Optimization of Monounsaturated Fatty Acids and Oil from Walnut Seed: Kinetics and Thermodynamics

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Abstract— The optimization, kinetics and thermodynamics of oil and monounsaturated fatty acid extraction from walnut seed using hexane were investigated. The effect of process parameters were studied and optimized using response surface methodology. The experimental data was fitted into first order kinetic model and Van't Hoff thermodynamic equation. The result revealed that the process parameters have significant effect on the yields of oil and monounsaturated fatty acid. The optimal conditions obtained were: solvent/solid ratio of 0.329mL/g and 0.342mL/g; extraction time of 46 minutes and 47 minutes; and extraction temperature of 42 °C with optimal yields of oil and monounsaturated acid of 53% and 72% respectively. The kinetic study indicated that rate constant increases as temperature increases with activation energy of 38.59kJ/mol. The thermodynamics study showed that the changes in enthalpy and entropy were positive with negative change in Gibbs free energy. This indicates that the extraction of oil is spontaneous and feasible.

Index Terms—Walnut, solvent, extraction, monounsaturated, optimization, spectrometer

I. INTRODUCTION

With increasing consumer concerns over oil with less or no cholesterol, there has been considerable interest in the extraction of oil from high nutritional seeds. Walnut is one of the top nutritious seeds known in the world. It is one of the oldest trees with edible fruit [1]. Its tree is among the few useful plants that naturally grow in both Eastern and Western hemispheres of the earth [2]. Walnut is scientifically called Juglans derived from the Latin word Jovis-Glans which means Jupiter Hazelnut [3].

From the nutritional perspective, walnut is a very nutritious nut with different composition depending on variety. Majority of walnut varieties have about 60% oil and 52 - 70% fat depending on variety and region [1]. The benefits of walnuts on cholesterol in human diet have been proven. It is shown that a balanced consumption of

walnuts reduces cholesterol or low-density lipoprotein levels to about 16 percent in men [1]. It has been proven that walnuts are effective in preventing heart disease.

Nevertheless, the ratio of fatty acids in the nutritional and economic value of oil is significant. The higher proportion of unsaturated fatty acids with one double bond cause additional durability against oxidation and increases its shelf life, but polyunsaturated fatty acids with multiple double bonds are more susceptible to oxidation, but they are more important regarding human health and nutrition [4]. Monounsaturated fatty acid has been found to be a useful aid to lower serum cholesterol levels and low-density lipoproteins in the human body [5]. Consumption of vegetable oil with Monounsaturated fatty acid will regulate cholesterol levels.

Many authors have reported several methods for extraction of oil from seeds among which are; supercritical carbon dioxide extraction, centrifugal extraction, microwave-assisted solvent extraction and Soxhlet extraction. Among these, soxhlet extraction is the simplest, cheapest and most practical process in extracting oil [6], [7]. Soxhlet extraction involves the use of solvents and it results in the production of base oils, which maintain some sulphur compounds which might be natural antioxidants. These base oils maintain a natural ability to stop oxidation, while hydrotreated base oils have to be similarly fortified with antioxidants to retain oxidation and thermal stability.

The solvent extraction process is carried out inside a predetermined space of the controllable factors that are known to have effects on the system response. The characterization (or screening) of these significant contributing variables to the process response is achieved through analysis of variance (ANOVA) and Design-of-Experiment (DOE) while the control and optimization tasks are gotten using Response Surface Methodology (RSM) [8]. An efficient and effective statistical technique used in optimizing experimental parameters is response surface methodology. It evaluates the outcome of a couple of factors and their interactions on one or extra

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response variables [9], [10], [11]. An advantage of RSM is that it reduces the number of experiments and provides a mathematical model. Therefore, this study focused on optimization of oil extraction from walnut using RSM and evaluation of a suitable kinetics mechanism for the oil extraction using n-hexane.

II. MATERIALS AND METHODS

A. Materials

Walnut was procured from Nkwo-Ezeagu Market Obinofia Ndiuno Enugu, Enugu State Nigeria. The nut was sun-dried, deshelled and ground for extraction of oil using analytical grade n-hexane. All chemicals and solvents utilized were of analytical grade and commercially sourced without treating them.

