Journal of Energy Technology and Environment Vol. 5(2) 2023 pp. 16 - 24 ISSN-2682-583x

NIPES

Journal of Energy Technology and Environment

Journal homepage: www.nipesjournals.org.ng

Characterization, Kinetics, and Thermodynamics Analysis of Palm Kernel Oil Extraction

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Article information

Article History
Received 27 March 2023
Revised 08 May 2023
Accepted 10May 2022
Available online 12 June 2023

Keywords:
Palm kernel, Kinetics, Thermodynamics, Oil extraction, Oil characterization

OpenAIRE
https://doi.org/10.5281/zenodo.8018158

https://nipes.org

Abstract

The inefficiency frequently encountered in oil extractors can be attributed to the insufficient availability of kinetics and thermodynamic data during the design phase. This study examined the kinetics and thermodynamics involved in the extraction of oil from palm kernel seeds. The mass transfer kinetic power model and the laws of thermodynamics were applied to describe the kinetics and the thermodynamics of the oil extraction process, respectively. The physicochemical parameters of the palm kernel oil extracted were determined according to the methods recommended by the Association of Official Analytical Chemists. The results showed that a maximum oil yield of 48.56% was obtained from the dried palm kernels under optimum conditions of 70 °C, a particle size of 2.0 mm, and an extraction duration of 90 min, using 250 ml of n-hexane. The oil extraction process was found to follow second-order kinetics, whose rate constant is dependent on temperature, and the activation energy (Ea) was 54.69 kJ/mol. The thermodynamic parameters of the extraction process were an enthalpy change (ΔH) of 24.94 kJ/mol, an entropy change (ΔS) of 0.08 kJ/mol, and negative values of Gibbs' free energy change (ΔG) at each prevailing temperature value. The results of the thermodynamic study implied that the palm kernel oil extraction process is endothermic and requires a constant supply of energy for effective and efficient extraction. Also, the physicochemical properties of the oil showed that it is edible and also suitable for use in soap production, pharmaceutical industries, and as a feedstock in the production of biodiesel.

1. Introduction

The need for oil has resulted in a comprehensive analysis of various oils [1]. Vegetable seed oils play a crucial role in the production of items such as soaps, paints, varnishes, lacquers, lubricants, hydraulic fluids, printing inks, dyes, pesticides, and insecticides [2 - 4]. The growing expense and insecurity of petroleum products have prompted the use of vegetable oil as a replacement fuel and in biodiesel manufacturing, thus resolving the energy shortage issue [5]. According to data obtained from Statista [6], the global output of vegetable oil has continuously increased from around 90.5 million metric tons in the year 2000/2001 to 207.5 million metric tons in 2019/2020, and a similar upward trend is forecast to continue in the future.
The palm kernel seed, which comes from the oil palm fruit tree (*Elaeis guineensis*), contains roughly 75-80% oil that can be extracted through several processes or a combination of techniques including mechanical screw-pressing, solvent extraction, and traditional methods. However, the mechanical

screw-press method is considered the most effective, as it can extract all available drops of oil, while the solvent extraction method is the next best option [7].
Palm kernel oil is a yellowish oil obtained from the kernels of the nuts of the palm tree (*Elaeis guineensis*), which is native to tropical regions in Africa and Asia. When processed locally, it takes on a dark brown color. 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 [8]. Due to its high content of lauric acid, palm kernel oil is sometimes referred to as lauric oil. Other significant fatty acids in the oil include myristic acid (16%) and oleic acid (15%) [9, 10]. In addition to being used as a lubricant or biodiesel in rural areas, palm kernel oil is also used in the food processing industry, soap production, cosmetics, pharmaceuticals, and traditional medicine [11].
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. For example, Osagiede et al. [12] 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. Orhevba et al. [13] 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, Ochi et al. [14] and Uzoh et al. [15] studied the extraction of *Gmelina arborea* oil and reported an oil yield of 52.60 and 49.90 wt%, respectively. Based on their findings, Uzoh et al. [2] reported that the extraction process follows a second-order rate mechanism.
The inadequate information regarding the kinetics data of extractors for seed oil extraction can result in suboptimal performance. To improve the design of efficient extractors for palm kernel seed oil extraction, it is crucial to conduct a study that generates kinetic and thermodynamic data. This data is essential in the design process and can significantly contribute to improving the performance of the extractors. This work is, therefore, aimed at investigating the kinetics and thermodynamics of oil extraction from palm kernel seeds using the solvent extraction method.

