Oil extraction from *Treculia africana* seeds: process conditions, kinetic and thermodynamic studies

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ABSTRACT: The declining global supply and sources of vegetable oil consumed across different parts of the world have become a source of growing concern. Finding alternative sources demands concerted efforts and studies on other agricultural products not adequately utilized. This study investigates the extraction of oil from *Treculia africana* seeds using n-hexane as a solvent. The effect of heat pre-treatment of the seed samples on the process was also investigated using oven-drying and sun-drying methods, respectively. The pre-treatment process had no effect on the physicochemical properties of the extract except the maximum yields at 60 min obtained as 42.5 and 40.31%, respectively. Characterization of the extract using the physicochemical properties of the oil showed specific gravity 0.931, saponification value 624.4 $mgNaOHg^{-1}$oil, acid value 2.57 $mgKOHg^{-1}$oil, and iodine value 14.13$mg100g^{-1}$ which indicates its suitability for consumption, soap making, production of pharmaceuticals and as a lubricant. The Kinetics of the process which was studied under different temperatures and time intervals indicate a first-order reaction. Several thermodynamic parameters were determined such as activation energy, enthalpy, and entropy. These physicochemical properties indicate that the extract is comparable to the vegetable oil obtained from other sources. The kinetics and thermodynamics studies indicate the spontaneity of the process showing that the energy required to break the solute-solvent/solvent-solvent interaction was more significant than that required to maintain the bonds between them thereby favouring the forward reaction and product formation.

KEYWORDS: *Treculia africana*, contact time, characterization, kinetics, thermodynamics, rate constant

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I. INTRODUCTION

Over the last few decades, there has been a disrupted global supply chain of essential commodities such as vegetable oil, cereal, and energy leading to rising consumer price inflation for these items. Owing to declining supplies, there are concerns about global food security risks due to several factors such as political and economic instability in addition to assess to raw materials. The supply of vegetable oil across the international market has dropped drastically forcing a surge in demand (FSIN, 2022).

Vegetable oil, a rich source of fat, accounts for about 10% of the daily caloric food supply second only to cereal. They provide a rich nutritional source of omega -3 and omega-6 fatty acids and vitamins E and K. Vegetable oils are essential cooking oil, aside from other more expensive butter or other animal fat-based products (Rana *et al*, 2022).

Treculia africana (african bread fruit) is of the inversa africana specie and moraceae family. It is a forest tree which fruits around February–March annually and grows as high as 27 m. Its fruit could contain as many as 1,500 seeds about 1.5 mm long and are very rich in protein (17%), crude fat (11%), carbohydrates, fibre, vitamins, amino acids, minerals and fatty acids (Ayoade *et al*, 2015; Ijet *et al*, 2010; Giami *et al*, 2000). These seeds are aromatic and flavoured like groundnuts and have been reported to be a rich source of oil containing as much as 20% semi-dried oil (Ajayi, 2008).

The plant is believed to originate from Guinea through the Indo-Malayan archipelago to western Micronesia spreading widely through the pacific area and is found in tropical countries such as Nigeria, Ghana, Sierra Leone, West Indies and Jamaica. Its use for nutritional, medical and other industrial purposes is well documented in literature (Ayoade *et al*, 2015). Chemical composition (Giami *et al*, 2000; Akubor and Badifu, 2004), physical, mechanical, aerodynamic (Omobuwajo *et al*, 1999) and other properties of Treculia africana have been examined. Osabor *et al* (2009), Okwari *et al* (2006), Fasasi *et al* (2004) investigated the chemical properties of Treculia africana. Ariahu *et al* (1999) examined its nutritional and organoleptic quality, whereas Ijeh *et al* (2010) and Nnorom *et al* (2015) examined the effect of processing and storage (Onyekwelu and Fayose, 2007) on some of these inherent properties. Shittu and Raji (2011) carried out a thin layer drying and investigated the rehydration capacity of Treculia africana, using various models to predict its drying profile; whereas Onyeike and Ancheru (2002) and

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Nwinuka *et al* (2001) compared the vegetable oil from Treculia africana with those from other sources.

Recently, Zahid *et al* (2023) studied the free fatty acid methyl ester (FAME) synthesized from plant oil with methanol using some suitable catalyst. They evaluated the physicochemical properties of the extract, and through a kinetic and thermodynamic study, assessed the rate of reaction, activation energy, enthalpy, entropy, and spontaneity of the process. The oil yield and optimum time for this process were equally examined. Similarly, Dos Santos *et al* (2015) and Menkiti *et al* (2015) have studied the yield and kinetic and thermodynamic parameters of the oil extraction process from *Jatropha curcas L*. and *Terminalia catappa L*., respectively using various solvents and at different operating conditions. The results of these studies showed the impact of contact time and the kinetic and thermodynamic properties of the process.

In spite of these efforts to assess the oil extraction process from several agricultural products, no study found in open literature has evaluated the effect of heat pre-treatment, kinetics and thermodynamics of the oil extraction process from *Treculia africana*. This assessment is crucial and will provide a novel approach to assessing the viability of the process as well as a suitable guide to encourage commercial-scale production. This study seeks to fill this research gap by investigating the kinetics and thermodynamics of the oil extraction process from *Treculia africana* using n-hexane as solvent.

II. MATERIALS AND METHODS

A. Materials

Freshly harvested Treculia africana seeds were used for this study.

Reagents used were obtained as pure grades namely: n-acetone, petroleum ether, paraffin oil, and carbon tetrachloride.

The following instruments were used: U-tube Ostwald viscometer (Model: PSL Rheotek BS188, USA), Lovibond tintometer (Model: PFXi-195/2, Germany), Thimble (supplied by GilZheng, China) Glasswares such as density bottles, burette, pipette, capillary tube and funnel were supplied by Thermo Fisher Scientific, China, while density bottles, condenser and flat-bottom flask were supplied by Sigma Aldrich, China.