B. Oil Extraction

The procedure of Reference [12] was adopted in carrying out walnut oil extraction. 200g of the ground kernel with a particle size of 950 μ m was mixed with n-hexane in a solvent/solute ratio of 0.5mL/g to 2.5ml/g. The mixture was then magnetically blended at a steady speed of 200rpm at a range of temperature of 30 °C to 55 °C for time 15 minutes to 75minutes hour. The yield of oil extracted was evaluated with Equation (1).

$$Y = \frac{W_o}{W} \times 100 \tag{1}$$

where Y is the oil yield (%),

 W_o is the amount of extracted oil (g) and

W is the amount of the walnut used.

C. Optimization of Oil Extraction

The optimization of the oil extraction was done using Central Composite Design of Response Surface Methodology of Design-Expert version 9.0.6. The experimental design employed in this work was a fivelevel-three factor full factorial design, involving 20 experiments. Extraction temperature, solvent/solute ratio and extraction time were chosen as independent variables. The responses chosen was the oil yield and monounsaturated acid obtained from solvent extraction. Six repeated centre points were utilized to predict with minimum errors and experiments were executed in a randomized order. The real and coded values are presented in Table I, and the range was selected based on the previous experiment performed by Reference [1]. The coded values are designated by -1 (minimum), 0 (centre), and +1 (maximum). The software employs the concept of the coded values for the examination of the significant terms. Therefore, equation in coded values is used to investigate the effect of the variables on the response. The empirical equation is represented as shown equation (2):

$$Y_{i} = \beta_{0} + \sum_{i=1}^{3} \beta_{i} X_{i} + \sum_{i=1}^{3} \beta_{ii} X^{2}_{i} + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \beta_{ij} X_{i} X_{j}$$
(2)

where Y_i is the predicted response for oil yield or monounsaturated acid, β_0 is the coefficient of the constant term, β_i is the coefficient of the linear term, β_{ij} is the coefficient of the interactive term while β_{ii} is the coefficient of quadratic term. The design matrix for the experimental data is presented in Table II.

Independent variables	Symbols	Range and levels				
		-2	-1	0	+1	+2
Solvent/solute ratio (ml/g)	А	0.1	0.2	0.3	0.4	0.5
Extraction Time (Minutes)	В	15	30	45	60	75
Extraction Temperature ($^{\circ}$ C)	С	30	35	40	45	50

TABLE I. RANGE OF INDEPENDENT VARIABLE IN ACTUAL AND CODED FORM

TABLE II. EXPERIMENTAL DESIGN MATRIX FOR EXTRACTION OF OIL FROM WALNUT USING N-HEX	KANE
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Std	A: Solvent/ solute ratio	B: Extraction time	C: Extraction temperature	Oil yield %	Monounsaturated
	mL/g	Minutes	Degree Celsius		acid %
1	0.2	30	35	39	43
2	0.4	30	35	42	53
3	0.2	60	35	43	67
4	0.4	60	35	48	67
5	0.2	30	45	46.7	63
6	0.4	30	45	49	72
7	0.2	60	45	43	65
8	0.4	60	45	48	64
9	0.131821	45	40	40	60
10	0.468179	45	40	47	72
11	0.3	19.7731	40	45	51
12	0.3	70.2269	40	48	66
13	0.3	45	31.591	43	55
14	0.3	45	48.409	49	63
15	0.3	45	40	52	68
16	0.3	45	40	53	71
17	0.3	45	40	52	73
18	0.3	45	40	53	72
19	0.3	45	40	52	67
20	0.3	45	40	52	73

D. Characterization of Oil

The extracted oil from walnut oil was characterized using American Society for Testing Material, (ASTM) for physicochemical properties and instrumentation such as Gas Chromatography-Mass Spectrometer, (GC-MS) and Fourier Transform Infrared Spectrometer, (FTIR) for the functional group and fatty acid profile respectively.

