Modelling esterification of palm kernel, neem, and jatropha seed oils using a simplex lattice approach

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Abstract. High concentrations of free fatty acids (FFAs) in many non-edible oils interfere with biodiesel conversion, causing soap formation throughout the transesterification reaction. Although esterification in single and binary oil systems has been well-researched, there is a lack of knowledge regarding ternary blends. The knowledge gap on interactions of multi-oils limits optimization of blended feedstocks for resource-efficient and scaled biodiesel generation. The investigation optimizes the pre-treatment of PKO, NSO, and JSO using SLMD. Esterification was carried out using methanol at 25 wt.% and sulfuric acid at 1 wt% for 1.5 h at 60 °C. In this study, SLMD was used to optimize blend composition to minimize FFA and improve the viability of hybrid biodiesel feedstocks. Fuel properties of ternary biodiesel (PNJO methyl ester) were determined using standard transesterification conditions, 6:1 methanol-to-oil ratio, 1 wt.% catalyst, 60 °C, according to density and viscosity requirements in diesel blends. ANOVA analysis confirmed the significance of the model by a p-value of less than 0.001, with very high values of R^2: 0.9983, adjusted R^2: 0.9957, and predicted R^2: 0.9295. The model validation revealed an RMSE value of 0.106 and SEP of 2.37%, MAE and AAD of 0.076 and 1.72%, respectively. The best formulation-0.0112 % JSO, 0.9653 % NSO, and 0.0235 % PKO gave 1.93 % FFA and produced biodiesel that met requirements according to both ASTM D6751 and EN 14214. This novel ternary optimization demonstrates that SLMD is a reliable predictive framework for sustainable biodiesel production.

1 Introduction

Biodiesel is a renewable and eco-friendly fuel that is biodegradable, emits reduced sulfur, and is compatible with diesel engines. Non-edible oils such as jatropha, neem, and palm

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kernel are abundant in tropical zones and are often utilised to avoid competition between food and fuel resources [1].

A major disadvantage of these oils is their high free fatty acid content (FFC), which results in the formation of soap during alkali-catalysed transesterification, thereby lowering biodiesel yield and making product separation more difficult [2]. Acid-catalysed esterification is normally adopted as a pre-treatment to reduce FFA and to ensure good performance of the following transesterification step [3]

Esterification is an important pre-treatment process used in lowering the FFC in NEOs before BCT. The efficiency of this process is influenced by various BCTs [2].

While a number of optimisation studies have been conducted on single or binary oil systems, three-component mixture studies are still scant, even though these may provide added advantages of fuel improvement due to synergistic effects [4,5]. NEOs include jatropha, neem, and palm kernel, which can be blended to overcome the weaknesses of each individual system and generally improve biodiesel properties [6].

The SLMD provides a very sound basis for modelling complex systems, thereby enabling appropriate prediction and optimization of feedstock performance [7]. Most of the previous optimization studies have been limited to individual single oils like Jatropha or neem, with a few studies on binary blends [4]. The ternary high-FFA systems are yet to be explored, though they have a great potential to increase feedstock flexibility and biodiesel quality [5].

1.1 Motivation, knowledge gaps, novelty, and objective

Biodiesel production from NEOs such as jatropha, neem, and palm kernel is often hindered by high FFC, which require esterification pretreatment. Table 1 presents a summary of studies on the esterification protocol for treating oily feedstocks. Earlier optimisation works have largely examined single or dual-oil feedstocks, utilizing statistical and intelligent modelling frameworks such as RSM, ANN, or Taguchi methods. However, these studies did not fully explore the complex interactions in ternary systems, where synergistic effects can improve fuel stability and address individual oil limitations. While jatropha and neem oils require pre-treatment due to their high FFA content, palm kernel oil offers good oxidative stability and low viscosity. Notably, there is a lack of systematic modelling of their combined behaviour and an absence of density and viscosity models for hybrid biodiesel blends.

This study introduces a new method using simplex lattice mixture design (SLMD) to optimise the esterification process of blends of palm kernel, neem, and jatropha oils. The research integrates multi-feedstock optimization with predictive modelling to reduce FFA levels, determine the optimal blend ratios, and assess the impact of ternary interactions on biodiesel quality. The objective is to establish a robust pre-treatment optimisation framework that enhance feedstock flexibility and complies with global biodiesel standards.

