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Best practices and methods

RSM optimization and yield prediction for biodiesel produced from alkali-catalytic transesterification of pawpaw seed extract: Thermodynamics, kinetics, and Multiple Linear Regression analysis

Godswill Adizue Ngige[a,b,c], Prosper Eguono Ovuoraye[d,*], Chinenye Adaobi Igwegbe[c,*], Endrit Fetahi[e], Jones A. Okeke[c], Alfred D. Yakubu[d], Pius Chukwukelue Onyechi[f]

[a] School of Science, Engineering and Environment, University of Salford, Salford, United Kingdom
[b] Department of Chemical Engineering, University of North Dakota, Upson, Centennial Dr Stop, United States
[c] Department of Chemical Engineering, Nnamdi Azikiwe University, P. M. B. 5025, Awka, Nigeria
[d] Department of Chemical Engineering, Federal University of Petroleum Resources, P.M.B. 1221, Effurun, Nigeria
[e] Department of Computer Science, University of Prizren, Prizren, Kosovo
[f] Department of Industrial/Production Engineering, Nnamdi Azikiwe University, P. M. B. 5025, Awka, Nigeria

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ABSTRACT

Optimization of alkali transesterification of pawpaw seed extract to biodiesel using NaOH catalyst was carried out to analyze kinetics, thermodynamic parameters, and optimum conditions. Response Surface Methodology (RSM) and Multiple Linear Regression (MLR) algorithms were used to confirm the optimum yield results. GC chromatography and X-ray diffraction (XRD) were used to determine the fatty acid profile and characteristics of the pawpaw seed oil (PSO). The maximum biodiesel yield of 80% was obtained at optimum temperature, catalyst weight, and methanol to oil ratio of 60 °C, 1.0 wt%, and 3:1 via the RSM. Kinetics shows that the effect of NaOH on the overall reaction rate was feasible at 30 min while MLR predictions exercised outside the design matrix confirmed that increasing catalyst weights and temperature increases biodiesel yield within the optimum conditions. The finding obtained from the MLR was consistent with the experimentally determined percentage yield practicable based on the experimentally determined value conducted to verify the predicted output. The predicted output indicated $a \pm 0.025$ standard deviation from the result practicable. Some key fuel properties derived from PSO satisfied ASTM (D6751) specifications and complied with EN141215 standards. The XRD patterns and GC/MC characterization confirm PSO is a good source for biodiesel production.

1. Introduction

Most of the energy that the world is using is derived from non-renewable fossil fuels with the present situation of increasing energy demand, rising energy prices, and reinforcement of countermeasures for global warming, renewable energy has taken the spotlight (Agunbiade and Adewole, 2014; P. C. Onyechi and Igwegbe, 2019; Uzoh et al., 2021). Natural resources such as coal, gas, or oil (non-renewable energy) that are once consumed, cannot be replaced over time, to overcome the challenges of fossil fuels, renewable and alternative energy sources are now being searched for more than ever before (Hosseinzadeh Samani et al., 2020), with a view of replacing the natural resource over time with renewable energy resources.

Biodiesel, a renewable fuel, is one of the most popular alternative fuels available today (Uzoh et al., 2021). It can be used in diesel engines, either purely or unified with diesel, to reduce exhaust pollutants (Simsek, 2020). Chemically, it is the outcome of a reaction called transesterification, where oils from animals and plants are reacted with any alcohol in the existence of a catalyst to yield fatty acid esters (Karmakar et al., 2010; Leung et al., 2010; Muniyappa et al., 1996). Biodiesel has been produced from Jatropha oil (Adeniyi et al., 2018; Sahoo and Das, 2009; Ude Callistus et al., 2016), rudder seeds oil (Uzoh et al., 2021), chicken fat (Kirubakaran and Selvan, 2018), kapok oil (Ong et al., 2013), cotton seeds oil (Araújo et al., 2012; Onukwuli et al., 2017), melon oil (Aliozo et al., 2017), and Caper spurge weed oil (Adeniyi et al., 2019).

However, the controversies about the conversion of eatable (edible) oils to fuel brought new dimensions to the transesterification process. Prolonged dependence and increasing demand for edible oil as feedstock for biodiesel created a siphon that drew a bigger portion of eatable oils into the fuel industry. This consequently threatened the supply of eatable oil to the food industry; therefore, looking for substitutes

* Corresponding authors.
E-mail addresses: pe.ovuoraye@gmail.com (P.E. Ovuoraye), ca.igwegbe@unizik.edu.ng, chinenyeigwegbe@gmail.com (C.A. Igwegbe).

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is necessary. Hence, the recent research work investigates biodiesel production from pawpaw (Carica papaya) seed oil, and non-edible oil by catalyzed transesterification.

Although, biodiesel has been accepted worldwide as the immediate solution to the heavy reliance on petroleum-based diesel oil from organic sources, the current commercial production technology of biodiesel through homogenous transesterification has a lot of limitations making the cost of biodiesel manufacture economically unviable (Chua et al., 2020; Oraegbunam et al., 2020). On the other hand, the heterogeneous transesterification process provides a cheaper, less problematic, and easier operation compared to homogenous and non-catalytic transesterification processes (Galadima and Muraza, 2014). However, the reactivity of the heterogeneous solid catalysts (such as CaO, MgO, ZnO/Al2O3) is a hindrance to its preservation (A. K. Singh and Fernando, 2007). Not many solid catalysts could produce a high yield of FAME (fatty acid methyl esters) in the transesterification process. Hence, creating a practical, durable, and highly reactive solid catalyst to utilize in the process becomes a challenge. Different types of catalysts homogeneous catalysts have been used in transesterification, including acid-based catalysts (H2SO4, HCl, etc.) (Marchetti et al., 2011; Nurhayati et al., 2017) and alkaline-based catalysts (NaOH, KOH, etc.) (Adeniyi et al., 2019; Anastopoulos et al., 2009; Ehsan and Chowdhury, 2015; Hassani et al., 2013). Alkali catalysts speed up transesterification (Elkady et al., 2015; A. Singh et al., 2006). Acidic catalysts are not recommended in the industry due to their corrosive nature and these catalysts are hard to be removed from the product (Faruque et al., 2020). The acid catalysis rate is much slower than that of base catalysis (Canakciand Van Gerpen, 1999). Agunbiade and Adewole (2014) used potassium hydroxide (KOH) on pawpaw seed oil extracted using n-hexane in the presence of methanol and Oraegbunam et al. (2020) used KOH and sodium hydroxide (NaOH) on refined pawpaw seed oil which resulted in a high yield of biodiesel. Production of biodiesel from pawpaw seed extract is at best functionally with the homogenous catalysts, NaOH or KOH (Sarianto et al., 2019; Umapathi, 2019).

There has been little research carried out on transesterification using pawpaw seed oil. Agunbiade and Adewole (2014) and Sarianto et al. (2019) experimented on pawpaw seed oil using varying catalyst and alcohol molar ratios. Agunbiade and Adewole (2014) produced biodiesel via methanolysis of crude pawpaw seed extract and confirmed the methyl ester formed as potential biodiesel resources. Umapathi (2019) experimented on pawpaw seed oil to form biodiesel blends to test engines, their work confirms the quality performance of the blend with less emission. Agunbiade and Adewole (2014) also characterized the methyl ester yield from pawpaw seed oil using CaO as the catalyst to describe the potency of biodiesel production using pawpaw seed extract.