B. Methods

This work involved the use of the following methods: sample collection and preparation, oil extraction, characterization of oil extract, and analysis. These methods were carried out at the reactions and particulate systems laboratories of the Chemical Engineering department, University of Port Harcourt, Nigeria. Statistical analysis and the evaluation of the kinetic and thermodynamic data were also considered.

1) Sample preparation

Inversa variety of Treculia africana samples used for this study was collected fresh from a local farm at Ifite-Ezinifite (5o96'0''N, 7o07'0''E) in Aguata local government area, Anambra State. The seeds were harvested and fermented for 5 days to degum them after which they were washed, dried for 72 h under atmospheric conditions, and dehulled while the dehusked pericarps and other impurities were separated from the seeds by winnowing.

The seed samples were dried using two (2) separate methods: oven and sun drying; weighed, dried and stored in two (2) different airtight containers. Sun drying was done for 5 days at a temperature of 32 oC, whereas oven drying was done using a microwave oven operating at a temperature of 60 oC for 1h. The oven temperature was carefully chosen so as not to denature the seed and to achieve the task of moisture removal from the seed. The moisture content was calculated as a ratio of the difference between the initial weight of seeds, W1, and the final weight on drying, W2 (indicated by constant weight) as shown in the correlation of Eqn. (1).

$$Moisure(\%) = \left(\frac{W_1 - W_2}{W_1}\right) * 100 \quad (1)$$

These samples were pulverized using a blender to increase the reaction surface area and also labelled accordingly.

2) Extraction process

The oil extraction from the *Treculia africana* seed samples using n-hexane as solvent. The oil extract was quantified whereas the Soxhlet process was employed in the extraction process. Solvent extraction was employed in this study over other extraction techniques such as mechanical extraction, traditional extraction and supercritical fluid extraction due to its cost-effectiveness and a high percentage of oil recovery from seed (Nwabanne, 2012). Also, the choice of n-hexane as a solvent in this study is due to its lower boiling point for easy separation after extraction, its non-polar nature which makes it suitable for extracting vegetable oils which are generally non-polar and its lower toxicity when compared to other solvents.

3)Effect of contact time

Using the batch settling procedure, the effect of contact time on the oil yield was determined. This was done by wrapping the powder samples in filter paper and adding 50 ml of n-hexane solvent batch-wise into six (6) weighed conical flasks amidst constant agitation while taking note of the time at regular intervals. The effect of contact time on oil yield was evaluated at a temperature of 303 K at time intervals of 10-65 min. The solvent mixture (miscella) was thereafter, subjected to heating to distil off the solvent for the recovery of the oil. The yield was evaluated using Eqn. (2).

$$Yield\ (\%) = \left(\frac{weight\ of\ oil}{weight\ of\ solution}\right) * 100 \quad (2)$$

C. Characterization of extracted oil sample

Physicochemical property tests were carried out to evaluate the quality of the oil extract. The physical tests include specific gravity, viscosity, boiling point, melting point, pH, and colour tests, whereas the chemical tests involved evaluation of the saponification value (SV), acid value (AV), free fatty acid (FFA), iodine value (IV), and peroxide value (PV). These tests were carried out using standard procedures as enumerated:

1) Specific gravity

The specific gravity of the oil extract was evaluated at 303 K by filling a density bottle of 10ml capacity with water and its was weight recorded. The bottle was subsequently emptied, dried in a microwave oven, filled with the oil sample and re-weighed. The specific gravity was evaluated as a ratio of the weight of the oil to that of water.

2) Viscosity (μ)

The method of Uyigue and Okwonna (2013) was employed by using a U-tube viscometer. The average time taken for the oil extract to move across the tube was recorded and used to evaluate the viscosity. The viscosity was calculated using Eqn. (3).

$$\mu = (t * m) \quad (3)$$

Where: m is a ratio of standard time and factor = 0.5487

3) Colour

This was evaluated using a lovibond tintometer following standard procedure (Oduola and Okwonna, 2016).

4) Boiling point

To obtain this, 10ml of the extract was measured into a capillary tube setup (big and small) contained within each other, and a thermometer suspended with a string. The temperature of the setup was maintained at 303 K (room temperature) and was immersed into a 100 ml beaker containing 50 ml of paraffin oil, held in position with a clamp. The entire setup was then heated while noting the temperature and time of appearance of the first, second, third, and fourth bubbles of the oil extract to appear in the smaller capillary tube.

5) Melting point

This was measured using 5 capillary tubes filled with the extract and allowed to freeze in a refrigerator. These were then transferred into a gallenkamp melting point apparatus which was used to determine the temperature at which the oil began to drift off the capillary tube. This temperature was recorded as the melting point of the oil.

6) Acid value (AV)

The acid value of the extract was determined by mixing 20 ml of equal-volume mixtures of diethyl ether and ethanol with 20 ml of the extract. This mixture was titrated against 0.1N NaOH solution using phenolphthalein as an indicator until an endpoint indicated by a colour change was reached. The acid value was calculated using Eqn. (4).

$$AV = \frac{56.1NV}{W} \quad (4)$$

Where: N = normality of NaOH used, V = volume of NaOH used, W = weight of oil extract (g)

7) Iodine value (IV)

This was evaluated using 10 ml of the extract mixed with 15 ml carbon tetrachloride (CCl_4) contained in 2 separate conical flasks. 25ml of iodine monochloride (Wijs) solution was added to each of these mixtures using a pipette. These mixtures were allowed to stand for 1 h without exposure to light in order to protect the oxidized material present in the sample mixture. In addition, 20 ml of potassium iodide (KI) solution diluted with 150 ml of water was added into both flasks and the entire solution was titrated with Sodium thiosulphate solution (0.1N) using freshly prepared starch as an indicator. The process was repeated under similar conditions without the oil extract (blank control). The IV was evaluated using Eqn. (5).

$$IV = \left(\frac{12.69N(V_2 - V_1)}{W}\right) \quad (5)$$

Where: V_1 = volume of sodium thiosulphate used in the test; V_2 = volume of sodium thiosulphate in blank; N = normality of thiosulphate; W = average weight of oil used.

