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Synthesis, Characterization and Property Evaluation of Biodiesel from Used Palm Oil

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ABSTRACT : *This work was aimed at synthesis of biodiesel from used fried palm oil (PFPO) via trans-esterification with optimization and kinetics of the process. The PFPO was pre-treated and characterized using American Society for Testing Materials (ASTM) D4067 (1986) methods to determine its physio-chemical properties. The oil was trans-esterified to biodiesel and the process parameters for trans-esterification, was optimized using response surface methodology (RSM). The physical and chemical properties of biodiesel were determined using (ASTM) 6751 (1973) methods. The kinetics of this trans-esterification to methyl ester using mechanisms of triglyceride to di-glyceride, di-glyceride to mono-glyceride and mono-glyceride to methyl ester. The results showed that the pre-treatment of fried palm oil reduced, its FFA less than 1%. The optimum value of the parameters for PFPO trans-esterification using RSM were catalyst concentration of 0.5 & 1.5 wt.%, methanol/oil molar ratio 4:1 & 8:1, reaction temperature of 45oC, reaction time of 60 minutes at constant stirring speed of 350 rpm and under these conditions the amount of methyl ester yield was 91.2 %. The properties of biodiesel produced under optimized protocol met the ASTM standard and was within the acceptable limits. The rate parameters showed that the trans-esterification of PFPO has conversion of triglyceride to di-glyceride as rate determining step (RDS). Also, the rate constant for RDS increased as temperature increased from 52 to 64oC. This indicates that the rate determining step of the trans-esterification of the oil was favoured at mild temperatures and heat is required for the reaction. The activation energies determined for PFPO (Tg =18.34, Dg = 9.83 and Mg = 4.9.KJ/mol) trans-esterification indicate that PFPO, mono glyceride trans-esterification requires less energy than di- and tri-glycerides.*

KEY WORDS: *Biodiesel, trans-esterification, optimization, kinetics, used fried palm oil.*

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I. INTRODUCTION

The ever-increasing energy cost and demands have ignited a global quest for sustainable alternatives to traditional fossil fuels, in which scholars and innovators across continents are joining forces (Saleh and Hassan, 2024). This urgency is particularly pronounced in Nigeria, a nation grappling, with the adverse effects of dwindling crude oil reserves and the consequent health and environmental challenges linked to fossil fuel reliance (Ighosewe et al., 2021). The political landscape, marred by economic mismanagement and unsustainable debt accumulation, has left the country in a precarious position, with hyperinflation and currency devaluation exacerbating the hardships faced by its citizens (Edy and Edy, 2024). As Nigeria's four refineries lie

abandoned and the national energy corporation seeks partnerships with private entities, the dependency on crude oil as the primary revenue source is no longer feasible (Alechenu et al., 2016).

Historically, Nigeria was a global leader in palm oil production, contributing significantly to the rural economy and sustaining local populations through the oil palm industry. In the years leading up to independence, Nigeria produced 43% of the world's crude palm oil, yet today, it has fallen to a mere 1.7% market share, overshadowed by Malaysia and Indonesia which command 83% of global production (NIFOR, 2021). This reduction not only highlights Nigeria's diminished agricultural prowess but also underscores the urgent need for economic diversification and self-sufficiency in palm oil production (FAO, 2022).

Amidst this backdrop, there lies a pressing opportunity for Nigeria to reinvigorate its agricultural sector and reclaim its erstwhile position in the palm oil market. Emphasizing the cultivation of cash crops, particularly oil palm, can provide a dual benefit: bolstering the economy and offering a sustainable source of clean energy through biofuels. Biodiesel synthesized from vegetable oils, such as used palm oil, presents a promising alternative to conventional fuels, owing to its low toxicity and biodegradability (Ude et al., 2021). Apart from palm oil, other vegetable oils sources from which oil recovered can be used for biofuel synthesis include soybean seed, sunflower seed, rap-seed, castor seed, linseed, neem seed, olive seed, and cotton seed etc. (Onukwuli and Ude, 2018).

This research endeavor, aims to synthesize biodiesel from waste palm oil through the trans-esterification process, optimizing the procedure and investigating its kinetics. By leveraging the abundant resource of used palm oil, we hope to contribute to waste reduction and energy sustainability while addressing the pressing economic challenges facing Nigeria. Through this synthesis, we aspire to pave the way for a cleaner energy future and a reimagined agricultural economy that honors Nigeria's rich heritage in palm oil production.