. **Table 1.** Tools for reducing high FFA oily feedstocks.

Feedstocks	**Modelling Tools**	**Key Outcomes**	**Density and viscosity models for biodiesel blends**	**Remarks**	**Knowledge gaps**	**References**
Castor and Neem oil (CNSO)	CCD	The model is unsuitable for synergizing the CNSO mix	×	Optimal conditions for the esterification of CNSO	No provision of density and viscosity model for CNSO methyl ester-diesel blends	Ayyub et al. [8]
Neem – Castor seed oil blend	RSM vs. ANFIS	ANFIS gave higher prediction accuracy for FFA reduction during esterification	×	Demonstrates the superiority of intelligent modelling tools	Predictive equation for robust esterification process absence	Samuel et al. [9]
Annona muricata–Calophyllum inophyllum oil (ACO)	OVAT	Lower acid value obtained by OVAT	×	Acid reduction for ACO mix conducted via OVAT	OVAT is unable to establish a perfect model for pre-treating ACO blends	Adepoju [10]
Jatropha curcus, Hevea brasiliensis, and Elaeis guineensis oil (JHEO)	CCRD	The optimal AV for esterification was determined using CCRD	×	CCRD has the ability to produce low a blend of JHEO	The CCRD is not robust enough to establish an explicitly built model for the esterified JHEO mixture	Adepoju et al. [11]

× = not considered

2 Material and methodology

The collection and characterisation of neem seed oil, castor seed oil, and palm kernel oil were carried out in accordance with the standards - ASTM D6751 and EN 14214. Various fuel-quality indices, such as FFA, density, viscosity, moisture, iodine, and saponification values, were determined according to ASTM and EN specifications. CSO was sourced from Oyo State; NSO was obtained from Agri Energy Ltd., while PKO was sourced from Benin City, Nigeria.

Acid esterification was carried out as a pre-treatment for NSO and CSO due to their high FFA content to avoid soap formation during base-catalysed transesterification. In this study, ternary blending was used as an approach to enhance feedstock stability and biodiesel quality by combining the three oils together. Before esterification, all the oils were heated to 110 °C and filtered to eliminate moisture and impurities. Ternary biodiesel of PNJO methyl ester was prepared through esterified PNJO under optimum conditions using classical parameters: 6:1 methanol-to-oil ratio, 1 wt.% catalyst, 60 °C, as earlier reported in [12]. For detailed experimental procedures, refer to Figure 1.

2.1 Blending and measurement of density and viscosity

The optimised PNJO methyl ester (B100) was blended with commercial diesel to create B5, B10, and B20 blends following ASTM guidelines. Pure diesel (B0) and B100 were also included in the analysis. Blending was carried out at ambient temperature using clean, dry glassware to prevent moisture contamination.

Kinematic viscosity (40 °C) was determined with a certified capillary viscometer following the procedures specified in ASTM D445 and EN ISO 3104 standards. Density at 15 °C was measured using a digital densitometer in accordance with ASTM D4052 and EN ISO 3675 methods. Each measurement was performed three times, and the average of the readings is reported as the final value.

The estimated measurement uncertainties were ± 2.3 kg m^{-3} for density and ± 0.05 mm^2 s^{-1} for viscosity (95 % confidence interval), consistent with the repeatability limits specified in ASTM D4052 (2023) and ASTM D445 (2022), as outlined in Appendix A

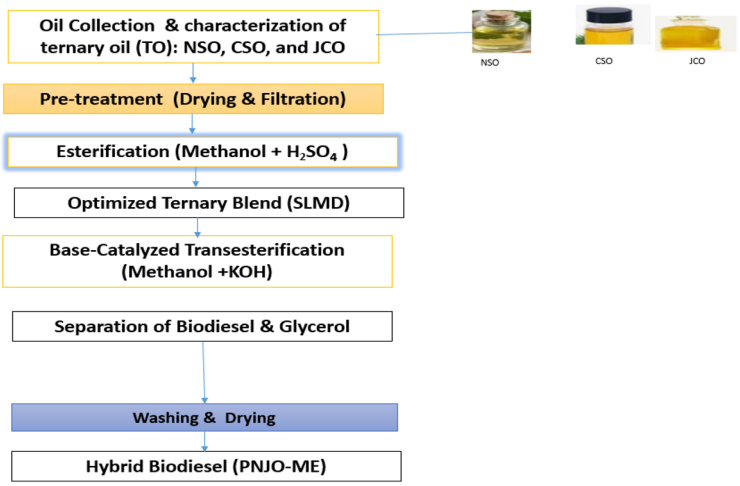


Fig. 1. Hybrid biodiesel production process using SLMD-optimised esterified PNJO blend.

