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Optimization and Kinetics Study of Oil Extraction from Pawpaw Seed

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***Abstract*-**The study involves optimization, kinetics, and thermodynamic study of Pawpaw seed oil extraction (PSOE). The effect of temperature, time, and volume of solvent as process variables, and their interaction on oil yield were evaluated. Experimental design for oil extraction and optimization of the extraction process was done with response surface methodology (RSM). The direct extraction (leaching) method with n-hexane was used for oil extraction according to Randall/Soxtec/hexane extraction-submersion method. The extracted oil was characterized for its physicochemical properties using standard methods. The mass transfer model and Van't Hoff Equations were employed to respectively evaluate the kinetics and thermodynamics of PSOE. The highest experimentally obtained oil yield was 25.48% at 51.50^{o}C, 78.50 minutes, and 182.00 ml, while out of 100 solutions found by the numerical optimization tool, the first solution with the desirability of 1.00, and oil yield of 25.533% at 55.852^{o}C, 105.663 minutes, and 210.2396 ml was selected as the optimal condition for PSOE. Oil yield increased with an increase in extraction parameters up to the optimal condition and then decreased. Physiochemical properties were saponification value (175.60mgKOH/100 g oil), acid value (1.28mg/g), iodine value (74.60gI_2/100g oil), peroxide value (1.24 meqO_2/kg oil),free fatty acid (0.64%), flash point (230.00 ^{o}C), and pour point(-14^{o}C). GC-MS revealed that oleic acid (74.40%) was the dominant fatty acid. The kinetic study showed that high coefficients of determinations (R^2) were obtained with activation energy (2,577.483J/mol), and Arrhenius Constant (0.030 S^{-1}). Values obtained for thermodynamic parameters were: $\Delta \boldsymbol{H}$ (1,413.46 kJ/mol), $\Delta \boldsymbol{S}$ (11.21 J/molK), and negative values for $\Delta \boldsymbol{G}$. PSOE was an endothermic, feasible, and spontaneous process, with appreciable oil yield. Extraction of oil from pawpaw seed in this study was successful and could be economical.

Keywords- *Pawpaw Seed Oil, Extraction, Optimization, Kinetics*

I. INTRODUCTION

There has been a global increase in the demand for vegetable oil due to a continuous increase in the global demand for oil for energy and industrial raw materials, depletion of fossil oil reserves, environmental challenges caused by the use of fossil oils, and non-renewability of the conventional petroleum sources [1;2]. The conventional sources of vegetable oil such as soybean, palm, rapeseed, and sunflower have little impact on meeting the increasing demand for vegetable oil for both human and industrial uses [3]. Hence, there is a need to supplement the supplies with other sources, especially underutilized oilseeds and seeds discarded as waste such as pawpaw seed. It has become observable in recent years bio-recovery of valuable by-products from agro-products that are underutilized such as skin, pulp, and seeds, as well as waste from agricultural biomass, namely corn stover, oat straw, nutshells, and rice husk. In many units that process fruits, these by-products (pulp, skin, seed, etc.) are discarded away as waste. Several studies have suggested the bio-recovery of different byproducts like enzymes, oils, ethanol, and pharmaceuticals from fruit wastes such as mango, banana, pineapple, and papaya waste [4]

Papaya (*Carica papaya* L.) is native of tropical America but has now spread all over the tropical world, Nigeria inclusive. The average production of pawpaw is about 10 million metric tons per annum globally with 1.9 and 3.6 million metric tons contributed by Brazil and India respectively as the major papaya producers in the world. The fruit is usually cylindrical, large (weighing 0.5-2.0 kg), and fleshy. The flesh is yellow-orange, soft, and juicy. The central cavity contains large quantities of seeds that comprise about 15 to 20% of the wet weight of the fruit which represents a considerable amount of papaya fruit waste in processing units. Papaya is grown mostly for fresh consumption and papain production; however, it can be processed into jelly, jam, candy, and pickles, and its seeds are usually discarded [5]. The papaya seeds normally discarded as waste have the potential to produce 20 to 34% oil with interesting physicochemical properties suitable for cosmetics, biodiesel, and bio lubricant production.

Reference [6] stated that solvent extraction was reported as the most efficient technique among different methods of extracting oil from oil-bearing seeds. Solvent extraction using n-hexane as extracting solvent can be achieved through either indirect extraction (Soxhlet extraction) method or direct extraction (leaching) method according to Randall/Soxtec/hexane extraction-submersion method [7].

Reference [8] and reference [9] reported 31.18 ± 0.1% and 22.93%respectively*as* the percentage oil yield of C. papaya with n-hexane as extracting solvent. The solvent extraction process must be carried out within a predetermined space of the controllable factors that have been reported to have significant effects on the system response (oil yield). Evaluation of these major contributing variables to the process response, control, and optimization tasks are accomplished through design-of-experiment (DOE), analysis of variance (ANOVA), and optimization tool of response surface methodology (RSM). While the rate constant of the extraction process, energy requirement, and the feasibility of the extraction process is achieved through kinetics and thermodynamic study of the process.