Other chemical properties such as: FFA, SV, and PV were determined using the method of Ajayi (2008).

D. Kinetics of the extraction process

Analysis and design of the oil extraction process requires adequate evaluation of the kinetic data and this was done using the method of Otaraku and Okwonna (2021). To achieve this, the yield at different time (10-60 min) and temperature (303-333K) intervals for the oven-dried pre-treatment process was considered. The rate of reaction of this process was evaluated with Eqn. (6).

$$dY/dt = kY^n \quad (6)$$

$$ln\frac{dY}{dt} = lnY + lnk \quad (7)$$

Where: Y = oil yield (wt %), k = rate constant (min^{-1}), t = extraction time (min), and n = extraction reaction order.

A plot ln (dY/dt) vs ln Y is shown in Figure 2 and fitted using XLSTAT 2016 to obtain the regression coefficient shown in Table 3 from where the rate constant of the process was evaluated.

E. Activation energy of the process

The activation energy was evaluated using the Arrhenius Equation (Eqn. 8) to access the minimum energy requirement for the oil extraction to occur.

$$k = Ae^{-Ea/RT} \quad (8)$$

Where: k = rate constant (min^{-1}); Ea = activation energy ($kJmol^{-1}$), R = universal gas constant ($kJmol^{-1}K^{-1}$), T = absolute temperature (K), and A = Arrhenius constant/ frequency factor.

The activation energy and Arrhenius constant were evaluated from the slope of the plot of ln k vs 1/T (Figure 3). However, only the temperatures suitable for the extraction process (based on the result of the rate constants) were considered.

F. Thermodynamic properties

The thermodynamic properties of the process were obtained on the basis of the transition state theory using Eqns. (9) – (11) to determine the spontaneity or otherwise of the extraction process.

$$A = \frac{RT}{Nh}e^{\Delta S^*/RT} \quad (9)$$

$$\Delta H^* = Ea - RT \quad (10)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (11)$$

Where: A = Arrhenius pre-exponential factor, N = Avogadro number (mol^{-1}), h = Planck constant (Joule-sec),

ΔS^* = activation entropy ($JmolK^{-1}$), ΔH^* = activation enthalpy ($kJmol^{-1}$), and ΔG^* = Gibbs free energy ($kJmol^{-1}$).

Furthermore, the equilibrium constant (K) and the thermodynamic parameters were evaluated using Eqns.12 and 13.

$$K = {}^{Y_T}/_{Y_u} \quad (12)$$

$$lnK = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (13)$$

Where: K = equilibrium constant, Y_T = oil yield at different temperatures (%), Y_u = unextracted oil (%)

The enthalpy change (ΔH) was obtained from the slope of the plot of $\ln Y_T$ vs 1/T in Fig. 4 while the values of K, ΔG, and ΔS were evaluated from Eqns. 12 and 13, respectively.

III. RESULTS AND DISCUSSION

A. *Effect of heat pre-treatment on oil yield*

The oven-drying pre-treatment of the *Treculia africana* seed sample gave a higher yield of the oil than the sun-dried process as shown in Figure 1. Uquiche *et al* (2008) reported that heat pre-treatment could give rise to changes in the microstructure of agricultural products which could enhance the oil yield and improved extraction efficiency. These changes rupture the spherosomes which are the oil-bearing materials or oil bodies contained within the fruits thereby giving rise to improved yield. A similar yield pattern was observed for both processes showing consistency with the yield from this seed. The observed pattern corroborates the work of Dos Santos *et al.* (2015) on *Jatropha curcas L.* In the control experiment, a maximum yield of 50.88 wt% was attained at a temperature of 333 K, beyond which equilibrium was reached and no further yield was observed. Based on the oil yield value (>22% dry basis), this product can be classified as a high-oil material in accordance with the work of Uquiche *et al* (2008).

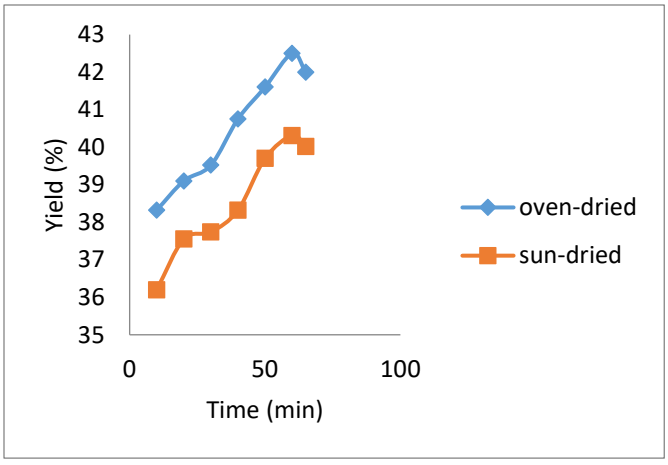

Fig. 1: Yield vs contact time at 303 K *Treculia africana*

B. *Effect of contact time on oil yield*

The yield of oil seems to be proportional to the extraction time (Fig. 1), with the maximum yield attained at 60 min. Hence, this can be considered as the optimum time to obtain maximum yield from this seed, subject to further studies. According to Dos Santos *et al* (2015), further increment in time could result in a decrease in the mass transfer rate of oil to the liquid phase until the attainment of equilibrium; hence the tendency of oil concentration in the liquid phase to remain constant after this time. An explanation of this phenomenon was presented by Meziane *et al* (2008) describing the vegetable oil extraction process from seeds to occur in two phases, namely: the exposure of the surface of the oil-bearing particle by the washing action of the solvent which maximizes oil yield and the latter phase where the extraction occurs by mass diffusion leading to a dependence of the process on the concentration of the oil in the solvent as well as on the average particle.