3 Results and discussion

3.1 Characterisation of feedstock oils

The physicochemical properties of Jatropha, neem, and PKO are summarised in Table 2 and are crucial for predicting transesterification performance, product quality, and compliance with standards. Acid values ranged from 8.08 to 17.46 mg KOH/g (FFA ≈ 4.0–8.7 %), exceeding the typical 0.50 mg KOH/g acid number limit for base-catalysed processes. PKO has a high saponification value of 214.9 mg KOH/g, which indicates abundant short-chain fatty acids. In contrast, Jatropha and neem have relatively lower values of 158.5 and 135.3 mg KOH/g, indicating longer chains. All the oils revealed high values of viscosity in a range of 34.6 to 69.8 cP at 30 °C, and thus, all require esterification in order to be used in engines. On the other hand, the very low moisture content less than 0.08 % minimizes the risk of hydrolysis reactions; however, high peroxide values-the highest for PKO at 16.2 mEq/kg-suggest severe oxidation problems. Employing a SLMD for the optimization of ternary blend ratios prior to transesterification will enable the production of high-quality biodiesel that is in agreement with the standard.

Table 2. Characteristics of WCO, jatropha and palm oils.

Parameter	Jatropha Oil	Neem Oil	PKO Oil
Acid value (mgKOH/g)	8.08	17.43	17.46
FFA (%)	4.040	8.715	8.730
Saponification value (mgKOH/g)	158.543	135.329	214.899
Viscosity @ 30°C (cP)	44.5	69.8	34.6
Density @ 30°C (g/cm^3)	0.934	0.948	0.936
Moisture content (%)	0.03	0.08	0.04
PV (mEq/kg)	1.5	8.2	16.2
Iodine value (I_2g/100g)	106.81	52.36	17.47

3.2 Statistical analysis

3.2.1 Regression model and coefficient estimates for FFA conversion

Eq. 1 presents the regression model in terms of coded factors, showing the forecast of esterified oil percentage and also the relative contribution of each feedstock component. Factors A (JSO), B (NSO) and C (PKO) all contributed positively individually to the esterification of mixtures of high-FFA feedstocks. The two-factor interactions AB (JSO × NSO) and BC (NSO × PKO) improved esterification, while a negative effect was recorded for AC (JSO × PKO), indicating that increased levels of this combination tend to decrease esterification efficiency and negatively affect pre-treatment efficiency. The model thus evidences how the interactions of the components are essential for promoting effective esterification and therefore enabling subsequent transesterification.

$$FFA = 3.51A + 1.79B + 7.98C - 3.86AB + 14.07AC + 1.83BC \qquad (1)$$

3.2.2 ANOVA for the model

ANOVA results (Table 3) confirmed the enhanced significance of the quadratic model ($F = 372.95$, $p < 0.0001$) in predicting FFA conversion during pre-treatment. Significant interaction effects were observed for AB (JSO × NSO) and AC (JSO × PKO), while BC (NSO × PKO) had a marginal contribution. Because the Lack-of-Fit was statistically

insignificant (p = 0.2323), the developed model accurately captured the observed experimental behaviour. Strong fit statistics (R^2 = 0.9983, Adj. R^2 = 0.9957, Pred. R^2 = 0.9295) and an adequate precision of 53.68 confirm the robustness and predictive reliability of the model in describing the pre-treatment process of high-FFA oil mixtures.

Table 3. ANOVA for FFA model (esterified Oil).

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	92.57	8	11.57	372.95	< 0.0001	Significant
[(1)]Linear Mixture	73.17	2	36.58	1179.14	< 0.0001	
AB	1.24	1	1.24	40.13	0.0014	
AC	9.99	1	9.99	322.02	< 0.0001	
BC	0.1682	1	0.1682	5.42	0.0673	
A^2BC	3.26	1	3.26	104.98	0.0002	
AB^2C	1.39	1	1.39	44.94	0.0011	
ABC^2	3.98	1	3.98	128.44	< 0.0001	
Residual	0.1551	5	0.031			
Lack of Fit	0.0513	1	0.0513	1.98	0.2323	Not significant
Pure Error	0.1038	4	0.0259			
Cor Total	92.72	13				
Statistical results	R^2 = 0.9983	Adj. R^2 = 0.9957	Pred. R^2 = 0.9295	AP = 53.68		

AP = adequate precision

3.2.3 Optimisation and validation of the model

The optimisation objective was to determine the best combination of Jatropha, neem, and palm kernel oils to maximise FFA conversion during pre-treatment. Through numerical optimization with a desirability function of 99.99%, the optimal blend ratio was found to be 0.0112 JSO: 0.9653 NSO:0.0235 PKO.