RSM can be said to be a collection of statistical and mathematical procedures/techniques employed in the modeling and analysis of problems with the aim of optimizing the output factor (response). Here, the response of interest is influenced by many independent factors (input variables). RSM has been extensively adopted in industries (drug and food industry), chemical and biological processes, in order to optimize the processes (operate the process more economically), ensure that the process operates in a more stable and reliable way, and produce high-quality products [10,11].

Appropriate kinetic data are required to analyze and design an extraction process, especially on an industrial scale. Usually, the mass transfer model is adopted to study the extraction of oil from plant seeds with n-hexane as extracting solvent due to the fact that the extraction process takes place at a non-steady-state and there are no chemical reactions during the process. Also, thermodynamic parameters, namely enthalpy change (**Δ**H) and entropy change (ΔS) for the oil extraction can be estimated using Van't Hoff Equations. However, there is scanty scientific research/reports on the optimization, kinetics, and thermodynamic studies of the pawpaw seed oil extraction process. Considering that pawpaw seed normally discarded as waste have the potential to produce 20 to 34% oil with interesting physicochemical properties, it is therefore very essential to carry out more studies and scientific analysis on the extraction process and pawpaw seed oil (PSO). Thus, this study focuses on characterization/screening of major variables significant to oil extraction, optimization, kinetics and thermodynamic study of pawpaw seed oil extraction process, and PSO characterization.

II. MATERIALS AND METHODS

A. *Materials Collection and Preparation*

Ripe and healthy pawpaw fruits were purchased from Eke Awka, Awka South L.G.A., Anambra State, Nigeria.The pawpaw fruits purchased were thoroughly washed with clean water, and then cut longitudinally into two parts to reveal the seeds which were removed and collected manually. The Papaya seeds (PS) were washed with clean water at least 4 times to remove the gelatinous, and then oven-dried at 60 ^{o}C for 24 hours in order to completely dry the fresh seeds.100g of the dried seeds of the samples were ground into homogenous powder. 5g of ground sample was weighed out into twenty different cellophane bags, labeled properly, and then preserved for oil extraction in twenty different runs. Before extraction, all apparatus was washed and oven-dried, to get rid of moisture.

B. *Design of Experiment for Oil Extraction and its Optimization*

Design-Expert software was used to design the experiment and to optimize the oil extraction conditions by employing the response surface methodology (RSM). Central composite design (CCD) was used as experimental design which yielded 20 experimental runs. The parameters varied or selected as independent variables (factors) were extraction temperature, extraction time, and solvent/solute ratio, while the dependent variable (or the response) selected was the oil yield obtained from solvent extraction. Six replications of center points were used in order to predict a good estimation of errors and experiments were performed in a randomized order. The actual and coded levels of each factor are shown in Table 1.The coded values were designated by -1 (minimum), 0 (center), and +1 (maximum).Since the software uses the concept of the coded values for the investigation of the significant terms, an equation in coded values was used to study the effect of the variables on the response. The empirical equation is presented in (1).

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

Where**,** $\beta_0$is a constant term**,** β_i is coefficient of the linear term, β_{ij} is coefficient of the interaction term, β_{ii} is coefficient of quadratic term, X_i,X_{ij}**,** andX_{ii} respectively, are the variables for linear, interactive, and quadratic terms.

TABLE I. STUDIED RANGE OF EACH FACTOR IN ACTUAL AND CODED FORM

Independent Variables	Symbols	Range of Factors and Levels				
		-2	-1	0	+1	+2
Temperature (^{o}C)	A	32.2	40	51.5	63	70.8
Time (Minutes)	B	30.6	50	78.5	107	126.4
Solvent/solute ratio (w/w)	C	26.4	40	60	80	93.6

C. *Oil Extractions*

The Oil extraction from papaya seed was carried out using the direct extraction (leaching) method with n-hexane as extracting solvent according to Randall/Soxtec/hexane extraction-submersion method, as recommended in [7].The weight of the extracted oil in the flask was calculated using (2)and then recorded.

$$W_o = W_{fo} - W_f \qquad (2)$$

Where: W_o is the weight of the oil, W_{fo} is the weight of the flask + oil, and W_f is the weight of the empty flask. The process was repeated for each run under the extraction conditions for that run. 20 experiments (runs) were carried out for the pawpaw seed and the percentage oil yield for each experiment (or run) was calculated using (3)

$$Y = \frac{W_o}{W_s} \times \frac{100}{1} \qquad (3)$$

Where: Y is the oil yield (%), W_o is the weight of pure oil extracted (g), and W_s is the weight of the sample (g) which in this experiment was 2g for each run.

