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KINETICS AND THERMODYNAMICS STUDIES ON OIL EXTRACTION FROM SOUTHERN KADUNA PALM KERNEL SEEDS USING SUBCRITICAL WATER EXTRACTION TECHNOLOGY

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Abstract

Subcritical water has the potential to be highly efficient, non-toxic and low-cost alternative extraction solvent due to unique properties under certain conditions. In this current study, we used the process variables (extraction temperature, time and particle size) to investigate the kinetics of palm kernel oil (PKO)

Keywords: Palm Kernel Oil, Subcritical Water, Oil Extraction, Kinetics, Thermodynamics

extraction using subcritical water as solvent by considering the power law

INTRODUCTION

Oil palm fruit tree (Elaeis guineensis), belongs to the tribe ceroxylimae of the family palmaceae.approximately contains 75-80% oil that can be extracted through several processes or a combination of techniques including mechanical screwsolvent pressing, extraction, and traditional methods [1]. Palm kernel oil (PKO) is a yellowish oil obtained from the kernels of the nuts of palm tree, which is native to tropical regions in Africa (Nigeria, Benin Republic, Congo, Cameroon Angola and Sierra Leone) and Asia (Malaysia and Indonesia) When processed locally, it takes on a dark brown color [3]. The oil is a rich source of fats, with its primary fatty acid being the saturated lauric acid, which makes up 48.20% of the oil [4]. Due to its high content of lauric acid, PKO is sometimes referred to as lauric oil. Other significant fatty acids in the oil include myristic acid (16%) and oleic acid (15%) [5, 6]. In addition to being used as a lubricant or biodiesel in rural areas,

and Elovich's kinetic law models. The laws of thermodynamics were employed to determine the spontaneity and nature of the PKO extraction process by evaluating thermodynamic parameters such as the Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS). The experimental result showed that the conditions for the optimum vield of PKO using subcritical water were established at 0.5 mm, 120 minutes and 493K (200 oC) where the highest oil yield was (49.02%). The experimental data was found to best fit the power

law model compared to the Elovich's model, as a result of its highest R² and lowest SDand RMS values. Thermodynamics analysis showed that **PKO** extraction has positive enthalpy and entropy values of 7.23×10-4kJ/mol and 0.0304kJ/molK respectively, indicating an endothermic and irreversible process. The negative values of Gibbs free energy (- 12.56 to -14.99kJ/molK) indicated that the extraction process spontaneous. Gas chromatography analysis showed that lauric acid (48.1%) appears as the predominant fatty acid in

the extracted oil followed by myristic acid (16.0%) and linoleic acid (14.9%). The subcritical water technology was therefore, highly recommended for the extraction of PKO due to its high potentials as shown in the high oil yield obtained. The power law model was also recommended due to the overall comparative fitness to the experimental data while the thermodynamics specifications as verified in work were this also recommended to be used for process design of PKO extraction.

alm kernel oil is also used in the food processing industry, soap production, cosmetics, pharmaceuticals, and traditional medicine [7].

A significant number of authors have dedicated their research to exploring the

A significant number of authors have dedicated their research to exploring the extraction of oils from seeds of various kinds, as well as conducting investigations into the characterization, kinetics, and thermodynamics of the process. [8] conducted a study on the kinetics and thermodynamics of mango seed oil extraction, which resulted in a 12.15 wt% oil yield, and the oil extraction process was reported to follow first-order kinetics. [9] investigated the extraction and characterization of Moringa oleifera seed based on solvent extraction method and found that Moringa oleifera contained 35 wt% oil. In a separate study, [10, 11] studied the extraction of Gmelina arborea oil and reported an oil yield of 35.1 and 49.90 wt%, respectively. Based on their findings, they both reported that the extraction process follows a second-order rate mechanism.

