Research article

Oil produced from Ghana Shea Nut crop for prospective industrial applications

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ABSTRACT

Though little research has been done, shea nut oil (Shea Butter), is a promising shea product with great potential for use in industrial shea product manufacture. To assess the oil obtained from the shea nuts for personal, commercial, and industrial use, this study focuses on the extraction process, the optimal solvent for extraction, thermodynamics and kinetic studies, and characterization of the oil. Using different solvents as well as extraction temperatures and times, the oil was extracted using the solvent extraction method. Moreover, models of thermodynamics and kinetics were used in examining the Shea nut oil extraction at different durations and temperatures. At the highest temperature of 333 K (at 130min), the highest oil yields of 70.2 % and 59.9 % for n-hexane and petroleum ether, respectively, were obtained, following first order kinetics. For both petroleum ether and n-hexane, the regression coefficient (R^2) was 1. For the extraction with n-hexane and petroleum ether, the mass transfer coefficient (K_m), activation energy (Ea), entropy change (ΔS), enthalpy change (ΔH), and Gibb's free energy (ΔG) were, respectively, (0.0098 ± 0.0061 and 0.0123 ± 0.0084) min^{-1}, 74.59 kJ mol^{-1} and 88.65 kJ mol^{-1}, (−236.15 ± 0.16 and −235.63 ± 0.17) J/mol K, (71.88 ± 0.06 and 85.94 ± 0.06) kJ/mol, and (148.75 ± 1.52 and 162.46 ± 1.52) kJ/mol. These values favor an irreversible, forward, endothermic, and spontaneous process. Gas chromatography analysis was used to identify the principal fatty acids in the oil, which include stearic acid (52 %), oleic acid (30 %), and linoleic acid (3 %), as well as various minor fatty acids. The oil's potential bonds and functional groups were identified using Fourier Transform Infrared analysis, and the physicochemical parameters such as the iodine value, peroxide value, acid and free fatty acid values were found to be within acceptable ranges for use in domestic, commercial, and industrial settings.

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1. Introduction

The Shea nut tree (Vitallaria Paradoxa) belongs to the family Sapotaceae, and its seeds are known as shea nuts [1–3]. Kenya, Senegal, Nigeria, Cote d'Ivoire, Cameroon, Burkina Faso, Mali, Togo, Sudan, Ghana, Benin, Niger, Uganda, Central African Republic, Chad, Guinea Bissau, and South Africa are among the roughly nineteen Sub-Saharan African nations, and other western and eastern African countries that have been least exploited, are home to this species, which is one of the most common and prevalent [4,5]. Shea nuts are usually processed and used for Shea butter extraction which have wide applications in the cosmetic, pharmaceutical and food industries [6–8]. It is used as cocoa butter equivalent (CBE) and enhancer in chocolate manufacturing, providing greater stability and extended shelf life [6,9]. Shea butter is an excellent choice for cooking oil, cosmetics, margarine, soaps, and candles because of its low level of cholesterol and high nutritional value [6,10–12].

Processed Shea kernel oil is typically liquefied at high temperatures in the industry, which makes it easy to use and suitable for industrial applications. However, the processed Shea kernel oil quickly solidifies at room temperature as a result of higher level of saturated fatty acid content in various Shea nuts which varies with geographical locations [11], which limits their applications in many industries. In order to maintain this state, the Shea kernel oil requires heating at elevated temperatures to avoid solidifying over a given processing duration. Therefore, a comprehensive study of the process of extracting oil from Shea kernels is essential to progress the large-scale processing of Shea kernel oil for commercial uses.

Also, much research has not been done to investigate the type of solvent best suitable for the large-scale extraction of the oil from the Shea kernels. Research conducted by Karl (1981) to determine the optimal solvent for extracting oil from Shea kernels using n–hexane, petroleum ether, chloroform, water and benzene. Extraction with n-hexane gave the maximum amount of oil from the Shea kernels. Therefore, n-hexane and petroleum ether were used in this study to extract the oil from the Shea kernels, and the kinetic and thermodynamic processes involved in the extraction were studied to determine the best solvent for the extraction.

Several methods for Shea kernel oil extraction have been reported in literature including solvent extraction, enzymatic extraction, mechanical method and others. However, solvent extraction method was employed in this study because of its ease of use, high efficiency, high degree of solvent recovery, quick process of extraction, safe operation, easy integration into industrial plants, and ability to control the duration and extraction temperatures to produce oil of high quality while studying the kinetics and thermodynamic processes of the oil extraction [13].

Therefore, this study was to extract and characterise oil derived from the Ghana Shea Nut crop. A solvent extraction method was applied for the extraction of the oil at different extraction temperatures and times. Kinetic and thermodynamic models were employed to the experimental data after the extraction was conducted at various temperatures. Moreover, the physicochemical properties of the oil were determined by measuring the oil's iodine value (IV), peroxide value (PV), and free fatty acid (FFA). The fatty acid composition and oxidative stability of the Shea Nut oil were characterised by gas chromatography (GC) and Fourier transform infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Materials and equipment

Well-processed Shea nut kernels, petroleum ether and n-hexane as extraction solvents, and distilled water were the materials used in this experiment. For this study, the reflux setup was employed. Equipment used in this study include the reflux apparatus, a water bath, a retort stand and clamp, glass beakers, containers, extraction thimbles, stopwatch, a thermometer, a condenser, cotton wool, and a calibrated hotplate with magnetic stirrer. Analytical grade reagents were all that were used in the characterization.

2.2. Sample preparation

Fresh, raw Shea kernels from a producer of Shea butter in the upper east region of Ghana were used for this study. The supplier stated that the Shea kernels were kept under ideal storage condition and that they had undergone sufficient pre-treatment to eliminate undesirable elements. In order to protect them from moisture and insects, the Shea kernels that were provided were thoroughly dried and sealed in sterile bags. For the extraction process, the Shea kernels were milled into powdered form to achieve a suitable mesh size of 2.0 μm and sealed in airtight polythene bags.

2.3. Solvent extraction

The reflux method was used for the experiment. A 250 ml flat bottom flask was mounted on a calibrated hotplate. 100 ml of the solvent was measured into the flask and heated to the desired temperature with a condenser fitted to condense the evaporating vapor back to the liquid. The extraction temperatures were; 45 °C, 50 °C, 55 °C and 60 °C and a time range of 50–130 min at interval of 20 min. The weight (g) to volume (ml) ratio was 1:10 for all extractions as employed by [13]. For the first extraction, 45 °C was the extraction temperature for 50 min. To control the temperature during the extraction, a calibrated hotplate was used for the heating and the temperature of the mixture was regularly monitored from time to time to ensure that it was maintained at the 45 °C extraction temperature. The mixture was then poured into a cellulose thimble to separate the extract from the residue by filtration. This procedure was repeated for time (70, 90, 110 and 130) minutes and for the temperatures 50 °C, 55 °C and 60 °C for both n-hexane and petroleum

ether extractions. The rotary evaporator was used to recover the solvent and the oil obtained was further dried in an oven at 70 °C for an hour to further remove residual solvent present in the oil before it was subjected to physicochemical analysis and characterization.

2.4. Kinetics and thermodynamics

For each extraction temperature (45, 50, 55 and 60 °C), the extraction procedure was repeated five times for the various time intervals of (50, 70, 90, 110 and 130 min) for the two solvents. The oil extraction yield data obtained from the extractions was then used for investigating the extraction kinetics, thermodynamics as well as mass transfer.

2.5. FTIR analysis

BRUKER ALPHA FTIR spectrometer fitted with platinum attenuated total reflectance (ATR FTIR, BRUKER, KARLSRUHE, GERMANY) was used to capture the FTIR spectra of Shea kernel oil, under conventional laboratory conditions. The analysis was carried out at the KNUST Central Laboratory in Kumasi, Ghana. All the equipment were thoroughly cleaned in between the samples and the background scans (4000–400 cm^{-1}). All FTIR spectra (32 scans: 4 cm resolution) were collected using the OPUS software (BRUKER, KARLSRUHE, GERMANY).

2.6. Physicochemical analysis

Free fatty acids (FFA) in the Shea kernel oils were identified and reported as percentages using the ISO 660:2009 protocol followed by [13]. The AOCS technique [14] was followed in the analysis of the iodine value (IV) in which the various iodine values were presented as Iodine (grams) per 100 g of oil. Peroxide value (PV) was determined by titration and the values were expressed as meq Kg^{-1}.

2.7. FAMEs analysis with gas chromatography

The fatty acid analysis of the Shea kernel oil was examined following the protocol used by [13], on oil extraction from cocoa beans. The preparation of Fatty acid methyl esters (FAMEs) was carried out using nonadecanoic acid methyl ester (Sigma Aldrich Chemical Co., Missouri, USA) in accordance with the European Method EN14103:2011 [15].