2. Materials and Methods

2.1. Material Collection and Preparation

The palm kernel nuts were collected from Nigeria Institute for oil palm Research (NIFOR), Benin city, Edo state, Nigeria. They were of Dura and Tenera varieties with thin and thicker mesocarps respectively. They were then cracked to separate the shells from the kernels. Afterward, a manual grinding machine was utilized to grind the kernels and the ground kernel was made to pass through a laboratory test sieve to obtain particles size of 2.0 mm [16]. To decrease the moisture content to the minimum level possible, the ground seeds were dried in an electric oven held at a constant temperature of 105 °C for 2 hours.

2.2 Methods

The palm kernel oil was extracted from its kernels using the solvent extraction method, which involved the use of a Soxhlet extractor and n-hexane as the solvent. To investigate the kinetics and thermodynamics of the extraction process, a total of 15 experimental runs were conducted. The extraction time was varied from 30 to 90 minutes, with 15-minute intervals, while keeping the volume of solvent and particle size constant at 250 ml and 2.0 mm, respectively, for each run. The extraction temperature was also varied from 50 °C to 70 °C, with 10 °C intervals, while maintaining the volume of solvent and particle size constant. In all 15 runs, a fixed weight of 100 g of ground palm kernel was used, and the percentage oil yield was calculated using Equation 1.

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

Where: Y = yield of the oil (%), W_o = weight of pure oil extracted (g), and W_s = weight of the seed sample (g).

2.3 Characterization of the extracted palm kernel oil

The physicochemical characteristics of the extracted palm kernel oil were evaluated, which included its specific gravity, oil content, refractive index, density, viscosity, moisture content, peroxide, iodine and acid values, free fatty acid content, saponification value, and ester value. These properties were measured using techniques specified by the standard association of official analytical chemists (AOAC, 1990).

2.4 Kinetic Modelling

The kinetics of the oil extraction process was investigated using the mass transfer kinetic power model shown in Equation 2.

$$\frac{dY}{dt} = kY^n \qquad 2$$

Where: t = extraction time (minutes); k = rate constant for the extraction, n = the extraction order, and $\frac{dY}{dt}$ = rate of change of oil yield (Y) with respect to time (t).

Equation 2 is then linearized to produce Equation 3.

$$\ln\left(\frac{dY}{dt}\right) = n\ln Y + \ln k \qquad 3$$

$\ln\left(\frac{dY}{dt}\right)$ was plotted against ln Y and the values of n and k were obtained from slope and intercept, respectively [17].

2.5 Thermodynamics Studies

The thermodynamic parameters of the process of oil extraction from palm kernel were determined using the Arrhenius equation which establishes the relationship between the rate constant (k) and temperature (T) as shown in Equation 4. The Arrhenius equation was then linearized to produce Equation 5, which was used to determine the activation energy and Arrhenius's constant. The changes in enthalpy (ΔH) and Entropy (ΔS) were determined using Equation 6 while Equation 7 was used to determine Gibb's free energy change (ΔG) at various temperatures [18].

$$k = Ae^{\left[\frac{-E_a}{RT}\right]} \qquad 4$$

$$\ln k = \left(\frac{-Ea}{R}\right)\frac{1}{T} + \ln A \qquad 5$$

$$\ln k = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad 6$$

$$\Delta G = \Delta H - T\Delta S \qquad 7$$

where k = extraction rate constant, A = Arrhenius's constant (frequency factor); E_a = Activation energy; R= Universal gas constant; T = absolute Temperature.