E. Kinetics of Oil Extraction

The analysis and design of an extraction process for industrial scale require a relevant kinetic data. Oil concentration gradient in the solid particle is the drag force involved in the extraction of oil, and this is controlled by diffusion. The kinetics of oil extraction is modeled with mass transfer occurring at the solid-liquid interface where mass flow by diffusion is equivalent to mass flow by convection [13]-[16].

Because extraction is carried out at non-steady state without chemical reactions, mass transfer kinetic model was adopted to study extraction of oil from walnut using n-hexane. The rate of change of oil concentration in the liquid phase (g L-1 min-1) is written as follows:

$$\frac{dC_L}{dt} = k \left(C_{Le} - C_L \right) \tag{3}$$

where C_L and C_{Le} are oil concentrations (g L-1) in the liquid phase at time t (minutes) and at equilibrium, respectively and k is the mass transfer coefficient (min-1). Boundary conditions applied to solve Equation (3) are:

(i) At the start of the extraction (t = 0), the concentration of the oil in the liquid phase is equal to zero $(C_L = 0)$.

(ii) At any time t, the concentration of walnut oil in the liquid phase is $C_L = C_{Le}$.

Integrating Equation (3) using the boundary conditions, gives Equation (4).

$$C_L = C_{Le} (1 - e^{-kt})$$
 (4)

Rewriting Equation (4) in terms of oil yield, (Y_t) , it gives Equation (5).

$$Y_t = Y_{Le} \left(1 - e^{-kt} \right)$$
 (5)

Re-arranging equation (5), gives Equation (6).

$$\ln Y_t = \ln Y_{Le} + kt \tag{6}$$

where Y_{Le} is the oil yield in the liquid phase at equilibrium in relation to the total oil content of the nut at time t = 0.

The oil content of the walnut in the liquid phase at equilibrium and mass transfer coefficient (k) was obtained from the intercept and slope of the plot of $\ln Y_t$ against t respectively.

The Arrhenius equation was used calculated the activation energy:

$$k = Ae^{-\frac{E_a}{RT}} \tag{7}$$

Re-arranging Equation (7) produces Equation (8)

$$\ln k = \ln A - \frac{E_a}{RT} \tag{8}$$

where k is the reaction rate (extraction) constant, A is the Arrhenius constant or frequency factor; Ea is the activation energy; R is the universal gas constant, and T is the absolute temperature. The activation energy and Arrhenius constant, A were determined from the plot of ln k vs 1/T.

III. THERMODYNAMICS OF OIL EXTRACTION

The thermodynamic parameters enthalpy change (ΔH) and entropy change (ΔS) for the oil extraction procedure were estimated using the Van't Hoff and Erying equations:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{9}$$

$$K = \frac{Y_{Le}}{Y_{se}} \tag{10}$$

$$\Delta G = \Delta H - T \Delta S \tag{11}$$

where k = rate constant/mass transfer coefficient, YLe is the average yield percent of oil at temperature T, YSe is percent of oil remaining in the seeds, T = temperature used in the extraction process (K), K is the equilibrium constant of the extraction process, and R is the universal gas constant (8.314 J mol-1 K-1).

The changes in enthalpy and entropy were calculated from the slope and intercept of the plot of $\ln K$ against $\frac{1}{T}$ respectively while ΔG was calculated using Equation (11).

IV. RESULT AND DISCUSSION

A. Model Fitting and Statistical Analysis

The experimental data of the design plan in Table II was used to generate multiple regression equations between the predicted responses (Y_o, Y_{ma}) and process variables and statistically analyze the significance of the models. The regression coefficients and significance analysis of the models for both oil yield and monounsaturated acid are presented in Tables III and IV respectively. From the tables, it is observed that the models for yields of oil and monounsaturated acid are both significant at p < 0.0001. The coefficients of determination (R2) for the models were very high. These show that the models adequately predicted the experimental data as described by Reference [17], who reported that a model is adequate when R2 > 0.75. The inability of a model to predict the experimental data at regions that are not included in the model is measured with lack-of-fit. From Tables III and IV, it is observed that the lack-of-fit for each of the model was insignificant (p > 0.05). Therefore, the quadratic model adequately predicted the data for both oil yield and the yield of monounsaturated acid.