C. *Characterization of the oil extract*

Characterization of the extract was done to determine the physical and chemical properties of the oil as shown in Table 1.

Table 1: Physicochemical properties of oil extract from *Treculia africana* seeds

S/N	Property	Pre-treatment	
		Sun-dried	Oven-dried
1	Physical state	Liquid	Liquid
2	pH	7.9	8
3	Melting point (°C)	21	22
4	Boiling point (°C)	118	120
5	Colour test	R3/Y24 max	R3/Y24 max
6	Viscosity (cSt)	7.902	7.902
7	Specific gravity	0.931	0.931
8	Saponification Value (mg $NaOHg^{-1}$ oil)	624.4	624.4
9	Acid Value (mg$KOHg^{-1}$ oil)	2.57	2.57
10	Free Fatty Acid (%)	1.28	1.29
11	Iodine Value ($mg100g^{-1}$)	14.13	14.13
12	Peroxide Value (mgg^{-1})	6.67	6.67

Samples obtained from both pre-treatment methods showed similar properties which is an indication of a minimal effect of heat pre-treatment on the properties of the extract. The liquid state of the extract is evidence of the unsaturated nature of the carbon chains present within these samples which explain the fluidity of the fatty acid (≈1.3). The fatty acid content makes the oil extract a suitable feedstock for soap making. The pH value indicates its suitability for consumption. The melting point obtained in this study were well within the acceptable range of -18 to 45°C reported as the ISO standard for melting points of vegetable oils obtained from organic sources such as olive, coconut, palm oil, palm kernel oil, cotton seed, soybean, castor seed (Engineering ToolBox, 2008). Similarly, the boiling point from this study justifies the fluidity of the FFA (Nwinuka *et al*, 2001). The golden yellow colour of this extract indicates that some coloured pigments of the seed were extracted with the oil. The viscosity of 7.902 cSt at 32 °C implies that the oil can be used as a lubricant due to its low viscosity index. Typical of most oils, this viscosity was observed to decrease with an increase in temperature which gives further proof of its unsaturated state although this can be enhanced by hydrogenation. The specific gravity of 0.931 for this oil indicates it is less dense than water and corroborates the values obtained from other vegetables such as pumpkin seed oil, rapeseed oil, olive oil, and sunflower seed oil (Nichols and Sanderson, 2003). FFA (%) and acid value (mgKOH g^{-1} oil) obtained from this study were less than 5.06 and 10.04

Table 2: Physicochemical properties of other vegetable oil grades

S/N	Property	Treculia africana oil	Arachis oil	Babassu oil	Coconut oil	Cotton seed oil	Grape seed oil	G/nut oil	Maize oil	Mustard seed oil	Olive oil	Palm oil	Palm Kernel oil	Palm olein	Rape-seed oil	Soyabean oil	Sunflower seed oil
1	Melting point (ºC)	21												24			
2	Colour test	R 3/Y 24 max.							R3/Y25 max.					R3 max./ Y30 max.		5 1/4" (R/Y) max. 1.5/15	
3	Specific gravity	0.931	0.912-0.920 x=20º C	0.914-0.917 x=25º C	0.908-0.921 x=40º C	0.918-0.926 x=20ºC	0.920-0.926 x=20º C	0.918-0.923	0.917-0.925 x=20ºC	0.910-0.921 x=20ºC	0.910-0.916	0.891 - 0.899 x=50 ºC	0.899-0.914 x=40º C	0.899-0.920 x=40ºC	0.910-0.925 x=20º C	0.919-0.925 x=20ºC	0.918-0.923 x=20ºC
4	Saponification Value (mg $NaOHg^{-1}$ oil)	624.4	187-196	245-256	248-265	189-198	188-194		187-195	168-184	184-196	190-209	230-254	194-202	182-193	189-195	188-194
5	Free Fatty Acid (%)	1.28						0.15 max	0.15 max		≤0.05			0.1 max	0.15 max		0.15 max.
6	Iodine Value ($mg100g^{-1}$)	14.13	86-107	*10-18	6.3-10.6	100-123	128-150	10 max	103-135	92-125	75-94	50.0-55.0	14.1-21.0	≥56	105-126	124-139	118-141
7	Peroxide Value (mgg^{-1})	6.67						10 max	10 max		<20 meq			2 meq max	10 meq max	10 meq max	2

(Source: ICRC, 2020; CAIFS, 2015; Woodbury *et al*, 1998)

