seed oil and *Mucuna* bean oil (primary lipid sources), *n*-hexane (used as the solvent for oil extraction), distilled water, and a nanostructured TiO_2 catalyst. pH indicators, including litmus paper and phenolphthalein, were used for acid-base titration during free fatty acid (FFA) determination. Titanium dioxide was selected as the heterogeneous catalyst for transesterification process in this study due to its practical and physicochemical advantages over conventional homogeneous alkaline catalysts such as potassium hydroxide. TiO_2 possesses a relatively high surface area, which enhances the availability of active sites for transesterification and promotes improved interaction between methanol and triglyceride molecules. Its excellent thermal stability ensures structural integrity and sustained catalytic performance under elevated reaction temperatures, thereby minimizing catalyst degradation during repeated cycles (Singh *et al.* 2019). Unlike homogeneous catalysts, TiO_2 can be readily separated from the reaction mixture by simple filtration, eliminating the need for neutralization and extensive water washing steps. This significantly reduces wastewater generation and simplifies downstream purification processes, which are major drawbacks associated with KOH-catalyzed biodiesel production (Nabgan *et al.* 2022). Furthermore, TiO_2 -based catalysts have demonstrated effective catalytic activity under relatively mild reaction conditions, enabling high biodiesel yields without excessive energy input. These characteristics collectively justify the selection of TiO_2 as a sustainable and operationally efficient catalyst for biodiesel production from blended non-edible feedstocks.

Titanium dioxide nanoparticles used in this study possessed the following properties: the predominant crystalline phase was anatase; purity was 99% (analytical grade); the average particle size ranged between 20-30 nm; and the specific surface area, determined using the Brunauer-Emmett-Teller (BET) method, was 50-65 m^2/g . The nanoparticles were procured from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany).

Oil extraction was carried out following the standard procedure described in Samuel *et al.* (2025). The process assessment was carried out using a two-level, five-factor factorial design to estimate the interactive effects of the primary process parameters on biodiesel production. Using design-expert software, 32 randomized experimental runs, including five center

points, were generated under a Central Composite Design (CCD) framework. Process optimization was achieved using CCD within RSM to determine optimal transesterification conditions. Oil characterization was subsequently performed, and oil properties were determined according to previously described methods (Samuel *et al.* 2023; John *et al.* 2025). Biodiesel characterization and blend property determinations were conducted in accordance with ASTM standard procedure. The biodiesel satisfied key ASTM standards, including appropriate kinematic viscosity (ASMT 455), acid value (ASTM D664), and flash point (ASTM D93). The density of the blend aligns with the ASTM D4052 standard range. For performance and emission analyses, biodiesel-diesel blends were prepared at different volumetric ratios and designated B100, B40, B30, B20, and B10, corresponding to the biodiesel content of each blend. B100 denotes pure biodiesel, while D100 represents conventional diesel fuel, which was used as the reference fuel in this study. The feedstocks and biodiesel blends are presented in Figures 1 and 2, respectively. Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD) analysis were performed under standard conditions and procedures.

3. RESULTS AND DISCUSSION

3.1 Oil Characterization of Gmelina-Mucuna Seed Oil

The properties of the blended Gmelina-Mucuna seed oil and their ranges classified by ASTM are presented in Table 1 (Christensen *et al.* 2020; ASTM 2017). The moisture content is about 0.037%, a value lower than those reported for comparable biodiesel feedstocks, indicating good quality. The mass density is 0.946 g/mL, with a refractive index of approximately 1.466 at 29 °C; both values fall within ASTM specifications, indicating suitable physical properties. The kinematic viscosity was 42.37 mm²/s, with an acid value of 0.756 mg KOH/kg, indicating seamless transesterification. The peroxide value of 1.64 meq/kg indicates minimal oxidation. The saponification value and molecular weight were within acceptable ranges, while the ester value of 99.66% shows good potential for biodiesel production.

3.1.2 Fourier Transform Infrared Analysis of Gmelina-Mucuna Oil Blend

Figure 3 presents the FTIR spectrum of the Gmelina-Mucuna oil blend. It reveals a dominant peak at approximately 1743 cm⁻¹, corresponding to a strong C=O (carbonyl) stretching vibration of ester functional groups. This peak confirms the presence of triglyceride structures. Additionally, distinct C-O stretching vibrations are observed in the region of 1160-1240 cm⁻¹, further indicating ester linkages within the oil matrix. The intensity and position of these peaks quantitatively

confirm that the blend possesses characteristic ester functional groups, validating its suitability as a biodiesel feedstock prior to transesterification.