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Source	Coefficient	Sum of	df	Mean	F -	p – value
	Estimate	Squares		Square	Value	Prob > F
Model		370.30	9	41.14	243.61	< 0.0001
Intercept	52.34					
А	1.98	53.67	1	53.67	317.76	< 0.0001
В	0.76	7.84	1	7.84	46.40	< 0.0001
С	1.82	45.00	1	45.00	266.45	< 0.0001
AB	0.59	2.76	1	2.76	16.35	0.0023
AC	-0.087	0.061	1	0.061	0.36	0.5604
BC	-1.84	27.01	1	27.01	159.93	< 0.0001
A^2	-3.14	141.92	1	141.92	840.27	< 0.0001
B^2	-2.08	62.19	1	62.19	368.25	< 0.0001
C^2	-2.25	73.23	1	73.23	433.59	< 0.0001
Residual		1.69	10	0.17		
Lack of Fit		0.36	5	0.071	0.27	0.9134
Pure Error		1.33	5	0.27		
Cor Total		371.99	19			
R^2	0.9955					

TABLE III. COEFFICIENTS AND ANALYSIS OF VARIANCE (ANOVA) FOR THE MODEL FITTING OF OIL YIELD.

TABLE IV. COEFFICIENTS AND ANALYSIS OF VARIANCE (ANOVA) FOR THE MODEL FITTING OF MONOUNSATURATED ACID

Source	Coefficient	Sum of	Df	Mean	F –	p-value
	Estimate	Squares		Square	Value	Prob > F
Model		1224.06	9	136.01	24.42	< 0.0001
Intercept	70.63					
А	2.80	106.75	1	106.75	19.17	0.0014
В	4.19	239.80	1	239.80	43.06	< 0.0001
С	3.47	164.89	1	164.89	29.61	0.0003
AB	-2.50	50.00	1	50.00	8.98	0.0134
AC	-0.25	0.50	1	0.50	0.090	0.7706
BC	-5.50	242.00	1	242.00	43.46	< 0.0001
A ²	-1.41	28.46	1	28.46	5.11	0.0473
B^2	-4.06	237.18	1	237.18	42.59	< 0.0001
C^2	-3.88	216.96	1	216.96	38.96	< 0.0001
Residual		55.69	10	5.57		
Lack of Fit		22.35	5	4.47	0.67	0.6641
Pure Error		33.33	5	6.67		
Cor Total		1279.75	19			
R^2	0.9565					

B. Response Surface Plotting for Oil and Monounsaturated Acid Yields



Figure 1. Interactive effect of solvent/solute ratio and extraction time on oil yield.



Figure 2. Interactive effect of solvent/solute ratio and extraction time on monounsaturated acid yield.

The yields of oil and monounsaturated acid were affected by solvent-to-solid ratio, extraction time and extraction temperature. Their linear effect was positive and significant at p < 0.05, and the interaction between solvent-to-solid ratio and extraction time; extraction time and extraction temperature was negative and significant at p < 0.05 while the interaction of solvent-to-solid ratio and extraction temperature was equally negative but insignificant at p > 0.05. Fig. 1 and Fig. 2 depict the interaction effects of solvent-to-solid ratio and extraction time on the yields of oil and monounsaturated acid respectively. Oil and monounsaturated acid vields had a significant increase with increasing both solvent-to-solid ratio and extraction time, but beyond 45 minutes and 0.3 mL/g, the oil yield decreased while monounsaturated acid remained constant. The decrease in oil yield may be attributed to the reduction of driving force due to the effectiveness of the solvent to extract the oil at short period while the constant value of monounsaturated acid was due to oxidative stability of the oil.

Fig. 3 and Fig. 4 show the interactive effect of extraction time and extraction temperature on both oil yield and monounsaturated acid respectively. Oil and monounsaturated acid yields had a continual increase with increasing both solvent-to-solid ratio and extraction

time, and this may be due to an increase in kinetic energy as well as boosting the effect of temperature on improving the rate of dissolution of oil in the solvent.