However, with the growing need for the application of artificial intelligence through the use of machine learning in modeling, prediction, and optimization of biological and chemical processes, using Multiple Linear Regression has become imperative in biodiesel production, with the aims of reducing cost and maximizing experimental analysis beyond pilot scale to solve future problems on energy from biodiesel production. It is pertinent to know that pawpaw seeds are currently undervalued in Nigeria and so there are no standardized processing methods available at present. Also kinetics model is necessary for the complete optimization of the biodiesel production process. Thus kinetics must be incorporated into transesterification studies for reactor design (Castillo Gonzalez et al., 2020; Trejo-Zárraga et al., 2018). Experimental results on biodiesel produced from pawpaw seed oil (Agunbiade and Adewole, 2014; Sarianto et al., 2019; Sendzikiene et al., 2004) were found to fit a first order kinetics rate law for the forward reaction.

The present research is focused on (i) the extraction of oil from pawpaw (Carica papaya) seeds using petroleum ether and n-hexane as extraction solvents, GC characterization and XRD analysis of the crude PSO extract and biodiesel produced to determine its fatty acid contents and physicochemical properties of the biofuel produced from alkali-transesterification of the oil using NaOH as catalyst, (ii) the determination of the influence of experimental factors (ethanol-to-oil molar ratio, temperature, and catalyst weight on ethyl-ester production at optimum conditions following the Box Benkhen design optimization from the RSM, (iii) the kinetics of the transesterification reaction was investigated to determine the rate constants and order of reaction, with the thermodynamics parameters (activation energy, and enthalpy) at optimum condition, (iv) to analyze the MLR algorithm used for the biodiesel yield prediction of the effect of changing variables beyond the experimental range on the PSO biodiesel yield was analyzed using Multiple Linear Regression Algorithm (MLRA), to determine the effect of changing parameter on the transesterification at optimum alcohol to oil molar ratio.

2. Materials and methods

2.1. Raw materials

320 kg of pawpaw (Carica papaya) seeds were obtained from local traders along the main market, Onitsha, Nigeria. 10 L of n-hexane was bought from a local vendor at Onitsha, Nigeria. 10 L each of ethanol and sodium hydroxide was also obtained from the research laboratory. All reagents were of analytical grade and required no further purification.

2.2. Batch extraction of pawpaw seed oil (PSO)

3.2 kg of pawpaw seeds was size-reduced to increase the surface area. The crushed sample was weighed, placed in a reactor and covered tightly, and left for a week. The sacs with the crushed seeds were transferred into the reflux condenser. 100 mL of n-hexane (extracting solvent) was added into a round bottom flask and the reflux condenser was attached. This set-up was placed on a heating mantle with a constant temperature of 50°C. The reaction time was maintained at 30 minutes and the PSO yield was calculated. The same procedure was also used for the petroleum-ether as the extracting solvent. The extracted PSO samples were then characterized using XRD and GC analysis.

2.3. Gas chromatography and XRD characterization of samples

The fatty acid composition/profile of the oil and biodiesel samples was determined using a bio-oil analyzer Gas Chromatography (GC) coupled with mass spectrometry (R Balasubramanian et al., 2018). The fatty acid composition/profile of the oil and biodiesel samples were determined using a GC–MS analysis performed with a Shimadzu (QP2010 SE, Japan) series gas chromatography, with mass spectrometer equipped with flame thermionic detector (FTD). The column oven temperature was initially set at 70 °C. The column temperature was then increased to 280 °C at 10 °C/min with a hold time of 5 min. The carrier gas was nitrogen at a column flow rate of 1.80 mL/min and the total flow rate of 40.8 mL/min. The analysis was performed at injector temperature of 250 °C and ion source temperature of 200 °C and a split ratio of 20:0. The peaks were identified by comparing with the retention time of standards and were quantified by area normalization using software.

The X-ray diffraction (XRD) technique following the ASTM standard was carried out using the XPERT X-ray diffraction unit (DMAX 2200/Ultima C, Japan) equipped with Cu radiation. The analysis was carried out to acquire diffraction patterns with the scan range from $2\theta = 10^0$ to 80°, step size of 0.0130, step time of 48.19 s, and at the rate of 30 mA and 45 Kv (Subramaniapillai Niju et al. 2019). The XRD characterization was carried out using (Cu, and k) radiations at a scanning rate of $20min^{-1}$. The FAME was identified by comparing their fragmentation pattern with authentic standards (Sigma) and also with the NIST library.

2.4. Determination of the yield of the biodiesel

A small quantity of PSO was added to a beaker and heated on a magnetic stirrer at a temperature of 50°C at a stirring speed of 700 rpm. A

2 M sodium hydroxide was added to the PSO at intervals. A phenolphthalein indicator was used to check for a color change. The mixture was heated at 55°C while the stirring speed was maintained at 550 rpm. The mixture was poured into the separating funnel where two different layers of the solution were observed. The mixture was washed with warm water and the yield was calculated. The procedure was repeated for various molar ratios, varying temperatures, and catalyst quantities.

20 ml of the neutralized oil was measured out and poured into a beaker. It was heated on a magnetic stirrer to remove any form of moisture. From the calculations made, it was seen that for the 1:1 molar ratio, 3.65 ml of ethanol and 0.17 g of sodium hydroxide catalyst (1% catalyst weight) were used. These two reagents, with the heated oil, were added into a conical flask which was covered tightly. The conical flask was placed on a magnetic stirrer and heated at a temperature of 65°C and an agitation speed of 550 rpm for 30 min. The solution was poured into a separating funnel and was allowed to stand for 6 h, after which two distinct layers were observed. The lower part (darker glycerol) was tapped off, while the upper biodiesel was washed with warm water to remove impurities.

2.5. Experimental conditions

The experimental procedure above was used to vary the PSO biodiesel yield at varied ethanol-to-oil molar ratios of 3:1, 6:1, 10:1, 15:1, 20:1, 25:1, and 30:1, respectively. The same procedure was used to also determine the yield at varying temperature conditions of 40°C, 50°C, 60°C, 70°C, 80°C, and 90°C, while biodiesel yield was also evaluated following Eq. (1) at varying catalyst weight of 0.75, 1.0, 1.25, 1.5, 1.75, and 2.0 wt%, respectively. A certain volume of ethanol (11 ml) obtained from the highest yield of ethanol to oil molar ratio was poured into a conical flask. 0.17 g of sodium hydroxide catalyst was also added and 0.5% catalyst weight (0.09 g of sodium hydroxide) was also added. The heated oil was also transferred into the conical flask. The percentage (%) yield of the biodiesel oil was calculated using Eq. (1):

$$\%\ \text{Yeild} = \frac{\text{Weight of biodiesel produced (g)}}{\text{Weight of oil used (g)}} \text{x } 100 \tag{1}$$

The conversions of oils used were based on the stoichiometric relation, that 100 cm^3 of oil gives approximately 100 cm^3 of methyl esters. However, the percentage weight per volume (%wt/v) of the catalyst was calculated using Eq. (2):

$$\%\frac{\text{Wt}}{\text{v}} = \frac{\text{weight of catalyst x } 100}{\text{Volume of the oil per run}} \tag{2}$$

2.6. Optimization design

The optimization of the significant parameters in the transesterification process is carried out to maximize the biodiesel yield where-in optimal value of each parameter is determined (Arunachalam Sivagurulingam et al., 2019; Ashokkumar et al., 2014) . The traditional method of optimizing more than one independent viable by one–factor–at–a–time (OFAT) method that is followed by keeping other factors constant is very complicated (Enyoh et al., 2022). This difficulty and complications associated with the application of the traditional method of optimizing the transesterification process can be overcome by employing a statistical method of optimization such as the Box-Behnken design (BBD) via the RSM (Senthilkumar et al., 2019). The BBD following the RSM was selected for the optimization study of the biodiesel yield. The experimental design consisted of three factors: temperature,alcoholto-oil, catalyst weight, and alcohol to oil molar ratio, respectively, were used to build the quadratic model for responses (biodiesel yield) with the need to control the design to three levels and provide information about interactions among experimental variables within the range studied, leading to a better knowledge of the process (Enyoh et al., 2022) (Deepalakshmi et al., 2015). The three levels of factors included the optimum values obtained from the 17 experimental runs of the design.