II. MATERIALS AND METHODS

A. MATERIALS

Used fried palm oil (PFPO) was obtained from Mama Uchechukwu, who fries beans balls (Akala), at Ukwuaki Bus stop, Ifite Street, Awka, Anambra state, Nigeria. Tea bag filter was used to filter and remove some adhering impurities. Other materials like methanol (99%), Potassium hydroxide (KOH, 97.5%), Hydrochloric acid (HCl, 96%), Sulphuric acid (H2SO4, 98%), Iso-propyl alcohol (99.5%), Sodium meth-oxide (98%) and phenolphthalein indicator, were secured at Head Bridge Market, Onitsha, Anambra State, Nigeria.

B. METHODS

i. Characterization of the oil

The oil was characterized using American Society for Testing Materials (ASTM) to determine their physiochemical properties and with GCMS to determine their free fatty acid composition.
Oil Esterification and Trans-esterification

To prevent saponification, waste fried palm oil's (PFPO) free full of fat acid (FFA) content was decrease by esterification. Esterification of the oil with methanol using sulphuric acid as a catalyst decreased the oil's high FFA (14.32%) concentration. After that, the raw oil was transferred to a two-necked closed reaction jar containing the methanol and catalyst (comp. H2SO4) combination. Within an hour, both were heated to 60 degrees Celsius in a water bath. Reducing the oil's free fatty acid content to 1% v/v sulphuric acid to oil volume is ideal. Since the percentage FFA was 0.25% as a result of refining, refined palm oil was not esterified.

With the use of sodium hydroxide as a catalyst, Ude et al. (2021) were able to Trans-esterify the oil sample with methanol. The oil was trans-esterified with methanol in 50 milliliters (50 ml). The catalyst utilized was 0.5% w/w of the oil, the weight ratio of oil to methanol was 3:1, and the reaction was carried out for 30 minutes at 60°C with an agitation speed of 250 rpm. In the presence of NaOH, the pre-treated fried palm oil (PFPO) and methanol interacted to form glycerol and methyl esters of fatty acids, or biodiesel. Using a heated magnetic stirrer, each oil was carefully and quantitatively put into a flask with a flat bottom. Next came the addition of a certain quantity of catalyst (by weight of the oil) dissolved in the necessary amount of methanol. Throughout the reaction, the reaction flask was maintained at a consistent temperature with precise agitation on a heated

magnetic stirrer. The sample was removed at the designated time, allowed to cool, and then allowed to settle overnight under ambient conditions in order to separate the biodiesel (the methyl ester in the top layer) from the by-product (the glycerol in the lower layer). By weighing the layer biodiesel and the oil utilized, the percentage of the biodiesel output was calculated.

$$\%\, Yield = \frac{weight\ of\ biodiesel}{weight\ of\ oil\ used} x100 \qquad (1)$$

Optimization of process parameters for biodiesel

This study used a two-level, four-factor factorial design with 30 trials. The optimisation research chose the following independent factors: catalyst concentration, methanol/oil molar ratio, reaction temperature, and reaction time. The methyl ester yields from the trans-esterification of PFPO were the selected answers. To forecast a decent assessment of errors, six replications of centre points were employed, and trials were conducted in a randomised sequence. Table 1 displays each factor's actual and coded levels. −1 (minimum), 0 (centre), +1 (maximum), −α, and +α identified the coded values. With a maximum value of 2n/4, where n is the number of elements, alpha is defined as the distance from the centre point that may be either within or outside the range. In this case, alpha is set at 2. It is important to highlight that the program investigates the significant terms using the notion of coded values; thus, the influence of the variables on the answer is studied using an equation in coded values. Equation (2) is a representation of the empirical equation.

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ii} X^2{}_i + \sum_{i=1}^{4} \sum_{j=i+1}^{4} \beta_{ij} X_i X_j \qquad (2)$$

The studies conducted to examine the impact of process factors on the use of NaOH catalyst for the trans-esterification reaction served as the basis for the selection of values for each factor.

Table 2: Experimental design matrix for oil trans-esterification studies

Std	A: Catalyst concentration	B: Methanol/oil molar ratio	C: Temperature	D: Time	Yield of biodiesel from PFPO
	wt%		Deg. Cel.	Minutes	
1	1	4	45	60	30.50
2	2	4	45	60	90.34
3	1	8	45	60	75.98
4	2	8	45	60	80.52
5	1	4	75	60	95.53
6	2	4	75	60	50.43
7	1	8	75	60	20.03
8	2	8	75	60	45.81
9	1	4	45	120	80.81
10	2	4	45	120	55.93
11	1	8	45	120	45.97
12	2	8	45	120	35.24
13	1	4	75	120	65.07
14	2	4	75	120	62.07
15	1	8	75	120	45.59
16	2	8	75	120	61.42
17	0.5	6	60	90	60.31
18	2.5	6	60	90	60.53
19	1.5	2	60	90	60.65
20	1.5	10	60	90	70.84
21	1.5	6	30	90	75.35
22	1.5	6	90	90	70.35
23	1.5	6	60	30	55.54
24	1.5	6	60	150	65.35
25	1.5	6	60	90	64.35
26	1.5	6	60	90	70.56
27	1.5	6	60	90	68.07