Figure 3. Interactive effect of extraction time and extraction temperature on oil yield.



Figure 4. Interactive effect of extraction time and extraction temperature on monounsaturated acid yield.

C. Optimization of the Extraction Process

Response surface methodology (RSM) of the Design Expert was used to optimize the three variables. The optimum conditions in terms of actual values obtained were: solvent/solid ratio of 0.329mL/g, extraction time of 46 minutes and extraction temperature of $42 \, \mathrm{C}$ with optimal yield of oil 53% while solvent/solid ratio of 0.342mL/g, extraction time of 47 minutes and extraction gave temperature of 42 °C optimal yield of monounsaturated acid 72%. The experimental values 52.5% oil and 71.3% monounsaturated acid obtained with their optimal conditions are inconsonant with the values predicted with the technique which suggested that RSM can accurately, reliably, and practically predicts the extraction [11].

D. Characterization of Oil Extracted at Optimal Conditions

1) Physio-chemical properties of the walnut seed oil

Table V depicts some physical and chemical properties of the crude walnut seed oil. The oil contains little quantity of acid and Free Fatty Acid (FFA) values of 7.5mgKOH/g and 3.75% respectively. The oxidation stability of the oil was low and suggests the heavy presence of unsaturated fatty acid in the oil.

TABLE V. PHYSICOCHEMICAL PROPERTIES OF WALNUT OIL

S/N	Physicochemical properties	Walnut seed oil
1	Specific gravity	0.880
2	Acid number (mgKOHg)	7.5
3	Free fatty acid (FFA) (%)	3.75
4	Spanofication value (mgKOH/g)	170

5	Iodine value (gI2/100g)	50.4
6	Kinematic viscosity at 40oC (mm2/s)	7.1
7	Peroxide value	3.5
8	Flash point (°C)	250
9	Cloud point ($^{\circ}$ C)	2
10	Pour point (°C)	13
11	Moisture content (%)	6
12	Refractive index	1.50
13	Oxidation stability 11 °C (Hour)	1.3
14	Molecular weight	867

2) Fatty acid profile of walnut Oil (GC – MS)

The fatty acid composition/profile of walnut seed oil was carried out with the aid of Gas Chromatography-Mass Spectrometry (GC-MS) and depicted in Table VI. From the table, it is observed that walnut oil comprises 6.44% of saturated acids (Lauric Acid, Myristica Acid, Palmitic acid and Arachidic Acid) and 93.76% unsaturated acids (oleic, linoleic linolenic). The dominant monounsaturated fatty acid of the oil was oleic, which accounted for 64.51% of the total fatty acid content. The oleic acid content of the seed is comparatively higher than 7-40% reported for coconut oil, palm oil, cottonseed oil and soya beans oil [18], [19]. This shows that walnut seed oil is highly unsaturated triglycerides (Triolein). The oleic content of the walnut oil obtained in this study is not in agreement with the result obtained by Reference [1]. This could be due to geographical differences. Nevertheless, the monounsaturated fatty acid components of the walnut seed oil contributed to its nutritional value with beneficial physiological effect in the prevention of heart diseases.

TABLE VI. FATTY ACID COMPOSITIONS OF WALNUT SEED OIL

S/N	FFA Profile		Walnut seed oil
	Fatty Acid	Component	Composition (%)
1	Capric acid	C ₁₀	-
2	Lauric acid	C ₁₂	0.003
3	Myristic acid	C ₁₄	0.034
4	Palmitic acid	C _{16:0}	6.21
5	Magaric acid	C ₁₇	-
6	Stearic acid	C _{18:0}	-
7	Oleic acid	C _{18:1}	64.51
8	Linoleic acid	C _{18:2}	26.13
9	Linolenic acid	C _{18:3}	3.12
10	Arachidic acid	C ₂₀	0.200
11	Euric acid	C ₂₁	-
	Total		100.2

