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Optimization and Kinetic Study of Soybean Oil Extraction Rate with Ternary Solvents Mixture

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Abstract
The rate of Soybean (Glycine max) oil (SBO) extraction with a ternary solvent mixture (water, ethanol, and ethyl acetate) optimised with I-optimal Design (IOD) under the Mixture Methodology of the Design Expert (12.0.1.0). The data obtained were analysed statistically. The effect of extraction time (60-180 mins) and temperature (65-70 °C) on SBO was investigated and data obtained were used to evaluate the suitable kinetic and thermodynamic properties of the extraction. The maximum Rate of Oil Yield (32.35 mg/min) was achieved at the solvent mixture of 9.17% water, 6.67% ethanol, and 84.17% ethyl acetate. The Quadratic model best describes the Rate of Oil Yield, with a correlation coefficient (R^2) of 0.9922 and an Adjusted R^2 of 0.9825. The rate equation for the extraction process is a first-order reaction with 'n' value of 1.12756 (≅ 1.000) while the activation energy (E_a) and Arrhenius constant were 6508.1 kJ/mol and 38.901 s^{-1}, respectively. The study has demonstrated the suitability of I-Optimal Design for the investigation of the Rate of Oil Yield from soybean and the result could be employed in oil extraction process design.

Keywords: Extraction Rate, Soybean Oil, Ternary Solvent, Optimisation.

Introduction
Mechanical expression of oil requires the application of pressure to force out oil from the desired oilseed (Ogunsina *et al.*, 2008). The oil obtained from Soybean (SB) by mechanical pressing has high oil qualities but lower yield because the mechanical presses are not operated at maximum efficiency and this has prompted a shift to the optimization of the operating variable of mechanical presses to obtain maximum SB oil yield. Besides, SB oil can be obtained through solvent extraction and several studies have investigated the use of mixed solvents, particularly binary mixture. Various alternative solvents such as trichloroethylene, *n*-heptane, ethanol, isopropanol, and propanol have been proposed as a substitute to hexane in oilseed extractions, (Gandhi *et al.*, 2003; Seth *et al.*, 2007; Thomas, 2003). Similarly, the use of other techniques such as supercritical fluid extraction (dos Santos Freitas *et al.*, 2008; Koubaa *et al.*, 2016; de Melo *et al.*, 2014; Rai *et al.*, 2016), compressed fluid extraction (dos Santos Freitas *et al.*, 2008; Pederssetti *et al.*, 2011, Coelho *et al.*, 2016), microwave and ultrasound-assisted extraction (Adam *et al.*, 2012; Hu *et al.*, 2012; Lee *et al.*, 2012; Araujo *et al.*, 2013) have been proposed for effective oil extraction from oilseeds.

The use of ethanol as alternative replacements for hexane is very promising in various applications and economical uses, particularly in countries such as Brazil, where ethanol production is abundant and relatively cheap (Baümler *et al.*, 2016; Toda *et al.*, 2016). Furthermore, ethanol presents lower health risks and flammability than hexane and its isomers, although hexane is completely miscible

in oil solubilization than ethanol, which is lower and partial, leading to a reduction in extraction efficiency (Baümler *et al.,* 2016; Gandhi *et al.,* 2003; Seth *et al.,* 2007).

It is very common to use co-solvent phase equilibrium studies to evaluate the performance of components solubility. For this purpose, the co-solvent should be soluble in both solvent and solute. Thus, using a co-solvent in the soybean crude oil extraction with ethanol as solvent could be a viable alternative to the process. Ethyl acetate is an oxygenated organic solvent, frequently used in chromatographic techniques and chemical, cosmetic, and food industries. This chemical presents a relatively low-boiling point (~350 K), is a renewable and low toxicity component, and is completely miscible with ethanol. Besides, the use of ethanol + ethyl acetate mixtures (instead of pure ethyl acetate) is justified mostly due to the lower price of ethanol. Organic solvents such as benzene and hexane have widely been used for the extraction of oil from seeds (Subroto *et al.,* 2015). However, due to environmental concern, poor oil quality, and the high cost of sourcing this petrochemical-based solvent, attention has been shifted toward searching for relatively cheap solvents, high yield of SB oil, and good oil quality. This thus portends the desire to use ternary azeotropic solvent mixtures such as Ethylacetate, ethanol, and water to extract SB oil.

Considering these characteristics, using ethyl acetate as a co-solvent in the ethanolic extraction of soybean oil emerges as a promising possibility. Furthermore, this solvent mixture (ethanol + ethyl acetate) could be completely removed by distillation, allowing separation in conventional extraction plants. In this context, this work aims to evaluate solubility, in terms of liquid-liquid equilibrium information, for the ternary system involving soybean oil (solute) + ethyl acetate (co-solvent) + ethanol (solvent) and also to investigate the kinetics of ethanolic extraction of soybean crude oil using ethyl acetate as co-solvent.

