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KINETIC, THERMODYNAMIC AND PARAMETRIC STUDIES OF OIL EXTRACTION FROM JATROPHA OILSEEDS

Sunday. U John
Department of Chemical Engineering, Faculty of Engineering,
Nnamdi Azikiwe University, Awka, Anambra State, Nigeria
* su.john@unizik.edu.ng

Philomena Igbokwe K.
Department of Chemical Engineering, Faculty of Engineering,
Nnamdi Azikiwe University, Awka, Anambra State, Nigeria
* pk.igbokwe@unizik.edu.ng

Joseph Nwabanne T.
Department of Chemical Engineering, Faculty of Engineering,
Nnamdi Azikiwe University, Awka, Anambra State, Nigeria
* jt.nwabanne@unizik.edu.ng

ABSTRACT

The kinetics, thermodynamics, and effects of process variables on Jatropha seed oil (JO) extraction were investigated via soxhlet extraction using petroleum ether. The kinetic models investigated were power law, pseudosecond-order, parabolic-diffusion, pseudo-first-order, Elovich, and hyperbolic models. The process parameters studied include, the extraction temperature, average particle size, and time. The thermodynamics parameters such as Gibb free energy, enthalpy, and entropy were determined. It was found that oil extraction yield varied directly proportional to an increase in temperature and time but inversely proportional to an increase in particle size. The maximum oil yield of 39.5 % was obtained at the extraction conditions of 74 ^{o}C, 0.1 mm, and 180 min. The best fitted kinetic models in order of performance were hyperbolic, parabolic, elovich, and power-law models. The average values of the absolute average relative error (AARE), the sum of the squares of errors (SSE), root mean squared error (RMSE), standard deviation (SD), total sum of squares (SST), coefficient of determination (R2), adjusted-coefficient of determination (adj-R2), hybrid fractional error function (HYBRID%), the Marquardt's percent standard deviation (MPSED%), and standard error of estimation (SEE) for power law as the best-fitted model is as follows: 0.0004, 0.4804, 0.0004, 6.72E-06, 16.6067, 96.8432, 96.4486, 0.0063, 0.0593, 0.0133, respectively. However, pseudo-second-order and pseudo-first-order models failed to give adequate fitting to the experimental data. The Gibb free energy, enthalpy, and entropy values of the Jatropha oil extraction process at 328K and 0.1mm were -3.53kJ/mol, 45.79kJ/mol, and 0.15kJ/mol, respectively, indicating endothermic, irreversible, and spontaneous process.

Keywords: kinetics, thermodynamics, Empirical-models, Jatropha-seeds-oil, liquid-solid-extraction, statistical-model-analysis

INTRODUCTION

The development of the vegetable oil sector and the oil extraction process is extremely valuable and important because of its relative advantage over petroleum base oils since the major vegetable oil resource used for both domestic and industrial applications are the nuts and seeds [1]. Concerning the overall economic importance of Jatropha oil cultivation and industrial application, the development and commercialization of the processes for both Jatropha oil extraction and its industrial applications are very attractive and crucial.

Kinetics and thermodynamics of the oil extraction process is an essential pillar that informs and drives the possibility of commercialization and industrial application of Jatropha seeds oil [2]. The extensive research on the thermodynamics and kinetics of the oil extraction process from Jatropha seeds is very important because it's pivotal to the design and development of the oil extraction process and plant for industrial application. Several studies on oil extraction from Jatropha seeds have majorly focused on the determination of oil yield and physicochemical characterization [1, 3, 4, 5, 6, 7, 8, 9, 10, 11]. As a result, the kinetics and thermodynamics studies of Jatropha seeds oil extraction has received very limited attention.

On the other hand, very few authors have investigated the kinetics of Jatropha seed oil extraction [12, 13, 14]. Amin et al. [13] applied the differential method to determine the order of reaction and reported the reaction order to be first-order kinetics. In their separate study, Sayyar et al. [12] and Silmara et al. [14] modeled the Jatropha oil extraction kinetics using a pseudo-second-order model. Their works were an effort to force the extraction process to follow the selected pseudo-second-order model and feigned the kinetics of oil extraction based on a second-order mechanism. Moreover, the exact extraction kinetics and reaction mechanisms are complex and partly comprehended, and hence, a very significant limitation to the oil extraction process and plant design and development.