3. Results and discussion

The results of the study showed that the palm kernel seeds contained 49.02% oil by mass, as determined through exhaustive extraction (repeated extraction of the same sample until all oil was extracted). However, a one-step extraction process using 250 ml of n-hexane and 100 g of 2.0 mm palm kernel seed particles at 70 °C for 90 minutes resulted in a maximum oil yield of 48.56%. In a similar study, Ibiam and Anosike [19] reported a maximum oil content of 47.5 wt% in the oil extraction from dura species of palm kernel, which is close to the value reported in this work.

However, in another study, a yield of 75-80% was reported in the extraction of oil from palm kernel oil [20]. The wide discrepancy observed may be attributed to the difference in the mode of extraction and the species of palm fruit used, which unfortunately were not specified in the study [19, 21].

3.1. Physicochemical properties of the palm kernel oil

The physicochemical properties of the extracted palm kernel oil are presented in Table 1. The specific gravity of the oil was found to be 0.901 and this value is comparable to those of other oils such as shea butter oil (0.920) and rubber seed oil (0.92) [22]. The specific gravity (0.901), obtained is close to those obtained for PKO by Ibiam et al. [19] and Olaniyi et al [23], which were 0.910 and 0.904, respectively.

Table 1: Physicochemical properties of the palm kernel oil

Property	Value
Specific gravity	0.9014
Refractive index	1.409
Oil content (%)	49.02
Viscosity of the oil at 35 ^{o}C (cP or mpa-s)	29.3
Moisture content of the oil (wt%)	0.91
Odour	Not offensive
Colour	Brown
Peroxide value (Meq/kg)	5.988
Acid value (mg KOH/g)	5.11
Free fatty acid (%)	2.555
Saponification value	240.43
Saponification value (mg KOH)	240.43
Iodine value (gI_2 /100g)	13.106
Ester value (mg KOH/g)	235.32

The refractive index measures the extent to which a light ray is bent as it passes from air into the oil, and its measurement is typically influenced by the oil's density. The refractive index of the oil was determined to be 1.409. This result can be compared with the refractive indices of other oils, such as coconut oil (1.449) and groundnut oil (1.47) [23], and fluted pumpkin seed oil (1.476) [16]. Furthermore, the value of 1.409 was found to be comparable to the 1.412 refractive index obtained for PKO [23].

The extracted palm kernel oil had a brown color and a non-offensive odor. The moisture content of the PKO obtained in this study was 0.91%, which was slightly higher than the 0.89% obtained by Ibiam and Anosike [19], but much lower than the values found in red palm oil (5%) and other vegetable oils such as cashew nut oil (8%), shea butter oil (10%), and rubber seed oil (8.60%) [20]. Low moisture content indicates a longer shelf life for the oil. The effectiveness of the distillation apparatus used to recover the oil might have contributed to the low moisture content [24].

The viscosity value of 29.3 cP that was determined in this study is an indication of the oil's resistance to shear stress. This value is higher than the values obtained for most other oils, except for fluted pumpkin seed oil (119 cP) as reported by Nwabanne [16]. For instance, the viscosity values for rubber seed oil (10.32 cP), castor oil (13.02 cP), and shear butter oil (17.78 cP) were lower than the value obtained in this study.

The peroxide value determined in this study was 5.988 meq/kg. This value is higher than the peroxide value of sesame seed oil (0.34 meq/kg) reported by Adeyemi et al. [25]. However, it is lower than the peroxide values for soybean oil (10 meq/kg) and sunflower oil (10 meq/kg) reported by Ebewele et al. [26], and shea butter oil (7.41 meq/kg) reported by Adeyemi et al. [25]. The peroxide value is a measure of the degree of deterioration of vegetable oils, where lower values indicate fresher oils and higher values suggest greater rancidity [27].

The iodine value of 13.106 gI_2/100g obtained was lower than those of other oils such as fluted pumpkin seed oil (123.83gI2/100g), rubber seed oil (142.45 gI_2/100g), soyabean oil ($1_2$4-139 gI_2/100g) and sunflower oil (110-144 gI_2/100g) [16, 26]. The lower iodine value (13.106 gI_2/100g) observed, was an indication of a low degree of unsaturation of the palm kernel oil. The iodine value measures the degree of unsaturation of a particular vegetable oil. The palm kernel oil extracted in this study was in good condition.