Thus, this present investigation aimed at modelling and optimization of the Rate of Oil Yield from the solvent extraction of Soybean oil. The rate of oil yield was rarely considered in previous studies. The I-optimal design, under the Mixture Methodology, was employed to examine the effect of the independent variables (solvent components): water, ethanol, and ethyl acetate together with their interactions on the dependent variable (rate of oil yield). The process variables optimization was carried out using the facilities embedded in the Design Expert Software (12.0.1.0). The kinetics and activation energy property of the process were investigated to understand the extraction rate with respect to the oil yield.

Materials and Method

Materials and Sample preparation

The Soybean (SB) samples (*Glycine Max (L*) were procured from the SB market, Benue State, Nigeria, and authenticated at the Forestry Research Institute of Nigeria (FRIN) Jericho, Ibadan, Nigeria. The reagents used for the experiments were of analytical grade and obtained from reputable chemical stores. The SB samples were cleaned thoroughly and conditioned to a constant moisture content (oven-dry weight) in an oven at 50 °C for 24 hours, before being blended and sieved to uniform particle size (2 mm), then stored (Araromi *et al.,* 2017).

Solvent Extraction of Soybean Oil

The accessories of the Soxhlet apparatus were washed and set up according to the manufacturer's specifications. A mixture of water, ethyl acetate, and ethanol solvents at various percentage compositions was used for the extraction process. The uniformly ground and sieved SB sample (50 g) was put in the thimble and inserted into the soxhlet. The round bottom flask (500 ml) was filled

with 300 ml of the ternary solvent mixture, while the condenser with its inlet and outlet tubing was firmly fixed. The flask was seated in the heating mantle and the set-up was heated to the azeotrope temperature (69.9 °C) of the solvent mixture for 4 hrs. The resulting rich solvent mixture was distilled and the rate of soybean oil yield was determined according to Eqn. (1)

$$Rate\ of\ oil\ yield = \frac{weight\ of\ extracted\ oil\ (mg)}{time\ (mins)} \quad (1)$$

Modeling of the experimental design for the rate of oil yield from SB

A three-level-three-components I-Optimal Design (IOD) under the Mixture Methodology of the Design Expert (12.0.1.0) was employed for the modeling of the rate of extraction of the process. The components were the ternary (water, ethanol, and ethyl acetate) solvents in the ranges 5-10%, 5-10%, and 80-85%, respectively (Table 1), and they were fed in the software as the independent variables, while the rate of oil yield (mg/min) was selected as the dependent variable.

Table 1: Levels Ternary Solvent Components considered for the Soybean Oil Extraction

Components	Symbols	Levels (%)		
		Low	Middle	High
Water	A	5	7.5	10
Ethanol	B	5	7.5	10
Ethyl acetate	C	80	82.5	85

The IOD generated the experimental runs with one replicate. The extraction experiments were conducted accordingly in triplicates and the average value was fed into the software for further analysis. Necessary statistical analysis was accomplished with the available tools embedded in the design Expert Software and suitable models were developed (Alabi *et al*., 2019). The relationship between the independent variables and the dependent variables is illustrated in the polynomial model (Equation 2)

$$Y = \alpha_0 + \alpha_1 A + \alpha_2 B + \alpha_3 C + \alpha_{12} AB \; ------ + \alpha_{33} C^2 \quad (2)$$

Where Y is the predicted Rate of SB oil yield, α_0 is the intercept, α_1-α_2 are the coefficients of partial regression, α_{12}-α_{33} are the coefficients for interaction regression, α_{12}-α_{33} are the coefficients for quadratic regression, while A, B, and C are the component variables representing water, ethanol and ethyl acetate in ml, respectively.

The fitted equation is represented in the surface and contour plots which expound the visual relationship between the response and the input variables. The Analysis of Variance (ANOVA) for the study was evaluated to determine the impact of the model terms (the component percentage compositions) on the rate of oil yield. The Coefficient of Determination (R^2), the Adjusted Coefficient of Determination (Adj R^2), and the Predicted Coefficient of Determination (Pred R^2) were evaluated to ascertain the fitness of the model equation developed. Other statistical variables such as the mean, Standard Deviation (SD), Coefficient of Variables (CV), Adequate Precision Ratio, p-value, and F-value for the data analysis were verified to adjudge their level of significance (Oladipo and Betiku, 2019).