2.8. Statistical analysis

In this study, each sample was performed at least twice, and the mean values were presented. The mean of triplicate measurements was presented with their standard deviations in the tables. All statistical data were analyzed with Origin Pro, (version 2021, Northampton, MA, USA). The one-way analysis of variance (ANOVA) was performed to detect any variance with the obtained data. The significant difference was evaluated by the P-values ($P < 0.05$), at 95 %, confidence level (95 %, CL).

3. Results and discussion

The two most crucial operating parameters for the majority of companies when processing Shea kernels are temperature and processing duration. The quality, yield, physicochemical and chemical properties, oxidative and thermal stability of the oil that is extracted are all influenced by these operational parameters. In order to keep track of how different temperatures and processing durations affect the extraction process and the amount of oil extracted, kinetic as well as thermodynamic parameters controlling the extraction were studied. Also, two non-polar solvents (n-hexane and petroleum ether) were used to extract the oil under the same

Table 1
Yield of Shea Kernel Oil at different times and temperatures.

Oil Yield at Different Temperatures and Times Using n-Hexane				
Time (min)	318 K	323 K	328 K	333 K
50	44.5	45.8	47.5	53.7
70	47.7	48.2	52.0	60.5
90	50.05	52.5	57.6	64.95
110	52.1	54.5	59.8	67.97
130	55.3	56.4	62.1	70.20
Oil Yield at Different Temperatures and Times Using Petroleum Ether				
50	17.2	19.4	24.05	32.1
70	21.5	24.7	30.55	38.0
90	25.5	27.6	37.95	48.95
110	31.05	33.0	44.25	55.1
130	34.5	37.5	51.05	59.95

extraction conditions. The purpose of this was to evaluate the solvent that is more efficient in extracting the oil from the powdered kernels under the same extraction conditions (temperature and time). Nonpolar solvents are commonly used in oil extraction because they can dissolve nonpolar compounds like fats, oils, and lipids [16]. This was also done to examine the effect of the solvents on the physicochemical properties of the oil as reported in literature. Previous research studies reported that the solubility of certain fatty acids present in the oil varies with the type of solvent used for the extraction. Thus, some nonpolar solvents have a higher affinity for certain fatty acids in the oil than others [17]. The choice of the two selected non-polar solvents was based on previous research works which reported that the selected solvents gave higher yields of the oil and have significant effect on the oil physicochemical properties compared to other solvents [18]. Additionally, these solvents can easily be recovered due to their high volatility [19].

3.1. Shea kernel oil extraction kinetics

Table 1 present the percentage yield (%) of shea kernel oil obtained using petroleum ether and n-hexane at different extraction durations and temperatures. Study on Shea kernel oil extraction was done at 45, 50, 55, and 60 °C within a time stretch of 50–130 min, at 20-min intervals. The oil output was significantly affected by the extraction temperatures and time changes according to Table 1. The maximum yields for n-hexane and petroleum ether at 318 K were found to be 55.3 % and 34.5 %, respectively, after 50 min of extraction. The extraction yield increased to 70.2 % and 59.95 %, respectively, when the temperature and extraction time were
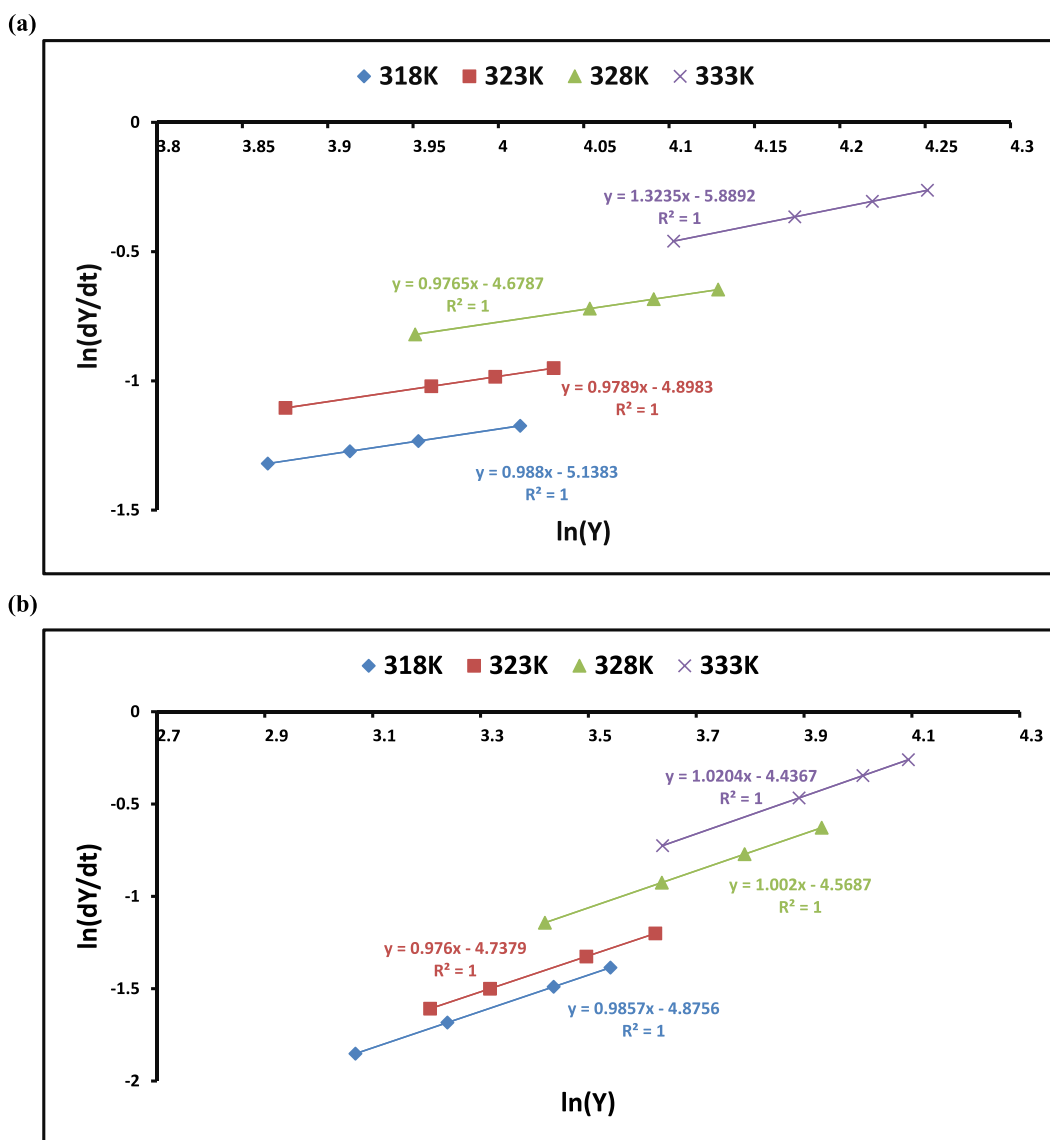

Fig. 1. (a) Kinetics graphs showing the extraction order at various temperatures using n-hexane. (b) Kinetics graphs showing the extraction order at various temperatures using petroleum ether.

increased to 333 K and 130 min, respectively. Equilibrium started to occur at 90 min, and depending on the temperature, a steady state was reached at 110–130 min thereafter. The observed pattern of increasing yield as temperature rises is consistent with related studies conducted by [13]. The oil yield was also dependent on the type of solvent used for the extraction. The results in Table 1 clearly indicated a higher yield obtained for the oil extracted using n-hexane at the various extraction temperatures. For instance, at the lowest extraction temperature 318 K, n-hexane extraction gave a higher yield of 55.3 % compared to the lower yield of 34.5 % obtained from the extraction with petroleum ether. Likewise, at the highest extraction temperature 333 K, the percent yield of the oil obtained from n-hexane (70.2 %) was higher than petroleum ether (59.95 %). The difference in the yield between the solvents can be accounted for by the differences in their polarity.

Using kinetic modelling, the impact of duration and temperatures on the extraction were further examined during the extraction process. For each extraction period 50–130 min at intervals of (20 min), the general rate law in Equaion 1 below was used to determine each rate of extraction.

$$\frac{dY}{dt} = k_a Y^n \tag{1}$$

where k_a stands for constant of extraction, Y for percentage yield of the oil, n represents the extraction order, and t for the extraction period. The positive dY/dt is due to the positive change in the extracted yield over time.

In order to determine the extraction constant (k_a) and the extraction order (n), Equation (1) was further linearized into Equation (2) as shown below.

$$ln\frac{dY}{dt} = nlnY + lnk_a \tag{2}$$

Linear graphs were generated by plotting ln(dY/dt) against ln(Y) at temperatures 318 K, 323 K, 328 K and 333 K with substantial regression coefficient (R^2) values and the slopes representing the extraction order which was approximately 1; indicating first order which is consistent with similar works reported by [13] on oil extraction from Ghanaian cocoa bean as shown in Fig. 1(a) and (b). Table 2(a) and (b) illustrate the results for the regression coefficient (R^2), the extraction order (n) and the constant of extraction (k_a).