D. Kinetics of Oil Extraction

The mass transfer model was adopted to study the extraction of oil from pawpaw seed with n-hexane as extracting solvent due to the fact that the extraction process takes place at non-steady-state and there are no chemical reactions during the process. The rate of variation of the oil concentration in the liquid phase (g $L^{-1}mim^{-1}$) can be represented with (4).

$$\frac{dC_L}{dt} = K(C_{Le} - C_L \quad (4)$$

Where C_L *and* C_{Le} are the oil concentration (g L^{-1}) in the liquid phase at time t (minutes) and at equilibrium, respectively, and K is the mass transfer coefficient (mim^{-1}).

In order to solve (4), the following boundary conditions were applied. The oil concentration in the liquid phase is equal to zero ($C_L = C_{Lo}$) at the start of the extraction process.The concentration of pawpaw seed oil in the liquid phase is $C_{Lo} = C_{Le}$) at any time t. Considering these boundary conditions, integration of (4) yields (5).

$$(C_L = C_{Le}(1 - e^{-kt}) \quad (5)$$

Equation (5) can be rewritten in terms of the percentage yield of extracted oil (Y_t) to give (6).

$$Y_t = Y_{Le}(1 - e^{-kt}) \quad (6)$$

Taking the logarithm of both sides in (6) and rearranging yield (7)

$$\mathrm{In}Y_t = \mathrm{In}\, Y_{Le} + kt \quad (7)$$

Where: Y_{Le} is the percentage of oil contained in the liquid phase at equilibrium in relation to the total oil content of the sample at time t = 0. Y_{Le} and K were respectively calculated from the intercept and slope of a plot (graph) of $\mathrm{In}Y_t$ against t. Employing Arrhenius equation expressed in (8), the activation energy was calculated.

$$k = Ae\frac{Ea}{RT} \quad (8)$$

Taking the logarithm of both sides in (8) and rearranging yield (9)

$$\mathrm{In}k = \mathrm{In}Ae - \frac{Ea}{RT} \quad (9)$$

Where: A is the Arrhenius constant (or frequency factor); R is the universal gas constant; k is the reaction or extraction rate constant (mass transfer coefficient), T is the absolute temperature, and Ea is the activation energy. Ea and A were respectively calculated from the slope (which is equal to E_a/R) and intercept (which is equal to $\mathrm{In}Ae$) of a plot of $\mathrm{In}K$ against$1/T$.

E. Thermodynamics of Oil Extraction

Van't Hoff Equations were used to estimate the thermodynamic parameters, namely enthalpy change (**Δ**H) and entropy change (ΔS) for the oil extraction as represented in (10) to (12).

$$\mathrm{In}K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (10)$$

$$K = \frac{Y_{La}}{Y_{se}} \quad (11)$$

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

Where Y_{La} and Y_{se} are respectively the average oil yield in percent at temperature T and the percentage of oil remaining in seeds, while *T*, *K*, and *R*are respectively the temperature of extraction, the equilibrium constant of extraction, and the universal gas constant ($8.314\, Jmol^{-1}K^{-1}$). ΔH *and* ΔSwere respectively calculated from the slope and the intercept of a plot of $\mathrm{In}K$ against $1/T$, while (12) was used to calculate ΔG.

F. Characterization of the Extracted Oil

The physicochemical properties of the pawpaw seed oil (PSO) were determined accordingly using standard test methods [12-25], while instrumentation such as Fourier Transform Infra-red (FTIR) Spectrometer and Gas Chromatography Mass Spectrometer (GC-MS) respectively were used to determine the functional group and fatty acid profile of the CSO. The molecular weight of the triglyceride of the oils (M_{wo}) was calculated using the free fatty acid profile evaluated from the gas chromatography analysis according to (13).

$$M_w = 3 \times M_{av} + 38.049 \quad (13)$$

Where: $M_w = Molecular\ weight\ of\ a\ triglyceride$, M_{av} = Average molecular weight of the oil, 3 = Number of chains of each fatty acid in a triglyceride, and 38.049 = Molecular mass of glycerol in the triglyceride (the glycerol backbone).

III. Result and Discussion

A. Oil Yield and Model Summary statistics

Extraction design matrix for PSO with actual yield, RSM predicted yield, and the residual is presented in Table 2. It can be observed from the table, that the maximum actual yield obtained in percentage (25.48%) is very close to the RSM predicted yield of 25.24%, and all the residual values, lie between ±0.5 which implies that the actual PSO yields agree very much with the RSM predicted values. Model summary statistics (Table 3) focus on the model maximizing the Adjusted R^2 and the Predicted R^2. The quadratic model comes out best for pawpaw seed oil extraction (PSOE). It exhibited low Std. Dev. (standard deviation), high values of R^2, and low PRESS values. These make the quadratic model the suggested model. The cubic model exhibited lower standard deviation as well as higher R-squared values, however, it was aliased (i.e distorted or misidentified).