Effect of Time and Temperature on oil yield from SB

The oil extraction from the SB samples was investigated under the effect of varying time (30-180 mins) and varying temperature (65–70 °C). The experiment was conducted with the Soxhlet apparatus, wherein the SB samples were leached with the solvent mixture composition established at the optimum in Section 2.2. The solvent-to-solid ratio was maintained at 6:1, with 50 g of the SB sample. The resulting solution at each 30 min extraction cycle was evaporated in a rotary evaporator to recover the solvent mixture and obtain pure SB oil (Araromi *et al.,* 2017). The SB oil obtained was cooled in a desiccator and the amount of oil yield was determined according to Eqn. 3.

$$oil\ yield = \frac{weight\ of\ extracted\ oil}{weight\ of\ soybean\ fed\ in}\ X\ 100\% \quad (3)$$

Kinetics of the Rate of Extraction

The rate equation (Eqns. 4-5) is a common model used to determine the kinetics of oil extraction from oilseed and it reveals the kinetic order of the extraction process (Ahmad *et al.,* 2014). The percentage of oil extraction, typically, increases with time and thus dY/dt is always positive

$$\frac{dY}{dt} = KY^n \quad (4)$$

$$\ln\left[\frac{dy}{dt}\right] = \text{n ln Y} + \ln \text{K} \quad (5)$$

Where, Y (%), is the oil extraction yield t (min) is the time of extraction, k (min^1) is the rate constant and n is the order number.

Activation energy of the extraction process

Experimental data needed for the thermodynamic study was obtained by investigating the rate of extraction o f Soy oil at 65, 67.5, and 70 °C, which are near the boiling point (68 °C) of the azeotropic solvent mixture. The Activation energy of the extraction process was calculated using the Arrhenius Equation (5) (Ahmad *et al.,* 2014). ln k was plotted against 1/T and the slope of the line ($-E_a/R$) was used to evaluate the activation energy ($-E_a$) of the extraction process, while the intercept of the line was used to evaluate the Arrhenius constant (A) (Ahmed *et al.,* 2014; Kadurumba *et al.,* 2018; Vishnu *et al.,* 2018). Activation thermodynamics parameters (ΔH*, ΔS*, and ΔG*) for the extraction were evaluated from Eqns. 6-9

$$lnk = lnA + \left(\frac{-E_a}{R}\right)\frac{1}{T} \quad (6)$$

$$A = \frac{RT}{Nh}e^{\Delta S^*/R} \quad (7)$$

$$\Delta H^* = E_a - RT \quad (8)$$

$$\Delta G^* = \Delta H^* - T\Delta S \quad (9)$$

Where A is the Arrhenius constant, Ea (kJ/mol) is the activation energy, k (s^{-1}) is the extraction rate constant, R (J/mol.K) is the universal gas constant, T (K) is the absolute temperature, *N* is Avogadro's constant, and *h* is Planck's constant, while ΔH*(kJ/mol), ΔS*(J/mol K) and ΔG* (kJ/mol) are the activation enthalpy, the activation entropy, and the activation Gibb's free energy, respectively, (Ahmad *et al.,* 2014).

Results and Discussion

Rate of Oil Yield

The trend of the Rate of Oil Yield, based on the I-Optimal experimental design with a three-level-three-component design is illustrated in Table 2. The relatively wide range between the minimum (19.03 mg/min) and maximum (32.35 mg/min) rate of oil yield with a standard deviation of 4.8 and a ratio of 1.70, indicates that the experimental design, the components, and the ranges selected are effective for the study. The composition of the component that led to the maximum rate of oil yield (32.35 mg/mm) is 9.17%, 6.61%, and 84.17% for water, ethanol, and ethyl-acetate, respectively, while the composition for the minimum rate of oil yield (19.03 mg/mm) was 7.50%, 10.00%, and 82.50% respectively. The difference in the percentage composition of the three components for the maximum and minimum yield justified further the effectiveness of the I-Optional experimental design. The residual values depict the difference between the experimental data (actual values) and the software-generated values (predicted). Positive residual is derivable when actual values are higher than predicted values, while negative residual is obtained on the contrary (Alade *et al*., 2020). The positive residual was generated for Runs 1, 3, 5, 6, 8, and 10, while the other Runs (2, 4, 7, and 9) displayed negative residuals.

Table 2: Response (Rate of Oil Yield) from the I-Optional Experimental Design

Run	Components			Response (Rate of Oil Yield mg/min)		
	A: Water (%)	B: Ethanol (%)	C: Ethyl acetate (%)	Actual	Predicted	Residual
1	5.00	10.00	85.00	29.4	29.15	0.2522
2	6.67	9.17	84.17	30.94	31.78	-0.8434
3	7.50	10.00	82.50	19.03	18.92	0.1103
4	10.00	7.50	82.50	20.89	21.06	-0.1660
5	9.17	6.67	84.17	32.35	31.74	0.6131
6	10.00	10.00	80.00	21.33	21.29	0.0435
7	10.00	5.00	85.00	26.66	26.87	-0.2121
8	7.92	9.16	82.92	25.47	24.97	0.5034
9	9.17	9.17	81.66	20.89	21.23	-0.3445
10	10.00	10.00	80.00	21.33	21.29	0.0435

Regression Equation Model

The best fit quadratic model equation which considered the relationship between the dependent and independent variables is given in Eqn 10. The software indicated that the equation, in terms of coded factors, can be used to make predictions about the response for a given level of each factor. The high levels of the mixture components, by default, are coded as '+1', and the low levels are coded as '-1'. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

$$Rate\ of\ Oil\ Yield\ = -35.03A - 56.67B + 139.16C + 263.56AB - 100.76AC - 48.37BC \quad (10)$$

Where A = water component, B = ethanol component and C = ethyl acetate component.