However, the most common empirical models fitting to the experimental data take either a linear, cubic, or quadratic form (Enyoh et al., 2022), with the coefficients of the model used to establish the BBD model equations showing the relationship and interactions of the catalyst weight, reaction time, and temperature and their significance with the biodiesel yield. A non-linear regression method was used to fit the second-order model into a quadratic, quadratic, or polynomial model that follows the model equation described in Eq. (3) below:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{3}$$

Where Y is the response; β_0 is a constant coefficient; ε is the error; β_i, β_{ii} and β_{ij} are interaction coefficients of linear, quadratic, and second-order terms, respectively; x_i and x_j are independent variables that determine the response (Y)The subscripts *i*and*j* are the integer variables (Igwegbe et al., 2021, 2019).

2.7. Prediction using Multiple Linear Regression Algorithm

The applications of machine learning and artificial intelligence are currently in high demand in experimental analysis (Ahmadi et al., 2021; Igwegbe et al., 2021). In many cases, due to financial constraints, limited data generated from the laboratory research data are not sufficient enough to cover a wide range of experimental analyses and investigations. Consequently, Artificial Intelligence (AI) models and algorithms are developed using machine learning to generate sufficient data from the regression analysis of the experimental data, to make predictions on the performance and quality of biodiesel produced from non-edible seeds. The present work explores the application of the prediction algorithm on experimental variables not initially covered within the scope of the design matrix, bet based on the regression table generated from the research data and following the Multiple Linear Regression (MLR) methodology incorporated into biodiesel prediction software (Bio-Predictor) following a simple CLI (Command Line Interface), which is based on Python programming language. The biofuel yield prediction software was developed in a way where; the input variables provided were entered from the regression table formulated, and following multiple regressions algorithm, consequently, prediction is made based on the experimental training data set integrated into the software, and MR is performed automatically by the software to predict output results on the biodiesel yield following the transesterification process. MR is a statistical procedure that utilizes a few illustrative factors to predict the result of a variable response. Multiple Regressions is the expansion of Common Least-Squares (OLS) regression since it includes more than one logical variable. This approach was effective for the prediction of biodiesel yield that covers a range of catalyst weights, and temperatures within and outside the range of the experimental scope. The overall model of the prediction and the training data set on which the prediction is performed followed the sequence shown in Fig. 1.

3. Results and discussion

3.1. Extraction of crude PSO

Solvent selection is a very important factor that can influence the extraction of bio-oil. There are several extracting solvents employed for transesterification (Vishnu Priya et al. 2019). The extracting solvents such as n-hexane and petroleum ether are recommended solvents used for extraction due to their higher lipid yield and good selectivity (Li et al., 2014). Hexane has gained favor due to the carrying capacity reported in the works of Vishnu Priya et al. (2019). The two solvent systems (n-hexane and petroleum ether) were chosen from the literature based on their proven effectiveness. The extraction of crude PSO from the crushed sample was carried out using petroleum ether and n-hexane. The results show that; the extraction of crude pawpaw seed was feasible using n-hexane compared to petroleum ether. A plot of the

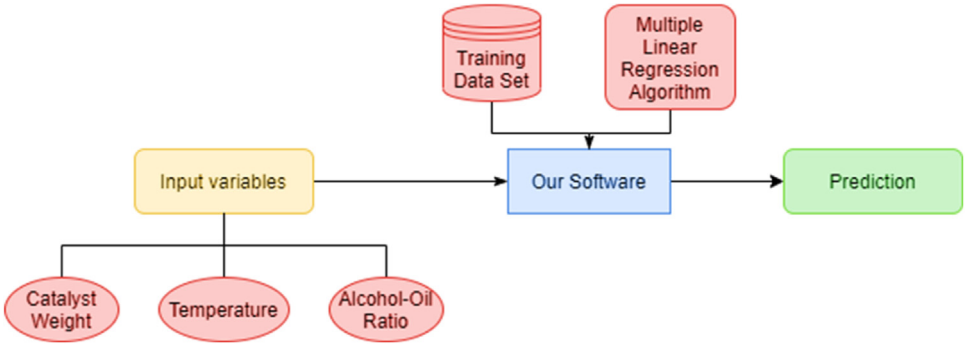

Fig. 1. Sequence for development of the MLR algorithm for biodiesel yield prediction.

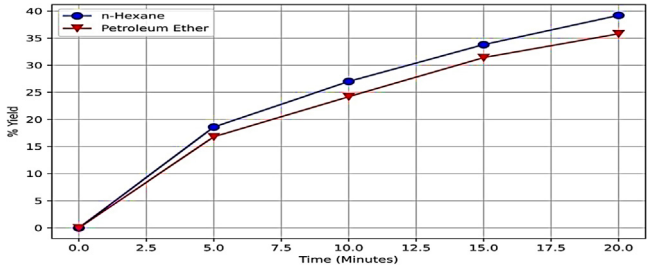

Fig. 2. Effect of extraction solvents on crude PSO.

percentage extract against time shows that; the percentage yield of the extract increases as the contact time increases from 0 to 20 min as shown in Fig. 2. The graph also shows that; the maximum crude PSO extract corresponds to 35% and 38% for n-hexane and petroleum ether, respectively at a maximum time of 20 min, this translates to the fact n-hexane is the better solvent of the two extraction solvents used in this research. The analysis of the crude PSO yield proved that n-hexane produced high PSO extract compared to petroleum ether; hence, we conclude that n-hexane remains the most suitable solvent for the extraction of crude pawpaw seed oil to be processed into biodiesel. This report is well represented in the graphical evaluation of the effect of extraction solvent on PSO yield at an equal interval of time (Fig. 2).

3.2. Characteristics of the crude PSO extract

The characterization of the seed extract was carried out to ascertain the compositions of fatty acid (FA) contents of the oil and other very important parameters of the crude PSO. The FA was determined following the chromatography techniques and the X-ray diffraction analysis (XRD) following the work by (Sarianto et al., 2019). The characterization and properties of the crude PSO extract were obtained following the GC/MC chromatography analysis and the XRD technique. The XRD result of the pawpaw seed extract shows that; the crude PSO contains higher proportions of pentadecanoate and arachidic acids corresponding to 65.27% and 9.93%, respectively as shown in the XRD presented in **Fig. S1 (see supplementary file)**. The proportions of palmitic acid, methyl-stearate, and melissic acids were, respectively less than 4% in the total weight of the FFA composition in crude PSO. The implication of the result is an indication of the presence of high molecular weight compounds present in the structure of crude PSO which corresponds to; greater C=C bonds present in the fat as such the engine operability will likely be minimal with the crude extract (Nayak and Vyas, et al. 2019; Sarianto et al., 2019).