The saponification value is a measure of the weight of alkalis required to saponify a fixed amount of oil. The saponification value obtained in this study was 240.43 mg KOH/g, which falls within the range of 230-254 mg KOH/g recommended by the Codex Alimentarius Commission [28]. The saponification value for PKO obtained in this study is similar to that of other oils such as coconut oil (257.5 mg KOH/g) and rubber seed oil (226.02 mg KOH/g) [23, 26]. This high saponification value of 240.43 mg KOH/g suggests that palm kernel oil has the potential for use in the industry and is suitable for soap production [29]. Additionally, it may be used for producing other cosmetic products, such as shampoo.

The acid value is the amount of free fatty acid present in fat as measured by the milligrams of potassium hydroxide needed to neutralize it. The lower the acid value of oil, the fewer the free fatty acids it contains, and vice versa [24]. The acid value of an oil may be used as a measure of quality. However, the acid value of the oil must not be too high, as this denotes an excessively high content of free fatty acids, which causes the oil to turn sour and may also lead to discoloration of the oil. The acid value obtained in this study for palm kernel oil was 5.11 mg KOH/g while the FFA was 2.55%. The acid value of 5.11 mg KOH/g obtained in this study was close to that obtained for coconut oil which was (5.5±0.5 mg KOH/g) (Olaniyi, Babalola and Mary, 2014), but was lower than those obtained for groundnut oil (9.0±0.5 mg/KOH/g), castor seed oil (14.8 mg KOH/g) and rubber seed oil (37.96 mg KOH/g) [23, 24, 26]. A low acidic value implies rather stable oil at the extraction temperature.

Ester value is the number of milligrams of potassium hydroxide (KOH) required to saponify the esters in 1 g of a sample. It is the difference between the saponification value and the acid value. The ester value of 235.32 mg KOH/g obtained was lower than that of coconut oil (252 mg KOH/g) but was higher than that of groundnut oil (182.5 mg KOH/g), rubber seed oil (191.93 mg KOH/g), shea butter oil (183.4) and castor seed oil (163.2) [20, 22, 23, 30]. The high ester value of the PKO 235.32 mg KOH/g) obtained in this study indicates the presence of a high amount of ester and low molecular weight fatty acid content.

3.2. Kinetics and Thermodynamics Study

The results of the 15 experimental runs that were conducted to investigate the kinetics and thermodynamics of palm kernel oil extraction are presented in Table 2. The experiments were conducted at different temperatures and times, while maintaining a constant particle size of 2.0 mm, solvent volume of 250 ml, and sample weight of 100g.

Table 2: Experimental oil yield at various temperatures and time

Extraction time (min)	Oil yield, Y (%)		
	323 K	333 K	343 K
30	25.46	28.66	31.8
45	27.92	31.69	34.78
60	30.66	35.73	38.75
75	34.43	40.51	43.48
90	39.51	46.61	48.56

The linearized form of the nth power model given by Equation (3) was used to obtain a linear plot of $\ln\left(\frac{dY}{dt}\right)$ versus lnY. Second-order kinetics was obtained from the slope of the straight lines. The extraction rate constants (k) were also determined from the intercepts of the plots as shown in Figure 1, with an average R^2 value of 0.9894, and the values are shown in Table 3.