This relationship shows that temperature variations have an impact on the pace at which shea kernel oil is extracted because higher temperatures enable quick mass transfer, which opens up the way for a higher extraction rate [13,20]. Fig. 3(a) and (b) and Fig. 4(a) and (b) distinctly display how the duration and temperature affects the yield of the oil extracted with the different solvents. The relationship from the graphs shows that the longer the duration (extraction time) and the higher temperature, the higher the yield. Because of the variation in oil concentration within the solid particles, the extraction process is controlled by convection mass transfer and diffusion [13]. In the seed, diffusion predominates, while in the solvent, advection does [13,21].

Since within the solid particles, the concentration gradient is unspecified, the mass transfer through convection between the solid and liquid interfaces employed by different published works to show the oil extraction kinetic approach [22] was used. Because there are no chemical reactions with convective mass transfer during the extraction and it takes place at a non-steady state, convective and diffusive mass flow are the same [22]. The variations in the oil mass concentration in the liquid state were determined using Equation (3) below.

$$\frac{dC}{dt} = K_m \times (C_f - C_t) \tag{3}$$

Considering the initial factors at time zero, the Shea kernel oil mass concentration is zero and Equation (3) above can be integrated and re-written as Equation (4) as shown below.

$$K_m t = -\ln\left(\frac{C_f - C_t}{C_f}\right) \tag{4}$$

where K_m is the mass transfer coefficient (min^{-1}) and C_f and C_t represent the oil mass concentrations at the liquid state at the respective times, t = 130 min and t. The yield Equation (4) of the Shea kernel oil above is then expressed as Equation (5) below.

$$K_m t = -\ln\left(\frac{Y_f - Y_t}{Y_f}\right) \tag{5}$$

Table 2(a)
Results showing the slope (order) and regression of the extraction using n-hexane.

Temperature (K)	R^2	n	ln K_a	K_a
318	1	0.9880	−5.1383	0.0058
323	1	0.9789	−4.8983	0.0074
328	1	0.9765	−4.6787	0.0093
333	1	1.3235	−5.8892	0.0027
Mean ± SD	1 ± 0.0000	1.0667 ± 0.1712	−5.1511 ± 0.5266	0.0063 ± 0.0027

SD; Standard Deviation, R^2; Regression Coefficient, n; Extraction Order, k_a; Extraction Constant.

Table 2(b)
Results showing the slope (order) and regression of the extraction using pet. ether.

| Temperature (K)	R^2	n	ln K_a	K_a
318	1	0.9857	−4.8756	0.0076
323	1	0.9760	−4.7379	0.0087
328	1	1.0020	−4.5687	0.0103
333	1	1.0204	−4.4367	0.0118
Mean ± SD	1 ± 0.0000	0.9960 ± 0.0195	−4.6547 ± 0.1920	0.0096 ± 0.0018

SD; Standard Deviation, R^2; Regression Coefficient, n; Extraction Order, k_a; Extraction Constant.

where Y_f stands for the percent yield at 130 min and Y_t for yield percent at a specific time, t. For every reaction temperature, a linear graph with K_m as the slope was produced by plotting $\ln[Y_f/(Y_f - Y_t)]$ versus t, as seen in Fig. 2(a) and (b).

For the oils extracted at different temperatures, the regression coefficient values were determined to be 1. Table 3(a) and (b) shows that as temperature rises, there is an increase in mass transfer due to reduced barrier within the boundary of the solid and liquid. This correlation compares favorably to earlier research on the extraction of oils [21,23]. For every temperature involved, the equilibrium state was attained, as shown in Fig. 4(a) and (b). At (90–110 and 110–130) min the yield variation measured 5 % and stayed steady and at 333 K, the highest temperature reached a constant state after 90 min, as opposed to 50–70 min and 70–90 min. The calculated equilibrium yields for 318 K, 323 K, 328 K, and 333 K, respectively, for both solvents were (55.3 and 34.5) %, (56.4 and 37.5) %, (62.1

(a)

(b)
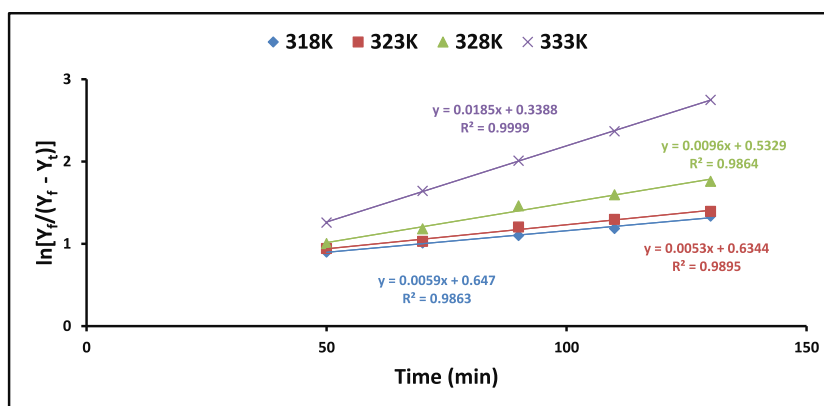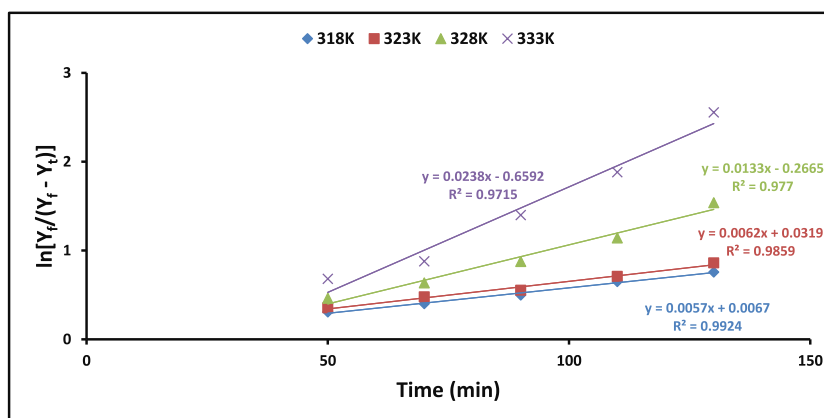
Fig. 2. (a) Graph of ln $[Y_f/(Y_f - Y_t)]$ against Time using n-hexane. (b) Graph of ln $[Y_f/(Y_f - Y_t)]$ against Time using pet. ether.

Table 3(a)
K_m values at different temperatures using hexane.

Temperature (K)	K_m (Min^{-1})	R^2
318	0.0058	0.9863
323	0.0053	0.9895
328	0.0096	0.9864
333	0.0185	0.9999
Mean $\pm$ SD	0.0098 ± 0.0061	0.9905 ± 0.0064

S.D; Standard Deviation, R^2; Regression Coefficient, K_m; Mass Transfer Coefficient.

Table 3(b)
K_m at different temperatures using pet. ether.

Temperature (K)	K_m (Min^{-1})	R^2
318	0.0057	0.9924
323	0.0062	0.9859
328	0.0133	0.9770
333	0.0238	0.9715
Mean $\pm$ SD	0.0123 ± 0.0084	0.9817 ± 0.0093

S.D; Standard Deviation, R^2; Regression Coefficient, K_m; Mass Transfer Coefficient.

and 51.05) %, and (70.2 and 59.95) %. Furthermore, Fig. 3(a), (b), and 4(a), and (b) demonstrate that for all conditions evaluated, the amount of oil extracted rose with extraction time and temperature. As can be seen in Fig. 3(a), (b), and 4(a), and (b), the maximum yield was obtained at 333 K. This confirmed the correlation between temperature and duration of extraction and oil yield. Several oilseed extraction experiments have documented and demonstrated this relationship for cocoa bean oil [13], using petroleum ether and sunflower [24], using n-hexane.

3.2. Thermodynamics study of shea kernel oil

The minimum energy needed for every reaction to occur is the activation energy (E_a). This is expressed using Equation (6) below. Equation (7) implies a linearized version of Equation (6).

$$K_m = Ae^{\frac{-E_a}{RT}} \tag{6}$$

$$lnK_m = \frac{-E_a}{RT} - lnA \tag{7}$$

It was determined that the mass transfer coefficients, k_m, and their corresponding temperatures, T, were related by using Equation (6). The Arrhenius constant, (frequency) factor, is denoted by A, while the universal molar gas constant (R), is expressed in kJ/mol.K. As illustrated in Fig. 5(a) and (b), the gradient; $-E_a/R$, and intercept; ln(A) were obtained by plotting a graph of ln(K_m) versus the inverse of temperature. The values of the E_a and the A were determined to be (74.59 kJ mol^{-1} and 88.65 kJ mol^{-1}) and (3.13 s^{-1} and 3.33 s^{-1}) for both n-hexane and petroleum ether extraction respectively. It is confirmed by this activation energy that diffusion over a narrow boundary layer limited the rate [13,21,25].