Figure 2 shows a contour plot exemplifying the non-linear interface effects of the oil blends on FFA reduction. Increasing JSO and NSO proportions while decreasing PKO, improved pre-treatment efficiency. The predicted optimal blend leaned towards higher NSO composition due to its favourable fatty acid profile and reactivity, complemented by the long-chain fatty acids in JSO. On the other hand, the inclusion of PKO had a less beneficial effect, consistent with its inhibitory interaction as observed in the model.

Three validation experiments at the predicted optimal blend ratio confirmed the model's reliability. The experimental FFA rate of 1.85% meticulously harmonized with the projected value of 1.93%, with a marginal inaccuracy of 0.04%. This adjacent agreement between predicted and detected values demonstrates the model's reliability in describing pre-treatment performance in high-FFA oil mixtures. Optimal conditions for JSO–NSO–PKO esterification is shown by Table 4.

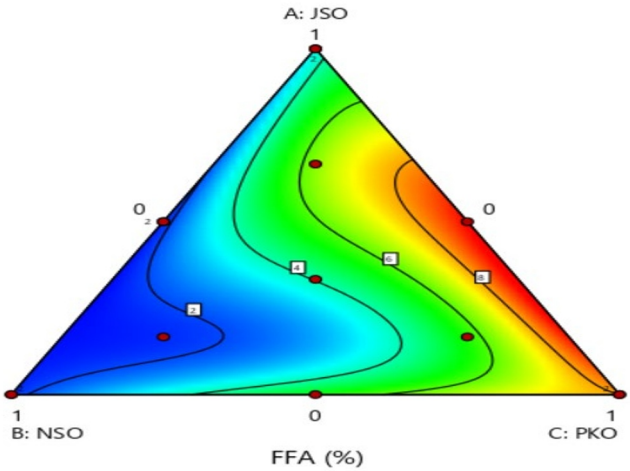


Fig. 2. Interaction contour plot of JSO, NSO, and PKO in SLMD-based esterification pre-treatment.

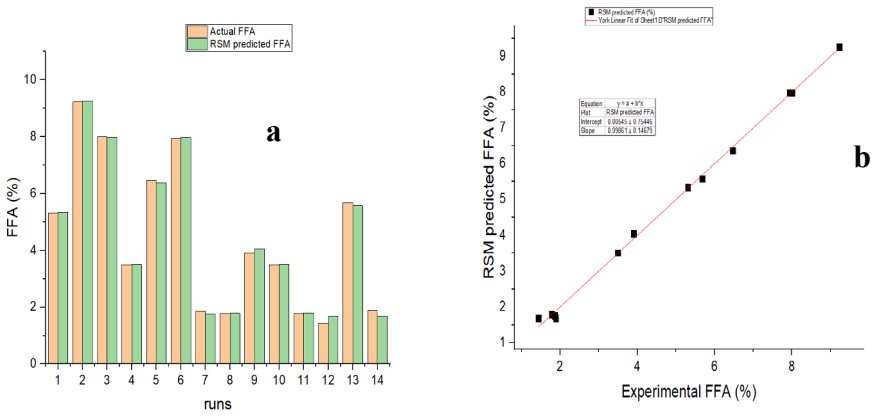
Table 4. Optimal conditions for JSO–NSO–PKO esterification.