The XRD pattern of the crude PSO extract in **Fig. S1** shows that the homogenous catalyst follows 2Theta= 12.31°, 20.84°, 39.44°, 45.7820, 62.248°, and 67.71°, respectively. This output is in agreement with the findings reported in reference (Sarianto et al., 2019) and confirms

Table 1
Physiochemical properties of bio-oil inaccordance with ASTM D6751 standard.

Crude PSO properties	Value	Unit
Density at 15° C	850	kg/m^3
Acid value	2.244	mgKOH/g
Viscosity at 30°C	2.224	Pa.s
Saponification value	35.76	mgKOH/g
Peroxide value	6.02	meq/Kg
Iodine value	8.35	meqI$_2$
Moisture content	1.98	%
Flashpoint temperature	80	°C
Kinematic viscosity at 40°C	7.69	cSt
Kinematic viscosity at 100°C	2.92	cSt
FA	1.122	%
Cetane number	25.472	-
Boiling point	198	-

that the homogenous catalyst used produced alkoxides from sodium hydroxide. The FA process contains predominantly, melissic and methyl-stearate acid contents that were relatively lesser than 9%. The fatty acid profile for the crude PSO was analyzed following the analysis reported shown in Fig. S1. Therefore, it becomes obvious to say that; the crude structure of pawpaw seed extract was made up of predominantly fatty acids (FA) with high compositions of carbon-carbon (C=C) bond, with molecular weight hydrocarbon compounds. Their respective molecular weights were greater than 240 gmol^{-1}, which transcends to higher weight hydrocarbon compounds with higher proportions of hydrocarbon contents ranging from C15 to C30, respectively. The confirmation of these reports is well represented in the XRD pattern showing the fatty acid profile of the crude PSO oil extract in Fig. S1.

However, the physicochemical characteristics of the crude PSO obtained following the American Oil and Chemical Society (AOCS) reference methods are well presented in Table 1. The acid value, iodine value, and saponification value were determined using titrimetry following the standard method stated (ASTM). The density and viscosity were analyzed using a hydrometer, and a viscosimeter (Redwood, model VT754, India). The results of the physicochemical properties of the crude extract show that; the extracted oil from the organic material has a density of 850 kg/m^3, and an acid value of 2.244 mg-KOH/g. The acid value is slightly higher than the ASTM specification (0.8). This outcome implies that the amount of hydroxide present in the oil is just sufficient to neutralize the FA content present. The iodine value of the crude PSO was recorded as 8.35 meqI$_2$, this value indicates the level of unsaturation of the double bonds present in the bio-oil based on the alkyl-ester made with sodium hydroxide and the fatty acid contents present in the crude PSO is sufficiently good enough to determine the oxidation stability of the biodiesel that is produced from the bio-oil.

Also, the cetane number corresponding to 25.472 and boiling point of 198°C were recorded for the PSO. The viscosity of the oil was ob-

Table 2
ANOVA for quadratic model developed.

Source	Sum of squares	df	Mean Square	F-value	p-value	
Model	3896.33	8	487.04	541.16	< 0.0001	**Significant**
A-Temperature	70.32	1	70.32	78.14	< 0.0001	
B-Catalyst weight	47.70	1	47.70	52.99	< 0.0001	
C-Alcohol-Oil Ratio	156.71	1	156.71	174.12	< 0.0001	
AB	164.27	1	164.27	182.52	< 0.0001	
AC	99.72	1	99.72	110.81	< 0.0001	
BC	39.54	1	39.54	43.93	0.0002	
A^2	839.17	1	839.17	932.41	< 0.0001	
B^2	608.44	1	608.44	676.05	< 0.0001	
C^2	0.0000	0	–	–	–	
Pure Error	7.20	8	0.9000	–	–	
Cor Total	3903.53	16	–			

Predicted R^2 = 0.999; Adjusted R^2 = 0.9963; R^2 = 0.9982; Stdv =0.9487; Mean value = 59.71.

tained as 2.24 Pa.s, with the saponification value of 35.76 (mg-KOH/g), flash point temperature of 80°C, and moisture content of 1.98%, respectively. The FA content of the crude PSO corresponds to 1.22%, with a kinematic viscosity of 2.92Cst at 100°C and kinematic viscosity of 7.2 Cst at 40°C. The peroxide value of the crude extract was recorded to be 6.20 (meq/Kg), respectively. The peroxide value of the crude PSO is an indication of moderate oxygen content that is sufficient enough to promote combustion. The physicochemical properties of the crude pawpaw seed extract are well presented in Table 1.

3.3. Optimization of the Alkali-Catalytic Transesterification Process

Response surface methodology (RSM) employing the Box-Behnken design was applied for the optimization of the Methyl-ester formation for 17 experimental runs. The reaction temperature (°C) = A, catalyst weight (wt%) = B, and the alcohol-to-oil molar ratio =C were varied to 3-levels based on the design matrix presented in **Table S1 (see supplementary file)**.

The quadratic model was developed following the Box-Behnken design to analyze the effect of the factors A, B, and C, respectively on the response parameter (biodiesel yield). The model F-value of 541.16 (Table 2) obtained following the Box-Behnken design implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The P-values less than 0.0500 obtained from the optimization analysis indicate model terms are significant. In this case, A, B, C, AB, AC, BC, A^2, and B^2 are significant model terms. Model values greater than 0.10 indicate the model terms are not significant Ovuoraye et al. (2021). In this case, the significance of the experimental variables follows the order:

$$\boldsymbol{AB} > \boldsymbol{A^2} > \boldsymbol{B^2} > \boldsymbol{C} > \boldsymbol{BC} > \boldsymbol{B} > \boldsymbol{A} > \boldsymbol{BC}$$

The correlation coefficient R^2 value of 0.9982 obtained at the adequacy of the precision value of 57.948 shows that; the model is significant. The predicted R^2 value of 0.999 and adjusted R^2 value of 0.9963 also show that the model terms are significant. The predicted R^2 value and the adjusted R^2 value are in reasonable agreement with the correlation coefficient R^2. These values are close to unity and confirm the predicted values from the quadratic model following the Box-Behnken design of the RSM are well correlated with the actual value Enyoh et al. (2022). This report is well represented by the linear graph in Fig. S2 (**see supplementary material**). The standard deviation value of 0.9487 and the mean value of 59.71 also confirmed that the quadratic model obtained following the Box-Behnken design is significant. These results are well presented in the analysis of variance (ANOVA) (Table 2).

The optimum alcohol-to-oil molar ratio of 3:1 was selected as the best point based on the results predicted in the optimization ramp plot in Fig. S3 **(see supplementary)**. The optimization results also proved that the maximum biodiesel yield which corresponds to 80% methyl-ester was obtained from the alkali-transesterification of pawpaw seed

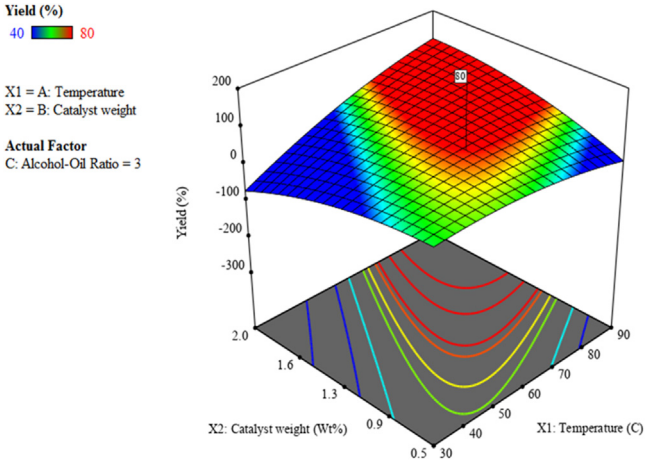

Fig. 3. 3D surface plot showing the values of optimum biodiesel yield.

oil. The process occurred at an optimum temperature of 60°Calcohol-to-oil molar ratio of 3:1. These values are derived from the analysis of the final model Eq. (4).

$$Y = 44 - 110A - 57\mathrm{B} - 38\mathrm{C} + 60\mathrm{AB} - 146\mathrm{AC} - 24A^2 - 28B^2 \quad (4)$$

The optimization analysis following the Box-Benkhen Design plot that, the optimum, temperature, catalyst weight, and alcohol-to-oil molar ratio are 60°C, 1.0wt%, and 3:1, respectively, which transcend to 80% biodiesel yield. These output results were obtained following the implementation of the optimization analysis executed using Design Expert Software Version 11.0. The ramp plot in Fig. S3 of ERM confirms that the optimal solutions fallwithin the experimental boundaries and these points are well represented in theflag point in the surface and contour plots in Figs. 3-5.