Using Equations (8)–(10) as done in similar works by [13,25], the activation parameters of thermodynamics, such as the enthalpy (ΔH^*), entropy (ΔS^*), and activation Gibb's free energy (ΔG^*), of the Shea kernel oil extraction were calculated for the individual temperatures. These equations agree with the notion of transition states [26].

$$A = \frac{RT}{N_A h} e^{\left(\frac{\Delta S^*}{R}\right)} \tag{8}$$

$$\Delta H^* = E_a - RT \tag{9}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{10}$$

The constants Na and h stand for Avogadro's and Plank's, respectively. Table 4(a) and (b) displays the average values of ΔS^*, ΔH^* and ΔG^* at 318 K, 323 K, 328 K and 333 K to be (-236.15 ± 0.16 and -235.63 ± 0.17) J/mol K, (71.88 ± 0.06 and 85.94 ± 0.06) kJ/mol and (148.75 ± 1.52 and 162.64 ± 1.52) kJ/mol for both solvents respectively.
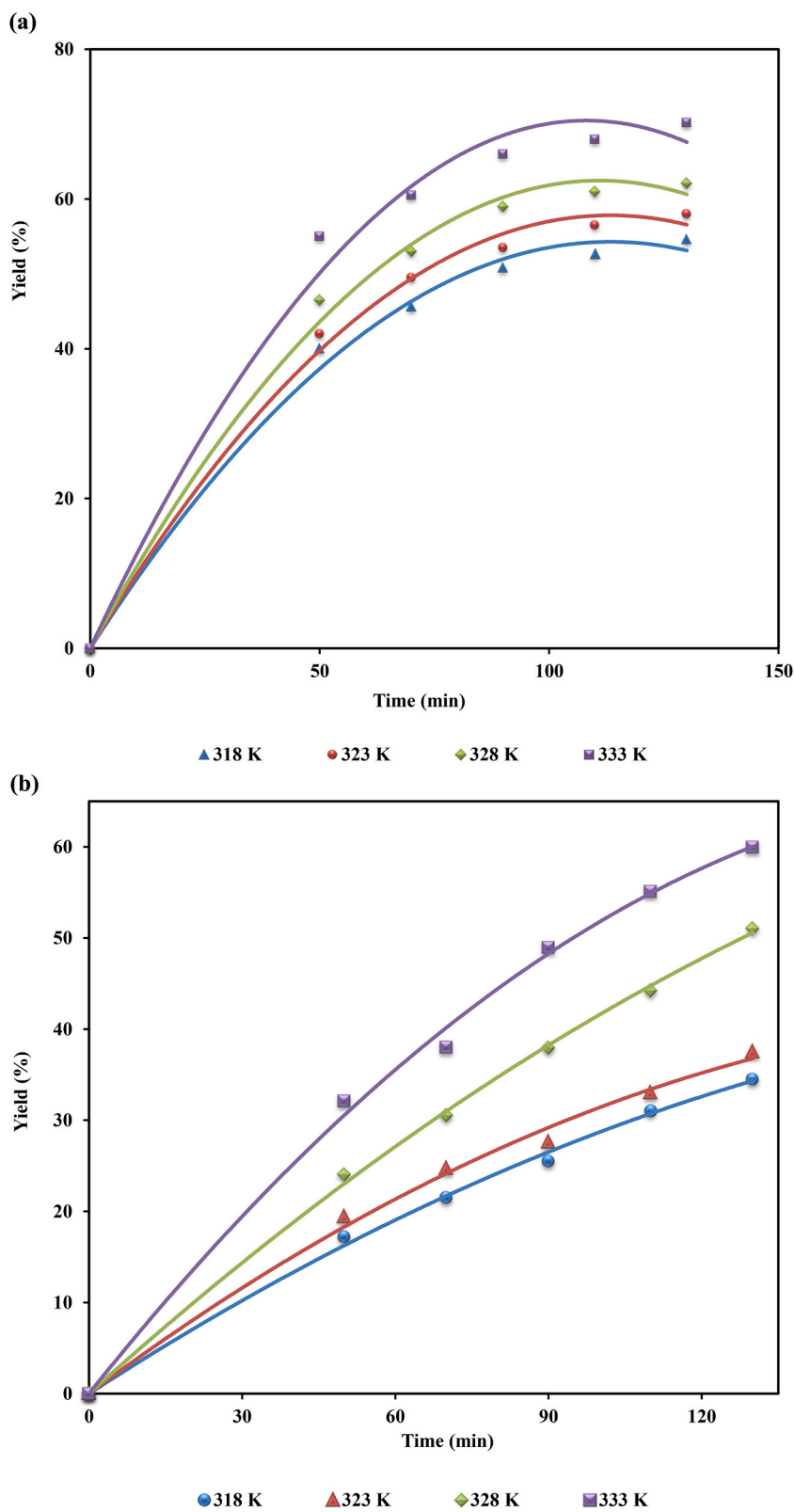
$$\frac{Y}{Y_U} = K = e^{kt} \tag{11}$$

Fig. 3. (a) Graph of Yield versus Time using n-hexane. (b) Graph of Yield versus Time using petroleum ether.
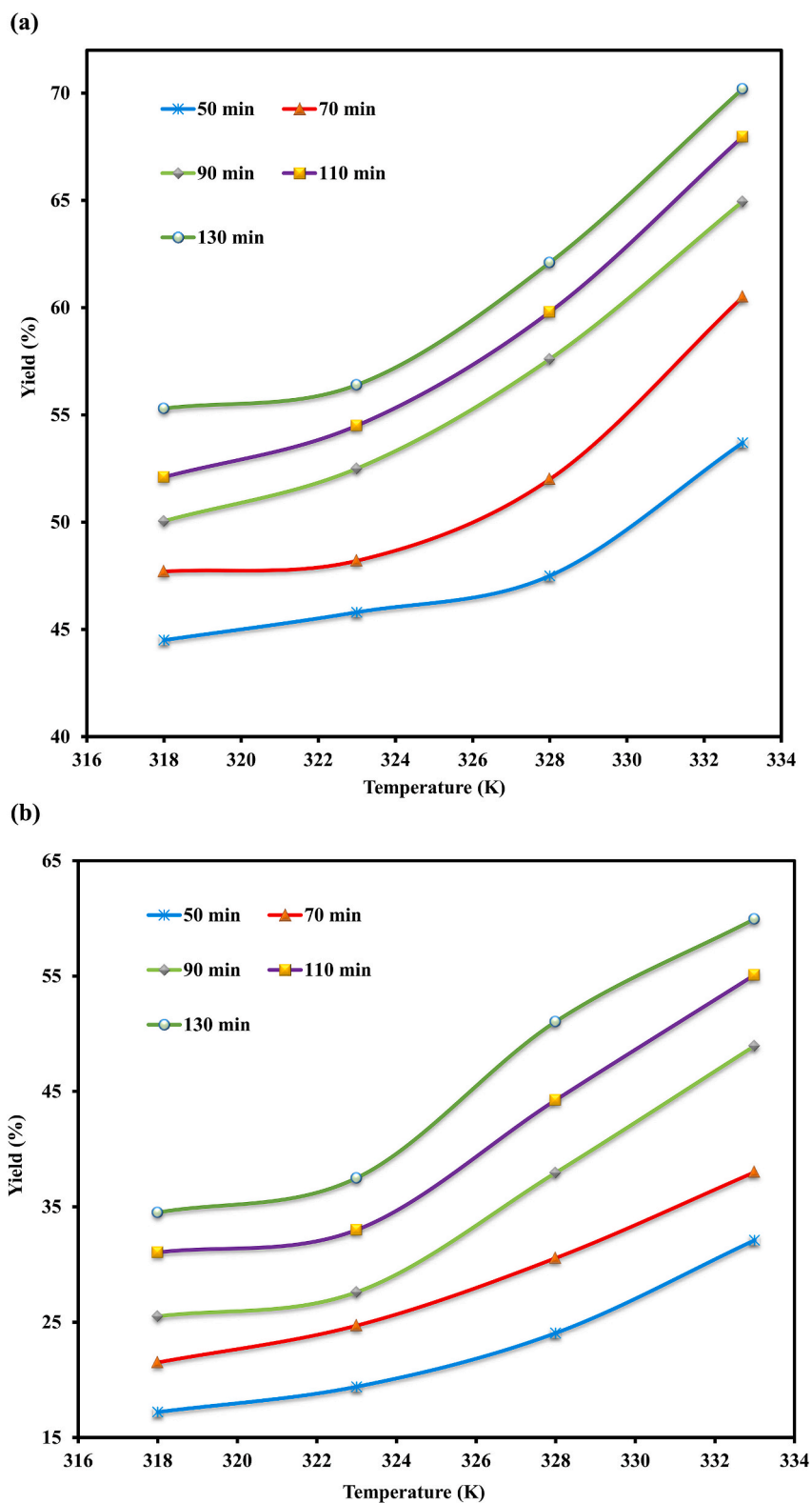
(a)

(b)