TABLE II. PSO CENTRAL COMPOSITE DESIGN (CCD) MATRIX OF INDEPENDENT VARIABLES AND THEIR CORRESPONDING EXPERIMENTAL, PREDICTED, AND RESIDUAL VALUES

Std Run Order	A: Temp	B: Time	C: Solvent/Solid Ratio	Actual Value	RSM Predicted Value	Residual
	(^{o}C)	(Minutes)		%	(%)	
1	40.00	50.00	40.00	24.37	24.60	-0.2273
2	63.00	50.00	40.00	22.39	22.56	-0.1666
3	40.00	107.00	40.00	24.35	24.20	0.1527
4	63.00	107.00	40.00	24.42	24.20	0.2227
5	40.00	50.00	80.00	24.33	24.20	0.1327
6	63.00	50.00	80.00	23.98	24.20	-0.2173
7	40.00	107.00	80.00	19.24	19.09	0.1505
8	63.00	107.00	80.00	21.04	20.73	0.3072
9	32.16	78.5.00	60.00	22.02	22.09	-0.0706
10	70.84	78.50	60.00	15.97	15.89	0.0786
11	51.50	30.57	60.00	15.99	16.28	-0.2921
12	51.50	126.43	60.00	22.01	22.09	-0.0821
13	51.50	78.50	26.36.	18.03	18.05	-0.0216
14	51.50	78.50	93.64	23.97	24.20	-0.2273
15	51.50	78.50	60.00	24.12	24.20	-0.0773
16	51.50	78.50	60.00	25.48	25.24	0.2356
17	51.50	78.50	60.00	23.41	23.44	-0.0349
18	51.50	78.50	60.00	21.32	21.29	0.0256
19	51.50	78.50	60.00	18.30	18.19	0.1101
20	51.50	78.50	60.00	24.10	24.10	0.0013

TABLE III. MODEL SUMMARY STATISTICS FOR PSO OIL EXTRACTION

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS
Linear	1.84	0.6710	0.6093	0.5309	77.05
2FI	2.00	0.6825	0.5360	0.2050	130.57
Quadratic	0.2377	0.9966	0.9935	0.9806	3.19
Cubic	0.1877	0.9987	0.9959	0.9768	3.81

The value of coefficients of determination (R^2), adjusted R^2, and predicted R^2 are all close to 1, and the closer the R^2values are to unity, the better the model. Also, the difference between the adjusted R^2 and predicted R^2 was 0.0153 (<0.2) which implies that there was reasonable agreement between Adjusted R^2 and Predicted R^2 for the quadratic model, thus, the adequacy of the model. The coefficients of determination R^2 values of 0.9966 obtained for the PSOE process showed that more than 99.7% of the overall system variability for the CSOE process can be explained by the empirical models of (1) which according to [26], is a specific case of the general predictive equation derived for the investigation from the multivariate regression analyses implemented on design expert.

B. Analysis of Variance (ANOVA) for Pawpaw Seed Oil Extraction (PSOE)

The model F-values of 321.91 (Table 4) implied that the model is significant with p-values (0.0001) <0.050 for PSOE. There is only a 0.01% chance that an F-value these large could occur due to noise for PSOE. In this study, the ANOVA results derived from the predictive model for PSOE showed that the main linear effects due to individual control factors such as temperature (x1), time (x2), and solvent/solid ratio (x3) coded as A, B, and C respectively, are all significant process variables, with the observed p-values <0.05 in the numerical analysis. Also, linear interaction effects between temperature and solvent/solid ratio (AC) and time and solvent/solid ratio (BC), as well as the quadratic effects of temperature (A^2), time (B^2), and solvent/solid ratio (C^2) for PSOE are all significant model terms with p-value <0.05. However, linear interaction effects between temperature and time (AB) are insignificant model terms with p-values greater than 0.100. The F-value shows how significant model terms are. The higher the value, the more significant the model term is. The Lack of Fit F-value of 1.89 and p-value of 0.2504 implies that the Lack of Fit is not significant relative to the pure error for PSOE. Thus, there is a 25.04% chance that a Lack of Fit F-value this large could occur due to noise. Since the model is required to fit, a non-significant lack of fit is good.

The predicted versus actual plot for PSO yield is showed in Fig. 1. The figure shows a straight line slopping upward from left to right with the values (points) uniformly distributed along the straight line which indicate that the differences between the actual values and predicted values were not much. This is in assertion with the low values of residual.

TABLE IV. ANALYSIS OF VARIANCE (ANOVA) FOR PAWPAW SEED OIL EXTRACTION PROCESS

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	163.68	9	18.19	321.91	< 0.0001
A-Temperature	18.03	1	18.03	319.07	< 0.0001
B-Time	81.31	1	81.31	1439.15	< 0.0001
C-Solvent/Solid Ratio	10.87	1	10.87	192.44	< 0.0001
AB	0.1540	1	0.1540	2.73	0.1297
AC	0.8911	1	0.8911	15.77	0.0026
BC	0.8515	1	0.8515	15.07	0.0030
A^2	4.23	1	4.23	74.86	< 0.0001
B^2	31.81	1	31.81	563.04	< 0.0001
C^2	23.44	1	23.44	414.89	< 0.0001
Residual	0.5650	10	0.0565		
Lack of Fit	0.3696	5	0.0739	1.89	0.2504
Pure Error	0.1954	5	0.0391		
Cor Total	164.25	19			