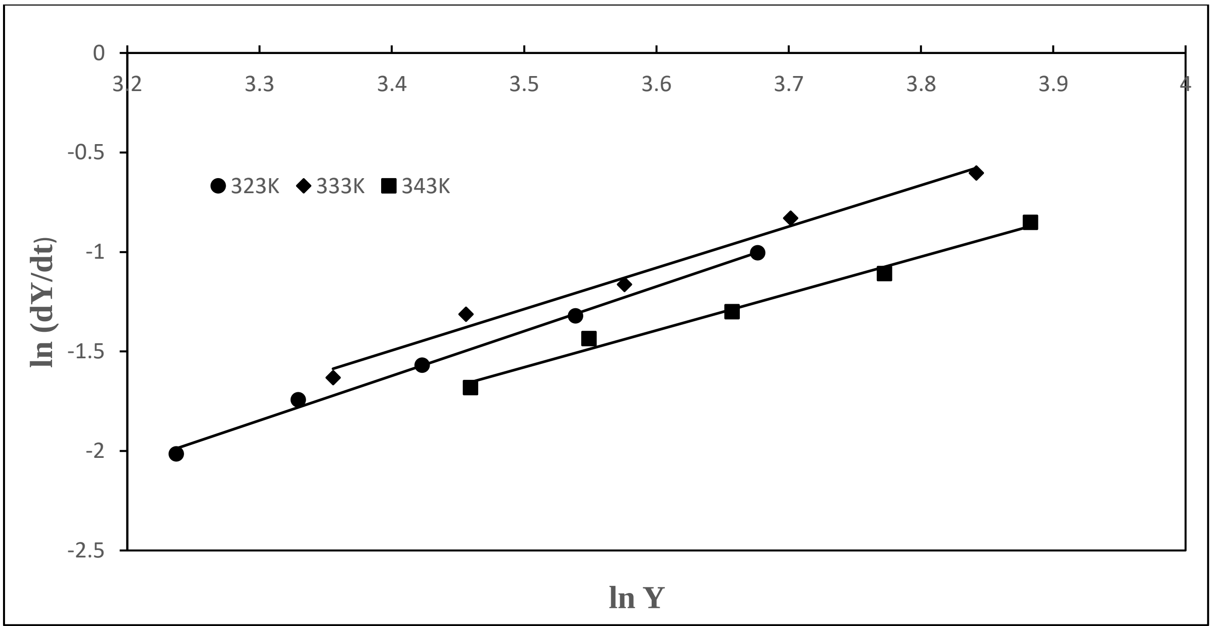

Figure 1: Plots of ln (dY/dt) Versus ln (Y) at 323, 333, and 343 K

Table 3: Estimated values of n and k at various temperatures

S/N	Temperature (K)	Slope(n)	Intercept (ln k)	k (min^{-1})	R^2
1	323	2.2429	-9.2481	0.00009629	0.9962
2	333	2.0747	-8.5486	0.00019382	0.9851
3	343	1.8522	-8.0622	0.00031523	0.9869

From the plot of ln k against 1/T shown in Figure 2, the activation energy (Ea), Arrhenius' constant (A), and thermodynamic parameters (ΔH and ΔS) of the extraction process were determined from the slope and intercept using Equations 5 and 6. The result is presented in Table 4. The Gibbs' free energy change ΔG of the extraction process, at each temperature value, was also calculated from Equation (7), and the results are shown in Table 5.