Fig. 4. (a) Graph of Yield versus Temperature using n-hexane. (b) Graph of Yield versus Temperature using petroleum ether.
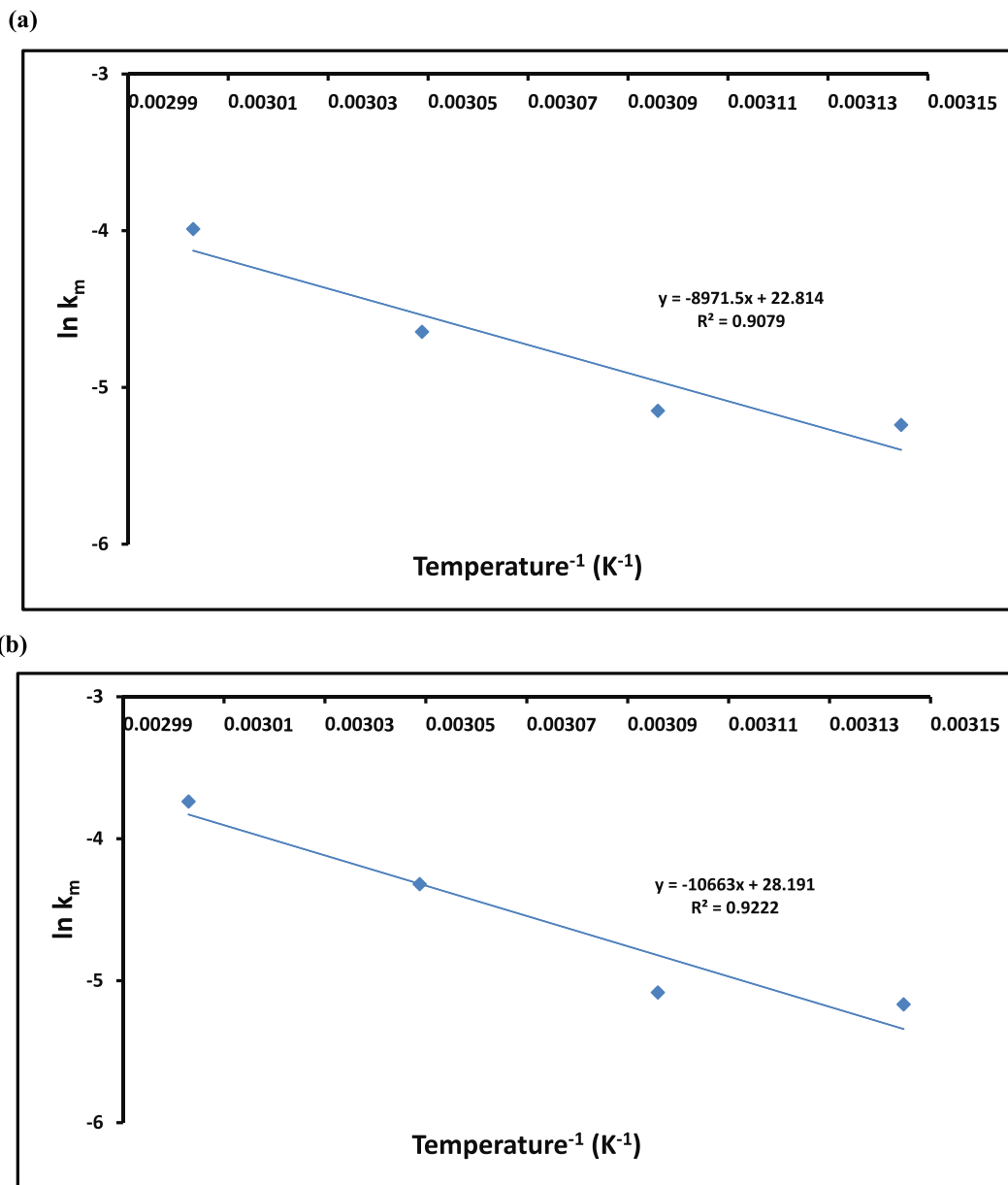
(a)

(b)

Fig. 5. (a) Graph of ln K_m versus 1/T, K using n-hexane. (b) Graph of ln K_m versus 1/T, K using pet. ether.

Table 4(a)
Results for Parameters of activation using hexane.

Temperature (K)	ΔS* (J/mol K)	ΔH* (kJ/mol)	ΔG* (kJ/mol)
318	−235.96	71.95	146.98
323	−236.10	71.90	148.16
328	−236.22	71.86	149.34
333	−236.34	71.82	150.52
Mean ± SD	−236.15 ± 0.16	71.88 ± 0.06	148.75 ± 1.52

SD; Standard Deviation, ΔS*; Entropy, ΔH*; Enthalpy, ΔG*; Gibb's Free Energy.

$$lnK = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{12}$$

Table 4(b)
Results for Parameters of activation using pet. ether.

Temperature (K)	ΔS^* (J/mol K)	ΔH^* (kJ/mol)	ΔG^* (kJ/mol)
318	−235.44	86.01	160.88
323	−235.57	85.96	162.05
328	−235.70	85.92	163.23
333	−235.83	85.88	164.41
Mean ± SD	−235.63 ± 0.17	85.94 ± 0.06	162.64 ± 1.52

SD; Standard Deviation, ΔS^*; Entropy, ΔH^*; Enthalpy, ΔG^*; Gibb's Free Energy.

Due to the internal energy content decreasing throughout the transition, a strongly negative value for ΔS^* indicates a more difficult transition and a lower extraction rate. Additionally, the Arrhenius model equation's Ea (74.59 kJ mol^{-1} and 88.65 kJ mol^{-1}) influence is equal to the Eyring equation's ΔH^* (71.88 ± 0.06 and 85.94 ± 0.06) kJ/mol. When ΔH^* values are large, the extraction rate decreases. Equation (11) below expresses the ratio of extracted and unextracted yield of the oil. Where T, K, R and Y_u represent absolute
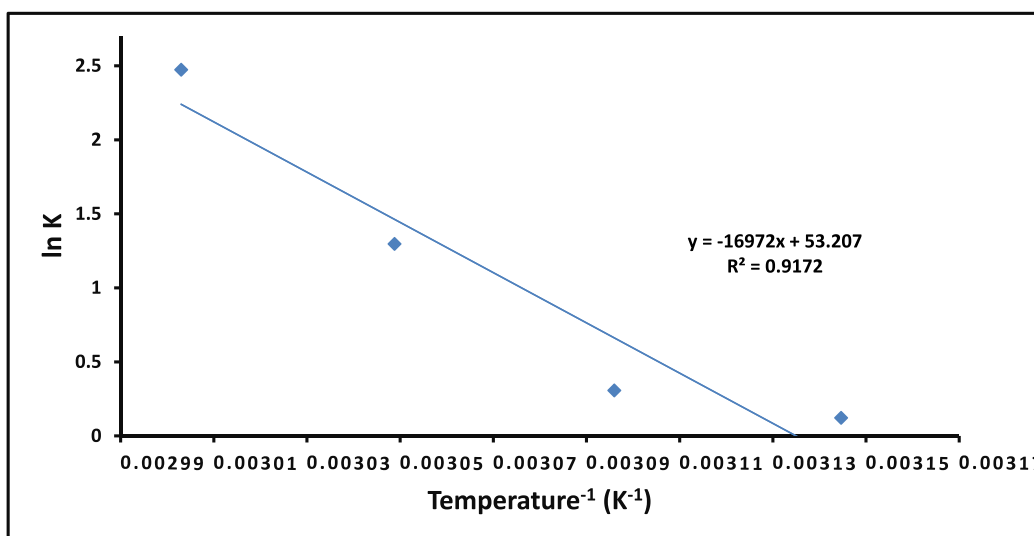
(a)

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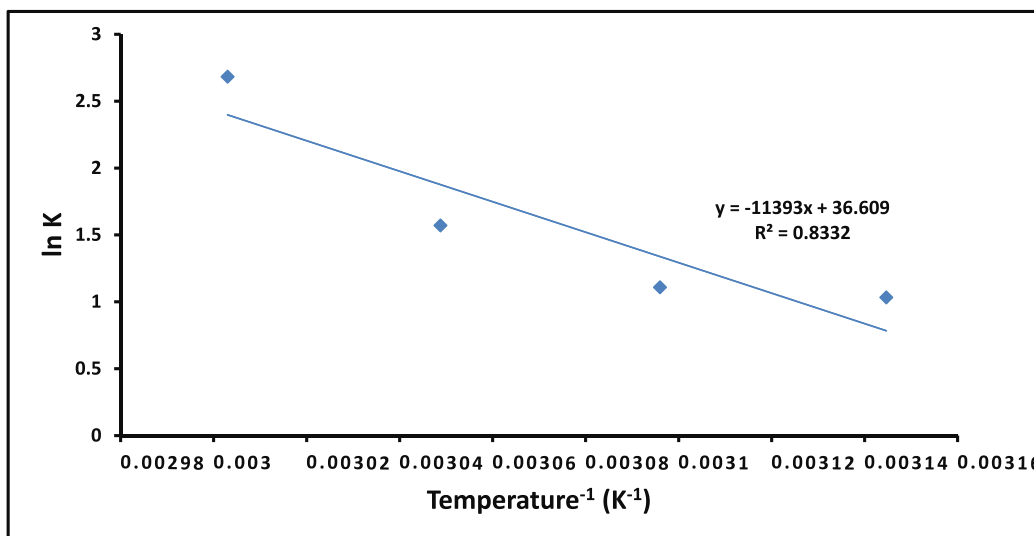
Fig. 6. (a) ln K against Temperature (K^{-1}) graph for hexane extraction. (b) Plot of ln K versus the inverse of Temperature (K^{-1}) for pet. ether extraction.

temperature, equilibrium constant, universal molar gas constant and percentage of unextracted oil respectively. Equation (12) above also known as the Van't Hoff Equation was used to graph ln(K) versus the inverse of temperature (T^{-1}) at 130 min. The results showed a straight line with $-\Delta H/R$ as slope and $\Delta S/R$ as intercept as shown on Fig. 6(a) and (b). For each of the two solvents, R^2, ΔH and ΔS were calculated to be (0.83 and 0.92), (94.72 and 141.11) kJ/mol, and (304.37 and 442.36) J/mol K.