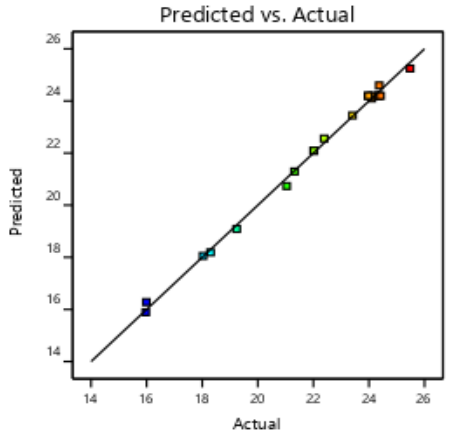

Figure 1. Predicted vs Actual for Pawpaw Seed Oil Yield

C. 3-D Surface for Pawpaw Seed Oil Extraction (PSOE)

The relationships between dependent and independent variables are illustrated in 3D surface representation of the response surfaces (Fig. 2-4) generated by the model for extraction yields [27]. An elliptical shape of the curve indicates good interaction of the two variables, while circular shape indicates no interaction between the variables. The response surface indicated that the percentage oil yield increased as time and solvent/solid ratio composition increased to optimum condition where further increase leads to decrease in percentage yield of oil, confirming that there was significant mutual interaction between the time and solvent composition (Fig. 4). When the solvent/solid ratio was increased beyond 65.035w/w, the increase in oil yield became less significant because the 65.035 w/w was sufficient to bring the oil solute to equilibrium.

It was observed from Fig. 2 and 3 that as the temperature increased from 32.2 to 63^{o}C, the oil yield increased and decreased beyond 63^{o}C.Reference [28], reported that the amount of salmon liver oil yield is increased by increasing temperature from 50°C to 68°Cin each of the considered times, denoting the direct impact of temperature increase on the increasing percentage of oil extraction, similar to the effect of extraction time. Similarly, cottonseed oil yield was reported by [29] to increase with temperature increase. Rupturing of oil cell walls which create voids that serve as migratory space for the contents of the oil-bearing cells is the primary reason for the positive effect of temperature on the seed oil yield. Also, increasing the temperature lowers the viscosity of the oil, draws moisture out, and releases the oil from the cell wall that was intact before the application of heat through temperature increase [30].The oil yield increased as the time increased from 30.60 to 100.713 minutes (Fig. 2 and 4) and decreased with a further increase in time. When the time was increased beyond 100.713 minutes, the increase in oil yield became less significant indicating that 100.713 minutes was sufficient to bring the oil solute to equilibrium. This is in agreement with [31] that emphasized that the more time given to the seeds for contact with the solvent, the higher the percentage of oil extraction. Little re-adsorption/re-absorption of oil by the seed might have occurred after 100.713 minutes of extraction. Reference [8] and [9] reported 31.18 ± 0.1% and 22.93%respectivelyas the percentage oil yield of C. papaya with n-hexane as extracting solvent. The current study may be economically advantageous in terms of energy savings considering the long operational time in the earlier reports.

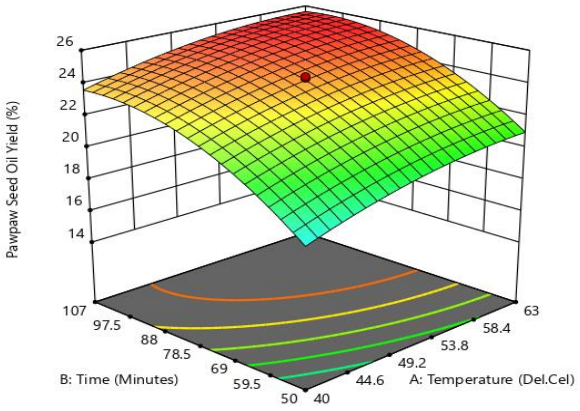

Figure 2. 3D Surface for temperature and time on the PSO oil yield

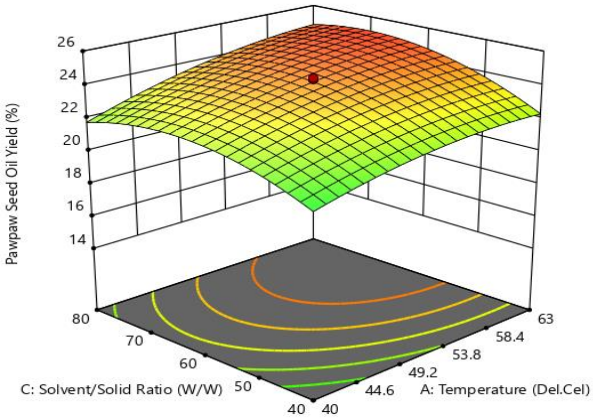

Figure 3. .3D Surface for temperature and solvent/solid ratio on the PSO oil yield