The positive coefficients (139.16 and 268.56) were obtained for components C and AB, while negative coefficients (-35.03, -56.67, -100.76, and -48.37) were obtained for components A, B, AC, and BC. These coefficients represent the expected change in the response (Rate of Oil Yield) per unit change in a factor value when all the remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the Runs. The coefficient was adjusted around the average based on the factor setting. It can be deduced that the interaction between the water (A) and the ethanol (B), has the highest coefficient (268.56) and this indicates a strong influence of the interacting factors on the Rate of Oil Yield from the SB while component C (ethyl acetate) with the positive coefficient of 139.16 has the most positive linear impact among the components (A, B and C).

Results of Statistical Analysis

The results of the analysis of variance (ANOVA) and other statistical parameters, related to the suggested quadratic model equation, are depicted in Table 3. The quadratic regression model is characterized by a high F-value (206.10) and a low p-value (0.0003), which indicated that the model developed is very significant. The p-value of 0.0002, 0.0007, and 0.0131 indicate that the interactive terms (AB, AC, and BC) of the model equation are significant at $p<0.05$ (95% confidence interactive level). The p-value (0.0002) obtained for the linear mixture simply suggests that the linear terms of A (water), B (ethanol), and C (ethyl acetate (C) are all significant. The properties of the filled model equation developed were examined and the results showed a high R^2 value of 0.9922, which means that the model regression equation could account for 99.22% variation of the quadratic model equation developed (Oladipo and Betiku; 2019). The predicted R^2 (0.9827) and predicted R^2 (0.8358) are close reasonable with a difference of 0.1467, which is less than 0.2 acceptable maximum differences set for Adj R^2 and pred R^2 (Alabi *et al.,* 2019). The adequate precision which is a measure of the signal-to-noise ratio is 26.165 and it is greater than the acceptable value of 4, thus indicating an adequate signal for the analysis. S.D (0.6347) obtained is relatively low and the CV (2.56%) explaining the extent of dispersion of the statistics (Sharifi *et al*., 2018). All these attests to the acceptability of the statistical analysis of the experimental data generated for the study (Myer et al; 2009).

Table 3: ANOVA for Quadratic model of Rate of Oil Yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	Statistical Parameters	Value
Model	206.10	5	41.22	102.32	0.0003*	R^2	0.9922
[(1)]Linear Mixture	117.37	2	58.69	145.68	0.0002*	Adjusted R^2	0.9825
AB	71.02	1	71.02	176.29	0.0002*	Predicted R^2	0.8358
AC	35.82	1	35.82	88.92	0.0007*	Adeq Precision	26.1650
BC	7.28	1	7.28	18.07	0.0131*	Std. Dev.	0.6347
Residual	1.61	4	0.4028			Mean	24.83
Lack of Fit	1.61	3	0.5371			C.V. %	2.56
Pure Error	0.0000	1	0.0000				
Cor Total	207.71	9					

[(1)] Inference for linear mixtures uses Type I sums of squares. * significant

Model Adequacy

The Normal Plot of Residual and the Plot of the Studentised Residual (Figure 1-2) were used to illustrate the adequacy of the model developed (Oladipo and Betiku, 2019). The fitted points in Figure 1 aligned closely, to the normal line that ran diagonally, and the degree of clustering to the line is depicted by the high R^2 (0.9922), which illustrates a very high degree of agreement between the observed and the predicted values. The experimental data spread between 5% and 95% Normal % probability on the Normal Plot of Residual (Figure 2). The extent indicates that wide speed was covered in the experimental design (Aremu *et al*., 2019).