Through the enthalpy of the reaction, the physicochemical characteristics of the oil are linked to the internal energy of the oil extraction. The disorderliness and randomness, as well as the reversibility level of a system once a process is completed, are indicated by the entropy (ΔS). Positive values of ΔH and ΔS indicate irreversible and endothermic extraction. This findings align with several research about extraction of oil by [23,27]. This indicates that for the extraction process to be effective, the system has to absorb heat energy and receive an external energy source as reported by [28]. Hence temperature is a key factor in the oil extraction process as asserted by [29].

When the temperature increases by 5 K, a significant increase in the equilibrium constant, K, was seen in Table 5(a) and (b). At 333 K, the maximum reported negative ΔG values (-6.64 and -6.20) kJ/mol, were found for both extractions respectively. This means that as a result of the chemical potential of the oil in the solid, more oil will naturally transit between the solid and liquid states as temperature surges. With K and ΔG values been positive and negative respectively, the extraction process was forward, feasible and thermodynamically spontaneous.

3.3. Characterization of the shea kernel oil

Oil extracted from oilseeds is extracted more quickly and with a higher yield and purity when heat is applied [30]. According to [13], several researches have indicated that the use of heat in the process of oil extraction and processing may lead to thermal oxidation and degradation, which could impact the oil's quality and shelf life. Peroxide value and iodine value of the oil are affected by the heating process. The mechanical method, also known as the cold press method does not require heating to extract the oil and hence does not affect the oil's peroxide value. However, the reflux method employed in this study to extract the oil at different temperatures helped to assess the impact of heating on the oil's quality and shelf life extracted at varying temperatures. Determining the oil suit-ability for commercial and industrial purposes required further characterization after the extraction process. The physicochemical analysis results for hexane and petroleum ether, respectively, of shea kernel oil are shown in Table 7(a) and (b).

3.4. Fatty acids compositions

Table 6(a) and (b) above displays the results for the characterization of the Shea kernel oil during heat treatment by fatty acid analysis. The Fatty acid profile of the Shea kernel oil was necessary for determining how fit the oil can be for optimal industrial processing, storage, application, and health benefits.

Four major fatty acids were discovered in Table 6(a) and (b): palmitic acid (PA), oleic acid (OA), linoleic acid (LA), stearic acid (SA), and several minor fatty acids with concentrations of less than 1 %. Table 6(a) and (b) shows that the oil comprised (55 % and 50 %) saturated fatty acids (SFAs), with (30 % and 29 %) and (3 % and 2.7 %) of the fat constituting monounsaturated (MUFAs) and polyunsaturated fatty acids (PUFAs), for both n-hexane and petroleum ether extractions respectively. Theoretically, oils with higher saturation levels need more energy to break down than oils with lower saturation levels [31].

The FA content of the Shea kernel oil used in this study was consistent with the FA composition stated by [11] and with numerous research indicating a significant level of linoleic acid [14,32]. Less concentration of linoleic acid of the oil (3.15 %) in comparison to the asserted value of 5.43 % [11] can be explained by two factors: The Vitellaria Paradoxa genome [4,13] or the geographic region corresponding to the many Shea tree kinds found at various locations [33]. Nonetheless, this study's linoleic acid concentration is more than the amounts stated by [13]. The polarity of the extraction solvents differs, as seen by the difference in FA values between Table 6 (a) and (b). Consequently, the more polar solvent during the extraction process has a higher affinity for the distinct free fatty acids. Shea kernel oil (Shea Butter) solidifies at room temperature, which can be explained by higher total saturated fatty acid [11] values seen in the data. The oil has a larger concentration of saturated fatty acids than unsaturated fatty acids, which are meant to maintain the oil's solid condition. From Table 6(a), the total Saturated Fatty Acids (SFAs) of the oil extracted using n-hexane at the four extraction temperatures were higher than that of the total Saturated Fatty Acids (SFAs) of the oil extracted with petroleum ether in Table 6(b). Also, the total Monounsaturated Fatty Acids (MUFAs) and Polyunsaturated Fatty Acids (PUFAs) of the oil extracted with n-hexane in Table 6(a) were higher than the values obtained using petroleum ether for the extraction as presented in Table 6(b). The observed difference in the results of this Fatty Acid profile data can be accorded to the differences in the solubility of the various Fatty acids in the solvents. This implies n-hexane has a higher affinity for the various fatty acids present in the oil than petroleum ether.

Table 5(a)
K and ΔG values for the Shea kernel oil extraction at different temperatures using hexane.

Temperature (K)	K	ΔG (kJ/mol)
318	2.81	-2.07
323	3.03	-3.59
328	4.81	-5.11
333	14.63	-6.64

K; Equilibrium Constant, ΔG; Gibb's Energy.

Table 5(b)
K and ΔG values for the Shea kernel oil extraction at different temperatures using pet. ether.

Temperature (K)	K	ΔG (kJ/mol)
318	1.13	0.43
323	1.36	−1.77
328	3.66	−3.98
333	11.87	−6.20

K; Equilibrium constant, ΔG; Gibb's Energy.

Table 6(a)
Shea kernel oil Fatty acid profile for the extraction using hexane (95 % Confidence Level).

Fatty Acid (%)	318 K	323 K	328 K	333 K
Stearic acid (C18:0)	52.031 ± 0.020	52.045 ± 0.021	52.054 ± 0.025	52.046 ± 0.021
Arachidic acid (C20:0)	0.599 ± 0.030	0.626 ± 0.025	0.620 ± 0.032	0.645 ± 0.031
Lauric acid (C12:0)	0.612 ± 0.020	0.687 ± 0.021	0.649 ± 0.025	0.654 ± 0.030
Palmitic acid (C16:0)	2.095 ± 0.015	2.066 ± 0.012	2.067 ± 0.010	2.079 ± 0.020
Total SFAs	55.337 ± 0.085	55.424 ± 0.079	55.290 ± 0.092	55.724 ± 0.102
Oleic acid (C18:1)	30.097 ± 0.050	30.307 ± 0.045	30.397 ± 0.050	30.419 ± 0.047
Total MUFAs	30.097 ± 0.050	30.307 ± 0.045	30.397 ± 0.050	30.419 ± 0.047
Linoleic acid (C18:2)	3.196 ± 0.021	3.119 ± 0.022	3.125 ± 0.020	3.171 ± 0.021
Total PUFAs	3.196 ± 0.021	3.119 ± 0.022	3.125 ± 0.020	3.171 ± 0.021

Data are given as mean values ± S.D, n (number of measurements) = 3, S.D; Standard Deviation, SFAs; Saturated Fatty Acids, MUFAs; Mono-unsaturated Fatty Acids, and PUFAs; Polyunsaturated Fatty Acids.

Hence higher amounts of the fatty acids present in the sample are dissolved by the solvent (n-hexane) during the extraction as compared to petroleum ether.

3.5. Physicochemical properties of the shea kernel oil

The main physicochemical properties of the Shea Kernel Oil are summarized in Table 7(a) and (b). The effects of heat during the extractions at various temperatures had no significant (p > 0.05) effects on the physicochemical properties of the oil extracted at different temperatures.

3.5.1. Iodine value

The amount of saturation or degree of unsaturation is indicated by the iodine value [18], which also determines the average

Table 6(b)
Shea kernel oil Fatty acid profile for the extraction using pet. Ether (95 % Confidence Level).