Numerous studies carried out on various methods of oil extraction from palm kernel seeds [12, 13,14] have mainly concentrated on the determination of oil yield using organic solvents and physicochemical characterization. None of these authors investigated the use of subcritical water extraction technology (SWET) in the extraction of PKO. Different applications of the SWET were reported [15 16, 17,18]. It was reported that relatively large amounts of oil, organic acids, and amino acids could be extracted from oil-containing biomasses, such as fish, squid entrails and meat wastes by subcritical water [19].

Recently, the use of subcritical water as an alternative to organic extraction solvents has gained more interest from many researchers. Subcritical water extraction technology

(SWET) involve the use of water within its boiling point (100°C) and critical point (temperature < 374.15°C, pressure 22.1 < MPa) under enough pressure to maintain the liquid state. Unique properties of water in this state are namely its low dielectric constant, greater diffusion rate, high ionic product, low viscosity and surface tension [20]. These properties make subcritical water more similar to less-polar organic solvent such as methanol and ethanol [21]. Consequently, it is considered as a potential solvent that can be used for the extraction of bioactive compounds or breaking down of biomass in hydrothermal operations [22].

The extraction rate of oil is an important factor considered in the design and development of oil extraction processes and plants. Normally, extraction rate depends on the nature of the solvent and the oil, reaction time between solvent and seeds, temperature of the process, particle size of the meal, and solvent-solid ratio. [23] observed that the oil extraction rate was largely dependent on particle size. [24] reported that oil from cracked particles (grits) of soybeans, cottonseed, flaxseed, and peanuts could be extracted more easily compared to flakes of equivalent thickness. Currently, there is no published work existing on the palm kernel seed oil extraction using subcritical water technology.

In this present work, the optimum conditions for the extraction of oil from palm kernel seed using subcritical water technology as well as the kinetics and thermodynamics of the extraction process were investigated. This new emerging technique for oil extraction utilizes water instead of organic solvents as extraction medium. The data obtained from the experiment conducted were analyzed using known extraction kinetics models which include the Power law model and Elovich's model. Also, the fitness of the selected kinetics models to the experimental data obtained were evaluated and compared using coefficient of determination R^2 , standard deviation SD and root mean square RMS. Lastly, thermodynamics considerations of the PKO extraction process was studied, where thermodynamics parameters such as entropy (Δ S), Gibb free energy (Δ G), and enthalpy (Δ H) were evaluated from thermodynamics laws. Afterward, these thermodynamics parameters were utilized to described the nature of the system and extraction process.

Materials and Methods Materials

The materials used in the experiment include palm kernel seeds, methanol(solvent) with boiling point 64 °C, hexane and distilled water. Also, the following laboratory equipment and apparatus were used in the study: stainless-steel reactor, steam distillation apparatus, heater, water bath, flasks, beakers, sample bottle, digital weighing balance, grinder, Gas Chromatography Mass Spectrometer (GC-MS), thermometer and stop watch.

Sample Preparation

Palm kernel seeds of the variety (Dura, Tenera) have been collected from local palm oil processors in Kaura and Jema'a Local Government areas of Southern Kaduna, Kaduna State, Nigeria. Manual cracking was used to separate the shells from the kernels. Afterward, the kernel seeds were milled using grinding machine then a laboratory test sieved was used to obtained particle size of 2.0 mm. To remove moisture and ensure its

content is reduced to a very low possible level, the milled seeds were dried in an electric oven held at a constant temperature of 110 °C for 45 minutes.

Chemicals and Solvent

All chemicals and solvent used in this study were of analytical grade purchased from Yokel's international company Jos, Plateau state, Nigeria. The solvent used for the experiment was distilled water while methanol was used to obtained the oil content of the palm kernel seeds. Distilled water was purchased from Akamai pure water distillery at Kagoro, Kaura Local Government, Kaduna State, Nigeria.