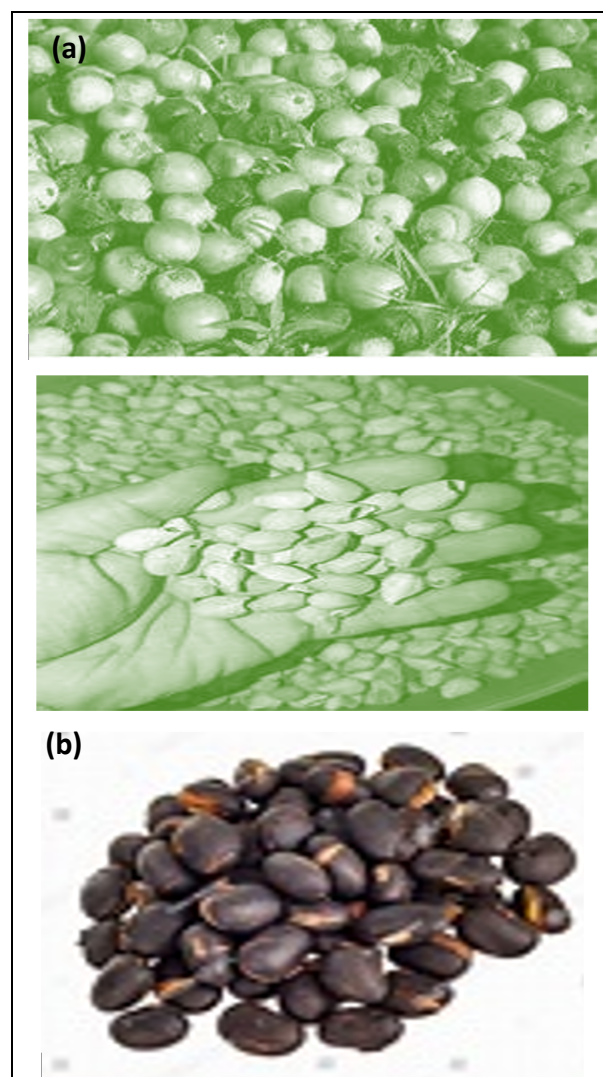


Fig. 1: Feedstocks, (a) *Gmelina arborea* seed and (b) Mucuna bean

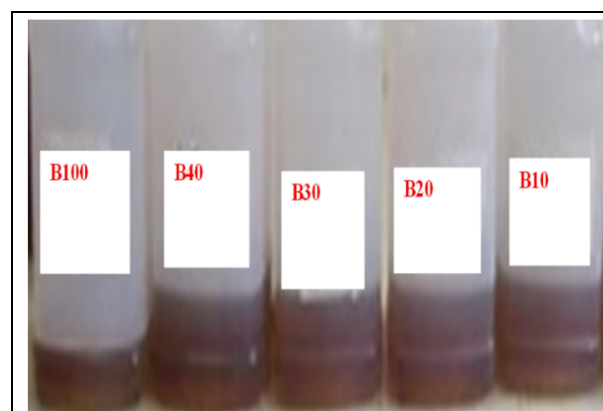
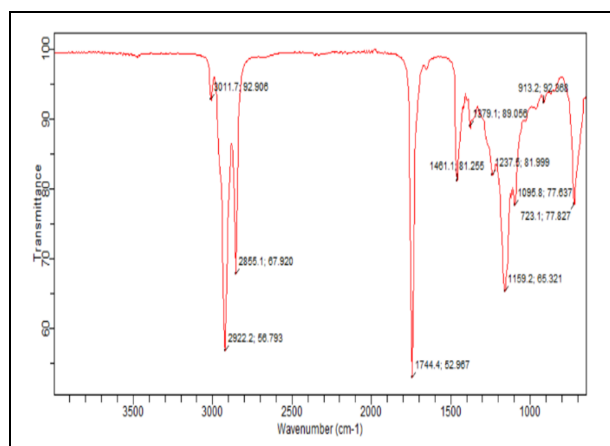


Fig. 2: Samples of blends produced from Gmelina-Mucuna oil-blends

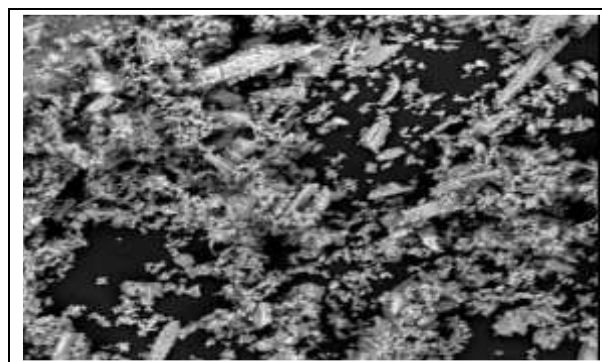
Table 1. Physicochemical properties of Gmelina-Mucuna seed oil compared with ASTM ranges

Parameter	Obtained Value	Relevant ASTM Method	Standard Range
Refractive Index @ 29 °C	1.466	ASTM D1218	1.44-1.48
Moisture Content (%)	0.037	ASTM D6304	≤ 0.05%
Mass Density (g/ml)	0.946	ASTM D1298	0.87 – 0.96 g/ml
Kinematic Viscosity @ 40 °C (mm ² /s)	42.37	ASTM D445	30 -50 mm ² /s
Energy Content (J/g)	27,564	ASTM D240	25,000 - 40,000 J/g
Flash Point (°C)	296	ASTM D93	> 200 °C
Fire Point (°C)	312	ASTM D92	> Flash point
Cloud Point (°C)	22	ASTM D2500	Feedstock-dependent
Pour Point (°C)	17	ASTM D97	Feedstock-dependent
Acid Value (mg KOH/g)	0.756	ASTM D664	≤ 2.0 mg KOH/g
Saponification Value (mg KOH/g)	236.96	ASTM D5558	180 –260 mg KOH/g
Peroxide Value (meq/kg)	1.64	ASTM D3703	≤ 10 meq/kg
Iodine Value (mg/100 g)	21.44	ASTM D5554	10 -120

**Fig. 3. FTIR of Gmelina-Mucuna oil blend**

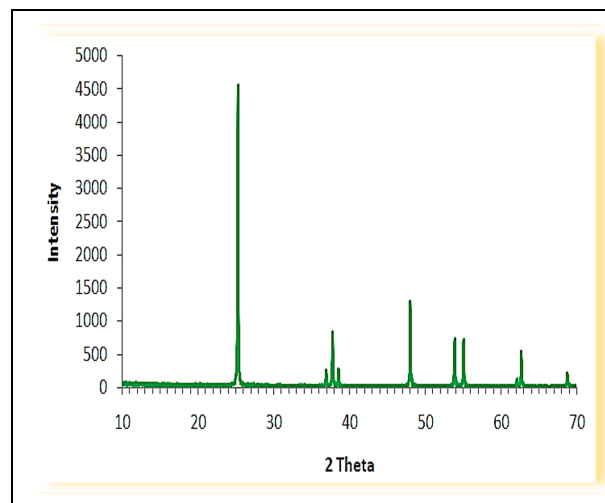
3.1.3 Scanning Electronic Microscopy (SEM)

Figure 4 shows the SEM image of the TiO₂ nanocatalyst. It shows a very fine, nearly spherical nanoparticles, predominantly fine, quasi-spherical particles with noticeable agglomeration, typical of nanosized anatase TiO₂ that are slightly clustered together. The latter is common for materials at the nanoscale. The particles appear fairly uniform and loosely packed, creating a rough surface texture. This structure provides more exposed active sites, allowing better interaction between the catalyst and reactants during transesterification. The nanosized morphology therefore supports improved reaction efficiency and enhanced biodiesel production.

**Fig. 4: SEM for TiO₂ catalyst**

3.1.4 X-ray Diffraction Analysis of TiO₂ Catalyst

The X-ray diffraction analysis of TiO₂ is presented in Figure 5 (Nkanang *et al.* 2024). The XRD pattern confirms the anatase crystalline phase, with dominant diffraction peaks observed at approximately 25.3°, 37.8°, 48.0°, 54.0°, and 62.7° (2θ). The strongest peak occurs at about 25.3°. Sharp peaks with high intensity show good crystallinity and phase purity. Generally, the catalyst reveals nanoscale particle size (approximately 20-30 nm), indicating appropriateness for catalytic transesterification.

**Fig. 5: XRD for TiO₂ catalyst**

3.2 Statistical Analysis

The results for the ANOVA are presented in Table 4, confirm that the quadratic response model for biodiesel yield using TiO₂ nanocatalysts is highly significant ($F = 2536.61$, $p < 0.0001$). Temperature showed the strongest effect, followed by MOR and catalyst concentration. Interaction terms (AD, BD, DE, BC) were significant, and squared terms confirmed non-linearity. Insignificant lack-of-fit indicates good model adequacy, supporting reliable prediction and process optimization (approximately 76% yield). Similarly, Table 5 compares actual and predicted biodiesel yields from 32

RSM-optimized runs. Yields ranged from 49.02–78.28%, while predictions closely matched (49.06-78.33%), with small residuals (-0.22 to +0.29). Most Cook's distance values were <0.10, indicating low influence; a few mild outliers reflected interaction effects. High correlation ($R^2 > 0.98$) confirms strong model accuracy and reliable process optimization. The final regression equation in coded factors describes how catalyst concentration (A), methanol-to-oil ratio (B), temperature (C), reaction time (D), and agitation speed (E) collectively affect biodiesel yield (Y). It incorporates linear, interaction, and quadratic terms to capture both direct and combined effects.