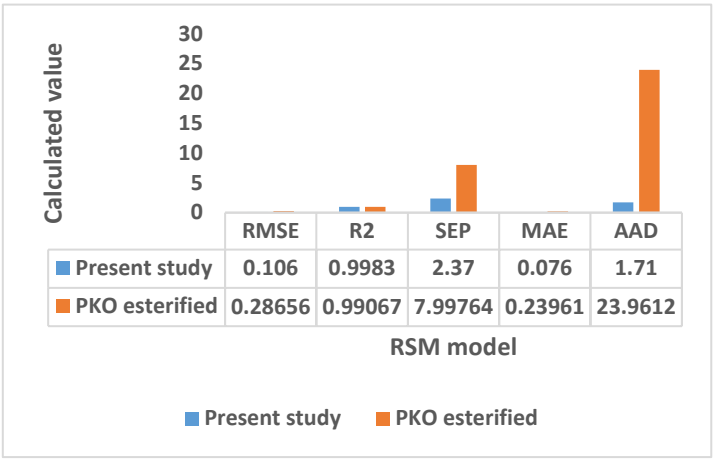
Samples of TO	JSO (%)	NSO (%)	PKO (%)	Predicted FFA level (%)	Experimental FFA level (%)	% Erro
Mixture ratio	0.0112	0.9653	0.0235	1.93	1.85	0.04

3.3 RSM model and assessment of its predictive fitness

Figure 3 (a-b) shows the experimental runs for the actual FFA compared to the RSM predicted FFA and the predicted and experimental FFA, respectively. In Figure 3a, the actual FFA closely matches the RSM-predicted FFA, indicating, a linear correlation $(0.99861x + 0.00545)$ that accurately represents the variation between the experimental and RSM predicted FFA,

Figure 3c shows the statistical indices evaluated, such as root mean square error (RMSE), coefficient of determination (R^2), standard error of prediction (SEP), mean average error (MAE), and average absolute deviation (AAD). The ASIs obtained in this study for the methyl ester of PNJO and palm kernel oil using the RSM model are comparable, showing high predictability and low errors [12].





(c)

Fig. 3. RSM model assessment: (a) Actual vs. predicted FFA, (b) Predicted vs. experimental FFA, and (c) Comparison of present and reported RSM results.

3.4 Fuel assessment of PNJOME obtained

For biodiesel to be considered a viable green diesel substitute, its production cost and quality must satisfy international sustainability benchmarks. Certain requirements must be met to ensure the efficiency of the diesel engine. The properties of palm kernel–neem–jatropha oil methyl ester (PNJOME) are summarized in Table 5. The kinematic viscosity of PNJOME (3.89 $mm^2\ s^{-1}$) was higher than that of PK-JCOB (2.40 $mm^2\ s^{-1}$) and NEAFJOEE (5.72 $mm^2\ s^{-1}$) reported by Okpala and Dibia [13] and Samuel et al. [14], respectively, and slightly above that of diesel (4.48 $mm^2\ s^{-1}$). This value also marginally exceeds the EN 14214 specification range of 3.5–5.0 $mm^2\ s^{-1}$. When the internal combustion engine operates on PNJOME, no notable variation in performance is expected due to the small difference between the kinematic viscosity of PNJOME and those previously reported. The density of PNJOME (915 kg m^{-3}) was slightly higher than that of pure diesel (B0, 842 kg m^{-3}), but comparable to the NEAFJOEE biodiesel (866 kg m^{-3}) reported by Samuel et al. [14] and within the EN 14214 specification range of 850–900 kg m^{-3}. This marginal increase in density is unlikely to cause significant changes in specific fuel consumption or spray penetration during injection.

The flash point of PNJOME (124 °C) exceeded that of pure diesel (68 °C), thus meeting international safety limits. Because of its high flash point, biodiesel is less flammable and hence safer to handle compared to diesel fuel.

Overall, PNJOME had a slightly lower heating value of 40.50 MJ kg^{-1} compared to diesel at 43.8 MJ kg^{-1}, owing mostly to the higher oxygen content that is characteristic of biodiesel compounds.

Figure 4 presents variations in the kinematic viscosity and density of the PNJOME–diesel blends. In internal combustion engines, fuel density is a key factor affecting spray characteristics and energy output. Although biodiesel typically has a lower heating value, its higher density can partially offset this factor, so that comparable performance to diesel can be achieved during engine operations. From Figure 4, the high R^2 value of 0.999 confirms that the quadratic equation obtained, $-0.0115x^2 + 1.903x + 840.19$, excellently predicts the blend density as a function of biodiesel content.