Experimental method

Determination of oil content of palm kernel seeds

Prior to the experiments, the amount of oil contained in the seeds was measured. Dried palm kernel seeds were used to extract palm kernel oil using methanol. Fifteen grams of grinded palm kernel seeds were extracted with 150ml of methanol. The content was mixed, and heated using a magnetic stirrer hot plate. The extraction was carried out at 55°C for 8 hours. Plastic container was then tightly closed and mixed using a rotating mixing machine, which was put inside an oven and adjusted at 45°C. filtration was then carried out and the extracted oil was recovered by evaporating the solvent. Measurements was repeated twice. The percentage oil yield of palm kernel seeds was estimated as the ratio of the weight of extracted oil to the total weight of the seed sample using equation (1).

$$Y_e = \frac{W_1}{W_0} \times 100 \% \tag{1}$$

Where Y_e is the extraction yield of PKO (%), W_1 is the mass of PKO extracted (g) and W_0 is the mass of the palm kernel seed sample used (g).

Fatty acid composition analysis of PKO

Before the fatty acid determination of PKO oil, the oil was first converted to fatty acid methyl ester (FAMEs) according to the method described by [25]. After changing the oil to FAMEs, the determination of fatty acids was then carried out according to the method described by [26]. 2µL of the petroleum ether aliquots obtained initially from FAMEs analysis was injected into the chromatographic column and peaks were recorded for their respective retention times and areas by the data processor unit of the GC-MS on the Agilent 7890B gas chromatography (GC) directly coupled with the mass spectrometer system (MS) of Agilent 5977 A. The ionization voltage and ion source were set at 72ev and 240°C respectively. The oven temperature of the GC was programmed from 80°C, increased at 15°C/min to 280°C. Helium was used as carrier gas with a flow rate of 1mL/min and the split ratio as 1: 10. the run time of one injection was 55minutes. The analysis was conducted at three injection replications. The FAME peaks were identified by comparing their retention time with certified 37-component FAME Mix reference standards (Supelco, Sigma-Aldrich, USA). The percentage of fatty acid was calculated based on the peak area ratios of a fatty acid species to the total peak area of all the fatty acids [27].

Subcritical water extraction Method

The experimental method for the extraction of oil from the palm kernel seeds made used of water between its boiling (100°C) point and subcritical point (374.15°C) as extraction solvent. The PKO was then extracted according to a method described by [15]. The subcritical water extraction was carried out in stainless steel pipes SUS 316, inner dimensions 1.68 cm×15cm (with a reactor volume of 34 cm³) and Swadgelock caps. The ground palm kernel seeds were charged into the reactor tube, and distilled water was added as an extraction solvent. The reactor was sealed and immersed in an oil heating bath (Thomas Kagaku Co. Ltd.). The extraction was carried out in the range of 140°C-220°C, and the pressure inside the reactor was estimated from the steam table for the subcritical conditions (saturated steam). After the desired reaction time, the reactor was immediately cooled down by immersing it into a cold-water bath. The extraction product was separated into three phases: the oil phase, the aqueous phase (including oil and water), and the solid phase. The three phases were separated through simple centrifugation and vacuum filtration processes. To recover any traces of oil from the aqueous phase, we added hexane to extract any oil that could be emulsified into the water phase. Then, the hexane was evaporated by heating it in a furnace at 60°C. The extracted oil was then weighed and the data was recorded.

Kinetic studies

To investigate the kinetics of PKO extraction via subcritical water extraction technology, the power law model and Elovich's law were used. These models have been studied by a number of researchers [28, 29, 30, 31, 32].

Power law model

The power-law model was employed to determine the rate at which oil in a solid substance dissolves into a solvent. The model equation is represented by equation (2). The variables $Y_t(\%)$ and t represents the dependent and independent variables, respectively.

$$Y_t = k.t^n \tag{2}$$

where Y_t is the oil concentration at time t, t is the extraction time(min), k is the extraction rate constant(min⁻¹), and n is the Power index which must always be <1 when extraction is carried out from plant cells [28]. Equation (2) was linearized to have equation (3) expressed as

$$InY_t = Ink + nInt$$
 (3)

A plot of InY_t against Int gives a slope equivalent to n and intercept as Ink from where k can be calculated.