28	1.5	6	60	90	45.18
29	1.5	6	60	90	75.98
30	1.5	6	60	90	58.40

Trans-esterification kinetics of Biodiesel (PFPO)

There were three steps involved in creating the kinetic model for this trans-esterified methyl ester. Initial conversion of the final triglyceride (Tg) concentration to final di-glyceride (Dg) and methyl esters, followed by final mono-glyceride (Mg) and methyl ester, occurs in the first stage. The last stage involves the conversion of magnesium to glycerol and methyl ester. Every molecule of glyceride that interacted produced a methyl ester. According to Theeragut et al. (2004), there is a fourth stage called a shunt reaction that involves the direct interaction of Tg and methanol to produce methyl ester and glycerol.

The overall reaction are

Tg + 3ROH = 3RCOOR +GL (3)

Stepwise reaction are

Tg +ROH = Dg +R´COOR (4)

Mg + ROH = GL + R´COOK (5)

Where K_1, K_2, K_3, K_4, K_5, and K_6 are rate constants, values of both forward and back reactions. The trans-esterification depends on the composition as noted by Sanji et al., (2004). A second order kinetic mechanism of palm oil trans-esterification with methanol and KOH as catalyst was adopted. The ideal trans-esterification values for palm oil were the main focus of the reaction conditions, and the predicted rate constants and activation energy of the reaction were based on the results.

According to research, second order model kinetics seems to be the kinetic model that fits the data the best. A model based on the kinetics of triglyceride alcoholysis was created in order to evaluate the notion (Darnoko and Chergan, 2000).

The second order reaction rate for triglyceride will be as follows:

$$\frac{-d(T_g)}{dt} = K(T_g)^2 \quad (6)$$

Integration of Equation (6) yields

$$KT_g t = \frac{1}{(T_g)} - \frac{1}{(T_g)_0} \quad (7)$$

Similarly $kD_g .t = \frac{1}{(D_g)} - \frac{1}{(D_g)0}$ (8)

$$KM_g.t = \frac{1}{(M_g)} - \frac{1}{(M_g)0} \quad (9)$$

Where K is the overall second order rate constant, t is the reaction time, $\frac{1}{(T_{g0})}$ is the initial T_g concentration. D_{g0} is the initial highest D_g concentration and Mg_0 is the initial highest Mg concentration. The model equation is valid only when the plot of reaction time (t) in terms of $\frac{1}{(T_g)}$ gives a straight line. Arrhenius equation was used to calculate the activation energy.

Arrhenius equation is given by; $k = Ae^{-\frac{E_a}{RT}}$ (10)

Taking the natural logarithm on both sides of the equation

$$\ln k = \ln A + \left(-\frac{E}{RT}\right) \quad (11)$$

The biodiesel was next characterized by GCMS to ascertain its methyl ester content and by the American Society for Testing Materials (ASTM) to ascertain its physiochemical characteristics.

III. RESULT AND DISCUSSION

Physiochemical Properties of PFPO

Table 3 presents the physiochemical properties of the fried palm oil (PFPO). The PFPO has high acid and high FFA values of 28.64 mgKOH/g and 14.32% before esterification. It was then esterified with sulphuric acid to reduce the FFA and it became pre-treated fried palm oil (PFPO). The oils have moderate acid number and free fatty acid values of 1.12 mgKOH/g and 0.56%. The FFA values of PFPO is greater than 1% signifying will hinder trans-esterification reaction, hence it was esterified to bring it down to 0.25%

The density and high viscosity of the oil will make their atomization difficult in internal combustion engine, hence they cannot be used directly as bio-fuel. The pour point shows that the oil will hardly solidify at room temperature hence can be stored for a long time. The oxidation stability of the oil was high and is good for production of biodiesel. The high oxidation stability of the oil could be as a result of method used in extracting the oils. Solvent refining result in the production of base oil, which retain some sulphur compounds that are natural antioxidants. This base oil retains a natural ability to prevent oxidation, while hydro treated base oil must be further fortified with antioxidants in order to maintain thermal and oxidation stability. The iodine value of the oil is less than 100g (I2/100g) indicating that it is a non-drying oil. The high saponification value (SAP) of the oil show that it has high tendency to form soap readily therefore the catalyst dosage should be effectively controlled during trans-esterification.