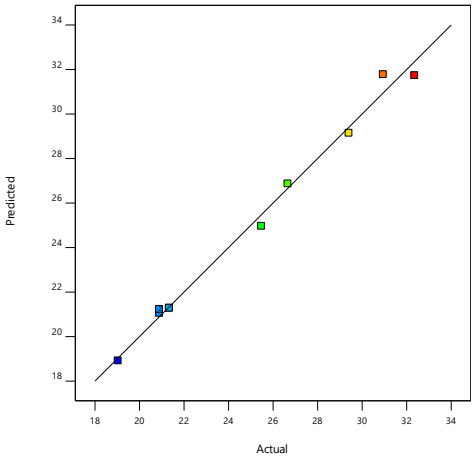


Figure 1: The Normal Plot of Residual for Rate of Oil Yield

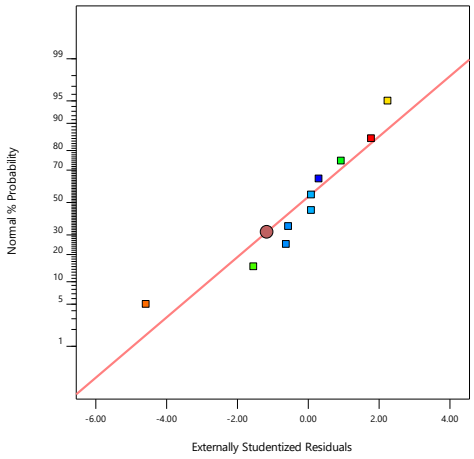


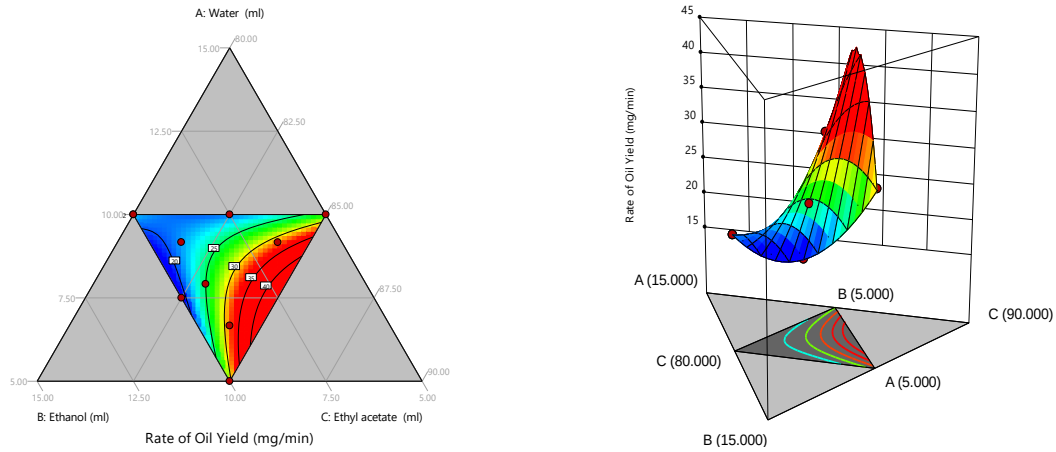
Figure 2: The plot of the Studentised Residual for Rate of Oil Yield

Effect of the experimental parameter on Rate of Oil

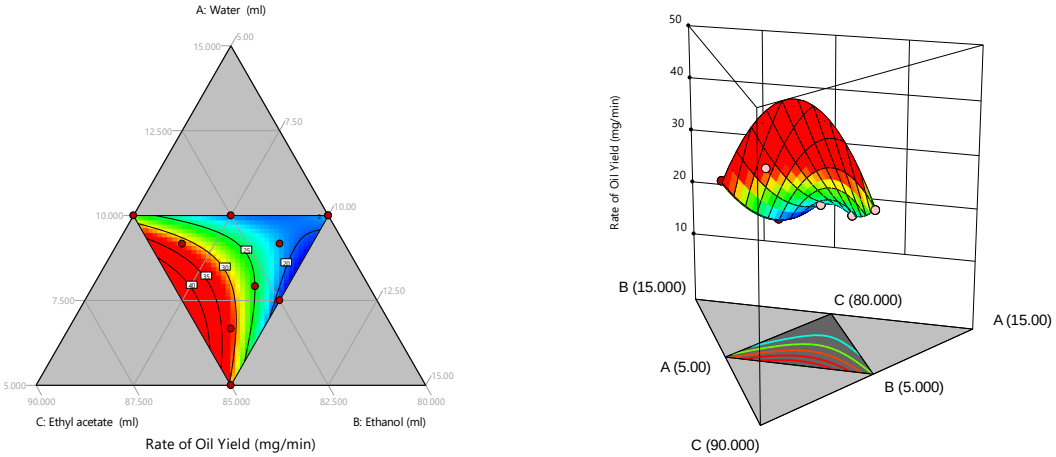
The Contour and 3D-surface plots for the effect of the components (water, ethanol, and ethyl-acetate) of the solvent mixture are illustrated in Figures 3. Generally, the 3D plot is characterized by elliptical or saddle curves indicates the existence of an interaction between the related variables being significant (Sharifi *et al*; 2018). The 3D plot, further, indicates the importance of the three-components (selected) on the rate of oil yield. The elliptical and saddle value of the curve proves that a suitable model is quadratic in nature (Alade *et al*; 2019) and the interaction between the related variables is very significant (Sharifi *et al*; 2018).