Elovich's model

The Elovich's model in equation (4) is stated mathematically as a logarithmic relation as shown below

$$q = E_0 + E_1 Int$$
 (4)

where q is extraction yield, E_0 is the initial yield (min⁻¹), E_1 the extraction rate(min⁻¹), and t the extraction time(min). This equation was formulated based on the assumption that the extraction rate decrease exponentially as the extraction time increases.

Statistical analysis

The model that best fit the experimental kinetic data was determined by evaluating the coefficient of determination (R²), standard deviation (SD) and root-mean square error (RMSE) [34,35] using the Sigma Plot version 20.00 (SPSS, Inc., Chicago, IL). Equations (11) to (14) present the formulas for R², RMSE and SD. The higher the value of R², and lower RMSE and SD the better would be the goodness of the model to fit the experimental data [36].

Thermodynamics study of PKO Extraction

The thermodynamic parameters such as entropy (ΔS), enthalpy (ΔH) and Gibbs free energy(ΔG) were evaluated in order to describe the nature of PKO extraction process. The relationship between entropy and enthalpy can be calculated using Van't Hoff Equation (16).

$$In K_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$
 (5)

where: ΔH is Change in enthalpy (kJ/mol), K_e is Equilibrium constant, ΔS is Change in entropy (kJ/mol.K), T is Temperature (K), and R = Gas constant (8.134 J/mol.K)

Equation (5) can be re-written to include Gibb's free energy as shown in equation (6)

In
$$K_e = -\frac{\Delta G}{RT} = \left(-\frac{\Delta H}{R}\right) \frac{1}{T} + \frac{\Delta S}{R}$$
 (6)

The values of K_e was obtained as the ratio of oil yield (Y_e) at temperature, T, to the percentage oil unextracted (Y_u) at the same temperature [33]. It is expressed as

$$K_{\rm e} = \frac{Y_e}{Y_{tt}} \tag{7}$$

Where
$$Y_u$$
 (%) = $\frac{\text{weight of cake after extraction(g)}}{\text{weight of particle (g)}} \times 100$ (8)

A plot of InK_e against $\frac{1}{T}$ gives slope $\frac{\Delta S}{R}$ and intercept $-\frac{\Delta H}{R}$ which were then used to calculate ΔH and ΔS . The Gibbs free energy change was calculated using Equation (21).

$$\Delta G = \Delta H - T \Delta S \tag{9}$$

Results and Discussions

Determination of oil content in the palm kernel seeds

The oil content in the palm kernel seeds used in this study was initially approximated. 15g mass of palm kernel was extracted with 150 ml of methanol as solvent at room temperature. It was found that the oil content represented 54% on dry weight basis of the

grinded palm kernel seeds. The percentage of oil extraction using subcritical water was based on this oil content measured.

Fatty acid composition of palm kernel oil

The composition of fatty acid in the extracted PKO was determine using GC-MS test. The result of the analysis is presented in Table 1.

Table 1: Fatty acid profile of PKO

| FA(%) | $\mathrm{C}_{8.0}$ | $\mathrm{C}_{10.0}$ | $\mathrm{C}_{12.0}$ | $\mathrm{C}_{14.0}$ | $\mathrm{C}_{16.0}$ | $C_{16:1}$ | $\mathrm{C}_{18.0}$ | $C_{18:1}$ | $\mathrm{C}_{18:2}$ | $\mathrm{C}_{18:3}$ | SFA |
|--------|--------------------|---------------------|---------------------|---------------------|---------------------|------------|---------------------|------------|---------------------|---------------------|----------|
| | | | | | | | | | | | MUFA |
| | | | | | | | | | | | PUFA |
| | | | | | | | | | | | |
| PKO(%) | 3.2 | 3.4 | 48.1 | 16.0 | 8.1 | N.D | 2.1 | 14.9 | 2.2 | N.D | 80.9 |
| , | | | | | | | | | | | 140 00 |
| | | | | | | | | | | | 14.9 2.2 |

Values are mean of two measurements (n = 2). FA: Fatty acids, ND= Not detected, SFA: Saturated fatty acid, MUFA: Monounsaturated fatty acids, PUFA: polyunsaturated sfatty acids. $C_{8:0} = \text{caprilic}$; $C_{10:0} = \text{capric}$; $C_{12:0} = \text{lauric}$; $C_{14:0} = \text{myristic}$; $C_{16:0} = \text{palmitic}$; $C_{16:1} = \text{Palmitoleic}$; $C_{18:0} = \text{stearic}$; $C_{18:1} = \text{Oleic}$; $C_{18:2} = \text{linoleic}$; $C_{18:3} = \text{linolenic}$.