The 3D surface and the corresponding contours in Figs. 3 and 4 plot the best biodiesel yield from the transesterification of PSO that occurred at an optimum temperature of 60°C. The darker red region of the contour gradient in Fig. 4 shows that the yield increases as temperature increases intermittently from 40°C through 70°C corresponding to an increase in yield from 35% to 90%. Further increase in temperature beyond 70 °C decreases the PSO biodiesel yield below 50% due to accelerated saponification of the glycerides produced at elevated temperatures. Hence, it can be reasoned that the temperature of 60°C gave the best degree of conversion at optimum alcohol to oil molar ratio of 3:1. Fig. 5 also plots that; the effect of the catalyst weight on the alkali-driven transesterification reaction, yield increase occurred with the increase in catalyst weight from 0.5wt% through 1.0wt% which translates to increase in biodiesel yield ≥70%. Beyond the optimum value of 1.0wt%, the biodiesel yield decreased below 50%. Increasing temperature be-

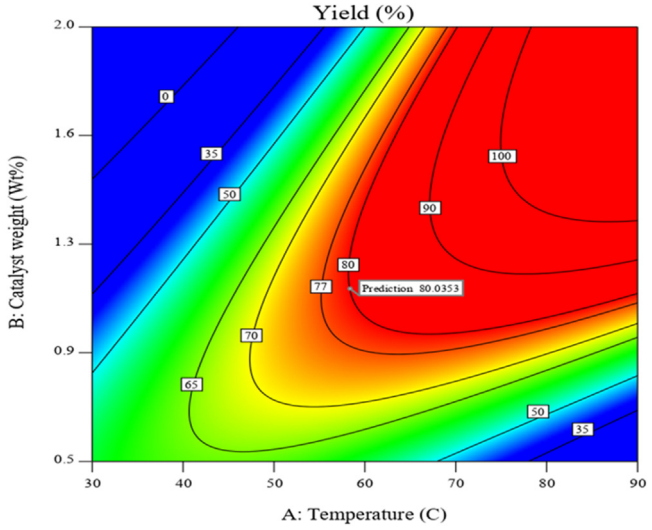

Fig. 4. Contour plot showing the interaction of temperature and catalyst weight.

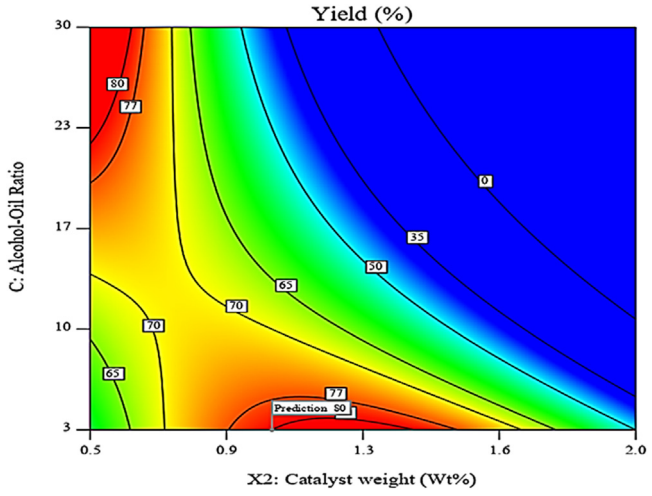

Fig. 5. Contour plot showing the interaction of temperature and catalyst weight.

yond 70°C at the optimum condition will lead to a decrease in PSO biodiesel yield below 50% due to the conversion of the methyl-esters to glycerol.

Also, the conversion of PSO to biodiesel was found to increase biodiesel yield as catalyst weight increased from 0.5wt% at the temperature increases from 60 °C through 70 °C. This analysis was well illustrated in the surface plot in Fig. 3 and the contour plot in Fig. 5. The percentage of biodiesel yield then decreases as catalyst weight increases beyond the optimum value of 1.0wt%. Further increase in the NaOH weight percent will lead to the formation of more glycerol conversion of the PSO. It can be concluded from the optimization analysis that the percentage contributions of each factor transcend to; temperature (60 °C) corresponded to 70% yield, and the alcohol-oil molar ratio (3:1) translates to ≥80%, while the optimum catalyst weight also produced a yield corresponding to 80%. It is believed that an insufficient amount of catalysts below the optimal weight will result in the incomplete conversion of the triglycerides into fatty acid esters (Anithaand Dawn, 2010), while excess catalyst weight beyond the optimum will decrease the yield leading to the formation of glycerol. Hence, a conclusion can be drawn from the optimization process that the best performance of alkali catalyst on the transesterification of pawpaw seed oil occurred at a temperature greater than 50°C, at an optimum molar ratio of 3:1 at sodium hydroxide (NaOH) catalyst greater than 0.5wt%, this result can be well interpreted from the contour plot in Fig. 5.

3.4. ASTM, XRD, and GC analysis of the biodiesel from PSO at optimum conditions

The XRD presented in Fig. S4 **(see supplementary file)** was used to confirm the FFA characteristics of the biodiesel and its properties at optimum conditions. Fig. S4 plots that the biodiesel produced from the alkali transesterification of the crude PSO with NaOH as catalyst contained higher weight contents of unsaturated fatty acid, which predominantly do not solidify at room temperature. It can be observed from the GC/MS analysis result and diffraction pattern in Fig. S4, the predominant fatty acid present in the biodiesel was linoleic, palmitoleate, and methyl-stearate acids which correspond to 34wt%, 17wt%, and 14wt%, respectively. The chromatograph also shows that the biodiesel contains low proportions of palmitoleate and palpric acids lesser than 3wt%, therefore, it can be concluded from the GC/MS chromatography report and XRD pattern that; the alkali-transesterification of pawpaw seed extract with sodium hydroxide biodiesel produced from PSO is categorically made up of high molecular weight C = C compounds. This report is well presented in Fig. S4 of ERM supplementary material.

The XRD analysis (Fig. S4) of the biodiesel produced from the alkaline transesterification reaction of PSO with NaOH as the catalyst, based on the International Center for Diffraction Data (ICDD) database follows 2Theta= 38.41°, 39.45°, 45.78°, 50.14°, 54.87°, 67.71°, 73.42°, and 75.61° which shows slight deviations from the biodiesel report presented in the study by Sarianto et al. (2019), the variations in their results was probably due to the nature of the different catalyst and the alcohol used, calcined CaO and methanol against NaOH and ethanol, respectively. The XRD profile (Fig. S4) also indicated major peaks at 2theta values of 59.97°, 50.14°, and 39.40°, respectively. The formation of the peaks at 2theta equal to 39.40 can be assigned to the effects of calcium ethoxide influence resulting from the interaction of water molecules formed as a product of synthesis and moisture absorbed when exposed to the atmosphere (Arun Prasad et al. 2019).