3.3 Effects of Combined Process Parameters on the Biodiesel Yield

Figure. 6a-6f present the effect of two process variables on biodiesel yield. Figure 6a shows the effect of catalyst concentration (CLC) and methanol-to-oil ratio (MOR) on biodiesel yield (BDY). The BDY gradually increases with increasing catalyst concentration and MOR up to the optimum region. The maximum BDY of about 78% was attained at a CLC of 1.5 wt% and a MOR of 8:1. When the catalyst concentration and methanol-to-oil ratio exceeded the optimum range, a decline in BDY was observed, which may be associated with catalyst oversaturation and excess methanol promoting reverse reactions and partial ester hydrolysis. At lower CLC (≤ 0.5 wt%), BDY remained relatively low (48-55%) due to inadequate active sites for complete transesterification. The interaction between CLC and temperature on BDY is illustrated in Figure 6b. Yield generally increased steadily with increasing CLC concentration. However, at low CLC values (< 0.8 wt.%), BDY decreased to 55-60%. As the CLC concentration increased from 0.8 to 1.2 wt.% and the temperature rose from 60 to 65 °C, BDY increased to 72-76%. Further increases in catalyst loading beyond the optimum resulted in a measurable reduction in BDY, which is likely due to enhanced soap formation that interferes with ester recovery.

Figure 6c illustrates the combined effects of CLC and agitation speed (AGS) on BDY. An increase in

BDY was recorded as both parameters increased toward their optimal values, with yield improving from approximately 55–60% at lower settings to about 73-77% at CLC levels of 0.8-1.2 wt.% and AGS of 300-500 rpm. Beyond this optimum region, excessive TiO_2 loading or high agitation speed reduced BDY due to increased soap formation, unstable emulsions, and difficulties in phase separation. Additionally, Figures 6d-6f illustrate the combined effects of temperature and MOR, reaction time and temperature, and AGS and MOR on BDY, respectively.

Figure 6d shows the yield increase as the MOR increases from 1:4 to 10:1. At a temperature increase of 52 °C, the yield increased to about 88-92 % and peaks to 95 % as the temperature approaches 52 °C before declining.

Figure 6e shows the effect of reaction time and temperature on BDY. At higher reaction time and temperature, around 70 min and 55 °C, respectively, BDY peaked at approximately 95% due to increased molecular activity and rapid conversion of triglycerides to esters. However, further heating above 65 °C likely led to methanol evaporation and soap formation, resulting in a slight reduction in BDY.

Figure 6f illustrates the combined effect of MOR and AGS on BDY. At low AGS (200 rpm), BDY remained moderate (70-82%) regardless of MOR. Yield increased as AGS rose to 300-500 rpm, reaching a maximum of about 96% at an MOR of 8:1. Beyond 500 rpm, BDY declined to 92-94% due to excessive shear, which may cause catalytic deactivation and reduced conversion efficiency. Taken together, the results indicate that biodiesel yield is strongly influenced by the interaction of process parameters, with maximum yield occurring within a clearly defined operational window. These findings suggest that the Gmelina-Mucuna oil blend is a viable feedstock for biodiesel production, provided that process parameters are appropriately selected and maintained within their optimal ranges.

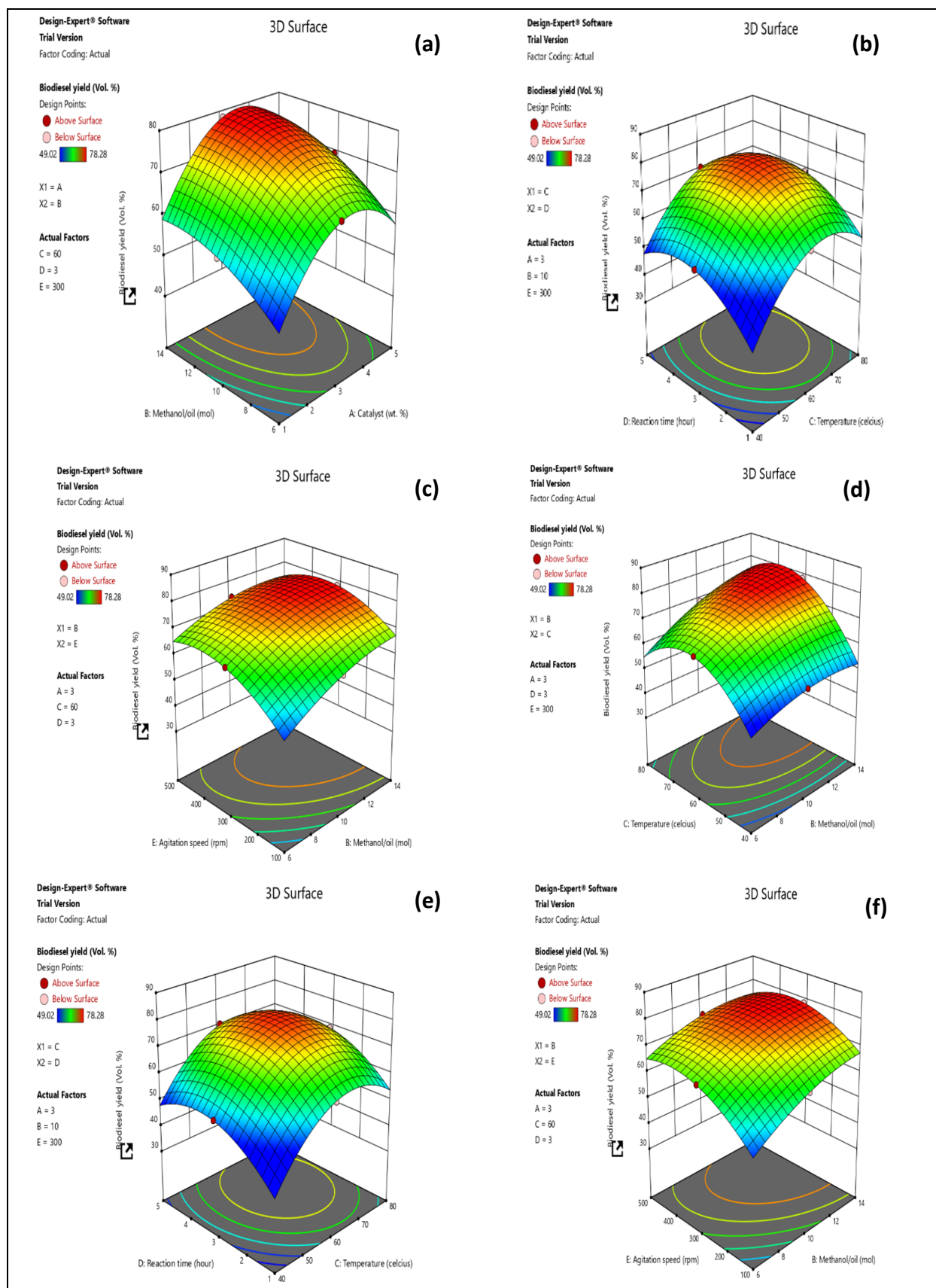


Fig. 6: Effect of process parameters on BDY (a) MOR and CLC, (b) Temperature and CLC, and (c) Agitation speed and CLC, (d) Temperature and MOR, (e) Reaction time and temperature and (f) AGS and MOR