Table 2 showed that lauric acid (C12:0) is in abundance in the oil with 48.1% fatty acid content, followed by myristic acid(C14:0), 16.0%, Oleic acid (C18:1), 14.9 and least being stearic acid (C18:0), 2.1%. The most abundant saturated and unsaturated fatty acids present in the extracted PKO in this study were lauric acid(C12:0) 48.1% and oleic acid(C18:1), 14.9% respectively. These results were similar with the findings of the study [37] who reported that lauric acid (41.8%) is the most abundant while the saturated and unsaturated fatty acids were 72.9% and 27.31% respectively. The difference in the values could be due to the geographical location and other factors such as fruit maturity and seed development [38].

Subcritical Water Extraction of PKO

PKO was extracted from 15g of grinded palm kernel seeds using 150 ml of distilled water as extraction solvent to evaluate the efficiency of the solvent on the extraction process. The oil yield was then examined by varying the extraction time; 30, 60, 90, 120, and 150minutes for a particular temperature (140, 160, 180, 200, and 240°C) at a constant particle size of 2.0mm. The result of the temperature variation influence on the oil extraction rate from palm kernel seeds using subcritical water as solvent is presented in Figures 2.

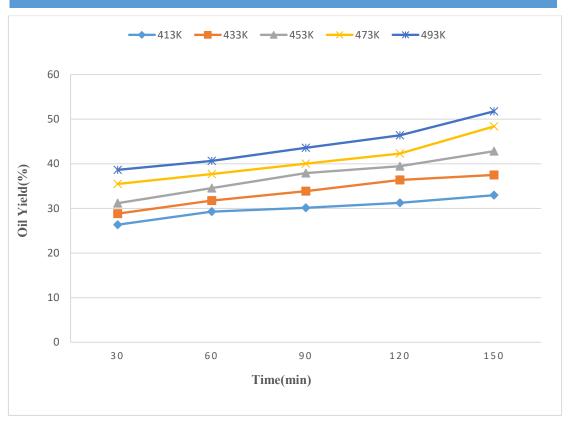


Figure 2: Oil yield versus extraction time at various temperatures

Figure 2 shows the percentage yield of PKO obtained at extraction times of 30 to 150 minutes and temperatures of 140°C(413K) to 220°C(493K). When the PKO was extracted using subcritical water as solvent at a particular temperature, the concentration of the PKO increases rapidly at the beginning, then slowed down with time. Generally, the oil yield increased as extraction time increased. Also, Figure 2 showed that for a given extraction time, the yield of oil increased with increase in temperature. Thus, the oil yield obtained between extraction time of 30 min and 90 min at 413(140°C) ranged between 26.34% and 30.13%. Similarly, at temperatures of 433, 453, 473, and 493K, the yield of oil obtained ranged between 28.82 -33.86%, 31.16 -34.54% and 35.47 -37.68% respectively, at extraction time of 30 to 90 min. The observed increase in oil yield with increase in temperature is as a result of the fact that increase in temperature would result in enhanced extraction mass transfer coefficient, decreased viscosity of oil, and increased diffusion [39,40,41,42]. The effects of temperature and extraction time on the oil yield as recorded in this work agreed with some previous studies on oil extraction from seed and nut of different plant species [43,44]. However, the maximum oil yield recorded (51.74%) after 150 minutes for particle size 0.5mm at temperature 220°C(493K) for PKO extraction using subcritical water, was above the percentages reported by some authors [45, 46]. This is because as the temperature rises, there is a marked and systematic decrease in permittivity, and increase in the diffusion rate and a decrease in the viscosity and surface tension [47]. This suggests that subcritical water extraction must be carried out at the

highest permitted temperature which should be determined experimentally for different plant materials to avoid degradation of certain essential components in the oil [48].