Numerical optimization

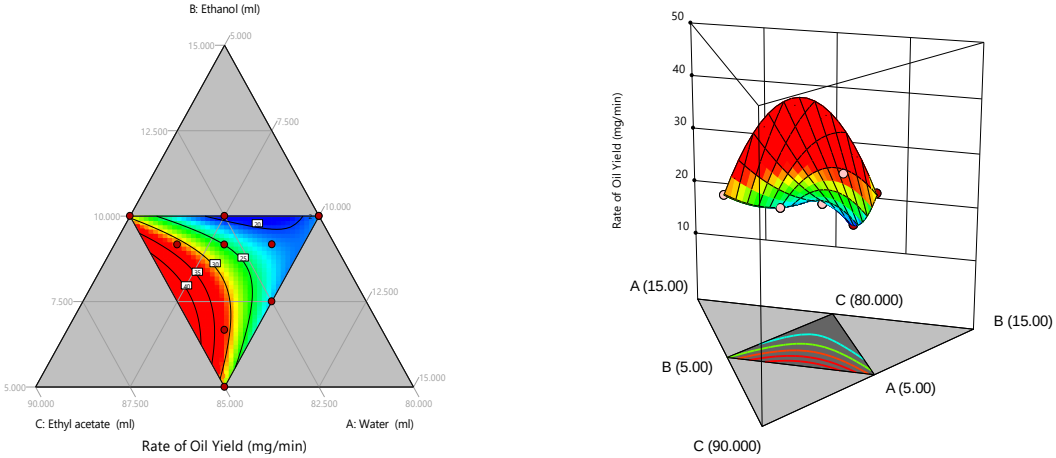
The software was incited to use the data fed and predict the best percentage composition and expected rate of oil yield, numerically. The upper and lower limits of the components were set within ranges while the response (Rate of oil yield) was set to 'maximum'. The selected numerical optimized percentage composition is 9.21% water, 6.14% ethanol, and 84.65% ethyl-acetate which gave the maximum rate of oil Yield of 34.16% (Figure 4). The percentage difference between the experimental and numerical values is 0.44%, 7.0%, 0.57%, and 5.30% for water, ethanol, ethyl-acetate, and rate of oil yield, respectively (Table 4). These percentage differences are less than 10% and thus established the suitability of the models and suggest that the experimental errors were minimal (Alade *et al*; 2019).



(a) Water-Ethyl acetate-Ethanol solvent mixture



(b) Water-Ethanol-Ethyl acetate solvent mixture



(c) Ethanol-Water-Ethyl acetate solvent mixture

Figure 3: Contour and Surface Plots of Ternary (Water, Ethanol, and Ethyl acetate) solvent mixture for the Rate of Oil Yield from Soybean

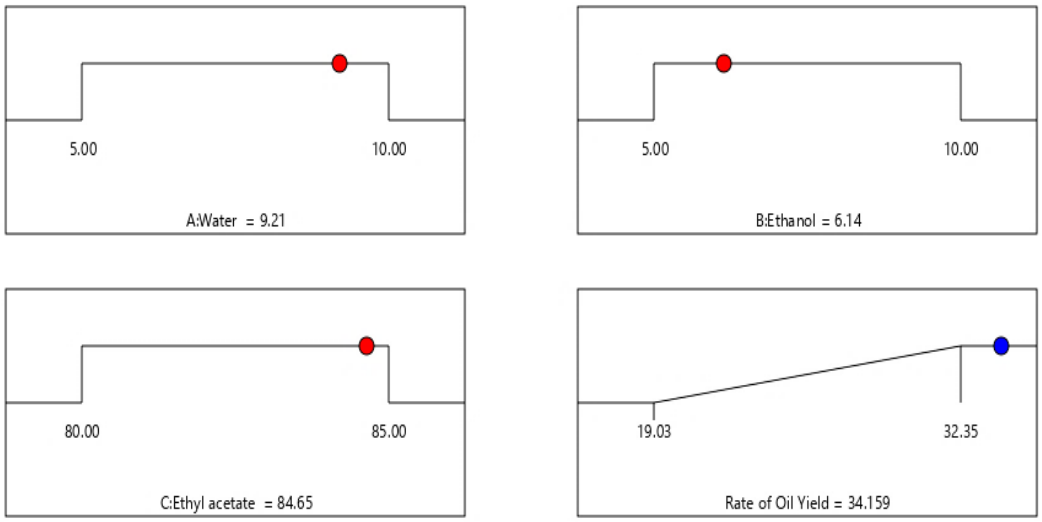


Figure 4: The Selected Numerical Optimized Percentage Composition

Table 4: The Percentage Difference Between the Experimental and Numerical value for Rate of Oil Yield

Run	Components			Response
	A: Water (ml)	B: Ethanol (ml)	C: Ethyl acetate (ml)	(Rate of Oil Yield mg/min)
Numerical	9.21	6.14	84.65	34.16
Experimental	9.17	6.67	84.17	32.35
Error (%)	0.44	7.0	0.57	5.30

Time and Temperature Effects on oil yield from SB

The SB oil yield increased from 3.37-8.9 %, 3.97-12.78 %, and 5.04-14.81 %, at 60 ºC, 65.7 ºC, and 70 ºC, as the time and temperature increased from 30-180 mins and 60-70 ºC, respectively (Figure 5). the SB oil yield increased from 8.9–14.81 %, at 180 mins and the results indicate that SB oil yield increased with an increase in temperature and time, proportionally, during the extraction process. This may be due to a decrease in the extraction solvent viscosity which facilities its flow and eventual increase in diffusion into the matrix of the beans (Menkiti *et al.*, 2015). Similarly, Bimaka *et al.*, (2011), and Suleiman *et al.*, (2013), reported that an increase in the extraction temperature enhanced the extraction mass transfer coefficient and consequently increased the amount of oil yield. A very rapid rate of extraction is expected at the beginning of the extraction process due to the availability of the oil on the surfaces of the blended soybeans, and this would enhance faster extraction (Menkiti *et al.*, 2015). The absence of this experience in his study may be attributed to the azeotropic nature of the solvent.