3.4 Environmental Performance and Heat Rate of Blends of Biodiesel Produced

This study focused on the environmental performance of biodiesel blends produced from the Gmelina-Mucuna oil blend, as well as the associated heat rate of the blends at different engine loads. This information is vital for system sustainability and optimization. To ascertain environmental sustainability,

experiments were conducted using a compression ignition diesel engine (Figure 7) with the following specifications: cylinder bore of 82 mm, stroke of 110 mm, compression ratio of 16.5:1, engine speed of 1500 rpm, rated power of 3.7 kW, and engine displacement of 556.24 cc (John *et al.* 2025). The study did not primarily focus on engine performance; instead, it evaluated the environmental sustainability of various biodiesel-diesel blends (B10, B20, B30, B40, and B100) compared with conventional diesel fuel (D100).

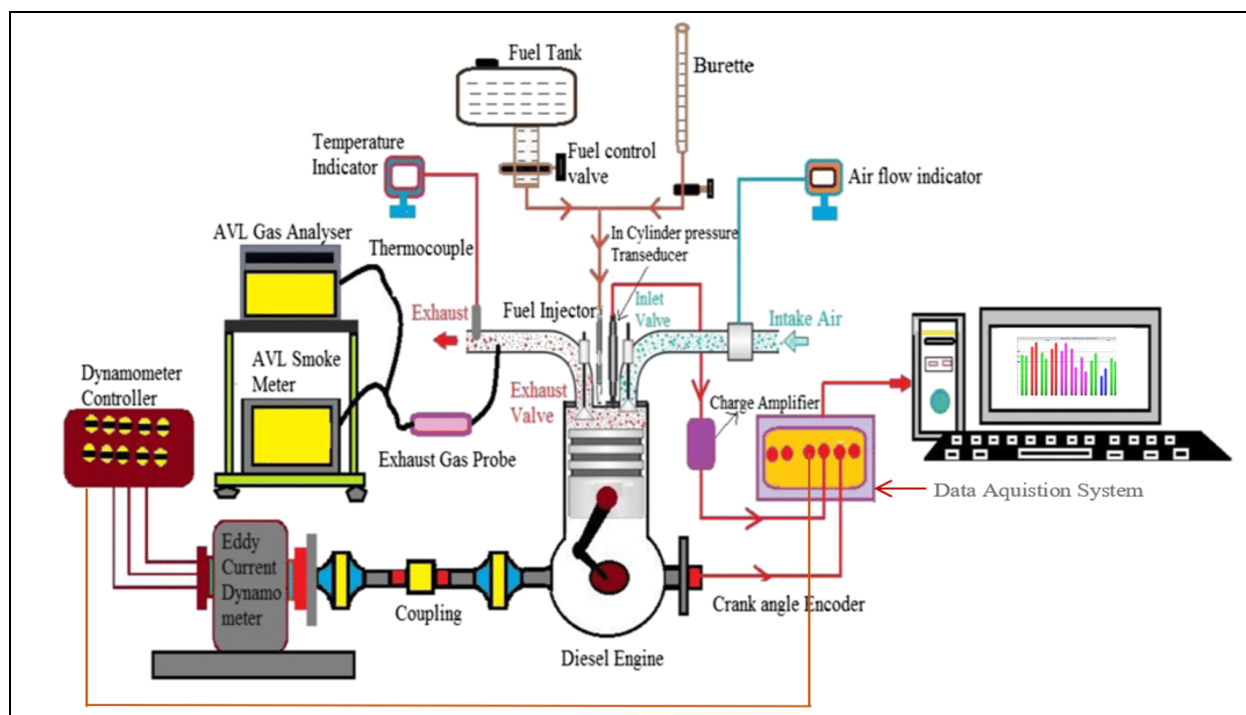


Fig. 7: Engine testing setup (John *et al.* 2025; Effiom *et al.* 2024)

Figure 8 presents the effect of brake power (BRP) on exhaust smoke intensity (ESI). The results show that ESI decreases gradually with increasing BRP for all fuel blends, indicating enhanced combustion efficiency under varying load conditions. At a low BRP of about 1.0 kW, D100 exhibited a smoke opacity of approximately 57%, whereas the biodiesel blends (BDB) showed reduced opacity values of about 55% (B10), 48% (B20), 45% (B30), 41% (B40), and 37% (B100). At a higher BRP of 2.5 kW, smoke levels decreased significantly to around 40% for D100 and 35%, 32%, 29%, 27%, and 23% for B10, B20, B30, B40, and B100, respectively. The observed inverse relationship indicates that increasing brake power increases in-cylinder temperature and turbulence, thereby supporting more complete oxidation of hydrocarbon chains and particulate matter.

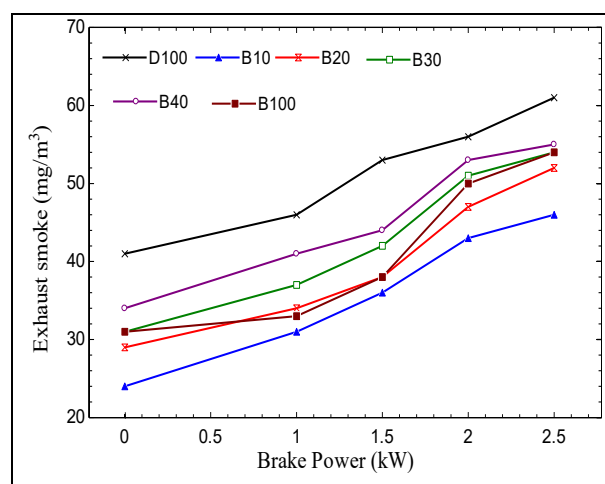


Fig.8. Effect of brake power on exhaust smoke

Figure 9 presents the changes in carbon dioxide emissions with brake power for diesel fuel and the biodiesel blends examined in this study. An overall rise in CO₂ emissions was observed as brake power increased, regardless of the fuel used. This trend is typical of diesel engines operating at higher loads, where combustion is more complete. At the lowest brake power of 1.0 kW, diesel fuel produced approximately 3.2% by volume of CO₂. Under the same operating conditions, the biodiesel blends emitted slightly higher levels of CO₂, and the emission concentration increased as the biodiesel fraction in the blend increased. When the brake power was increased to 2.5 kW, CO₂ emissions rose noticeably for all fuels. This increase can be linked to improved fuel atomization and elevated in-cylinder temperatures at higher loads, which favor more complete oxidation of carbon during combustion. Across the full range of brake power tested, the biodiesel blends consistently emitted more CO₂ than conventional diesel. This behaviour suggests a more complete combustion process when biodiesel is present, which can be attributed to the oxygenated nature of biodiesel fuels. Although pure biodiesel (B100) exhibited the highest CO₂ emissions, this outcome should not be viewed as undesirable, since higher CO₂ formation is generally associated with reduced emissions of incomplete combustion products such as carbon monoxide. The trends observed in this study are in good agreement with previously reported results for biodiesel-operated diesel engines (Nkanang *et al.* 2024).