Influence of Particle Size on PKO extraction using SWET

The starting material characteristics like the particle size, generally, influence the oil extraction process, [49,50]. The effect of the mean particle size on the efficiency of subcritical water extraction of PKO was studied at 493K as shown in Figure 3. The mean ground kernel seed particles were 0.5 1.0, 1.5, 2 and 2.5 mm.

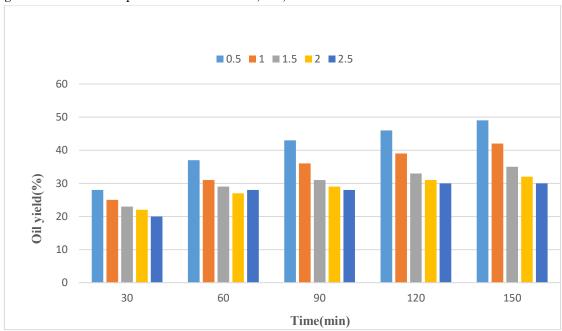


Figure 3: Effect of particle size variation on palm kernel oil yield

Figure 3 presents the particle size effect on palm kernel seeds oil yield. It is clear that at 0.5 mm particle size, maximum oil yield of 49.02% was obtained. The inverse relationship between oil yield and particle size has been attributed to the solid surface area [31]. The smaller the particle sizes, the larger the surface area which leads to easy the penetration of the solvent into the pores of the seed particles. Consequently, diffusion of the solvent into the solid matrix becomes easier due to decrease intra-particle diffusion resistance. On the other hand, diffusion tends to be slower in large particle sizes because of the difficulty of solvent to penetrate the seed particles. Consequently, significant quantity of oil was not extracted from larger particle sizes, especially 2.0 and 2.5mm particle sizes. This was because of minimal contact surface area, as well as limited solvent entrainment into the solute [51]. Therefore, as particle size increases, oil yield decreases and vice versa.

Kinetic Parameters

This work was undertaken to study the kinetics of palm kernel oil extraction using subcritical water technology. In order to explore the kinetics of the mass transfer process in extraction of PKO from palm kernel seeds, the following two mathematical models were analyzed.

Power-law model

The plot of InY_t versus Int (Figure 4) shows that the extraction of PKO can be represented in a linear form according to the power-law model presented in equation (3). From the slope and the intercept of the plot, n, k, and the coefficient of determination, R^2 , were calculated (Table 2).

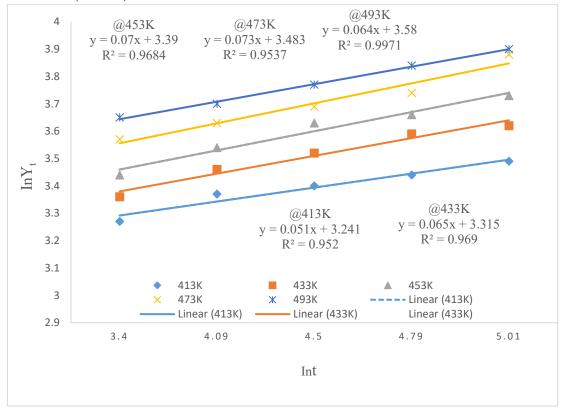


Figure 4: Power law kinetic parameters

Figure 4 shows the variation of temperature on PKO extraction rate. It is evidence that increase in temperature leads to higher PKO yield since higher temperatures leads to faster mass transfer and consequently increases the extraction rate [52, 53]. It was observed that the parameters n and k for the power-law model varied proportionally with increasing temperature.