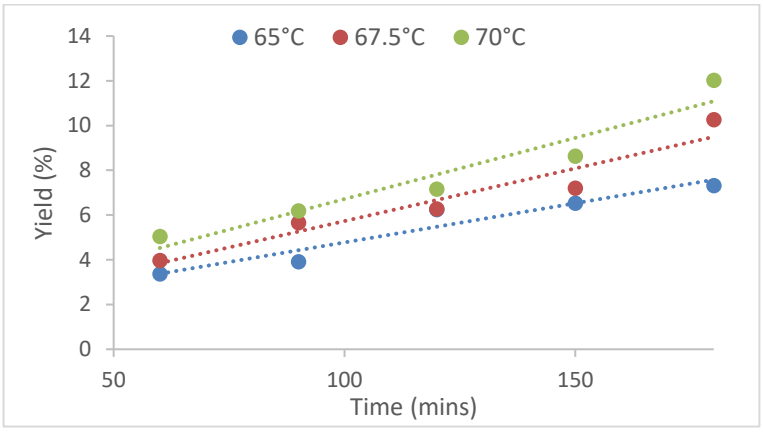


Figure 5: Plot of Yield (%) against Time (mins) at varying Temperature

Kinetic of extraction rate

The general extraction rate equation evaluated by plotting ln (dY/dt) against lnY (Figure 6) at 65 ºC, 67.5 ºC, and 70 ºC gave 'n' as 1.2487, 1.0196, and 1.1142, respectively (Table 5). This gave an average of 1.12756 which would have suggested a fractional kinetic order. (Ahmad *et al.*, 2014), but these values, as well as their average, can be approximated to 1.0 and this would suggest first-order kinetics (Vishnu *et al.*, 2018). The regression coefficient (R^2) for 65 ºC, 67.5 ºC, and 70 ºC were 0.9626, 0.9755, and 0.972 with an average of 0.9717. This implied that there were fewer errors in the extraction rate recorded at each temperature and their closeness to the average R^2, further suggested that they possessed similar extraction properties at the selected temperatures. The reaction rate constants (K) were 6.19×10^{-3}, 1.09×10^{-2} and 8.17×10^{-3} min^{-1} at 65 ºC, 67.5 ºC, and 70 ºC. This were related to the time required to achieve maximum soy oil extraction and it was expected to increase with the increase in temperature (Ahmad *et al.*, 2014), particularly at higher temperature as observed for sunflower seeds (Topallar and Geogel, 2000), *Jatropha Curcas* (Amin *et al.*, 2010) and *Chlorella sp*. (Ahmad *et al.*, 2014). By evaluating the reciprocals of these values, based on the unit (min^{-1}), suggested that the theoretical maximum extraction time for Soy oil extraction at 60 °C, 67.5 °C, and 70 °C were 161.29, 91.74, and 121.95 min, respectively. The extraction time was expected to reduce as the temperature increase, and this meant that lesser time was expected for better oil extraction at high temperatures (Ahmad *et al.*, 2014, Menkiti *et al.*, 2016, and Kadurumba *et al.*, 2018).

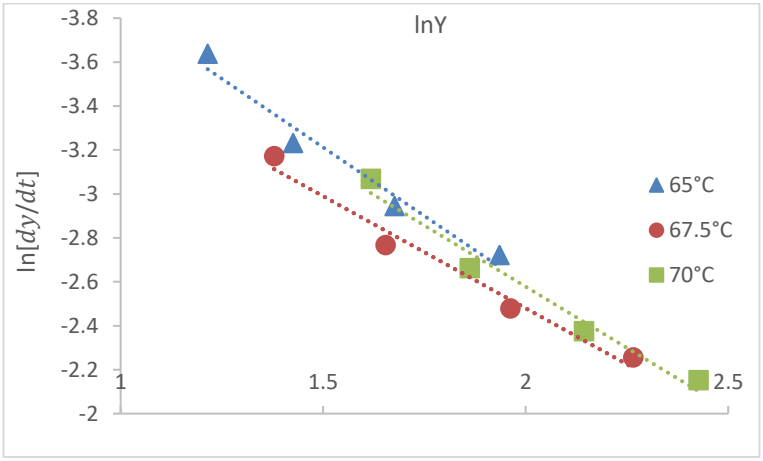


Figure 6: Plot of $\ln[dy/dt]$ *against* ln Y at varying Temperature

Table 5: Soy oil Extraction rate constants at different temperatures for extraction time