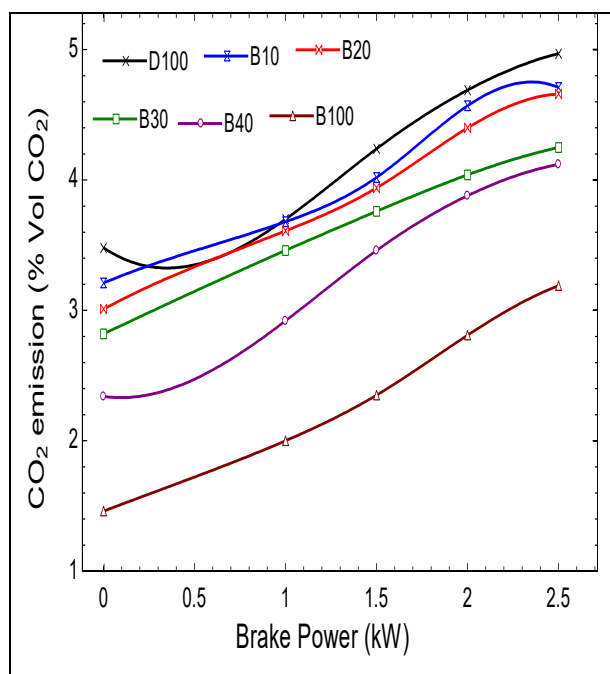


Fig. 9: Effect of brake power on CO₂ emissions

The relationship between brake power and carbon monoxide emissions for diesel and biodiesel-diesel blends is presented in Figure 10. An apparent

reduction in CO emissions was observed as brake power increased for all fuels tested. This indicates that the combustion process became more effective at higher loads, mainly due to higher cylinder temperatures and better air-fuel mixing, which enhance the oxidation of carbon monoxide. At a brake power of 1.0 kW, the highest CO emissions were recorded for conventional diesel (D100). Introducing biodiesel into the fuel blend led to a noticeable decrease in CO emissions, with the lowest values observed when the engine was operated on pure biodiesel (B100). When the brake power was raised to 2.5 kW, CO emissions decreased further across all fuels, reinforcing the observation that higher engine loads improve combustion quality. In comparison with neat diesel, biodiesel-containing fuels achieved a reduction in CO emissions in the range of approximately 35-45%. This improvement can be attributed to the oxygenated nature of biodiesel, which facilitates more complete combustion. The results of this study agree with trends reported in the literature Effiom *et al.* (2023), confirming the suitability of biodiesel blends for reducing exhaust CO emissions in diesel engines.

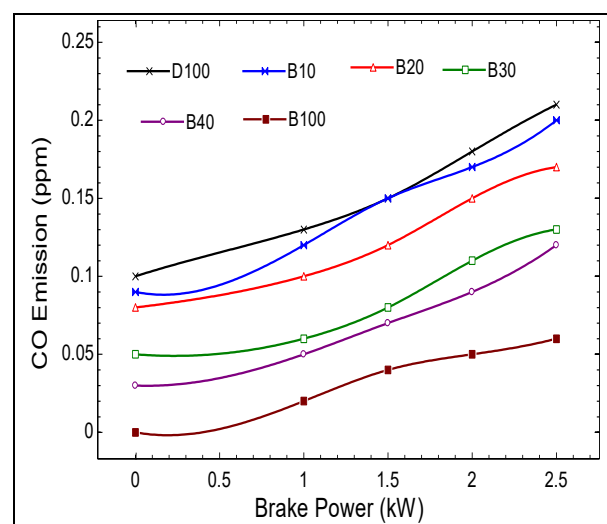


Fig.10: Effect of brake power on CO emissions

Figure 11 presents the heat release rate (HRR) behaviour of diesel and biodiesel blends during engine operation. A rapid increase in HRR was observed at the start of combustion, corresponding to the premixed phase. Diesel fuel showed the highest peak HRR, while the peak value gradually decreased as the biodiesel percentage increased, reaching the lowest level for B100. This reduction can be linked to the shorter ignition delay of biodiesel, which limits the amount of fuel available for rapid premixed burning. During the diffusion combustion stage, biodiesel blends produced smoother and more evenly spread HRR curves, indicating a more gradual energy release. Overall, the results suggest that biodiesel blending moderates combustion intensity and promotes a steadier heat release process, which can contribute to improved combustion stability and reduced engine stress.

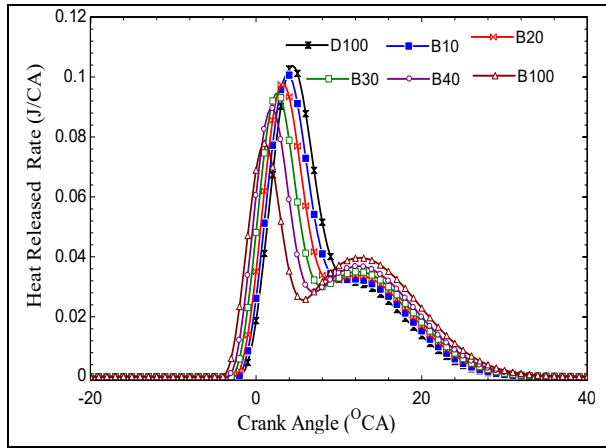


Fig. 11: Heat release rate characteristics against Crank angle of diesel and biodiesel

The changes in cylinder pressure and crank angle are depicted in Figure 12. The results show that the highest peak pressure is achieved with D100 at full load. The peak pressure for neat diesel is about 65 bar, occurring at a crank angle of 8° after top dead centre. The cylinder pressure initially increases with increasing blend ratio. However, at higher blends, the peak pressure decreases. This reduction is primarily due to the lower calorific value of biodiesel and its shorter ignition delay, which limit the amount of fuel accumulated during the premixed combustion stage, thereby reducing the pressure rise. At very low blend ratios, the combustion process remains close to that of D100, with only a slight deviation in combustion timing. However, at higher blends, the peak pressure occurs somewhat earlier in the crank angle domain. This shift is ascribed to the higher viscosity of biodiesel, which adversely affects fuel evaporation, atomization, and air-fuel mixing, particularly under high-load conditions.