Table 2: Kinetic parameters of power-law model

| Temperature(K) | Ink (min ⁻¹) | $k(\min^{-1}$ |) n | ${f R^2}$ |
|----------------|--------------------------|---------------|-------|-----------|
| 413 | 3.24 | 25.56 | 0.051 | 0.952 |
| 433 | 3.32 | 27.52 | 0.065 | 0.969 |
| 453 | 3.39 | 29.67 | 0.07 | 0.9684 |
| 473 | 3.48 | 32.56 | 0.073 | 0.9537 |
| 493 | 3.58 | 35.87 | 0.064 | 0.9971 |

Generally, the observed consistent increase of the kinetic parameter values with temperature is attributed to the prevalence and power of diffusion rate above the washing mechanism process, therefore, leads to better/greater oil extraction yield in the models [23, 27]

Elovich's model

The constant E_0 and E_1 in the Elovich's model, were determined by fitting experimental results into equation (4) and then, plotted as shown in Figure 5.

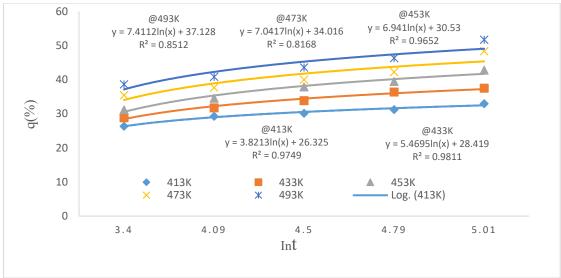


Figure 5: Plot of q vs Int for calculating Elovich's model parameters

From Figure 5, the values of the initial PKO yield (E_0) and the extraction rate (E_1) at various temperatures were obtained as shown in table2. The slope of the graph represents the extraction rate, $E_1(\min^{-1})$ while the intercept is the initial oil yield, E_0 .

Table 3: Elovich's model paramters

| Temperature(K) | E_0 (%) | $E_1(min^{-1})$ | ${f R}^2$ | |
|----------------|-----------|-----------------|-----------|--|
| 413 | 26.325 | 3.8213 | 0.9749 | |
| 433 | 28.419 | 5.4695 | 0.9811 | |
| 453 | 30.54 | 6.941 | 0.9652 | |
| 473 | 34.016 | 7.041 | 0.8168 | |
| 493 | 37.1128 | 7.4112 | 0.8512 | |

The kinetic parameters in table 2 indicated that the values E₀, and E₁ for the Elovich's model varies with temperature, which shows the direct proportionality of temperature to oil yield and extraction rate respectively. This is similar with what was reported by [28] and [54] for Neem and Terminalia catappa L. kernel seeds, respectively.

Comparison of the kinetics models

The model that best fit the experimental data obtained in this study was determined using the values of R^2 , RMS and SD. Figure 2 shows the yield of oil at various time and temperature while Figure 3 is a histogram which shows the yield of oil for different particle sizes. Also, Figure 4 and Figure 5 are kinetic plots comparing the R^2 values obtained for the two models investigated, at 413, 433, 453, 473, and 493K. From Table 2, and Table 3, Power law model presented the maximum average R^2 value. Based on the results obtained from the statistical analysis, Power-law model was selected as the best model for extracting PKO because it has the highest R^2 values and least RMS and SD values at the optimum conditions

Thermodynamics Parameters

The thermodynamics consideration of the PKO extraction using subcritical water was carried out to evaluate the process parameters which were then used to describe the nature of the process. The plots of Ink against $\frac{1}{T}$ was used for the estimation of the thermodynamics parameters.