Table 3: Physic-chemical properties of (PFPO) sample

S/N	Parameters	Unit	PFPO	Test Method
1	Moisture content	%	0.25	ASTMD6871-03
2	Specific gravity (Spg)	-	0.8994	ASTM D792
3	Boiling point	^{o}C	302	ASTM D2887
4	Density	g/mol	0.8786	ASTM D5002
5	Pour point	^{o}C ± 2^{o}C	23.0	ASTM D97
6	Cloud point	^{o}C	25.2	ASTM D97
7	Flash point	^{o}C	325	ASTM D6871
8	Fire point	^{o}C	332	ASTM D6871
9	Oxidative stability	^{o}C	176	ASTM D2440
10	Acid value	MgKOH/g	1.122 (28.64[a])	ASTM D6751
11	FFA	%	0.25 (14.32[b])	ASTM D5555
12	SAP value	Mg	142	ASTM D 1962
13	Viscosity @ 40^{o}C	Cst	40.21	ASTM D6871
14	Viscosity @ 100^{o}C	Cst	6.17	ASTM D6871
15	Viscosity index	-	186	ASTM D 2270
16	Iodine value	g	52.3	ASTM D4607

[a] = acid value of PFPO before pretreatment, [b] = FFA of PFPO before pretreatment.

Fatty Acid Profile of PFPO

The free fatty acid profile of the fried palm oil is presented in Table 4. From the table, the dominant fatty acid in PFPO is stearic acid. The oil has more unsaturated fatty acid than the saturated fatty acid, making it appropriate feedstock for biodiesel and bio-lubricant production.

Table 4: Fatty acid profile of the trans-esterification of PFPO.

Component	Concentration of PFPO (ppm)
C12	4.66
C14	0.2415
C16	4.35
C18:0	11.58
C18:1	2.855
C18:2	6.77
C18:3	4.23
C20:2	5.10
C20:3	1.81
C20:4	3.88
C20:5	6.94
C22:6	4.51
C24:5	2.52

Statistical analysis of biodiesel production from PFPO

Design Expert version 10 was employed to develop model and statistically analyse the model for the production of biodiesel from both PFPO.

Statistical analysis of PFPO biodiesel production

The responses of the experimental design matrix of trans-esterification of purified fried palm oil (PFPO) with methanol using NaOH is presented in Table 3. The data were fitted to the central composite design (CCD) second order mathematical equation. The equation which relates response (purified fried palm oil biodiesel, PFPOBD) to the process parameters in terms of the coded form and actual forms is described in equations (12 a & b).

$$\text{Yield, } Y = +64.87 - 8.42 * A + 3.50 * B - 5.08 * C - 1.92 * D + 7.53 * AB + 7.75 * AC + 0.63 * AD + 0.64 * BC + 5.61 * BD - 7.56 * CD + 1.79 * A^2 - 0.93 * B^2 - 0.060 * C^2 - 0.65 * D^2 \quad (12a)$$

Where purified fried palm oil biodiesel yield respectively, A = catalyst loading, B = methanol/oil molar ratio, C = Temperature and D = time

Final Equation in Terms of Actual Factors:	
Yield	=
+167.58275	
-142.13175	* Cat. Loading
-12.67019	* MOR
+0.044958	* Temp
+0.47169	* Time
+7.52644	* Cat. Loading * MOR
+1.03358	* Cat. Loading * Temp
+0.041896	* Cat. Loading * Time
+0.021210	* MOR * Temp
+0.093532	* MOR * Time
-0.016803	* Temp * Time
+7.17121	* Cat. Loading^2
-0.23317	* MOR^2
-2.65880E-004	* Temp^2
-7.25498E-004	* Time^2

(12b)

The statistical significance of the mathematical regression model was tested using analysis of variance (ANOVA) and presented in Table 5 for purified fried palm oil biodiesel yield. From the table, it was observed that the model was significant at the 95% confidence level; the p value and F value of the model were <0.0001 and 116.63. The level of significance of each parameters using ANOVA at 5% significance level showed that all the linear terms, all the interactive terms except AD and BC, and only quadratic terms of A and B were significant. Therefore, the model was reduced to equations (13a & 13b)). The equations in coded form and actual form are given by:

$$\text{Yield, } Y = +64.87 - 8.42 * A + 3.50 * B - 5.08 * C - 1.92 * D + 7.53 * AB + 7.75 * AC + 5.61 * BD - 7.56 * CD + 1.79 * A^2 - 0.93 * B^2 \quad (13a)$$

Final Equation in Terms of Actual Factors:	
Yield	=
+167.58275	
-142.13175	* Cat. Loading
-12.67019	* MOR
+0.044958	* Temp
+0.47169	* Time
+7.52644	* Cat. Loading * MOR

+1.03358	* Cat. Loading * Temp
+0.093532	* MOR * Time
-0.016803	* Temp * Time
+7.17121	* Cat. Loading^2
-0.23317	* MOR^2
-2.65880E-004	* Temp^2
-7.25498E-004	* Time^2

(13b)

The performance of the mathematical model was evaluated using statistical indicators and the results obtained are:; adjusted = 0.99824; predicted = 0.9484. The predicted and adjusted were approximately in reasonable agreement. These indicate good correlation between the experimental and predicted values as well as good fit of the model. Betiku et al. (2018) reported that a good model should have at least = 0.8. Adequate precision, which measures the signal to noise ratio, was 319.91. A ratio greater than 4 is required; thus, the model can be used to navigate the design space. The coefficient of variance (CV) was 0.43% for the model. The lower the CV, the smaller the residuals relative to the predicted value. The low CV obtained indicated good model.