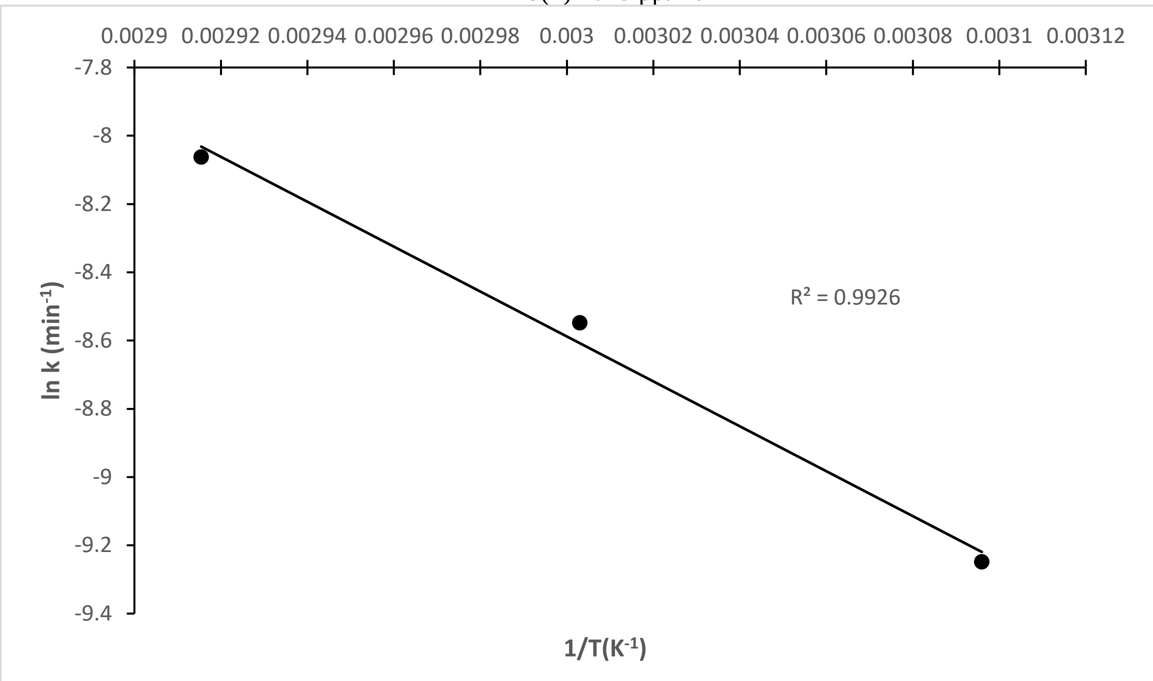

Figure 2: A Plot of ln k Versus 1/T for palm kernel oil extraction

Table 4: Comparison of thermodynamic parameters

Reference	ΔH (kJ/mol)	ΔS (kJ/mol.K)
This study	24.94	0.08
Osagiede et al. [12]	32.78	0.108
Nwabanne [16]	78.84	0.234
Liauw et al. [31]	25.33	0.09

Table 5: Estimated values of change in Gibb's free energy at various temperatures

Temperature. (K)	323	333	343
ΔG (kJ/mol)	-0.90	-1.70	-2.50

The activation energy and the frequency factor for the palm kernel oil extraction process were found to be 54.69 kJ/mol and 6.96×10^4 min^{-1}. The values of the thermodynamic parameters obtained in this study in comparison with those reported in the literature are shown in Table 4. It can be seen from Table 4 that the values of ΔH and ΔS obtained in this study compare favorably with the results reported by Liauw et al. [31] in the study of the extraction of neem seed oil using n-hexane. Also, the values of ΔH and ΔS in this study are lower than those reported by Osagiede et al. [12] for the extraction of oil from mango seed, Nwabanne [16] for the extraction of oil from fluted pumpkin seed, and Liauw et al. [31] for the extraction of oil from neem seed. The lower values of the thermodynamic parameters obtained in this study suggest that the extraction of palm kernel oil is an energy-efficient process that requires less energy input when compared to the extraction of oil from seeds such as mango seed, fluted pumpkin, and neem seed. The negative values of Gibb's free energy shown in Table 5 indicate there is a decrease in the free energy with an increase in temperature. This observation suggests that the extraction process is spontaneous, which is consistent with earlier studies [17, 18, 31, 32]. This also suggests that the process is thermodynamically viable.

4. Conclusion

The present study has demonstrated that palm kernel seeds are oil-rich, containing approximately 49.02% total oil content, and thus hold promise as a commercially valuable source of vegetable oil. The oil yield from the extraction of palm kernel oil using n-hexane as solvent is affected by operating conditions such as temperature and time under constant particle size and volume of solvent. The palm kernel oil possesses desirable qualities that render it appropriate for various applications, including pharmaceuticals, soap production, margarine production, and consumption. The low iodine value, indicating a low degree of unsaturation, as observed in this study, makes it feasible to store the palm kernel oil in a plastic container for an extended period without the risk of rancidity. Furthermore, the evaluation of kinetic and thermodynamic parameters revealed that the extraction data of palm kernel oil were suitably described by a second-order kinetics model, where the rate constant was significantly influenced by the extraction temperature. The positive value of entropy implies that the extraction process is characterized by randomness, whereas the positive value of enthalpy and the negative value of the Gibbs free energy change indicate that the extraction process is endothermic and spontaneous, respectively

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