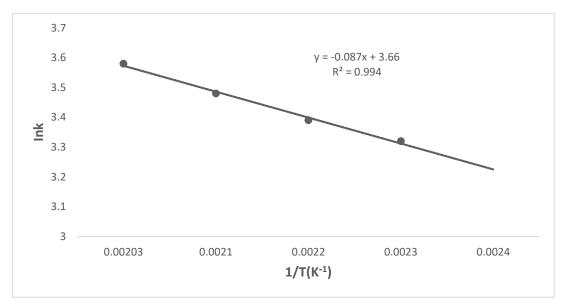


Figure 7: Plot of InK vs $\frac{1}{T}$ (K-1)

The values of ΔH and ΔS were determined from the above plot of Ink against 1/T by comparing the linear equation in Figure 7 with equation (6). Thus, by comparing equation (6) with the equation in the graph and equating the slope with the ratio of enthalpy to the universal gas constant, R, the value of ΔH was obtained as $+7.23 \times 10^{-4} \text{kJ/mol}$ which showed that the extraction process was endothermic, also, from the intercept, a positive entropy value, ΔS was obtained as 0.0304 kJ/mol.K indicating an increase disorderliness of the system and an irreversible process. The results of ΔH and ΔS calculations, were similar to the results found in literature for the extraction of oils from plant seeds/nuts [55, 56]. The differences in the enthalpy values of the seeds can be associated with the

seed morphology [57]. The Gibb's free energy was then evaluated from the values of ΔH and ΔS using equation (9). The result is shown on Table 2.

Table 2: Equilibrium constant and Gibb's free energy

| Temp(K) | 1/T(K ⁻¹) | k | ${ m In} k$ | ΔH ×10-4 | (kJ/mol) | $\Delta S(kJ/mol)$ |
|------------|-----------------------|-------|-------------|-----------------|----------|--------------------|
| ΔG | | | | | | |
| 413 | 0.00242 | 25.53 | 3.24 | 7.24 | 0.030 | -12.56 |
| 433 | 0.00231 | 27.66 | 3.32 | | | -13.16 |
| 453 | 0.00221 | 29.67 | 3.39 | | | -13.77 |
| 473 | 0.00211 | 32.46 | 3.48 | | | -14.37 |
| 493 | 0.00202 | 35.87 | 3.58 | | | -14.99 |

Table 2 clearly show the calculated values for the Gibb's free energy. Gibbs free energy change (ΔG) values recorded for the oil extraction were found to be negative, showing that the process is feasible and spontaneous under the experimental conditions studied. The relatively high negative values of Gibbs free energy change showed that the oil extraction process was highly spontaneous. This is due to the high energy necessary to destroy the solid-liquid interaction [58]

Conclusion

The findings of this research show that process parameters (extraction temperature, time and particle size) affect the yield of palm kernel oil (PKO). High oil yield was obtained for smaller particle size while increase in particle size results in the decrease of oil yield. On the other hand, increasing time of extraction and extraction temperature increases the amount of oil extracted. Therefore, temperature of extraction is directly proportional to yield of PKO, while particles size varies inversely to PKO yield. The conditions for the optimum yield of PKO using subcritical water were recorded at 0.5 mm, 120 minutes and 493K (200 °C) where the highest oil yield was (49.02%). The gas chromatography result shows that PKO contains lauric acid as the major fatty acids. The experimental model that gave the best description of the experimental data out of the two that were investigated was the power law model, due to its closeness to experimentally obtained results. Nonetheless, the two models significantly depicted the kinetics of the process; because they all gave low RMS and SD values and high R2 values. The extraction process can be described as spontaneous (ΔG), endothermic ($\pm \Delta H$) and irreversible ($\pm \Delta S$). This study is limited to kinetic and thermodynamics analysis of oil extraction from Palm kernel seeds using subcritical water extraction technology. Therefore, subcritical water was recommended for solvent extraction of palm kernel oil and other seed/nuts oil due to its high potency as shown in the high oil yield obtained. The power law model was also highly recommended for oil kinetic modeling due to the overall comparative fitness to the experimental data.

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Author Contributions

Confidence, M. K., Abel, A., Ibrahim, A: Writing-original draft, Conceptualization. Methodology, formal analysis. Confidence, M. K., Abel, A., Ibrahim, A: Investigation. Confidence, M. K., Abel, A., Ibrahim, A: Writing—review and editing.

Data availability statement

The data that supported the findings can be made available upon reasonable request.

Conflicts of Interest: The authors declared that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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