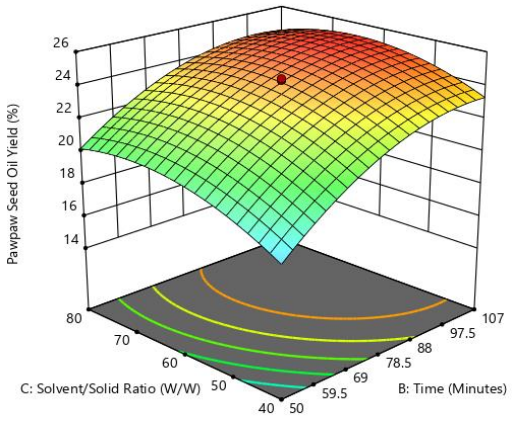

Figure 4. .3D surface plot for time and solvent/solid ratio on the PSO oil yield

D. Physicochemical Properties of Pawpaw Seed Oil (PSO)

Table 5 showed the physicochemical properties of PSO. The PSO refractive index (1.465) obtained in this study falls within the range of the refractive index (1.45 – 1.49) reported by [32] for some vegetable oil. The refractive index of oil is a measure of how much a light ray is bent when it passes from air into the oil and it usually depends on the density of the oil. The adulteration of vegetable oils is measured physically by the values of refractive index and specific gravity/density generally, given that different oils have a typical refractive index and specific gravity/density [33]. The high density and high viscosity of the oil suggest that atomization in an internal combustion engine will be difficult when the oil is used in its natural form; hence the oil cannot be used directly as bio-fuel.

The pH of the PSO indicated that the oil is slightly acidic signifying the presence of a small amount of free fatty acid (unsaturated fatty acid in the oil). The acid value (1.28 mg/g) obtained for PSO in the current study is comparable to 1.61mg/g reported by [34] but higher than 0.98 mg/g reported by [35]. The acid value is an indicator of the edibility and suitability of the oil in the soap and biodiesel industries. The acid values and the percentage of free fatty acid (0.64) obtained for PSO in the present study agreed with the result of the pH value (low acidity) obtained which suggests that transesterification reaction can be carried out on the oil without going through esterification reaction first. It has been reported that oil with a percentage free fatty acid greater than 1% will need to go through an esterification reaction before transesterification to avoid the formation of soap (saponification) during the transesterification reaction. In addition, the free fatty acids (FFA) content of raw oil is a parameter that affects the optimal conversion of vegetable oils to fatty acids methyl esters and also dictates the selectivity of a suitable catalyst for the transesterification reaction [36,37]. Free fatty acids value obtained for the oil fall within the category of oils that may optimally yield ester on a single-step alkaline transesterification reaction [37]. Oil having a high FFA value (> 3%) will deactivate alkaline catalyst on single-stage transesterification reaction thus, pre-treatment is required prior to transesterification.

The high saponification value (mg KOH/100g oil) obtained in this study for PSO (175.60) is comparable with the values reported by [38] for common oils; palm oil (196–205), groundnut oil (188–196), and corn oil (187–196). The high values are indicative that the oils also have the potential for the production of soap, shampoo, and other cosmetics products [39]. The obtained iodine value (74.60 gI_2/100g oil) fails within the standard value of 50 – 140 gI_2/100g oil [40]. The iodine value shows the measure of unsaturation in oil which is an indicator of the viability of oil for biodiesel production. Thus, the iodine value of the oil was appreciable, which implies that it contains an appreciable amount of unsaturated fatty acid making the oil a good candidate for transesterification reaction into fatty acid methyl ester (biodiesel).

The low pour point of the oil indicates that the oil will hardly solidify at room temperature, and thus can be stored as a liquid at room temperature for a long period. The high oxidation stability of the oil signifies that the oil is a good candidate for the production of biodiesel. The high oxidation stability of the oil could be a result of the solvent extraction method employed in oil extraction. Solvent refining yields base oils that retain some sulfur compounds which are natural antioxidants. To maintain thermal and oxidation stability, hydro-treated base oils have to be fortified further with antioxidants whereas base oils from solvent extraction maintain a natural ability to prevent oxidation. Also, the flash point (112.0 ^oC) indicates that the oil can be handled at temperatures well above room temperature without ignition.