Fatty Acid (%)	318 K	323 K	328 K	333 K
Stearic acid (C18:0)	50.099 ± 0.030	50.105 ± 0.031	50.110 ± 0.030	50.120 ± 0.030
Arachidic acid (C20:0)	1.084 ± 0.010	1.047 ± 0.010	1.056 ± 0.011	1.060 ± 0.010
Lauric acid (C12:0)	0.518 ± 0.040	0.509 ± 0.041	0.525 ± 0.040	0.538 ± 0.041
Palmitic acid (C16:0)	1.555 ± 0.025	1.597 ± 0.024	1.556 ± 0.023	1.560 ± 0.025
Total SFAs	53.256 ± 0.105	53.258 ± 0.106	53.247 ± 0.104	53.278 ± 0.106
Oleic acid (C18:1)	29.139 ± 0.030	29.250 ± 0.031	29.245 ± 0.030	30.001 ± 0.031
Total MUFAs	29.139 ± 0.030	29.250 ± 0.031	29.245 ± 0.030	30.001 ± 0.031
Linoleic acid (C18:2)	2.776 ± 0.020	2.817 ± 0.021	2.652 ± 0.020	2.895 ± 0.021
Total PUFAs	2.776 ± 0.020	2.817 ± 0.021	2.652 ± 0.020	2.895 ± 0.021

Data are given as mean values ± S.D, n (number of measurements) = 3, S.D; Standard Deviation, SFAs; Saturated Fatty Acids, MUFAs; Mono-unsaturated Fatty Acids, and PUFAs; Polyunsaturated Fatty Acids.

Table 7(a)
Physicochemical properties of Shea kernel oil with n-hexane.

Parameter (s)	Shea Kernel Oil			
	318 K	323 K	328 K	333 K
Iodine Value (g/100g)	34.52 ± 0.03	35.53 ± 0.02	33.76 ± 0.03	35.02 ± 0.02
Peroxide Value (meq/kg)	0.60 ± 0.04	0.65 ± 0.03	0.50 ± 0.04	0.65 ± 0.03
Acid Value (mgKOH/g)	39.80 ± 0.02	37.60 ± 0.02	41.50 ± 0.03	29.10 ± 0.02
Free fatty acids (%)	19.90 ± 0.01	18.80 ± 0.02	20.75 ± 0.02	14.55 ± 0.01

Data are given as mean values ± S.D, n (number of measurements) = 3, S.D; Standard Deviation.

Table 7(b)
Physicochemical properties of Shea kernel oil extracted using pet. ether.

Parameter (s)	Shea Kernel Oil			
	318 K	323 K	328 K	333 K
Iodine Value (g/100g)	34.26 ± 0.02	35.41 ± 0.03	38.07 ± 0.02	37.05 ± 0.03
Peroxide Value (meq/kg)	0.50 ± 0.03	0.50 ± 0.04	0.65 ± 0.03	0.65 ± 0.04
Acid Value (mgKOH/g)	6.73 ± 0.02	6.62 ± 0.03	7.52 ± 0.02	5.27 ± 0.03
Free fatty acids (%)	3.37 ± 0.02	3.31 ± 0.03	3.76 ± 0.01	2.64 ± 0.02

Data are given as mean values $\pm$ S.D, n (number of measurements) = 3, S.D; Standard Deviation.

number of double bonds in the oil. It measures the oil's shelf life and is defined as the amount of iodine in grams that can be added to 100g of the oil. Lower iodine concentrations in oils or fats mean that they are higher in saturated fatty acids, which protect food cooked in them against oxidation and rancidity. Higher iodine values in fats or oils, however, also mean that the fat or oil is rich in poly-unsaturated fatty acids, which raises the nutritional value of the food products that use the fat or oil [34].

The iodine values for n-hexane and petroleum ether that were found in this study, respectively, (33.76–35.53 I₂g/100g and 34.26–38.07 I₂g/100g), are lower than the 45.6 I₂g/100g stated by [11] for Shea butter and higher than (28.03–30.01 I₂g/100g) reported by [13] for cocoa bean oil. Higher saturation and lower unsaturation levels in the Shea butter used in this study are indicative of a lower concentration of unsaturated fatty acids in the oil. On a global scale, Shea butter iodine values usually range between (30–75 I₂g/100g) [35]. The iodine values obtained from the extraction with n-hexane was appreciably lower as compared to that of the values obtained from the extraction with petroleum ether. This implies that the oil extracted using n-hexane contains higher amounts of unsaturated fatty acids hence, a lower iodine value and otherwise. As a result of the higher degree of unsaturation of the oil extracted with n-hexane, it easily solidified at room temperature, compared to the oil extracted with petroleum ether which required a longer time to solidify under the same condition. The oil's lower iodine content accounts for its ability to solidify at room temperature and its low susceptibility to oxidative rancidity, making it an ideal option for cooking [11].

3.5.2. Peroxide value

The peroxide number reveals the extent to which the fat or oil has been oxidized. The typical cause of this is when the oil is exposed to heat, light, metals, moisture, and other initiators [13]. The unit of measurement is milliequivalents, or mEq, of oxygen per 1000 g of fat. In this study, the peroxide values for the Shea kernel oil were found to be between 0.5 and 0.65 meq/kg for both petroleum ether and hexane. Comparing the peroxide values of the oil extracted with n-hexane and petroleum ether, there was no significant difference observed. Hence it showed that the type of solvent had no significant effect on the peroxide value of the oil. As the peroxide value is mainly affected by heat, light, metals, moisture and other initiators, as reported by [13]. Lower peroxide values indicate a lesser amount of primary oxidative substances present in the oil as well as a higher degree of saturated fatty acids, which provide stability against oxidation [13]. According to [35], the oil in this study is appropriate for the food and cosmetic industries since oils or fats with (PV < 10meq/kg) are beneficial for these sectors.

3.5.3. Free fatty acids and acid value

The Shea kernel oil was subjected to free fatty acid analysis to ascertain its optimal industrial applicability, processing, storage, and health benefits. The fatty acids found in oil that have not been neutralized are known as free fatty acids (FFA). This analysis yielded free fatty acid values for petroleum ether and n-hexane of (2.64–3.76 % and 14.55–20.75 %), respectively. These numbers were calculated based on the oil's acidity levels. The acid value of a gram of oil or fat is the amount of potassium hydroxide, expressed in milligrams, required to neutralize its free fatty acid content [36]. The acid value is twice the oil's free fatty acid content. This suggests that free fatty acids (%) will decrease with decreasing acid value. A low acidity value lowers the oil's susceptibility to rancidification since it contains fewer free fatty acids [36]**.**

The acid values recorded for the shea kernel oil in this study ranged from (29.1–41.5 mgKOH/g) and (5.27–7.52 mgKOH/g) for n-hexane and petroleum ether respectively. The acid values for the n-hexane were higher than that of the petroleum ether. The results showed that the acid values depend on the type of solvent just as the yield. The results can be further explained by the reality that free fatty acids are more soluble in n-hexane than in petroleum ether, due to the difference in the polarity between the two solvents [37].

The span of storage, processing, packaging, and environmental factors all have an impact on the amount of free fatty acids in Shea butter [38].

3.6. Fourier Transform Infrared spectroscopy (FTIR) analysis on the shea kernel oil

An infrared transmittance spectrum was obtained by further subjecting the shea kernel oil (Shea Butter), which was extracted using petroleum ether and n-hexane at different temperatures, to FTIR analysis. The different peak spectra for every sample were used to identify the potential kind of bond or functional group found in the oil samples. The FTIR spectra of the Shea butter extracted at different temperatures using n-hexane and petroleum ether are displayed in Fig. 7(a–h). Each sample's spectrum has a similar pattern, with the fingerprint region's frequency being 1163–449 cm⁻¹, and the major peaks at 2920.67–1176.29 cm⁻¹. Alkanes were perceived to be responsible for the stretching of C–H bonds, as seen by the peaks at 2920.67 cm⁻¹ and 2851 cm⁻¹.