However, the analysis also shows that the content of biodiesel produced from pawpaw seed extract contained high concentrations of linoleic acid ethyl ester, ethyl-stearate, and melistic acids ethyl-ester which increases increased with the formation of smaller concentrations of FFA content such as caparic ethyl-ester and lauric acids ethyl-ester, respectively. The weight of pentantenoic acid decreased in concentration, while the weights of myrsteste ethyl-ester and palmitic acids ethyl-ester conversion increased in weights of the fatty acid, this observation is a clear indication of biodiesel yield with some degree of unsaturation. We reasoned that; the more highly unsaturated a fatty acid is, the lower the melting point. Unsaturated fats are excellent for cold weather conditions. Biodiesel that has unsaturated fatty acid as its predominant acid does not solidify at room temperature.

However, fuel properties such as flash point values of the biodiesel were measured to be 120°C at the optimum conditions and were compared to American Society for Testing and Materials ASTM (D6751-02) standards to determine the suitability of the sample as biodiesel fuel. The flash point satisfied standard ≥ 120°C. This result is an indication that the fuel will require a very low temperature for it to cease to flow through systems, the reason being that; this property translates to the suitability of the fuel in a cold and warm region. Also, the biodiesel was characterized with an FA content of 0.3, this value was less than 1 as such; we concluded that the biofuel is presumed to contain very little amount of soap. High FA content (>1%) would lead to soap formation AOCS (1998) and the separation of products would be exceedingly difficult, resulting in a low yield of biodiesel products. The pawpaw seed oil showed an FAEE value of 0.34, which was slightly below the 1% stipulated as standard in the literature. Therefore, it can be concluded that;

Table 3
Physicochemical characteristics of the biodiesel to ASTM (D6751) and EN 14214.

Biodiesel properties	Composition	ASTM specification	EN 14214
Color	Yellowish brown	NA	-
Specific gravity	0.75	0.8–0.9	0.8–0.9
Flash point temperature	120^0C	100–170	NA
Kinematic viscosity at 40°C	5.43	1.9–6.0	-
Moisture content	0.64	Max 0.05	-
Kinematic viscosity at 100°C	2.75	-	120
Cetane number	44.725	Min 47	51
Cloud point	155	NA	-
Acid value	0.785	max 0.8	0.5
Sulfur content (mg/l)	2.717	max 10	-
Carbon contents	0.2	Max 0.3	-
Boiling temperature	158	NA	NA
FA %	0.393	-	12

the pawpaw seed oil was well neutralized to produce a higher yield of biodiesel. This report is well presented in Table 3.

The PSO biodiesel GC techniques characteristics a result presented in Table 3 show that the kinematic viscosity of the fuel which plots 5.43 at was obtained the oil translates to 92% yield. The kinematic viscosity value was 5.43 Pa.s at 40°C and 2.75 Pa s at 100 °C was recorded for the biodiesel at the optimum condition. The viscosity value was minimal, hence, we concluded that the low viscosity suggests hydrogen peroxide that can suppress the negative constraints of high viscosity and poor spray formation. While, the boiling point temperature was measured to be 158, and its specific gravity value was measured to 0.75, compared to ASTM (D6751–02) standards was found to be ≤ 0.8 mm/s^2. The cold flow characteristics of biodiesel depict the temperature at which the biodiesel oil is least soluble, since the cloud point of the PSO biodiesel was accounted for, evidence to determine its solubility can be ascertained, consequently, it can be reasoned that the biodiesel produced might probably not be problematic based on variable analysis results in accordance to ASTM (D6751-02) standards.

However, the carbon content of the biodiesel produced from crude PSO was found to be < 0.3, and the sulfur content of the biofuel was measured to be equal to 0.2.This result is less than 10 as specified in the acceptable value of ASTM Specification (D6751-02). The moisture content of 0.64 with the centane number of 44.7, and an acid value of 0.78 was consistently lesser than 47 and 0.8, respectively at a boiling point of 158°C. The%FA content of the biofuel was found to be equal to 0.39 with a cloud point value of 155. The kinematic viscosities of the biofuel at 100 °C were recorded to be equal to 2.75 and 5.43 at 40 °C which was close to the results published for the pawpaw seed oil biodiesel blend presented in Umapathi (2019). These values were found within the range specified by the ASTM (D6751-02) and EN 14214 specifications for biofuel presented in Table 3. Thus, the comparative physiochemical analysis of the properties of the biodiesel produced from crude PSO at 350 rpm and 30 min satisfied the acceptable ASTM Specification (D6751-02) for biofuel presented in Table 3. The flash point value of 120°C is in close range with the ASTM (D6751) value specified for biofuel; this value was slightly less than 159°C reported for pawpaw seed oil biodiesel blend in Umapathi (2019). Hence, the bio-fuel produced from crude PSO extract satisfied the minimum requirement of EN 14,214 standards which was in obvious agreement with the biodiesel properties presented in (Okolie et al., 2012; Oraegbunam et al., 2020; Sarianto et al., 2019) showing only slight deviations due to the difference in the alcohol used. Thus the biodiesel produced from the alkali transesterification employed in this study might be suitable for diesel engines. The characteristics of the biodiesel oil are presented in Table 3. The fatty acid ethyl ester (FAEE) composition of the biodiesel contains a low amount of unsaturated and poly-unsaturated esters, suggesting that; the biofuel will offer moderate resistance to oxidation, this report is in agreement with the research works of Okolie et al. (2012) and Oraegbunam et al. (2020).

Conclusively, key biodiesel properties such as specific gravity, sulfur content, acid value, carbon content, and specific gravity suit the essential fuel standard prescribed by the American limits. The moderate values of the viscosity, specific gravity, acid value, sulfur, and carbon contents of the biodiesel obtained from PSO are indications of the key influence on good efficiency of atomization, promoting air-fuel-mixing, and confirming the stability of the biofuel against corrosiveness, ensuring aging, and maintain good combustion system. However, the centane number and moisture content showed slight deviation from the American limits suggesting little modification was required to use this fuel (R. Balasubramanian et al., 2018). The centane number is an indication of the fatty acid carbon chain and more saturated molecules were present in the biodiesel obtained. The required modification will minimize the moisture content of the biofuel while improving the ignition properties of the biofuel.

3.5. Multiple Regressions (MR) modeling result on PSO biodiesel prediction

In this research paper, bio-oil yield prediction based on the training data sets obtained from the transesterification experiment was also surveyed. The co-purpose of this paper is to gain knowledge from the data generated and for this reason, various technologies are used. Artificial Intelligence is used relatively much in the technological aspect in almost every field of life. Various algorithms have been developed on a large scale so that technologies can advance. One area of AI that deals with the automation of analytical models is Machine Learning. Machine Learning is a method through which different patterns can be identified, which is valuable to gain knowledge from the generated data. Machine Learning is widely used for prediction, which is the main focus of this chapter. Various algorithms that are used to make predictions also Support Vector Machines, Artificial Neural Networks, Linear Regression, and Decision Trees.