As a result of the significance of kinetics with regards to the oil extraction process, a good number of physical and empirical kinetic models have been suggested to examine the oil extraction process kinetics for various oil seeds and nuts such as, however not limited to, olive cake, sunflower, sunflower collets, Terminalia catappa, rapeseed, Colocynthis vulgaris Schrad, fluted pumpkin [15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. Normally, the empirical models such as the hyperbolic model, Elovich's model, Peleg’s model, parabolic diffusion model, powerlaw model, Weibull's model, pseudo-first-order, and Pseudo-second order models are easier, plainer, and simpler than physical models, and hence, more appropriate for engineering drives.

However, there is little or no published work existing on the kinetics study of Jatropha seed oil extraction using hyperbolic, parabolic diffusion, elovich models, and pseudo-first-order models. As a pivotal and significant clincher to the achievable industrial application of Jatropha oil, extensive kinetics and thermodynamics studies on the oil extraction process from seeds/nuts are a functionality that is vital to the development and commercialization/industrialization of the extraction process and the vegetable oil sector. Therefore, this study focuses on the application of empirical models (such as power law, parabolic, Elovich, hyperbolic, pseudo-secondorder, and pseudo-first-order) to investigate the kinetics of Jatropha oil extraction using petroleum ether as a solvent medium. Besides, the thermodynamic parameters (enthalpy, entropy, and Gibb free energy) were also determined.

MATERIALS AND METHODS

Feedstock preparation

In the extraction of oil from jatropha seeds, the first step is to remove the seed-coat and husk, called seed cleaning. Seed cleaning involves the removal of the seed coat or shell and the separation of the chaff. The adequate screening was done on the seed samples to remove damaged or spoilt ones and clean the remaining good seeds. This was very necessary to ensure that no debris was left in the seeds before the extraction of oil. After the nuts were cracked, the separated oil-bearing seeds or kernels were sieved, cleaned, dried, and stored at room temperature. The seed drying was done by sun-drying or by heating carefully on the fire for a short while [25], to remove moisture. To reduce the moisture content to 1.3%, further seed drying was conducted in the oven at 65 °C. The dried seeds were milled with an electric grinder. The milled seeds were sieved into different average standard particle sizes (0.1 mm to 0.5 mm), using standard sieve plates. After this was completed, the next step was to commence the crucial extraction process. The extraction solvents were of analytical grades and were used without further purification.

Extraction of Jatropha seed oil

Soxhlet extraction was carried out using petroleum ether as the extracting solvent in a soxhlet apparatus. The dried seeds of Jatropha were crushed using a commercial grinder. A determined amount of extracting solvent and milled seeds of jatropha of particular average particle size was placed in a Soxhlet extractor connected to a condenser. The extraction cycle was carried out at different temperatures (32–74 °C), average particle sizes (0.1–0.5 mm), and time (30 – 180 min). The extracted oil yield was calculated and recorded at the end of every cycle of extraction. The residual solvent was removed or evaporated employing a simple method of evaporation or rotary evaporator, at 65 °C. The percentage oil yield of Jatropha seeds was determined as a ratio of the weight of oil extract to the total weight of the seeds used using the equation (1):

$$\text{Oil yield }(\%) = \frac{\text{weight of extracted oil (g)}}{\text{weight of sample (g)}} \text{ x } 100 \qquad (1)$$

One-factor-at-a-time analysis

To examine the influence of extraction time, temperature, and particle size on the percentage oil yield from Jatropha seeds using petroleum ether, one-factor-at-a-time (OFAT) experiments were designed and carried out in the batch form. The range of variables studied were extraction temperature (32 ºC – 74 ºC), particle size (0.1 mm – 0.5 mm) and extraction time (30 – 180 min). Figures 1-2 summarize the result of the effects of the different extraction process variables on the oil yield.

Kinetic models

To investigate the kinetics of Jatropha seeds oil extraction route using petroleum ether, the six kinetic models studied were power law, Elovich's, hyperbolic, parabolic diffusion, pseudo-first-order, and pseudo-second-order models. The kinetic equations of the aforementioned models were presented in Table 1.