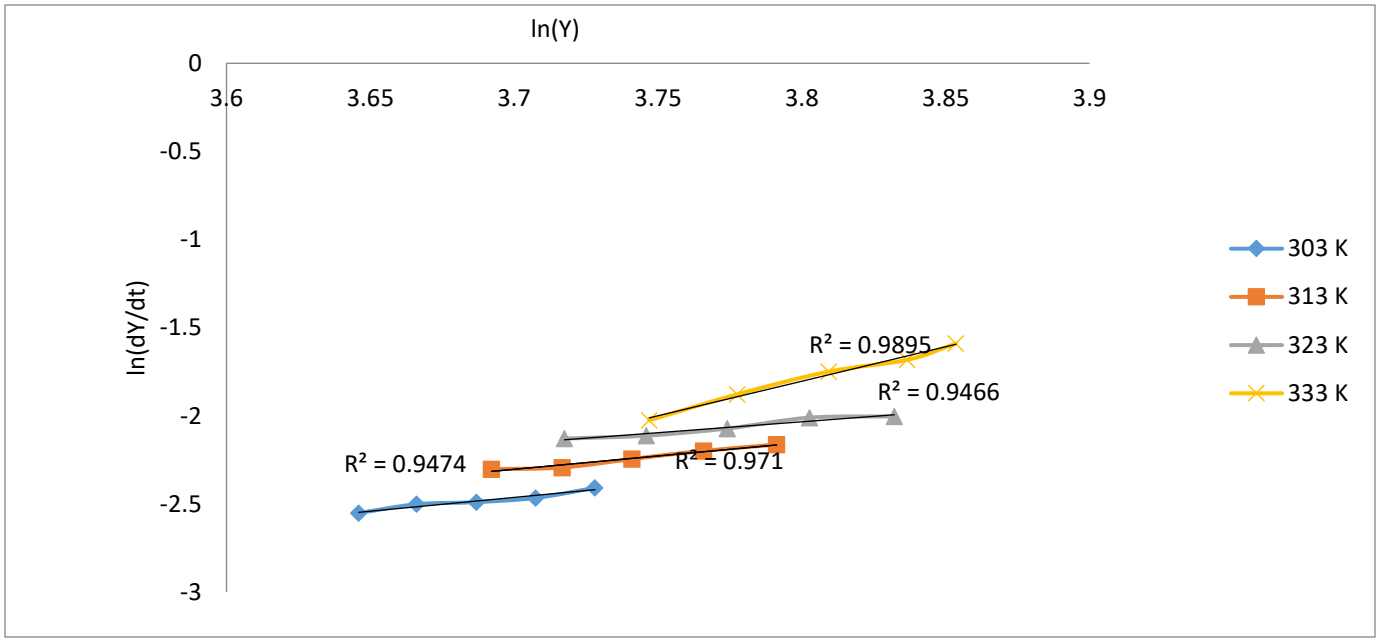

Fig. 2: Plot of ln (dY/dt) vs ln (Y)

respectively reported by Ajayi (2008), although a similar peroxide value of 6.67 mgg-1 were obtained in both studies. The iodine value obtained in this work was well within the reported limit of < 90 (Nichols and Sanderson, 2003). Hence, this oil can be classified as non-drying oil grade suitable for consumption, soap-making, production of pharmaceuticals and as a lubricant. Moreover, the SV of 624.4mg $NaOHg^{-1}$oil, which is a measure of the alkali-reactive groups in fats and oils which helps to evaluate the grades of glycerides present in a sample, indicates that this oil could be very well utilized in the soap making industry. This value also corroborates the values reported for other vegetable oils (Nichols and Sanderson, 2003).

An important factor for the assessment of the sample purity is the acid value of the oil. The value obtained in this study is higher than that of the vegetable oil obtained from pre-treated Chilean hazelnut (Uquiche *et al*, 2008) and this difference is attributable to the hydrolysis of triacylglycerols by the oven drying pre-treatment in the production of FFA (Anjum *et al*, 2006). The unsaturation of the fats and oil contained in the obtained vegetable oil was evaluated from its IV, on the basis of the ability of the unsaturated bond between carbon atoms to accept halogen atoms. The pre-treatment process led to a reduction in the IV. Additionally, a measurement of the PV gave an indication of the intermediate peroxides in the oil which decompose at high temperatures through irradiation of transition metals to form free radicals (Decker, 2004). A correlation exists between PV, organoleptic flavour and freshness of vegetable oils as a result of oxidation (O'Brien, 2004; Vieira and Regitano-d'Arce, 2001).

A comparative analysis of the physicochemical properties of the extract oil from this study with other oil grades is shown in Table 2.

Compared to other vegetable oil grades as shown in Table 2, the specific gravity of the oil extract from this study compared favourably with that of coconut oil, groundnut oil, maize oil, mustard seed oil, rapeseed oil, soyabean oil, as well as sunflower oil and as such could serve as suitable alternatives to these grades especially when refined. The higher SV and FFA values of the extract from this study further justify its suitability for consumption, soap making, production of pharmaceuticals and as a lubricant.

D. Kinetics of oil extraction

The predicted yield at different temperatures is shown in Table 3, while the rate constant shown in Table 4 is an indication of the time required for the extraction process to attain maximum yield. These values increased linearly with temperature (303-323K). A decline was observed at 333K which implies that although temperature improves the reactivity and extraction rate, attaining such a high temperature might give a very rapid reaction which could lead to the destruction of the microstructure of the seed (Uquiche *et al*, 2008). The rate constants obtained in this study corroborate that of vegetable oil obtained from *Daturametel Linn* oil (Mathiarasi and Partha, 2016).

Table 3: Oil yield at different extraction conditions

Time (min)	Oil yield (%)			
	303K	313K	323K	333K
10	38.32	40.13	41.16	42.39
20	39.1	41.13	42.35	43.71
30	39.92	42.14	43.56	45.24
40	40.75	43.2	44.82	46.98
50	41.6	44.31	46.16	48.84
60	42.5	45.46	47.51	50.88

Table 4: Regression coefficient and kinetic parameters

Temp (K)	R^2	Kinetic parameters		
		k (min^{-1})	Ea ($kJmol^{-1}$)	A (sec^{-1})
303	0.947	2.59 x 10-4	61.5	6.72
313	0.971	3.711 x 10-4		
323	0.946	1.186 x 10-3		
333	0.989	5.759 x 10-8		