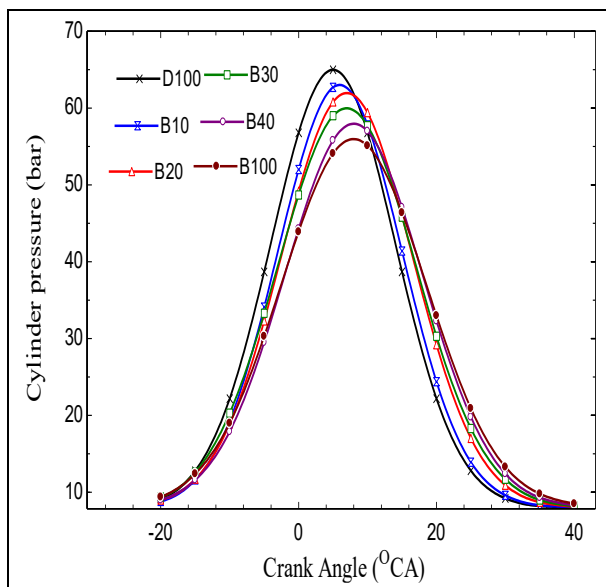


Fig. 12: Influence of biodiesel blends on cylinder pressure

3.5 Uncertainty Analysis

In this study, a Type-A statistical uncertainty analysis was performed. This method uses the spread of experimental data to estimate random variation. Since multiple CO₂ values were available at each brake power (from different blends), their mean and standard deviation were used to determine the uncertainty of the average value. Because the sample size was small ($n = 6$), the student's t-distribution was applied to calculate the expanded uncertainty at a 95% confidence level.

The formular use in the uncertainty calculations are:

x_i = Individual gas component measurement (CO₂, exhaust smoke or CO)

n = Number of measurements

$\bar{x}$ = Mean value of gas component

s = Sample standard deviation

u = Standard uncertainty of the mean

t = Student's t-value (for 95% confidence and $n-1$ degree of freedom)

U_{95} = Expanded uncertainty at 95% confidence

Mean value for any measured gas,

$$G = \frac{\sum_{i=1}^n x_i}{n} \quad \dots (1)$$

This gives the degree of G value at a given brake power or any other parameter considered as input for G measurement. The sample standard deviation is obtained as:

$$s = \frac{\sqrt{\sum_{i=1}^n \sum_{i=1}^n (x_i - \bar{x})^2}}{n-1} \quad \dots (2)$$

Standard uncertainty of the mean is obtained as:

$$u = \frac{s}{\sqrt{n}} \quad \dots (3)$$

Equation (3) represent the uncertainty associated with $\bar{x} \pm U_{95}$. A typical calculation for CO₂ emission is presented in Table 6.

3.6 Techno-economic Analysis of Biodiesel Production

The estimated overhead costs related to biodiesel production are shown in Figure 13. The total cost of production is in two categories: the fixed production costs, which remain constant irrespective of the production capacity, and the variable production

costs, which rise proportionately with the measure of production activities. Following the overall production outflow of ₦32,000, the process yielded 50 liters of biodiesel and liters of glycerin, equivalent to a unit biodiesel production cost of ₦440 per liter. With non-recurring laboratory costs exclusion and methanol recovery taken into account, the adjusted unit cost of production reduced to nearly ₦400 per liter (variable operating cost). Considering the prevailing market price of fossil diesel, which ranges from ₦1,000 to ₦1,200 per

liter, as at the time of this study, the biodiesel could be competitively marketed at an estimated price of ₦650 per liter. This indicates a probable cost saving of ₦350 to ₦550 per liter compared to conventional diesel. For large-scale commercial operation, the projected capital investment in essential processing equipment and plant infrastructure is ₦1,021,500,000, corresponding to nearly USD 681,000 at an exchange rate of ₦1,500 per US dollar, as shown in Table 2.

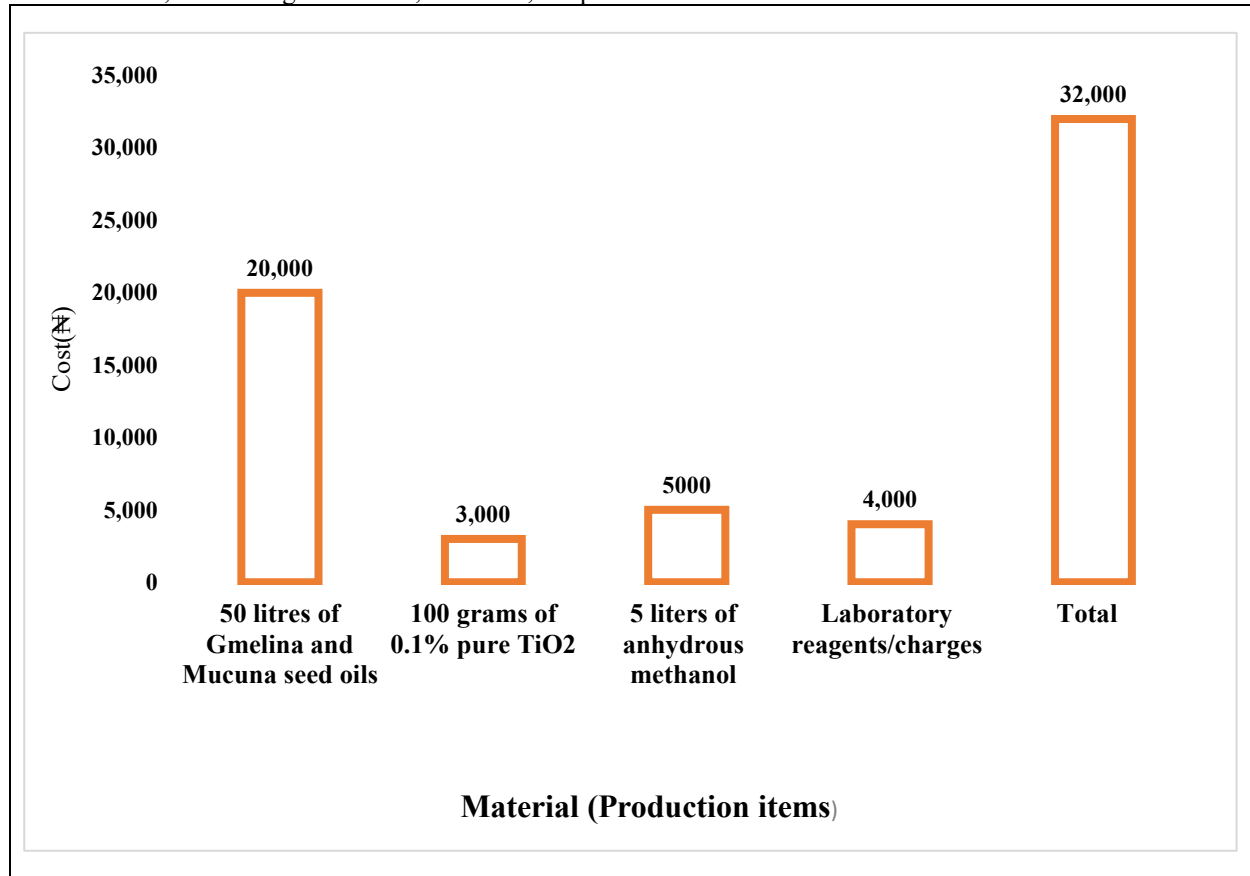


Fig. 13: Estimate overheads in biodiesel production

3.7 Capital Expenditure and its Effect Per Litre and Capital Recovery Factor

Total equipment capital expenditure (CAPEX) (Table 2) is \$681,000 = ₦1,021,500,000. The Capital Recovery Factor (CRF) is a financial coefficient applied in Techno-economic analysis (TEA) to convert the entire CAPEX into an even, yearly cost over the economic life of a plant, reflecting the time value of money (Effiom *et al.* 2016).