TABLE V. PHYSICOCHEMICAL PROPERTIES OF PAWPAW SEED OIL EXTRACTED AT OPTIMAL CONDITION

Parameters	Values
Oil Yield (%)	25.48
pH at 29.1^oC	5.96
Specific gravity at 60^oC	0.927
Refractive index at 30^oC	1.465
Melting point (^oC)	46.85
Saponification value (mgKOH/100 g oil)	175.60
Acid Value (mg/g)	1.28
Iodine value (gI_2/100g oil)	74.60
Peroxide value (meqKOH/g)	1.24
Free fatty acid (%)	0.64
Moisture content (%)	0.18
Kinematic viscosityat 40^oC (cSt)	27.36
Viscosity at 20^oC (mPa.s)	27.40
Flash point (^oC)	230.00
Pour point(^oC)	-14
Cloud point (^oC)	9
Oxidation stability 11 ^oC (Hour)	5.2
Molecular weight ($gmol^{-1}$)	844.16

E. Fatty acid Profile of PSO from GC –MS Analysis

The fatty acid composition of PSO is shown in Table 6. It could be seen from the table that PSO contain 21.01% of saturated acids (myristics acid: 0.23 %, palmitic acid: 13.22%, stearic acid: 5.35%, arachidic acid: 0.46%, heneicosylic acid: 1.18%, and behenic acid: 0.57%) and 78.99% unsaturated acids (Palmitoleic: 0.67 %, oleic: 74.40%, linoleic: 3.57% and linolenic acid: 0.35%). The study revealed that oleic acid (monounsaturated) was the dominant fatty acid in the studied pawpaw seed oil. This result for oleic acid is comparable to 66.74% [41], 70.50-74.70% [42], 71.52% [43], and 75.89% [44]; implying that oil from pawpaw seed belongs to oleic category.

TABLE VI. FATTY ACID PROFILE OF PAWPAW SEED OIL

Common Name	IUPAC name	Formula	Composition (%)
Myristic acid	Tetradecanoic acid	C14:0	0.23
Palmitic acid	Hexadecanoic acid	C16:0	13.22
Palmitoleic acid	Hexadecenoic acid	C16:1	0.67
Stearic acid	Octedecanoic acid	C18:0	5.35
Oleic acid	Octadecenoic acid	C18:1	74.40
Linoleic acid	9,12-Octadecadienoic acid	C18:2	3.57
Linolenic acid		C18:3	0.35
Arachidic acid	Eicosanoic acid	C20:0	0.46
Heneicosylic acid	Heneicosanoic acid	C21:0	1.18
Behenic acid	Docosanoic acid	C22:0	0.57
Total			100

F. Kinetics of Pawpaw Seed Oil Extraction (PSOE)

The kinetics plots at temperatures of 30 °C, 40 °C, 50 °C, and 60 °C for oil extraction from pawpaw seed using n-hexane are respectively shown in Fig. 5, 6, 7, and 8. It could be observed from the figures that high R^2 values (coefficients of determinations) were obtained which implied that the oil extraction from the seeds using n-hexane obeyed the mass transfer kinetic model (4) and (5). Table 7 shows the kinetic parameters. It could be seen from the table that the rate constant increases as temperature increases which suggests that the oil extraction from the pawpaw seed using n-hexane occurs at moderate temperature. The activation energy for PSOE evaluated from Fig. 9and depicted in Table 8 was low indicating that the oil extraction from the seed using n-hexane requires lesser energy which makes the process economical.