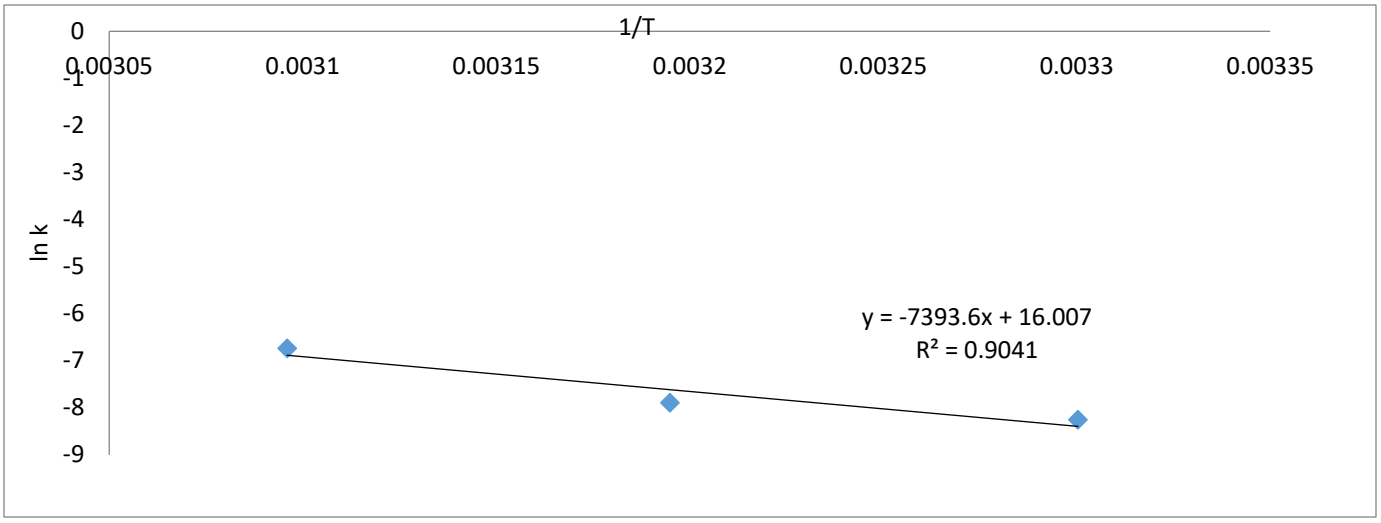

Fig. 3: lnk vs 1/T

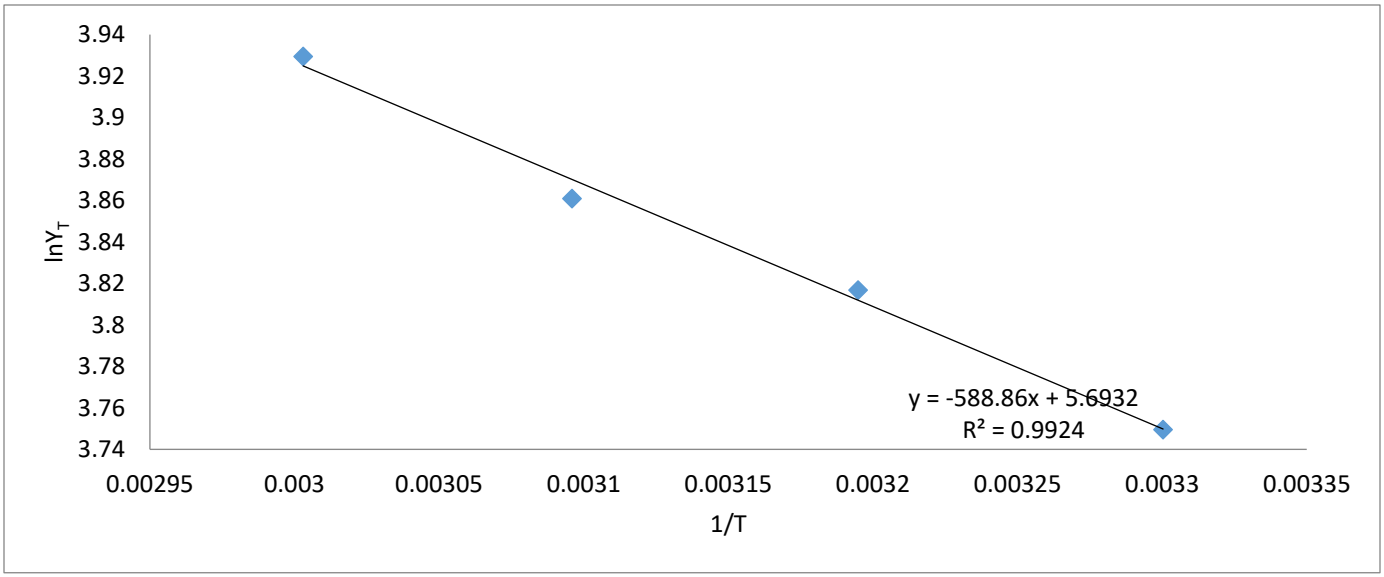

Fig. 4: lnY vs 1/T

Activation energy and Arrhenius constant values obtained in this work also corroborate the works of Mathiarasi and Partha (2016) and Amin *et al* (2010) on *Daturametel Linn* oil and jatropha seed oil, respectively.

E. Thermodynamic properties

An enthalpy changes of 0.071 kJmol^{-1}shows evidence of the endothermic nature and energy requirement of this process in agreement with the values reported for other agricultural products (Otaraku and Okwonna, 2021; Amin *et al*, 2010). These parameters are shown in Table 5.

The Gibbs free energy ($\Delta G<0$) shows a steady decrease in the free energy after activation and hence the oil extraction from the *Treculia africana* seed is spontaneous whereas the positive enthalpy value indicates its energy requirement. Moreover, the entropy, which is a measure of the molecular disorder of the extract, increased linearly with temperature. This is an indication of the effect of temperature on this process. Furthermore, based on these results, it is obvious the energy required to break the solute-solvent/solvent-solvent interaction was greater than that required to maintain these bonds, and as such favours the forward reaction. These values indicate the spontaneity of the process and also corroborate the thermodynamic properties of vegetable oil obtained from other agricultural products (Otaraku and Okwonna, 2021; Mathiarasi and Partha, 2016).