Table 5: Significance of regression coefficients of the yield of biodiesel produced from PFPOBD using the design-expert version 2010

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	6146.74	14	439.05	116.63	< 0.0001	significant
A- Cat. Loading	*1702.64*	*1*	*1702.64*	*452.29*	*< 0.0001*	
B-MOR	*293.56*	*1*	*293.56*	*77.98*	*< 0.0001*	
C-Temp	*618.37*	*1*	*618.37*	*164.26*	*< 0.0001*	
D-Time	*88.49*	*1*	*88.49*	*23.51*	*0.0002*	
AB	*906.36*	*1*	*906.36*	*240.77*	*< 0.0001*	
AC	*961.45*	*1*	*961.45*	*255.40*	*< 0.0001*	
AD	*6.32*	*1*	*6.32*	*1.68*	*0.2147*	
BC	*6.48*	*1*	*6.48*	*1.72*	*0.2093*	
BD	*503.90*	*1*	*503.90*	*133.86*	*< 0.0001*	
CD	*914.81*	*1*	*914.81*	*243.01*	*< 0.0001*	
A^2	*88.16*	*1*	*88.16*	*23.42*	*0.0002*	
B^2	*23.86*	*1*	*23.86*	*6.34*	*0.0237*	
C^2	*0.098*	*1*	*0.098*	*0.026*	*0.8739*	
D^2	*11.69*	*1*	*11.69*	*3.11*	*0.0983*	
Residual	56.47	15	3.76			
Lack of Fit	*55.23*	*10*	*5.52*	*22.35*	*0.0016*	*significant*
Pure Error	*1.24*	*5*	*0.25*			
Cor Total	6203.21	29				

PRESS = 319.91, R^2 = 0.9909, Adj. R^2 = 0.9824, Pred.R^2 = 0.9484

Fig.s 1 to 4 are the surface plots of the predicted biodiesel yield which can be generated by equation (13). The synergistic effect of catalyst concentration and methanol/oil molar ratio on yield of biodiesel is shown in Fig. 1. The Fig. shows that the amount of methyl ester yield increases with methanol/oil molar ratio and catalyst

concentration. However, at higher catalyst concentration and methanol/oil molar ratio, a reduction in the yield was observed due to saponification.

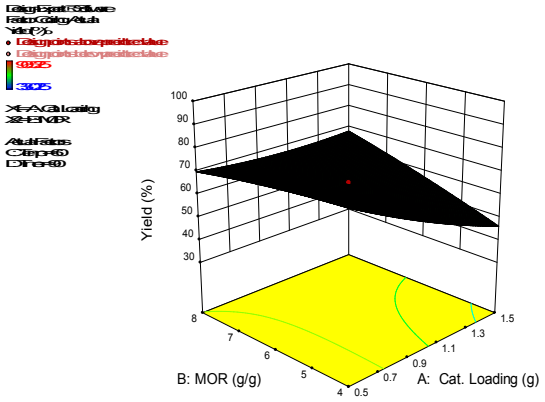

Fig.1: Interaction effect of catalyst concentration and methanol/oil molar ratio on PFPOBD yield.

The interaction effect of catalyst concentration and MOR on yield of biodiesel is significant and shown in Fig.2. The Fig. indicates that the yield of biodiesel increases with MOR and catalyst concentration. However, at higher catalyst concentration and MOR, a decrease in the yield can be observed due to evaporation of methanol at higher temperature (Onukwuli et al., 2017). The finding is similar to the results obtained by Ude et al., (2020) and Ude et al. (2021).

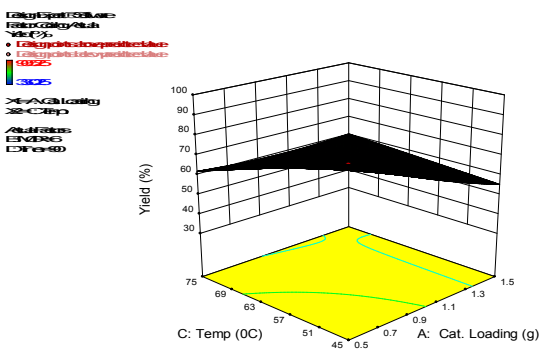

Fig.2: Interaction effect of catalyst concentration and temperature on PFPOBD yield.