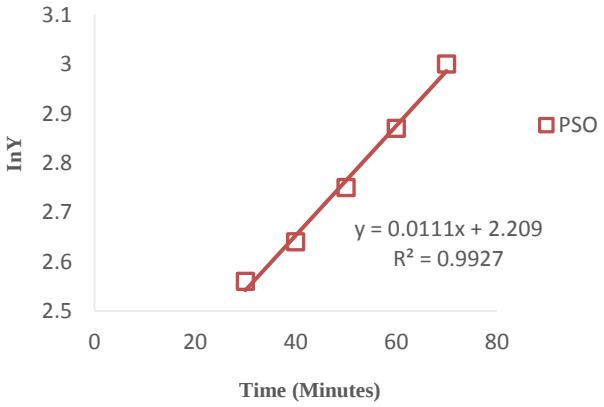

Figure 5. Kinetic plot for oil extraction from Pawpaw seed at 30 °C

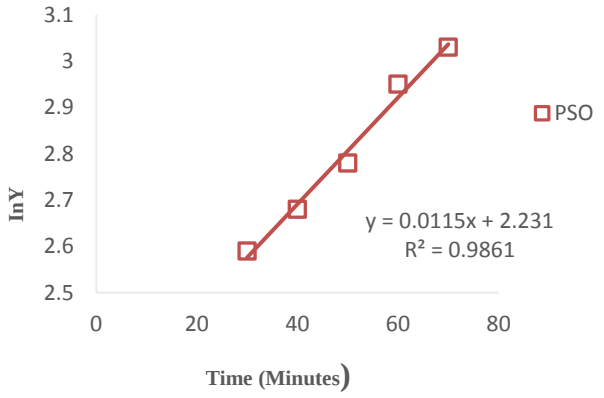

Figure 6. Kinetic plot for oil extraction from Pawpaw seed at 40 °C

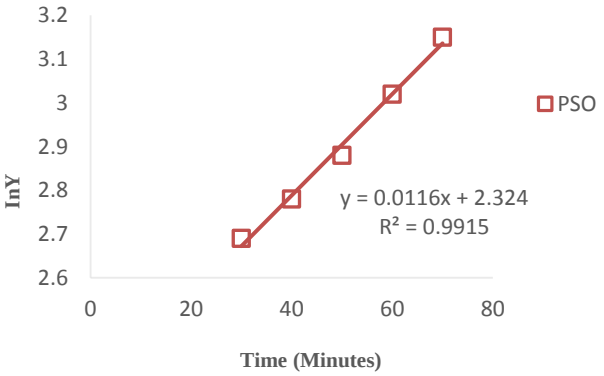

Figure 7. Kinetic plot for oil extraction from Pawpaw seed at 50 °C

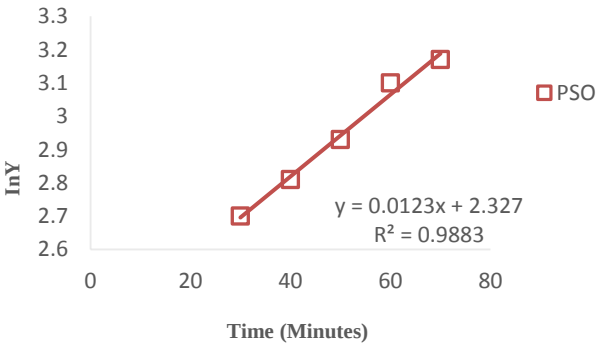

Figure 8. Kinetic plot for oil extraction from Pawpaw seed at 60 °C

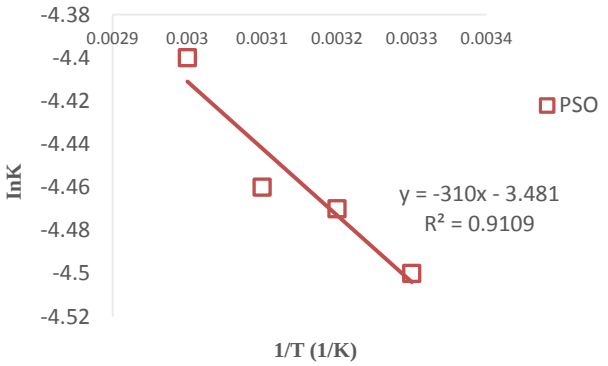

Figure 9. Activation energy plot for oil extraction from Pawpaw seed

TABLE VII. KINETIC DATA OF OIL EXTRACTION FROM PAWPAW SEED

Temperature (K)	k(min^{-1})	R^2	Ea (J/mol)	*A* (S^{-1})
303	0.0111	0.9927	2,577.483	0.031
313	0.0115	0.9861		
323	0.0116	0.9915		
333	0.0123	0.9883		

G. Thermodynamics Studies of Pawpaw Seed Oil Extraction (PSOE) Process

The values of equilibrium constant (K), enthalpy change (ΔH), and entropy change (ΔS)for oil extraction from pawpaw seed using n-hexane were determined and calculated from Fig. 10 and (10), while the Gibb's free energy change (ΔG)for the oil extraction were calculated using (12), and their values presented in Table 9. The positive and low value of the enthalpy signify that the process is endothermic, implying that the extraction process requires heat energy but at low temperature. The negative values of ΔG implied that the oil extractions from pawpaw seed using n-hexane are feasible, and the process is spontaneous.

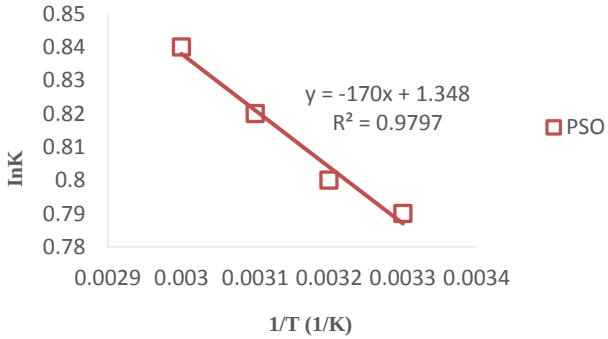

Figure 10. A Plot of InK versus 1/T for Thermodynamic Data of PSO Extraction

TABLE VIII. THERMODYNAMICS DATA FOR PSO EXTRACTION

ΔH (J/mol)	ΔS (J/mol)	Temperature (K)	ΔG (J/mol)
1,413.458	11.208	303	-2,004.054
		313	-2,094.612
		323	-2,206.691
		333	-2,318.770

IV. CONCLUSION

The oil yield from pawpaw seed is very much appreciable and could be a potential source of oil for consumption and industrial application – a case of waste to wealth. The response surface methodology proved to be an effective tool for the experimental design of the oil extraction process and optimization, with the quadratic model as the best fit for this oil extraction. The study also showed that oil extraction from pawpaw seed was feasible, spontaneous, and economical which proceeded at moderate temperature. In addition, the extracted pawpaw seed oil (PSO) belongs to the oleic category and has potential for industrial applications due to its interesting physicochemical properties, thus, it is recommended for cosmetic, biodiesel, and biolubricant production.

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