In this research work, a python program written Software based on CLI (Command Line Interface), was applied to predict biodiesel yield based on the training data set obtained from the transesterification experiments and MLR algorithm. The software requires input variables (Catalyst weight, Temperature, and Alcohol-oil molar ratio) based on the experimental training data set integrated into the software. The software performs multiple linear regression algorithms, through which the results are the predicted values of the biodiesel yield. The trend of the output from the multiple regressions was investigated to verify the trend of experimental optimum conditions obtained from the RSM optimization output to create a better understanding of how the production system works. The general model prediction is shown in **Table S2 (see supplementary),** Figs. 6 and 7.

The ML result showed that a predicted biodiesel yield translating to 40.334% was achieved at predicted operating conditions corresponding to catalyst weight (0.1 wt%), temperature (20°C), and alcohol-oil molar

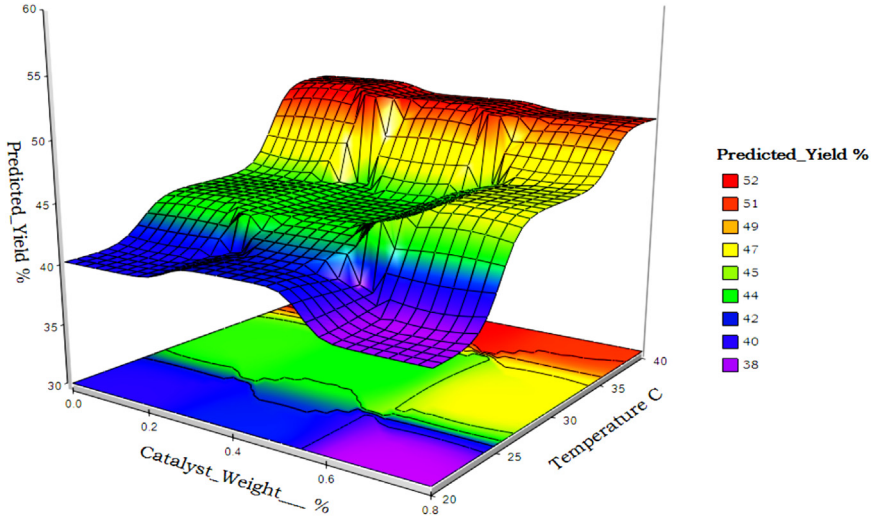

Fig. 6. MLR prediction of showing the effect of catalyst and temperature on ethyl-ester yield.

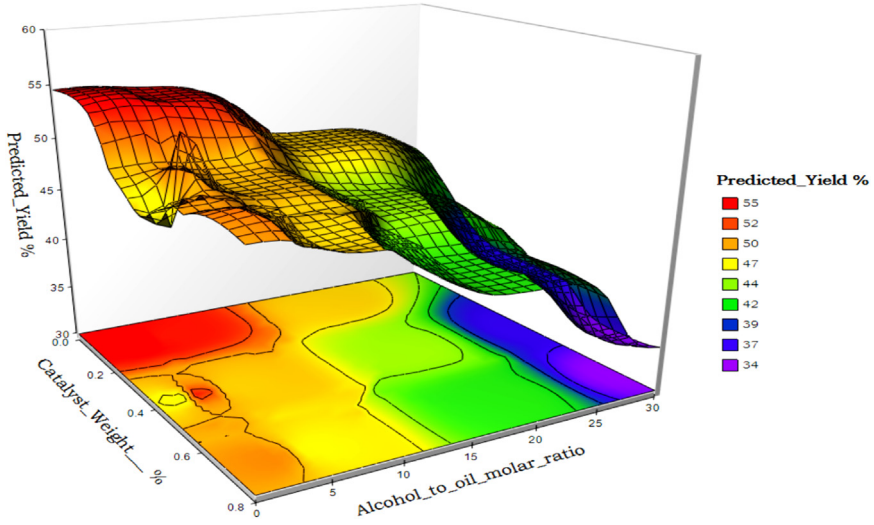

Fig. 7. MLR prediction of showing the effect of catalyst and alcohol molar ratio on ethyl-ester yield.

ratio (20:1). This output was consistent with the experimentally determined 39.85% biodiesel yield practicable based on the experimentation conducted to verify the ML optimization indicating $a \pm 0.025$ deviation of the ML output from the result practicable.

However, the nature of the curvature of the 3D surface plot in Fig. 6 shows that at the optimum alcohol-to-oil molar ratio of 3:1, ethyl-ester biodiesel yield increases as the temperature increases from 30°C to the optimum temperature of 60°C. However, the 3D surface in Fig. 6 also confirms that; homogenous catalyst weight below the optimum 1.0wt% will not increase the biodiesel yield beyond 52%. The light orange color of the respective contour gradient on the floor of Fig. 6 proved that better performance of alkoxide (NaOH mix ethanol) on PSO conversion to ethyl-ester yield occurred at a temperature beyond 40°C which corresponds to 52% yield, this result is in obvious agreement with the contour patterns following the RSM optimization reported in Figs. 4 and 5, where the darker red region of the contour gradient indicates areas of better performances of the catalyst between 0.9wt% to 1.3wt% beyond these points a decrease in ethyl ester yield (≤42%) indicated by the darker blue region of the plots in Figs. 4 and 5. The surface plot in Fig. 7 confirms that increasing the alcohol-to-oil molar ratio beyond the optimal molar oil ratio will lead to a decrease in biodiesel yield due to the formation of soap. It can be concluded from the MLRA that; the alcohol to oil molar ratio of 3:1 is most influential to the biodiesel yield at optimum catalyst and temperature of 60°C. This result showing the effects of operational variables of the ethyl-ester conversion from pawpaw seed oil are well interpreted from the analysis of variance (**Interface 1, see supplementary file**). The drawback in the prediction results is the very fewer data training sets available for the prediction.

3.6. Kinetics and thermodynamics parameters of ethyl-ester at optimum condition

Most alkali-catalyzed transesterification reaction for the methyl or ethyl ester conversion between 55°C and 65°C obeys uni-molecular first-order kinetics concerning PSO (Sarianto et al., 2019; Umapathi, 2019) or bi-molecular second-order kinetics concerning homogenous catalyst on methanol or ethanol, respectively (Sarianto et al., 2019). Assuming the visible the irreversible transesterification reaction is given by:

$$\text{Triglycerol (PSO)} + \text{Ethanol} \rightarrow 3\text{PSOEE} + \text{Glycerols}$$

The assumptions made for converting the three-step reversible transesterification were based on reducing the complexity associated with the three-step reactions to a simplified single step forward (overall reaction) such that, due to the excess alcohol (ethanol) used is considered a limiting factor, there's a shift in the equilibrium to the right side of

Table 4
Kinetics parameter of the alkaoxide driven transesterification of PSO at Optimum catalyst weight.