The interaction effect of catalyst loading and temperature on yield of biodiesel is shown in Fig. 3. The Fig. indicates that the amount of biodiesel yield increased with cat. loading and temperature. This may be as a result of adequate time provided for conversion of the triglyceride. At higher cat. loading and temperature, a reduction in biodiesel yield can be observed due to excess alcohol that hindered more conversion of triglyceride (Ude et al., 2020). This trend was observed by Onukwuli et al. (2017) and Ezekannagha et al. (2017).

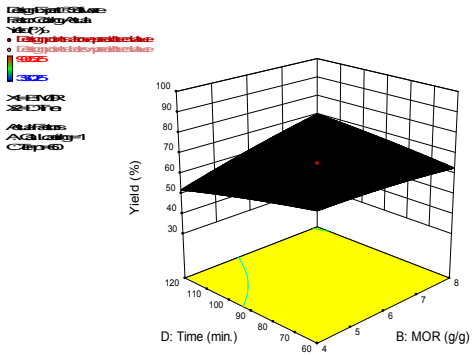

Fig. 3: Interaction effect of methanol/oil molar ratio and time on PFPOBD yield.

The interaction effect of MOR and time on yield of biodiesel is shown in Fig.4. At lower temperature, below 60^{o}C the yield increased with increase in time. However, at a temperature above 60^{o}C, there was reduction in yield. This may be as a result of evaporation of methanol which inhibited the reaction (Ezekannagha et al., 2017; Ude et al., 2020). Onukwuli et al. (2017) and Ude et al. (2021) observed similar results.

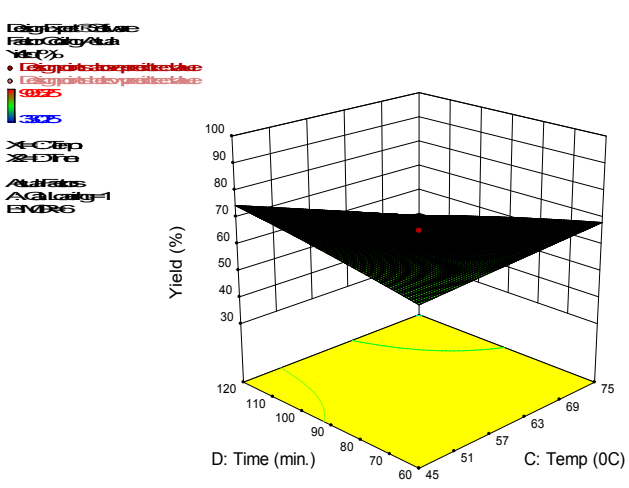

Fig.4: Interaction effect of temperature and time on PFPOBD yield.

Optimization of Biodiesel Process Parameters

The value of desirability was approximately unity (1) which signifies that the optimization result is highly desirable. The optimal conditions are shown in table 6. Therefore, it is observed from the table that the optimal yields of biodiesel or fatty acid methyl ester (FAME) from PFPO is 91.5% at optimized conditions of catalyst concentration = 0.5wt%, methanol/oil molar ratio = 4:1, temperature = 45oC for and time = 60 minutes.

Table 6 also depicts the validation of the optimal results of the trans-esterification process and was observed that the percentage error of response was less than 1%. This shows that the model was adequate in predicting the response.

Table 6: Validation of the optimal values for PFPO biodiesel

S/N	Responses	Catalyst conc. (wt. %)	Methanol/oil molar ratio (mol/mol)	Temperature (°C)	Time (minutes)	Experimental Yield (%)	Predicted Yield (%)	% Error
1	Yield PFPOBD by author	0.5	4:1	45	60	91.2	91.5	0.33

Physiochemical properties of the biodiesel

Table 7 gives a summary of all the fuel properties analysed and the limits that they were compared with (ASTM D 6751 (2002) standards).

Biodiesel generally has a higher density than petro-diesel. This can impact on fuel consumption as fuel introduced into the combustion chamber is determined volumetrically. The density of the PFPOBD evaluated at 30oC was within the ASTM limits for biodiesel (Table 7). It is also observed that the viscosity of the biodiesel produced from the oil falls within the ASTM limits (1.6-6.0 Cst) for biodiesel.

The flash point is a determinant for flammability classification of materials. The typical flash point of pure methyl ester is >200oC, classifying them as "non-flammable". However, during production and purification of biodiesel, not all the methanol may be removed, making the fuel flammable and dangerous to handle and store if the flash point falls below 130oC. The flash points were >130oC, which fall within the ASTM standard making it safe for storage.

High fuel acidity is linked with corrosion and engine deposits. The PFPOB has acid value 0.6mgKOH/g . The ASTM value for TAN is 0.8mgKOH/g; this implies that the acid values of the biodiesel are acceptable.