Temperature (°C)	K_1	n	lnK	Time (mins)				
				60	90	120	150	180
65	6.19×10^{-3}	1.2487	-5.0848	3.37	4.16	5.345	6.925	8.90
67.5	1.09×10^{-2}	1.0198	-4.5189	3.97	5.228	7.115	9.631	12.77
70	8.18×10^{-3}	1.1142	-4.8062	5.04	6.436	8.53	11.322	14.81

Activation Energy

The activation energy property of the soy oil extraction from its bean using azeotropic solvent (9.17 % Water, 6.67 % Ethanol, and 84.17 % Ethyl acetate) was evaluated from the plot of InK versus 1/T (Figure 7). The slope of the straight line obtained is equivalent $-E_a/R$ and this was used to determine the values of E_a, while, the intercept of the straight line is equivalent to lnA, used to evaluate 'A' (Arrhenius constant). E_a and A, obtained were 6508.1 KJ/mol and 38.901 s^{-1}. The E_a obtained in this study is higher than 38.893 KJ/mol, 25.8 KJ/mol, and 10.0765 KJ/mol reported by Ahmad *et al.*, (2014), Mathiarasi and Partha (2016), and Vishnu *et al.*, (2018) for the extraction of oil from *Chlorella sp.*, Daturametelin, and *Chlorella*, respectively. The value of 'A' (38.901 s^{-1}), is lower than 2684 s^{-1} reported by Ahmad *et al.*, (2014), but higher than 1.738 s^{-1} and 0.090 s^{-1} reported by Mathiarasi and Partha (2016) and Vishnu *et al.*, (2018). The activation energy is well related to the influence of solvent diffusion through the limited boundary layer. The activation enthalpy (ΔH*), activation entropy (ΔS*), and the activation of Gibb's free energy (ΔG*) evaluated for the extraction process are indicated in Table 6. The activation entropy (ΔH*) were -47.477, -47.526, and -47.594 J/mole while the activation enthalpy was 51.30, 51.28 and 51.26 KJ/mol. These two quantities decreased as the extraction temperature increased, while the ΔG*(67.34, 67.463, and 67.584 KJ/mol) increased with increased extraction temperature, similar to the trends observed by Ahmad *et al.*, (2014), Mathiarasi and Partha (2016), and Vishnu *et al*, (2018) for the extraction of oil from *Chlorella sp.*, Detrimental Linn and *Chlorella v.*, respectively.

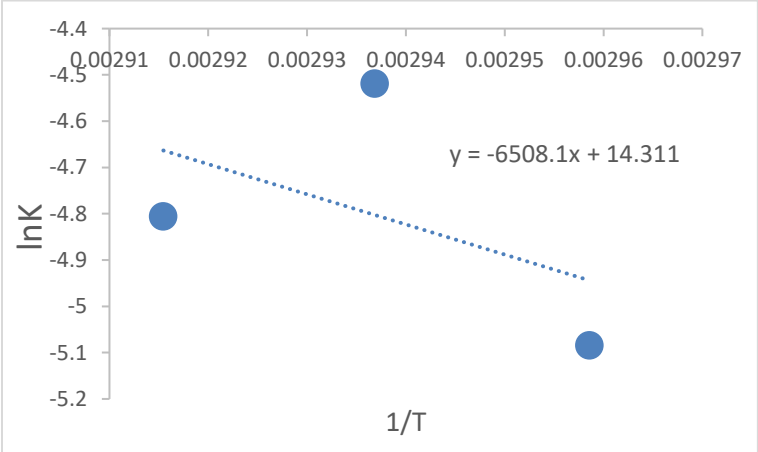


Figure 7: The plot of ln k versus 1/T

Table 6: Thermodynamic Activation Parameters for Soy Oil Extraction at Various Temperatures

Temperature (K)	ΔS*(J/molk)	ΔH*(KJ/mol)	ΔG*(KJ/mol)
338	-47.477	51.30	67.346
340.5	-47.526	51.28	67.463
343	-47.594	51.26	67.584

Conclusions

The composition of the component that led to the maximum rate of oil yield (32.35 mg/mm) is 9.17%, 6.61%, and 84.17% for water, ethanol, and ethyl-acetate, with the I-optimal Design under the Mixture Methodology. The general rate equation for the oil extraction gave average Fractional kinetic order (n) of 1.12756 ($\cong 1.000$) suggesting a first-order reaction for the extraction process. The activation energy properties of the extraction indicate a relatively high activation energy (E_a) (6508.1 KJ/mol) and a low Arrhenius constant (38.901 s^{-1}). The thermodynamic properties (ΔH* and ΔS*) of the activation energy decreased, while ΔG* increased, as the extraction temperature increased. This information obtained in this study can be employed effectively in the process design of soybean extraction from its bean and possible scale-up.

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