3) Fourier transform infra-red spectrum of walnut seed oil

The FTIR spectrum of walnut seed oil is shown in Table VII. This was done to find out the different functional groups present in the feedstock. From the result, discernible peaks of note were recorded. The region 679.61 cm⁻¹ – 886.65 cm⁻¹ shows the presence of =C-H(alkenes) functional groups. They possess bending form of vibrations appearing at low energy and frequency region inside the spectrum, and they are all double bounded. They are attributed to olefinic (alkenes) functional groups and are unsaturated. This confirmed the presence of unsaturated fatty acid in the oil. They could be part of the unsaturated bond in the oil. The characteristics peaks found in the region 1050.15–1297.23cm⁻¹ indicate stretching vibrations of C-O and C-

O-C. They can also show the bending vibration of O-CH₃ in the spectrum [20], [21]. The band region of 1387.88 cm⁻¹ can be ascribed to the bending vibration of C-H methyl groups, while the band at 1631.85cm⁻¹ is ascribed to C=C bending vibrations [22]. The region 1861-2003 cm⁻¹ shows the presence of aromatic combination. Region 2179.68-2281 cm⁻¹ indicates the presence of O-H group stretched in a carboxylic acid. The peaks at 2874.75 cm⁻¹ and 2982.07cm⁻¹ show symmetric and asymmetric

stretching vibrations of C-H alkane groups respectively. The peak at 3160.41 cm⁻¹ is attributed to the stretching vibration of =C-H alkene groups. They are detected above wave number 3000 cm⁻¹ in the spectrum compared to corresponding alkane C-H stretching groups detected below 3000 cm⁻¹. The peak at 3911.89 cm⁻¹ with stretching mode of vibration is attributed to the presence of O-H groups. They are single bounded and at high energy region in the spectrum.

	Group Frequency (cm-1) of	Functional group/Asigment
	extracted oil	
S/N	Raw walnut seed oil	
1	679.61-886.65	=C-H Alkenes of unsaturated fatty acid
2	1050.15-1297.23	C-O, C-O-C stretching vibration, O-
		CH ₃ bending vibration
3	1387.88	C-H methyl groups
4	1631.85	-C=C- bending vibration
5	1861-2003	Aromatic combination
6	2179.68-2281	O-H group stretched in carboxylic acid
7	2874.75-2982.07	Symmetric and asymmetric stretching
		vibrations of C-H alkane groups
8	3000-3160.41	=C-H alkene group, C-H alkane
9	3498.02	-OH stretch of unsaturated fatty acid.
10	3911.89	Double bond $C = C$, primary alcohol –
		OH stretch

TABLE VII. FTIR ANALYSIS OF THE EXTRACTED OIL

E. Kinetics and Thermodynamics

The experimental data were fitted into the first order kinetic model and depicted in Fig. 5 while the kinetic parameters for the extraction of the oil were determined and presented in Table VIII. From the table, it is observed that the experimental data fitted the kinetic model employed at a temperature of 35, 40 and 45 $^{\circ}$ with high coefficients of determination. The extraction rate constant was found to increase as temperature increases. The activation was determined to be 38.59kJ/mol.

TABLE VIII. KINETIC PARAMETERS FOR THE EXTRACTION PROCESS

Temperature (K)	Rate constant, k	\mathbb{R}^2	ΔΕ
	(Min^{-1})		(kJ/mol)
308	0.003	0.96	
313	0.004	0.94	38.59
318	0.005	0.95	

The extraction thermodynamics was determined using Van't Hoff equation and shows in Fig. 6 and Table IX. From Table IX, changes in enthalpy and entropy are positive signifying that the extraction process is endothermic which increased the disorder of the solids-oil-hexane system. Similar results were noted for extraction of other vegetable oils with a different solvent. Reference [23] reported entropy change of 36.73J/mol K and enthalpy change of 12.16kJ/mol. Reference [24] determined enthalpy and entropy changes for olive oil using hexane as 12.91kJ/mol and respectively 59.33J/mol K.