Cetane number serves as a measure of ignition quality. Fuels with low cetane numbers show an increase in emission due to incomplete combustion. The lower limit for cetane index is 47 by ASTM standards. The cetane numbers of the PFPOBD was >50, which are above the lower limit for cetane number. Thus, the result obtained is acceptable. Oxidation stability is one of the most important factors used to determine how long an oil/diesel will last in a particular application. From table 7, it could be observed that the oxidation stabilities of the biodiesel produced was within the ASTM acceptable limits for biodiesel. This shows that the biodiesel is good for application in a diesel engine but blending it with little diesel from mineral oil will improve its engine performance.

Table 7: PFPOB properties compared with ASTM limits

PROPERTY	UNITS	ASTM METHODS	PFPOB	ASTM LIMITS
Density	kg/m^3	ASTM D-1298	860.1	830-880
Kinematics Viscosity	Cst	ASTM D-445	4.5	1.6-6.0
Flash Point	°C	ASTM D-93	150	≥130
Pour Point	°C	ASTM D-97	6.5	+15 max
Cloud Point	°C	ASTM D-2500	3	-15 to 5
Acid Value	mgKOH/g	ASTM D-974	0.60	≤ 0.80
Low Heating Value	MJ/kg		37	≥ 35
Aniline Point	(°C)	ASTM D-4737	19.5	
Higher Heating Value	MJ/Kg		71	
Oxidative stability	Hour	ASTM D-6751/EN 14112	9	3 min
Cetane number		ASTM D-130	58.1	47 min

GCMS of biodiesel

The gas chromatography flame ionization detection (GCFID) analysis of the biodiesel from PFPO was performed and presented in Fig.s 5. It is observed from the Fig.s that the triglyceride was converted to fatty acid methyl esters with appearance of intermediates (mono-glycerides and di-glycerides). The biodiesel has highest concentration of 22.49 ppm at retention time of 9.5 minutes.

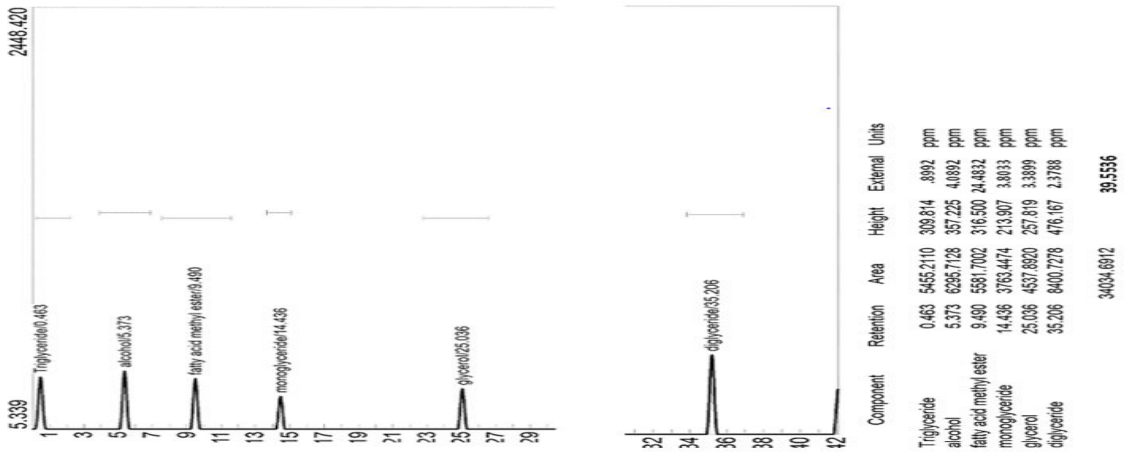

Fig. 5: GCMS of purified fried palm oil biodiesel (PFPOBD)

Product and reactants distribution

The formation of products and disappearance of reactants at various temperatures and time for trans-esterification of PFPO is depicted in Fig.6. From the graph, it could be observed that the products (methyl esters and glycerol) concentration increased as both time and temperature increased and the reactants (triglyceride, methanol) with the intermediates (di-glyceride and mono-glyceride) concentration decrease as both time and temperature increased. The Fig.s show that biodiesel is more predominate in the product with a higher concentration at temperature of 64°C. This shows that higher yield is obtained at temperature of 64°C.