$$CRF = \frac{i(1+i)^n}{i(1+i)^n - 1} \quad \dots (4),$$

where i = yearly reduction (interest) rate and n = plant life cycle (years). Several Nigerian banks offer finance

loans with interest rates of roughly 14%-18% per annum, while organized term loans are about 17% per annum. For specific equipment financing, the facilities are about 13% per annum, depending on the tenor and security. From this study, the interest rate is = 13%, machine operation life = 10 years, substituted in Equation (1) to give a CRF of 0.15

$$\text{Annualized CAPEX} = CRF \times \text{CAPEX}$$

$$= \text{₦1.0215 billion} \times 0.15$$

$$= \text{₦153.225 million per year.}$$

$$\text{The cost per litre} = OPEX + CAPEX,$$

Table 2: Essential factory assets for biodiesel production

Equipment	Cost (\$)	Cost (NGN)
Catalyst pre-mixer	50,000	75,000, 000
Transesterification reactor	350,000	525,000, 000
Neutralizer reactor	13,500	20,250, 000
Distillation column to purify biodiesel	60,000	90,000, 000
Distillation column to separate the methanol	40,000	60,000, 000
Distillation column to separate the glycerol	77,500	116,250, 000
3 decanters	90,000	135,000, 000
Total	681,000	1, 021, 500, 000

Table 3: Technoeconomic analysis of biodiesel production

S. No.	Annualized Capital Cost (Million/year)	Annual Production (Liter/Year)	Operating Expenditure (OPEX) (₹/L)	Capital Cost Per Litre (CAPEX) (₹/L)	Total Cost (CAPEX)+ (OPEX) (₹/L)
1	153.225	500000	674	306.5	980.50
2	153.225	1000000	674	153.2	827.20
3	153.225	1.50E+06	674	102.2	776.20
4	153.225	2.00E+06	674	76.61	750.60
5	153.225	2.50E+06	674	61.29	735.30
6	153.225	3.00E+06	674	51.08	725.10
7	153.225	3.50E+06	674	43.78	717.80
8	153.225	4.00E+06	674	38.31	712.30
9	153.225	4.50E+06	674	34.05	708.10
10	153.225	5.00E+06	674	30.65	704.60
11	153.225	6.00E+06	674	25.53	699.50
12	153.225	6.50E+06	674	23.57	697.6
13	153.225	7.00E+06	674	21.89	695.9

4. CONCLUSION

where OPEX is operating expenditure per litre, which is ₦674/L. Table 3 depicts the TEA of biodiesel production at varying yearly production volumes, using a continuous annualized capital cost of ₦153,225 million/year and a fixed operational expenditure (OPEX) of ₦674 per litre. As yearly production rises from 0.5 million to 7.0 million

litres per annum, the capital cost per litre (CAPEX element) declines meaningfully from ₦306.5/L to ₦21.89/L. This reverse relationship confirms that capital investment is a fixed cost whose per-unit burden declines as production volume rises. The overall production cost (CAPEX + OPEX) declines gradually from ₦980.5/L at 500,000 L/year to ₦695.9/L at 7,000,000 L/year, demonstrating a strong economy of scale, with the substantial cost discounts existing at a reduced production range of (0.5-2.0 million L/year).

This study has established the technical viability, environmental returns, and economic potential of producing biodiesel from a blended non-edible feedstock of *Gmelina arborea* and *Mucuna pruriens* oils using TiO₂ nanocatalyst. The oil blend showed good physicochemical properties, including a low moisture content (0.037%) and an acid value (0.756 mg KOH/kg), demonstrating its suitability for transesterification without pretreatment. The process optimization using RSM revealed that biodiesel yield is sturdily controlled by the interface of operational parameters, with the optimal yield of nearly 96% attained at 1.2 wt% catalyst loading, MOR of 8:1, a reaction temperature of 55 °C, and a reaction period of 70 minutes. The catalyst characterization showed a high specific surface area and a well-developed pore structure, which contribute to enhanced catalytic activity and conversion efficiency. Environmental valuation based on engine emission testing indicated that biodiesel blends significantly reduced exhaust smoke opacity and show slight increase in CO₂ emissions at higher biodiesel blend, with smoke opacity decreasing from approximately 57 % for diesel to 23% for biodiesel at increased engine loads. Though CO₂ emissions rise slightly, the trend reflects better combustion efficiency due to the oxygenated nature of biodiesel fuels. The combustion breakdown further showed a smoother heat-release pattern and moderated peak cylinder pressures for biodiesel blends, suggesting enhanced combustion stability and reduced engine stress. A techno-economic study showed that biodiesel from the *Gmelina-Mucuna* oil blend is economically viable, with an estimated production cost of approximately ₦400 per liter, given potential savings of about ₦550 per liter compared with conventional diesel. Generally, the findings indicate that TiO₂-catalyzed *Gmelina-Mucuna* biodiesel is a sustainable, eco-friendly, and cost-effective substitute fuel for compression-ignition engines, with potential for extensive application in tropical areas.

Table 4: ANOVA table for quadratic model response 1: Biodiesel yield

Source	Sum of Squares	Df	Mean Square	F-value	p-value	Remarks
Model	2097.22	20	104.86	2536.61	< 0.0001	significant
A-Catalyst	223.14	1	223.14	5397.76	< 0.0001	
B-Methanol/oil	266.13	1	266.13	6437.84	< 0.0001	
C-Temperature	384.80	1	384.80	9308.42	< 0.0001	
D-Reaction time	153.42	1	153.42	3711.25	< 0.0001	
E-Agitation speed	184.26	1	184.26	4457.30	< 0.0001	
AB	0.7310	1	0.7310	17.68	0.0015	
AC	2.37	1	2.37	57.37	< 0.0001	
AD	8.50	1	8.50	205.55	< 0.0001	
AE	5.38	1	5.38	130.20	< 0.0001	
BC	12.46	1	12.46	301.43	< 0.0001	
BD	28.78	1	28.78	696.27	< 0.0001	
BE	3.72	1	3.72	90.11	< 0.0001	
CD	0.2304	1	0.2304	5.57	0.0378	
CE	1.40	1	1.40	33.97	0.0001	
DE	29.38	1	29.38	710.62	< 0.0001	
A ²	281.19	1	281.19	6802.08	< 0.0001	
B ²	25.36	1	25.36	613.57	< 0.0001	
C ²	389.16	1	389.16	9413.99	< 0.0001	
D ²	200.57	1	200.57	4851.85	< 0.0001	
E ²	99.84	1	99.84	2415.13	< 0.0001	
Residual	0.4547	11	0.0413			
Lack of Fit	0.4547	6	0.0758			
Pure Error	0.0000	5	0.0000			
Cor Total	2097.67	31				