The changes in Gibbs' free energy at various temperatures considered were determined and presented in Table IX. The results gotten showed that the extraction of oil from the walnut is feasible and occurred spontaneously. The values are inconsonant with ΔG for Jatropha oil (-4.93 kJ/mol) at 333K as reported by Reference [24] and close to the range reported for olive cake oil, which was between -4.47kJ/mol and - 6.25kJ/mol for temperatures ranging from 293 to 323K as reported by Reference [25].

TABLE IX. THERMODYNAMIC PARAMETERS FOR THE EXTRACTION $$\operatorname{Process}$

Temperature (K)	ΔH (kJ/mol)	ΔS (kJ/mol.K)	ΔG (kJ/mol)
308			-6.51
313	23.94	98.85	-7.00
318			-7.49



Figure 5. First order kinetic model plot for walnut oil extraction



Figure 6. Plot for the determination of activation energy.



Figure 7. Van't Hoff equation fit to experimental thermodynamic data.

V. CONCLUSION

The optimization, kinetics and thermodynamics of oil extraction with adequate monounsaturated fatty acid from walnut seed using n-hexane were studied. The process parameters have a significant effect on the yields of oil and monounsaturated fatty acid. The optimal conditions obtained were: solvent/solid ratio of 0.329mL/g, extraction time of 46 minutes and extraction temperature of 42 °C with optimal yield of oil 53% while solvent/solid ratio of 0.342mL/g, extraction time of 47 minutes and extraction temperature of 42 °C with optimal yield of monounsaturated acid of 72%. The characterization shows that the oil contains more of unsaturated fatty acid than saturated fatty acid. The kinetic study shows that rate constant increases as temperature increases and the thermodynamics study shows that the enthalpy and entropy are positive with negative Gibbs free energy. This indicates that the extraction of oil is spontaneous and feasible.

REFERENCES

- M. A. Gonabad, M. S. Noghabi, and R. Niazmand, "Evaluation of extraction percentage and physicochemical properties of walnut oil," *Journal of Applied Environmental and Biological Science*, vol. 4, no. 11S, pp. 74–82, 2015.
- [2] G. McGranahan and C. Leslie, Walnuts (Juglans). Acta Hortic, vol. 290, pp. 907-974, 1991.
- [3] X. Jiang and H. K. Lee, "Solvent bar microextraction," *Analytical Chemistry*, vol. 76, pp. 5591 5596, 2004.
- [4] M. Dogan and A. Akgul, "Fatty acid composition of some walnut (Juglans regia L.) cultivars from east Anatolia," *Grasas y Aceites*, vol. 56, pp. 328 – 331, 2005.
- [5] G. L. Gatbonton, A. P. De Jesus, K. M. L. Lorenzo, and M. M. Uy, Soxhlet extraction of Philippine avocado fruit pulp variety 240. Research Congress, De La Salle University Manila March 7 – 9, 2013.
- [6] C. M. D. Luque and F. Priego-Capate, "Solvent extraction: Past and present panacea," *Journal of Chromatography*, vol. 1217, no. 16, pp. 2383-2389, 2010.
- [7] L. Wang and C. L. Weller, "Recent advances in extraction of nutraceuticals from plants," *Trends in Food Science and Technology*, vol. 17, pp. 300–312, 2006.
- [8] F. C. Uzoh and D. O. Onukwuli, "Extraction and characterization of Gmelina seed oil; Kinetics and optimization studies," *Open Journal of Chemical Engineering and Science*, vol. 1, no. 2, pp. 1 –18, 2014.
- [9] J. Azmir, I. S. M. Zaidul, M. M. Rahman, K. M. Sharif, F. Sahena, M. H. A. Jahurul, and A. Mohamed, "Optimization of oil yield of Phaleria macrocarpa seed using response surface methodology and its fatty acids constituents," *Industrial Crops and Products*, vol. 52, pp. 405–412, 2014.