1.0wt% Catalyst Concentration							
T (°C) K(min^{-1}) α	30°C 0.0170 1.0	40°C 0.01993 1.0	50°C 0.03054 1.0	60°C 0.05634 1.0	70°C 0.0591 1.0	80°C 0.0475 1.0	90°C 0.0401 1.0

the reaction (Senthilkumar et al., 2019). Therefore, the overall reaction was assumed to be a single-step forward reaction (uni-molecular pseudo-first-order) (Vishnu Priya et al. 2019).

$$TG + MeOH \rightarrow 3ME + GL \tag{5}$$

With respect to the above reaction, the rate equation can be expressed in terms of TG and [MeOH]^3 described by:

$$r_A = \frac{-d[TG]}{dt} = -k^I[TG][MeOH]^3 \tag{6}$$

Taking$\boldsymbol{k = k^I[Me]^3}$to arrive at Eq. (7)

$$\frac{-d[TG]}{dt} = -[TG] = kt \tag{7}$$

Rearranging the overall rate, and taking integral of both sides

$$\int_{TG_0}^{TG} \frac{1}{TG} = -\frac{1}{TG}d[TG] = k\int_{t=0}^{t=1} dt \tag{8}$$

$$In\left[\frac{TG_t}{TG_0}\right] = kt \tag{9}$$

where [TG_t] is the triglyceride concentration at time t (minutes), and TG_0] is the initial triglyceride concentration. Applying material balance to arrive at:

$$\int_{TG_0}^{TG} \frac{1}{TG} = -\frac{1}{TG}d[TG] = k\int_{t=0}^{t=1} dt \tag{10}$$

Applying mass balance;

$$In[1 - X_A] = kt \tag{11}$$

Rearranging Eq. (11) analytically to express k in terms of X_A and t, we arrive at Eq. (12). Thus, the kinetics for PSO and ethanol over NaOH catalyst for the production of pawpaw seed-oil ethylester analysis can thus be described by:

$$\frac{-In(1 - X_A)}{t} = k \tag{12}$$

where; X_A is the fractional conversion of PSO to ethyl-ester. k is the rate constant following the transesterification reaction and t is the time taken. In this work, the kinetics was expressed in terms of fractional conversion X_A and t. The kinetics studies were determined following the pseudo-first-order kinetic assumptions expressed in terms of fractional conversion of the FAME (X_A). The fractional conversion were determined following the expression $X_A = 1 - \frac{TG_t}{TG_0}$ where TG_t is the values of the triglyceride measured at reaction time t = 30minutes, and at varying experimental temperatures range (30°C-90°C), and TG_0 is the initial value of triglyceride measured at time t = 0. Hence, fitting the data for X_A in terms of fractional conversion and time t = 30minutes at varying temperatures and the optimum alcohol to oil molar ratio of 3:1 and catalyst weight of 1wt%, we obtained the rate constant K following the pseudo-first-order kinetics using Eq. (12).

It can be observed from the kinetics distribution of the rate constants (Table 4) following the alkaoxide conversion of the PSO to ethyl ester that the value of the rate constant $k = 1.7\text{x}10^{-2}$ min^{-1} was obtained at a temperature of 30 °C, $k = 1.993\text{x}10^{-2}$ min^{-1} at 40 °C, $k = 3.054\text{x}10^{-2}$ min^{-1} at 50 °C, $k = 5.634\text{x}10^{-2}$ min^{-1} at 60 °C, and $k = 5.91\text{x}10^{-2}$ min^{-1} at 70 °C, respectively. The rate constant increased intermittently as the temperature increased from 30 °C and terminates at 70°C, whereas the value of rate constant decreased from 80°C through 90°C which corresponds to values of$k = 4.75\text{x}10^{-2}$min^{-1}, and $k = 4.01\text{x}10^{-2}$ min^{-1}. The kinetics results showed that the maximum rate constant was obtained at a temperature of 70°C which corresponds to $5.63\text{x}10^{-2}$ min^{-1} while the minimum rate constant of $1.7\text{x}10^{-2}$ min^{-1} was obtained at the lowest temperature of 30°C. The kinetics of transesterification result is in obvious agreement with the prediction and optimization reports, which confirmed that the ethylester biodiesel yield from PSO in the presence of the homogenous catalyst decreases beyond the optimum temperature at optimum catalyst weight of 1.0wt% and ethanol to oil molar ratio of 3:1. This result is well presented in Table 4.

The determination of the E_A at the optimal ethanol to oil ratio and catalyst weight of 3:1 and 1.0wt% were evaluated from Eq. (7) this was done per the works of Angilelli et al. (2017) and Tucki et al. (2019). The connection between temperature and reaction rate is established by Arrhenius (K. K. Onyechi and Igwegbe, 2018). The activation energy following the transesterification reaction leading to the formation of the ethyl ester biodiesel can be estimated by an expression similar to the Arrhenius equation given by:

$$\text{Ae}^{\frac{-\text{Ea}}{\text{RT}}} = K \tag{13}$$

Where is E_a is the apparent activation energy of reaction rate and K = apparent rate constant; R is the molar gas constant and T is the temperature. Rearranging Eq. (13) to obtain Eq. (14), taking the Log of both sides of Eq. (14), the Arrhenius equation was modified to become:

$$\text{InK} = \text{LogK} = \frac{[-\text{Ea/R}]}{(\text{T} + \text{C})} \tag{14}$$

where R is the molar gas constant R = 8.314 J/mole K; T is the temperature, and k is the transition coefficient assumed to be equal to 1 (Tucki et al., 2019). The enthalphy of activation($\Delta \boldsymbol{H}‡$)can be found by applying Eq. (15) given by:

$$\Delta \boldsymbol{H}‡ = E_a - RT \tag{15}$$

Thus from Eq. (14), the graph of In(K) plotted against 1/T produces linear traces with the slope representing ($\frac{Ea}{R}$) while the intercept is represented by In(A) (Angilelli et al., 2017); where A is the pre-exponential factor and E_a is the activation energy, respectively. From the analysis of **Fig. S5 (see supplementary file)**, the activation energy of 18,024.7 kJmol, was obtained for the biodiesel produced from the transesterification of the PSO at the optimum condition with a pre-exponential factor of 24 as can be read from **Fig. S5**. The value of the calculated enthalpy of activation is 15,422.4 kJmol. It can thus be concluded that the positive value of enthalpy indicates that the process is endothermic and requires energy (Sivakumar P et al. 2012).

4. Conclusion

In the analysis of the production of biodiesel following the extraction of oil from pawpaw seeds and alkali transesterification, the following conclusions were drawn from the present study: biodiesel from the alkali-catalyzed transesterification method with optimal ethanol to oil molar ratio of 3:1, catalyst weight of 1.0wt%, the temperature of 60°C and constant time of 30 min when NaOH was used as the catalyst. The transesterification temperature controls the yield of the product while purification is fundamental to fulfill the characteristics of biodiesel as a fuel. Temperatures between ranges of 60°C – 70°C have a noticeable effect on the optimal yield of biodiesel from the transesterification process corresponding to ≥80%. The flash points and kinematic viscosity of the biodiesel samples produced were found to have satisfied the ASTM

(D6751) specifications and EN141215 standard for biodiesel and the specific gravity of biodiesel samples was temperature-dependent which follows a predominant first-order degree of the kinetics of transesterification reaction. Prediction results of the biodiesel yield show that the biodiesel yield was temperature-dependent at the optimum conditions following the RSM and ML reports. The XRD patterns and GC/MC chromatography characterization report confirms pawpaw seed oil as a good source for biofuel production.

Compliance with ethical standards

This article does not contain any studies involving human or animal subjects.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Godswill Adizue Ngige: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft, Writing – review & editing, Validation. **Prosper Eguono Ovuoraye:** Methodology, Software, Writing – original draft, Writing – review & editing, Validation. **Chinenye Adaobi Igwegbe:** Supervision, Project administration, Data curation, Writing – original draft, Writing – review & editing, Validation. **Endrit Fetahi:** Software, Writing – original draft, Writing – review & editing, Validation. **Jones A. Okeke:** Conceptualization, Supervision, Methodology, Writing – review & editing, Validation. **Alfred D. Yakubu:** Writing – review & editing, Validation. **Pius Chukwukelue Onyechi:** Supervision, Writing – review & editing, Validation.

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Supplementary materials

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