Table 5: Actual and predicted combined effects of process parameters to produce biodiesel

Run Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residuals	Externally Studentized Residuals	Cook's Distance	Influence on Fitted Value DFFITS	Standard Order
1	55.47	55.42	0.0454	0.879	0.641	0.623	0.142	1.677	2
2	49.02	49.06	-0.0388	0.879	-0.548	-0.530	0.104	-1.426	16
3	55.02	54.89	0.1295	0.879	1.830	2.092	1.156 ⁽¹⁾	5.634 ⁽¹⁾	8
4	67.03	67.07	-0.0380	0.879	-0.536	-0.518	0.099	-1.395	5
5	53.21	53.08	0.1287	0.879	1.818	2.073	1.141 ⁽¹⁾	5.582 ⁽¹⁾	28
6	66.65	66.69	-0.0388	0.879	-0.548	-0.530	0.104	-1.426	27
7	70.39	70.26	0.1295	0.879	1.830	2.092	1.156 ⁽¹⁾	5.634 ⁽¹⁾	13
8	69.45	69.40	0.0454	0.879	0.641	0.623	0.142	1.677	4
9	55.97	56.01	-0.0371	0.879	-0.524	-0.506	0.095	-1.363	22
10	66.55	66.75	-0.2046	0.879	-2.891	-5.622 ⁽²⁾	2.885 ⁽¹⁾	-15.137 ⁽¹⁾	11
11	60.02	60.06	-0.0363	0.879	-0.513	-0.495	0.091	-1.332	18
12	64.69	64.81	-0.1205	0.879	-1.702	-1.890	1.000	-5.090 ⁽¹⁾	6
13	63.84	63.88	-0.0371	0.879	-0.524	-0.506	0.095	-1.363	24
14	68.45	68.57	-0.1213	0.879	-1.713	-1.908	1.014 ⁽¹⁾	-5.138 ⁽¹⁾	23
15	68.16	68.11	0.0470	0.879	0.665	0.647	0.152	1.742	29
16	78.02	78.14	-0.1205	0.879	-1.702	-1.890	1.000	-5.090 ⁽¹⁾	25
17	56.69	56.91	-0.2183	0.598	-1.694	-1.879	0.204	-2.294	1
18	69.39	69.10	0.2851	0.598	2.213	2.832	0.348	3.458 ⁽¹⁾	20
19	65.13	65.01	0.1184	0.598	0.919	0.912	0.060	1.113	31
20	78.28	78.33	-0.0516	0.598	-0.400	-0.385	0.011	-0.470	9
21	52.93	52.81	0.1167	0.598	0.906	0.898	0.058	1.097	21
22	68.78	68.83	-0.0499	0.598	-0.388	-0.372	0.011	-0.454	3
23	59.66	59.87	-0.2149	0.598	-1.668	-1.840	0.198	-2.247	19
24	70.27	69.99	0.2817	0.598	2.187	2.773	0.339	3.386 ⁽¹⁾	30
25	62.42	62.47	-0.0499	0.598	-0.388	-0.372	0.011	-0.454	15
26	73.67	73.55	0.1167	0.598	0.906	0.898	0.058	1.097	12
27	75.38	75.39	-0.0111	0.159	-0.060	-0.057	0.000	-0.025	10
28	75.38	75.39	-0.0111	0.159	-0.060	-0.057	0.000	-0.025	17
29	75.38	75.39	-0.0111	0.159	-0.060	-0.057	0.000	-0.025	7
30	75.38	75.39	-0.0111	0.159	-0.060	-0.057	0.000	-0.025	14
31	75.38	75.39	-0.0111	0.159	-0.060	-0.057	0.000	-0.025	32
32	75.38	75.39	-0.0111	0.159	-0.060	-0.057	0.000	-0.025	26

Ultimate Equation in Terms of Coded Factors

$$Y = +75.39 + 6.10A + 6.66B + 8.01C + 5.06D + 5.54E + 0.8550AB + 1.54AC + 2.91AD + 2.32AE + 3.53BC - 5.37BD - 1.93BE - 0.4800CD - 1.18CE - 5.42DE - 12.38A^2 - 3.72B^2 - 14.57C^2 - 10.46D^2 - 7.38E^2 \quad \dots (A)$$

Y denotes the predicted biodiesel yield (%) and the coefficients represent how strongly each variable or interaction affects that yield.

1. The intercept (75.39) represents the mean yield when all coded variables are at their central levels (zero).
2. The linear terms (A, B, C, D, E) show the main effects of each variable. Positive coefficients (e.g., for temperature and methanol/oil ratio) indicate that increasing those parameters increases yield, up to an optimum level.
3. The interaction terms (e.g., AB, AD, BC) describe how two variables jointly affect yield. For instance, AD (2.91) suggests that increasing catalyst and reaction time together enhances yield, while BD (-5.37) implies that increasing methanol/oil ratio and reaction time simultaneously reduces yield.
4. The quadratic terms (A^2 , B^2 , C^2 , etc.) have negative coefficients, showing that beyond certain optimum points, further increases in these factors decrease yield likely due to side reactions, excessive methanol dilution, or catalyst saturation.

Uncertainty Analysis

Table 6. CO₂ emissions at varying brake power and blend ratio

Brake Power (kW)	CO ₂ Emissions (% Vol/CO ₂)					
0	3.48	3.21	3.01	2.82	2.34	1.46
1	3.7	3.68	3.61	3.46	2.92	2
1.5	4.24	4.02	3.94	3.76	3.46	2.35
2	4.69	4.57	4.4	4.04	3.88	2.81
2.5	4.97	4.71	4.66	4.25	4.12	3.19

Table 6 shows measured values of CO₂ for different brake power and different blend ratio. The expanded uncertainty (95 % confidence level) is obtained as:

$$U_{95} = t(0.95, 5n - 1) \times u$$

For $n = 6$, $t = (0.95, 5) = 2.59$

$$U_{95} = 2.57 \times \frac{s}{\sqrt{6}}$$

The CO₂ result at each brake power is reported and calculated as:

$\bar{x} \pm U_{95}$, where $\bar{x}$ is mean CO₂. The calculated mean values of CO₂ for different blends at varying brake power are presented in Table 7. This uncertainty is based on variation across different brake powers, not measurement repeatability at the same brake power. The same calculation can be extended to CO and exhaust smoke.

Table 7. mean CO₂ values for different brake power

Brake Power	Mean CO ₂ Across Blends	SD (s)	Std unc. (u)	Expanded (U ₉₅)	Mean $\pm$ U ₉₅
0.0	2.720	0.727	0.297	0.763	2.720 $\pm$ 0.763
1.0	3.228	0.650	0.265	0.681	3.228 $\pm$ 0.681
1.5	3.628	0.664	0.271	0.697	3.628 $\pm$ 0.697
2.0	4.065	0.653	0.267	0.686	4.065 $\pm$ 0.686
2.5	4.317	0.663	0.271	0.697	4.317 $\pm$ 0.697

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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