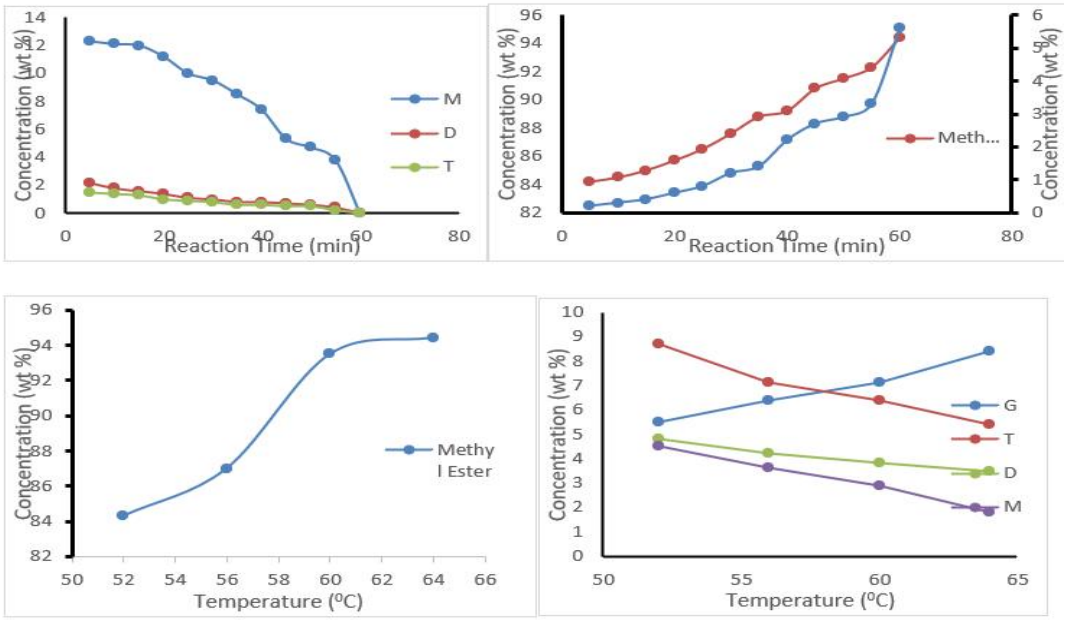

Fig.6: Product distribution for trans-esterification of PFPO.

Kinetic study of trans-esterification reaction of PFPO

The kinetics of trans-esterification of purified fried palm oil (PFPO) to fatty acid methyl ester was studied at the four different temperatures (52, 56, 60 and 64ºC). The rate constants, k for the proposed reactions mechanism (triglyceride to di-glyceride; di-glyceride to mono-glyceride; and mono-glyceride to methyl esters) were calculated from the plots of first order rate equation. The rate constants are presented in Table 8 and it could be observed from the tables that the rate constants of conversion of triglyceride to di-glyceride was least with more fitting. Hence, it is the determine step (RDS) for trans-esterification of PFPO. It could also be observed that the rate constant for RDS increased as temperature increased from 52 to 64ºC. This indicates that the rate determining step of the trans-esterification of PFPO was favoured at higher temperatures and heat is required for the reaction. The activation energy for the trans-esterification of PFPO was determined using Arrhenius equation plot and presented in the Table 8. The activation energy determined is 18.34kJ/mol for RDS of PFPO trans-esterification. It indicates that PFPO trans-esterification requires more energy than RPO trans-esterification.

Table 8: Kinetic parameters of RDS for trans-esterification of PFPO

Trans-esterification of PFPO (RDS = Tg to Dg)	52ºC	56ºC	60ºC	64ºC	ΔE (kJ/mol)	A (min^{-1})
k_1 (min^{-1})	0.0180	0.0188	0.0208	0.0244	18.34	6.97
R^2	1.0000	0.9951	0.9996	1.000	0.9331	

IV. CONCLUSION

The production of biodiesel from fried palm oil via tran-esterification with optimization and kinetics of the process were carried out. The fried palm oil (PFPO) was treated by esterification. The purified fried oil (PFPO) was used to produce biodiesel via trans-esterification. It was deduced that the fried palm oil has FFA > 1% and was pre-treated. The pre-treated fried palm oil and was then trans-esterified to produce biodiesel and the variation in process parameters of biodiesel production significantly affected the yields. The optimum value of the parameters for PFPO trans-esterification using RSM were catalyst concentration of 0.5 wt.%, methanol/oil molar ratio 4:1, reaction temperature of 45ºC, reaction time of 60 minutes at constant stirring speed of 350 rpm and under these conditions the amounts of methyl ester yield was 91.2%. The properties of biodiesel produced under optimized protocol met the ASTM standard and was within the acceptable limits. The rate parameters showed that the trans-esterification of PFPO has conversion of triglyceride to di-glyceride as rate determining step (RDS). Also, the rate constant for RDS increased as temperature increased from 52 to 64ºC. This indicates that the rate determining step of the trans-esterification of the oil was favoured at mild temperatures and heat is required for the reaction. The activation energy determined for PFPO (Tg =18.34, Dg = 9.83 and Mg = 4.9KJ/mol) trans-esterification indicates that PFPO trans-esterification requires more energy.

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