IV. CONCLUSION

In this study, the extraction of vegetable oil from *Treculia africana* seed has been successfully carried out using n-hexane as solvent. The effect of heat pre-treatment on the process was investigated using sun and oven drying treatments. The results indicate that the pre-treatment process had no effect on the physicochemical properties of the extract although the oven-dried samples gave a better yield of 42.5%. Properties of the vegetable oil produced such as specific gravity 0.931,

Table 5: Thermodynamic parameters at different temperatures

Temp (K)	ΔH^* (kJmol^{-1})	ΔS^* (Jmol^{-1}K^{-1})	ΔG^* (kJmol^{-1})	K	ΔG (kJmol^{-1})	ΔS (Jmol^{-1}K^{-1})
303	58.981	-229.21	128.432	5.23	-4.17	14
313	58.898	-229.48	130.725	7.13	-5.11	16.55
323	58.815	-229.74	133.021	11.15	-6.48	20.28
333	58.731	-229.99	135.318	15.32	-7.56	22.92

Saponification value of 624.4 mgNaOHg^{-1}oil, acid value of 2.57 mgKOHg^{-1}oil, free fatty acid of 1.28%, Iodine value of 14. 13 mg100g^{-1} and peroxide value of 6.67 mgg^{-1}, indicate that extract can be classified as non-drying oil grade suitable for consumption, soap making, production of pharmaceuticals and as a lubricant and compares favourably with the vegetable oil from other sources. The kinetics of the extraction process was studied in detail considering all the basic parameters. The reaction was seen to be a first-order reaction with activation energy (Ea) of 61.5 kJmol^{-}, while the rate of reaction was determined. The thermodynamic properties such as enthalpy and entropy of the process were evaluated. The enthalpy changes of 0.071 kJmol^{-1}shows evidence of the endothermic nature, energy requirement and spontaneity of the process. From the result of this study, based on its easy and affordable synthesis technique as well as the properties of the extract, *Treculia africana* seed oil provides a suitable alternative to commercial-grade vegetable oil.

DECLARATIONS

Availability of data and materials

All data generated or analyzed during this study are provided.

COMPETING INTERESTS

The authors declare they have no competing interests.

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AUTHORS' CONTRIBUTIONS

O.O.O. provided data curation, draft manuscript preparation, data analysis and modelling. **A.A.O.** provided data analysis and modelling. **I.J.O.** provided the conceptualization, supervision and bench work. All authors read and approved the final manuscript.

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REFERENCES

Ajayi, I. A. (2008). Comparative study of the chemical composition and mineral element content of *Artocarpus heterophyllus* and *Treculia africana* seeds and seed oils. Journal of Bioresource Technology, 99 (11): 5125–5129.

Akubor, P.I. and Badifu, I.O. (2004). Chemical composition, functional properties and baking potential of African breadfruit kernel and wheat blends. International Journal of Food Science and Technology, 39 (2): 223- 229.

Amin, S. K., Hawash, S., El Diwani, G., and El Rafei, S. (2010). Kinetics and thermodynamics of oil extraction from *Jatropha curcas* in aqueous acidic hexane solutions. Journal of American Science, 6(11): 293-300.

Anjum, F., Anwar, F., Jamil, A., and Iqbal, M. (2006). Microwave roasting effects on the physico-chemical composition and oxidative stability of sunflower seed oil. Journal of the American Oil Chemists' Society, 83(9): 777-784.

Ariahu, C. C., Ukpabi, U., and Mbajunwa, K. O. (1999). Production of African breadfruit (*Treculia africana*) and soybean (Glycine max) seed based food formulations, 1: Effects of germination and fermentation on nutritional and organoleptic quality. *Plant* Foods for Human Nutrition (Dordrecht, Netherlands), 54(3):193-206.

Ayoade, G.W., Aderibigbe, A.D., Amoo, I.A. (2015). Effects of Different Processing Operations on Chemical Composition and Functional Properties of African Breadfruit (*Treculia africana*) Seed. American Journal of Food Science and Nutrition Research, 2(1): 180-185.

Codex Alimentarius International Food Standards, CAIFS (2015). Standard for named vegetable oil. CODEX-STAN- 210-1999, 1-13.

Decker, E. A. (2004). Antioxidant mechanisms, in: Akoh, C. C., Min, D. B. (Eds.), Food lipids, chemistry, nutrition, and biotechnology, Marcel-Dekker, New York, .pp. 397−422.

Dos Santos, S. B., Martins, M. A., Caneschi, A. L., Aguilar, P. R. M., Dos Reis Coimbra, S., (2015). Kinetics and thermodynamics of oil extraction from Jatropha curcas L. using ethanol as a solvent.International Journal of Chemical Engineering, 2015.

Engineering ToolBox, (2008). Melting points of oil. https://www.engineeringtoolbox.com/oil-melting-point-d1088.html. Accessed on June 15, 2021.

Fasasi, O.S., Eleyinmi, A.F., Fasasi, A.R., Karim, O.R. (2004). Chemical properties of raw and processed breadfruit (*Treculia africana*) seed flour. Journal of Food, Agriculture & Environment, 2: 65-68.

Food Security Information Network, FSIN (2022). 2022 Global report on food crises: Joint analysis for better decisions: Mid-year update. Rome, Italy; and Washington, DC. Food and Agriculture Organization (FAO); World Food Programme (WFP); and International Food Policy Research Institute (IFPRI).

Giami, S.Y., Adindu, M.N., Akusu, M.O., Emelike, J.N.T. (2000). Compositional, functional and storage properties of flours from raw and heat processed African breadfruit (*Treculia africana Decne*) seeds. Journal of Plant Foods for Human Nutrition, 55(4):357–368.