Fig. 7(f) with a peak of 2139.42 cm⁻¹ demonstrates how the expansion of the C–C triple bond is brought about by the presence of an
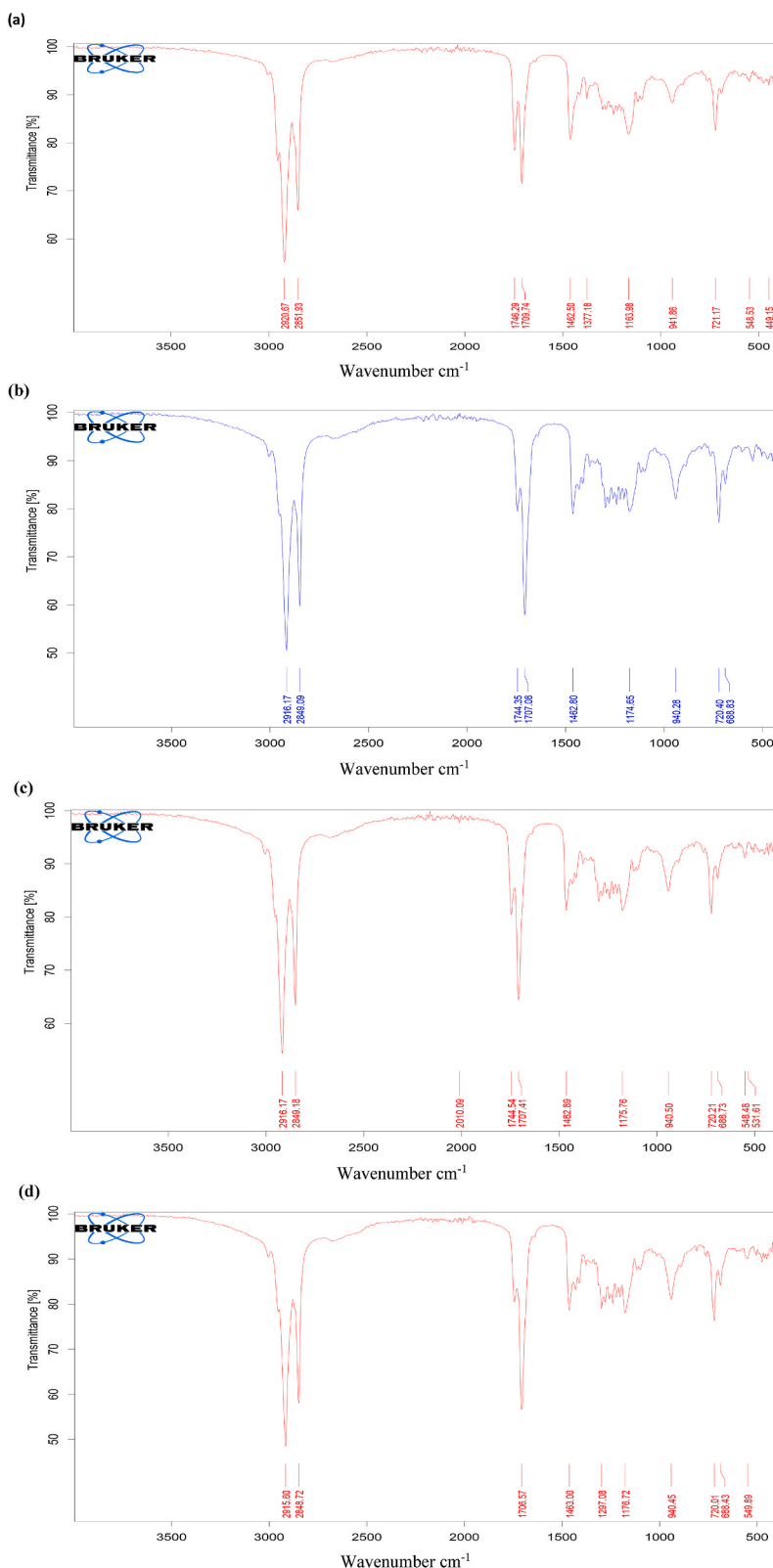
Fig. 7. FTIR Spectra for (a),(b),(c),(d),(e),(f),(g), and (h) at different temperatures and solvents; a, b, c and d (FTIR spectrum for the extraction with n-hexane at 60 °C, 55 °C, 50°C and 45°C, respectively), e, f, g, and h (FTIR spectrum for the extraction with pet. ether at 60 °C, 55 °C, 50 °C and 45 °C, respectively).
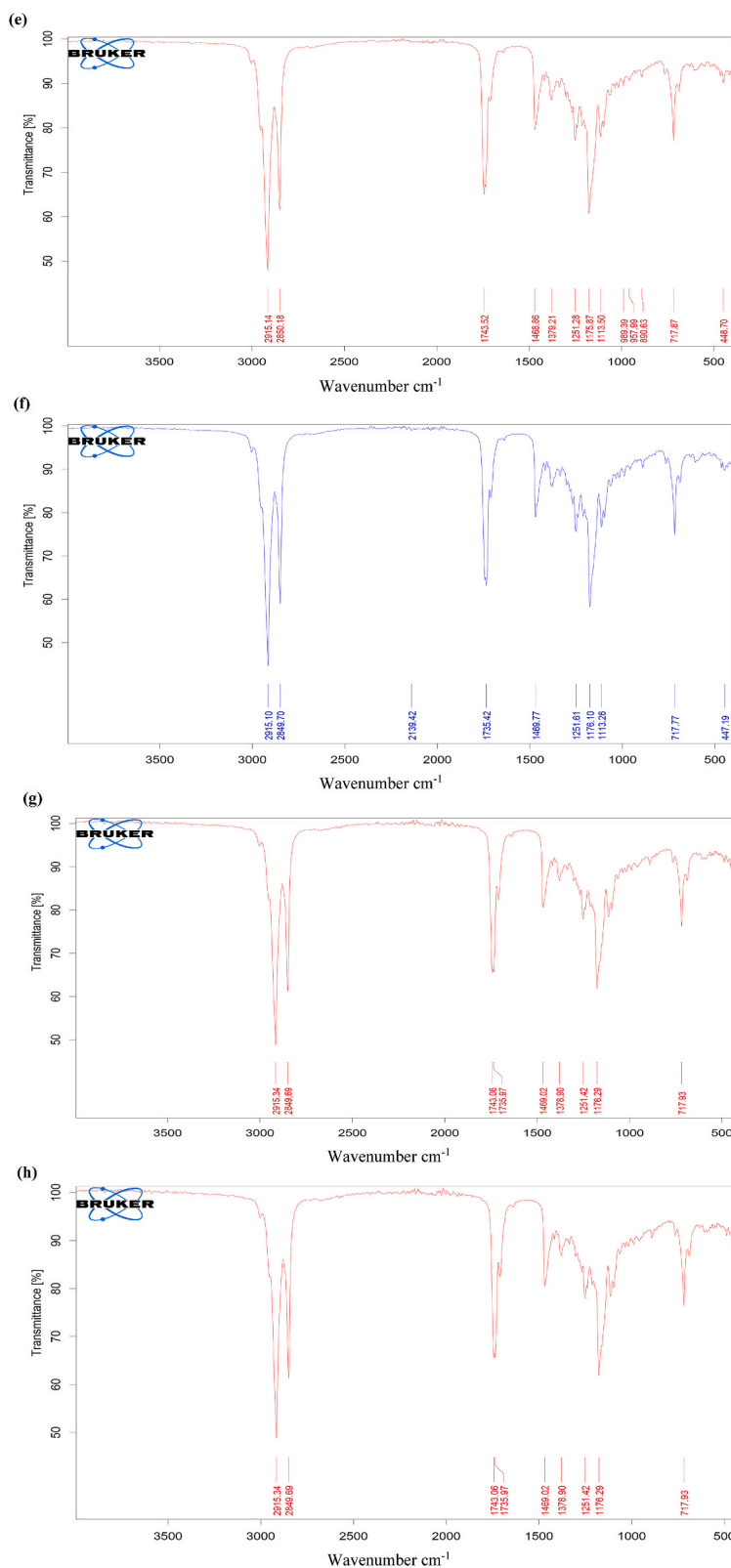
Fig. 7. (*continued*).

alkyne group. The existence of an ester group is suggested by the peaks at 1750 and 1735 cm^{-1}, which implies C=O stretching. This frequency is typical of vegetable oils that contain a high concentration of saturated fatty acids [39]. Peaks between 1706.57 and 1709.74 cm^{-1} signify C=O stretching caused by the presence of ketones or unsaturated aldehydes. According to C–H bending, the peaks at 1469.77–1462.80 cm^{-1} suggest the presence of alkane. As a result of aromatic amines, the C–N stretch is indicated by the peak at 1379 cm^{-1} and 1377 cm^{-1}. The extension of the ester group C–O is responsible for the vibrations around 1252 cm^{-1} and 1174 cm^{-1}, while aromatic bending vibration is responsible for the vibrations at 719 cm^{-1} and 448 cm^{-1} as reported in similar works by [39].

4. Conclusion

Oil from Ghanaian Shea kernels was extracted for this studyto assess its suitability for commercial, industrial, and personal uses and the process followed first order kinetics. According to the thermodynamic studies, the process of extracting the Shea kernel oil was endothermic, spontaneous, and irreversible with ($+K_a, + \Delta S, +\Delta H \ and -\Delta G$) and activation energy of 74.59 kJ mol^{-1} and 88.65 kJ mol^{-1} for the extraction with n-hexane and petroleum ether respectively. The various fatty acids present in the oil were identified as Stearic Acid, Palmitic Acid, Lauric Acid, Oleic Acid Arachidic Acid, and Linoleic Acid by Gas Chromatography analysis. FTIR analysis was carried out to determine the possible bonds and functional groups contained in the oil. The extracted oil possesses good quality, making it suitable for use in industries and commercial settings, based on the physicochemical results.

Data availability

The data that support the findings of this study are available in the article and will be made available upon request.

CRediT authorship contribution statement

Enoch Mbawin Alale: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **Samuel Kofi Tulashie:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Conceptualization. **Michael Miyittah:** Writing – review & editing, Resources, Investigation, Formal analysis. **Emmanuel Boafo Baidoo:** Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **Kingsley Enoch Adukpoh:** Software, Methodology, Investigation, Formal analysis. **Enock Opare Dadzie:** Software, Formal analysis, Data curation. **Clement Akonnor Osei:** Methodology, Investigation, Formal analysis, Data curation. **Bright Komla Gah:** Software, Formal analysis, Data curation. **Desmond Acquah:** Software, Formal analysis, Data curation. **Philip Agudah Quasi:** Software, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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