- [10] A. R. Karnopp, A. M. Figueroa, P. R. Los, *et al.*, "Effects of whole-wheat flour and bordeaux grape pomace (Vitis labrusca L.) on the sensory, physicochemical and functional properties of cookies," *Food Science and Technology*, vol. 35, no. 4, pp. 750 – 756, 2015.
- [11] Q. Xu, Y. Shen, H. Wang, N. Zhang, S. Xu, and L. Zhang, "Application of response surface methodology to optimise extraction of flavonoids from fructus sophorae," *Food Chemistry*, vol. 138, no. 4, pp. 2122–2129, 2013.
- [12] B. Sanjay, C. D. Dinesh, and C. D. Dibakar, "Composition of biodiesel from Gmelina arborea seed oil," *Advances in Applied Science Research*, vol. 3, no. 5, pp. 2745 – 2753, 2012.
- [13] I. S. Adeib, I. Norhuda, R. N. Roslina, and M. S. Ruzitah, "Mass transfer and solubility of Hibiscus cannabinus l. seed oil in supercritical carbon dioxide," *Journal of Applied Sciences*, vol. 10, vol. 12, pp. 1140 – 1145, 2010.
- [14] M. Y. Liauw, F. A. Natan, P. Widiyanti, D. Ikasari, N. Indraswati, and F. E. Soetaredjo, "Extraction of neem oil (Azadirachta indica A. Juss) using n-hexane and ethanol: Studies of oil quality, kinetic and thermodynamic," *Journal of Engineering and Applied Sciences*, vol. 3, no. 3, pp. 49 – 54, 2008.
- [15] S. Sulaiman, A. R. A. Aziz, and M. K. Aroua, "Optimization and modeling of extraction of solid coconut waste oil," *Journal of Food Engineering*, vol. 114, no. 2, pp. 228 – 234, 2013.
- [16] B. S. Silmara, A. M. Marcio, L. C. Ana, M. A. P. Rafael, and R. C. J. S. dos, "Kinetics and thermodynamics of oil extraction from Jatropha curcas using ethanol as a solvent," *International Journal of Chemical Engineering*, 2015.
- [17] H. L. Man, S. K. Behera, and H. S. Park, "Optimization of operational parameters for ethanol production from Korean food waste leachate," *International Journal of Environmental Science* and Technology, vol. 7, no. 1, pp. 157–164, 2010.
- [18] A. Singhabhandhu, M. Kurosawa, and T. Tezuka, "Life cycle analysis of biodiesel fuel production: Case study of using used cooking oil as a raw material in Kyoto, Japan," in *Proc. 2nd Joint International Conference on Sustainable Energy and Environment*, Bangkok, 2006.
- [19] U.Rashid, A. Farooq, and K. Gerhard, "Evaluation of biodiesel obtained from Cottonseed oil," *Fuel Processing Technology*, vol. 90, no. 9, pp. 1157–1163, 2009.
- [20] J. Coates, "Interpretation of infrared spectra, a practical approach," *Encyclopedia of Analytical Chemistry*, vol. 12, pp. 10815–10837, 2000.
- [21] I. Y. Mohammed, A. A. Yousif, K. K. Feroz, Y. Suzana, A. Ibraheem, and A. C. Soh, "Comprehensive characterization of napier grass as feedstock for thermochemical conversion," *Energies Journal*, vol. 8, pp. 3403–3417, 2015.
- [22] S. H. Shuit, K. T. Lee, A. H. Kamaruddin, and S. Yusup, "Reactive extraction of Jatropha curcas seed for production of biodiesel: Process optimization study," *Environmental Science* and Technology, vol. 44, no. 11, pp. 4361–4367, 2010.
- [23] H. Topallar and U. Geçgel, "Kinetics and thermodynamics of oil extraction from sunflower seeds in the presence of aqueous acidic hexane solutions," *Turkey Journal of Chemistry*, vol. 24, pp. 247 – 253, 2000.
- [24] S. K. Amin, S. Hawash, G. El Diwani, and S. El Rafei, "Kinetics and thermodynamics of oil extraction from jatropha curcas in aqueous acidic hexane solutions," *Journal of American Science*, vol. 6, pp. 293–300, 2010.
- [25] S. Meziane and H. Kadi, "Kinetics and thermodynamics of oil extraction from olive cake," *Journal of American Oil Chemistry Society*, vol. 85, pp. 391–396, 2008.



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