Ijeh, I.I., Ejike, C.E., Nkwonta, O.M., Njoku, B.C. (2010). Effect of traditional processing techniques on the nutritional and phytochemical composition of African Bread-Fruit (*Treculia africana*) Seeds. Journal of Applied Sciences Environmental Management,14(4):169–173.

International Federation of Red Cross and Red Crescent Societies, ICRC (2020). Standard product catalogue.

Mathiarasi, R. and Partha, N. (2016). Optimization, kinetics and thermodynamic studies on oil extraction from *Daturametel Linn* oil seed for biodiesel production. Renewable Energy, 96: 583-590.

Menkiti, M.C., Agu, C.M., Udeigwe, T.K. (2015). Extraction of oil from Terminalia catappa L.: Process parameterimpacts, kinetics, and thermodynamics. Industrial Crops and Products, 77: 713–723.

Meziane, S. and Kadi, H. (2008). Kinetics and thermodynamics of oil extraction from olive cake. Journal of the American oil Chemists' society, 85(4): 391-396.

Nichols, D. S and Sanderson, K. (2003). The nomenclature, structure, and properties of food lipids, in: Sikorski, & Kolakowska (Eds.), Chemical and functional properties of foods lipids. Boca Raton, FL: CRC Press Llc., pp. 29−59.

Nnorom, I. C., Ewuzie, U., Ogbuagu, F., Okereke, M., Agwu, P., and Enyinnaya, I. P. (2015). Mineral Contents of Ukwa, African Breadfruit (*Treculia africana*), from South-Eastern Nigeria: Effect of Methods of Preparation. International Journal of Plant & Soil Science, 4(3), 230-240.

Nwabanne, J. T. (2012). Kinetics and thermodynamics study of oil extraction from fluted pumpkin seed. International Journal of Multidisciplinary Sciences and Engineering, 3 (6): 11-15.

Nwinuka, N.M., Ogbonda, J. and Ayalogu, E.O.(2001). Physicochemical characterization of breadnut (*Artocarpus*) seed oil. Global Journal of Pure and Applied Sciences, 7(3): 451-454.

O'Brien, R. D. (2004). Fats and oils: Formulating and processing for applications, 2nd ed. CRC Press LLC, Boca Raton, pp. 174−233.

Oduola, M. K. and Okwonna, O. O. (2016). Kinetic Modelling of the Adsorption Treatment of Waste Lubricating Oil using Activated Ukpor Clay (Bentonite). International Journal of Engineering Research & Science (IJOER), 2(5): 113 – 123.

Okwari, O. O., Ofem, O. E., Ettarh, R. R., and Eyong, E. U. (2006). Blood glucose level and lipid profile in rats fed on *Treculia africana* (Breadfruit) diet: A sub-chronic study. Nigerian Journal of Health and Biomedical Sciences, 5(2):21-25.

Omobuwajo, T.O., Akande, E.A. and Sanni, L.A. (1999). Selected physical, mechanical and aerodynamic properties of African breadfruit (*Treculia africana*) seeds. Journal of Food Engineering, 40 (4): 241-244.

Onyeike, E. N and Acheru, G. N. (2002). Chemical composition of selected Nigerian oil seeds and physicochemical properties of the oil extracts. Food chemistry, *77*(4): 431-437.

Onyekwelu, J. C. and Fayose, O. J. (2007). Effect of storage methods on the germination and proximate composition of *Treculia africana* seeds. In Proceedings of the International Conference on Agricultural Research for Development.

Osabor, V. N., Ogar, D. A., Okafor, P. C., and Egbung, G. E. (2009). Profile of the African breadfruit (*Treculia africana*). Pakistan Journal of Nutrition, *8*(7): 1005-1008.

Otaraku, I. J. and Okwonna, O. O. (2021). Evaluation of Transformer Grade Oil from Coconut Seed Waste. Global Journals of Research in Engineering, 21(1): 13-24.

Rana, A.W., Gill, S., and Akram, I. (2022). Promoting oil seed crops in Pakistan: Prospects and constraints. PACE Policy Research Paper February 2022. Washington, DC: International Food Policy Research Institute (IFPRI).

Shittu, T. A. and Raji, A. O. (2011). Thin layer drying of African Breadfruit (*Treculia africana*) seeds: modeling and rehydration capacity. Food and Bioprocess Technology, 4(2): 224-231.

Uquiche, E., Jeréz, M. and Ortíz, J. (2008). Effect of pretreatment with microwaves on mechanical extraction yield and quality of vegetable oil from Chilean hazelnuts (*Gevuina avellana Mol*). Innovative Food Science & Emerging Technologies, 9(4): 495-500.

Uyigue, L. and Okwonna, O. O. (2013). Conversion of post-consumer (or waste) printers' paper grades into microcrystalline cellulose powder. Journal of Emerging Trends in Engineering and Applied Sciences, 4(1): 126-132.

Woodbury, S.P., Evershed, R.P., and Rossell, J.B. (1998). Gamma 13C analysis of vegetable oil, fatty acid components, determined by gas chromatographycombustion-isotope ratio mass spectrometry, after saponification or regiospecific hydrolysis. Journal of Chromatography A, 805: 249-257.

Vieira, T. M. and Regitano-d'Arce, M. A. (2001). Canola oil thermal oxidation during oven test and microwave heating. Lebensmittel Wissenschaft und Technologie Food Science and Technology, 34(4): 215-221.

Zahid, A.; Z. Mukhtar; M.A. Qamar; S. Shahid; S.K. Ali; M. Shariq; H.J. Alathlawi; M.A. Hasan; M.S. Khan; S. Islam. (2023). Synthesis of Mn-doped ZnO nanoparticles and their application in the transesterification of castor oil. Catalysts, 13, 105.