Viscosity is one of the most critical factors governing fuel atomization and injection in a diesel engine. The high R^2 value of 0.9856 explains that the second-order polynomial as stated by the equation, $-0.0002x^2 + 0.0358x + 2.4275$, becomes increasingly accurate to model the kinematic viscosity of the different PNJOME–diesel blends with respect to the biodiesel fraction. These findings agree with the trends reported by Alptekin and Canakci [15] and validate the sufficiency of a quadratic model to predict the viscosity variation of biodiesel–diesel blends.

Table 5. Fuel properties of PNJOME.

Properties	**Present study***	**PK-JCOB [13]**	**NEAFJOEE [14]**	**ASTM D6751**	**EN 41214**	**B0**
Viscosity (mm^2/s)	3.89	2.40	5.72	1.9–6.0	3.5–5.0	2.5
Density @ 15 °C (kg/m^3)	915	ND	866	Nil	850–900	842
FLP (°C)	124	112.00	153	130 min	120 min	68
Calorific value (MJ/kg)	40.50	41.26	41.4	---	---	43.814

*PNJOME; PK-JCOB=Palm kernel oil -Jatropha curcas oil biodiesel; NEAFJOEE = neem, animal fat, and jatropha oil ethyl ester.

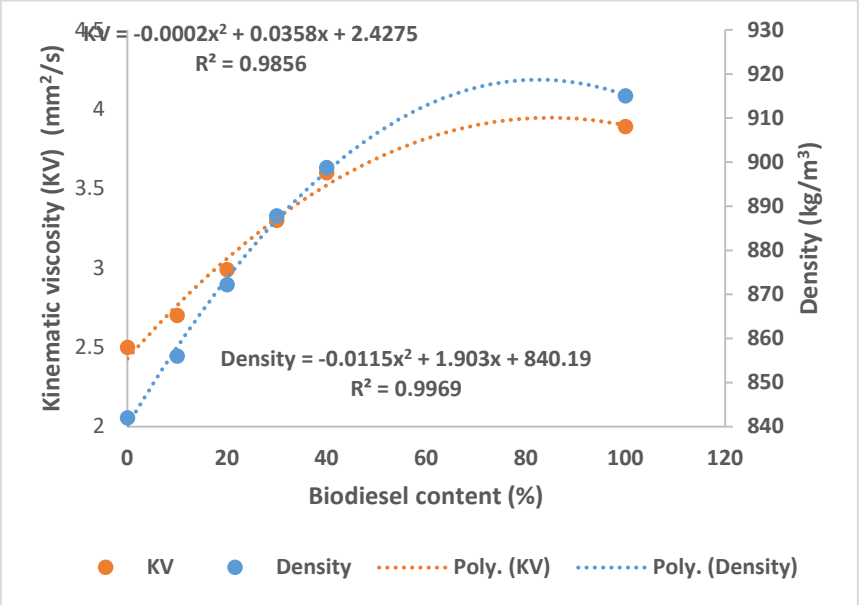


Fig. 4. Variation of kinematic viscosity and density with biodiesel content.

Conclusion

This study systematically modelled and optimized high-FFA ternary blends of jatropha, neem, and palm kernel oils using a simplex lattice mixture design (SLMD). It also assessed the commercial viability of biodiesel produced from the optimized esterified ternary blend through classical transesterification. Predictive models for key thermophysical properties, such as density and viscosity, were developed by correlating these parameters with biodiesel fraction in PNJOME–diesel blends using Excel-based regression tools.

The optimized quadratic regression model afforded a high predictive accuracy with an R^2 of 0.9983 and an RMSE of 0.106, which gave close approximations to experimental observations where experimental values were close to predictions with error <0.05%. With an optimized ternary mixture of 0.0112 JSO, 0.9653 NSO, and 0.0235 PKO, a minimum value of FFA of 1.85% was obtained that allowed effective downstream transesterification. Furthermore, quadratic equations developed for density, R^2 = 0.999, and viscosity, R^2 = 0.9856, of the different PNJOME-diesel blends indicated strong predictability, thereby affirming its application in the prediction of fuel behavior at any variable blend ratio. biodiesel obtained met both ASTM D6751 and EN 14214 standards to emerge as a promising renewable alternative for diesel fuel.

The focus of future studies should be on: comprehensive fuel characterization; life cycle assessment of ternary biodiesel to assess environmental sustainability; testing of the performance and emissions of PNJOME-diesel blends under realistic operating conditions; scaling up and carrying out techno-economic feasibility analyses for industrial deployment; integration of AI-based predictive frameworks to complement and extend SLMD modeling approaches.

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