Table 1: Model names, nonlinear, linear and linear prediction equations and plotting parameters

Kinetic models	Nonlinear equation	Linear equation	Linear predicted response	Linear plot	Slope	Intercept
Pseudo 1st order	$Y,(\%) = \frac{d(q_t)}{dt} = K(q_e - q_t)$	$Ln(q_e - q_t) = Inq_e - Kt$	$q_t = q_e - exp(Inq_e - Kt)$	$Ln(q_e - q_t)\ VS\ t$	-K	Inq_e
Pseudo 2nd order	$Y,(\%) = \frac{q_e{}^2Kt}{1 + q_eKt}$	$\frac{t}{q_t} = \frac{1}{Kq_e{}^2} + \frac{t}{q_e}$ $\frac{1}{h} = \frac{1}{Kq_e{}^2}$	$q_t = \frac{t}{(\frac{1}{Kq_e{}^2} + \frac{t}{q_e})}$	$\frac{t}{q_t} VS\ t$	$\frac{1}{q_e}$	$\frac{1}{Kq_e{}^2}$
Hyperbolic	$Y,(\%) = \frac{C_1t}{1 + C_2t}$	$\frac{1}{Y}(\%) = \frac{1}{C_1} X \frac{1}{t} + \frac{C_2}{C_1}$	$Y,(\%) = \frac{1}{\left(\frac{1}{C_1} X \frac{1}{t} + \frac{C_2}{C_1}\right)}$	$\frac{1}{Y}(\%)\ VS \frac{1}{t}$	$\frac{1}{C_1}$	$\frac{C_2}{C_1}$
Parabolic diffusion	$Y,(\%) = A_0 + A_1t^{1/2}$	$Y,(\%) = A_0 + A_1lnt$	$Y,(\%) = A_0 + A_1lnt$	$Y,(\%) VS\ lnt$	A_1	A_0
Elovich's	$Y,(\%) = E_0 + E_1lnt$	$Y,(\%) = E_0 + E_1lnt$	$Y,(\%) = E_0 + E_1lnt$	$Y,(\%) VS\ lnt$	E_1	E_0
Power law	$Y\ (\%) = Bt^{1/2}$	$InY\ (\%) = InB + nLnt$	$Y,(\%) = exp(InB + nLnt)$	$InY\ (\%)\ VS\ Lnt$	n	InB

Initial extraction rate, h = Kq_e; q_e acts for the pseudo-first and seconder order model oil concentration parameter in the mixture extract (gL^{-1}); E_o and E_1 represents Elovich model parameters relating initial rate and rate constant (L); ^{n}power law exponential diffusion; ^{K}rate constant; ^{Ao,A1}denote parabolic diffusion model parameters; washing coefficient (initial extraction rate) and rate of diffusion constant ($\min^{-1}$), respectively. B represents power law model parameter relating the extraction rate constant characteristic ($\min^{-1}$). C1, C2 acts for the initial extraction rate and rate constant for the maximum oil extraction yield ($\min^{-1}$); Y" oil extraction yield; ^{t}time (min); $^{qe,\ qt}$ equilibrium extraction capacity or yield (mmol/g) and extraction capacity at a time t, respectively.

Statistical method

The statistical degree of fitness of the kinetic models on the experimental data was determined by the assessment of the root mean squared error (RMSE), coefficient of determination (R^2), adjusted-coefficient of determination (adj-R^2), absolute average relative error (AARE), hybrid fractional error function (HYBRID%), the sum of squares of the errors (SSE), the Marquardt's percent standard deviation (MPSED%), standard deviation (SD), the total sum of squares (SST) and standard error of estimation (SEE) [2, 20, 22, 26, 27, 28]. The R^2, adj-R^2, RMSE, AARE, HYBRID%, SSE, MPSED%, SD, SST and SEE were computed by applying the given equations (2) - (11).

$$RSME = \sqrt{\frac{\sum\left[\frac{q_{\exp(i)} - q_{model(i)}}{q_{\exp(i)}}\right]^2}{n}} \tag{2}$$

$$AARE = \frac{\sum_{i=1}^{N}\left[\frac{q_{\exp} - q_{model}}{q_{\exp}}\right]}{n} \tag{3}$$

$$SD = \sqrt{\frac{\sum_{i=1}^{N}\left[q_{\exp(i)} - q_{model(i)}\right]^2}{n-1}} \tag{4}$$

$$HYBDBRID\% = \frac{\sum_{i=0}^{n}\left(\frac{y_i - \hat{y_i}}{y_i}\right)}{N - P_r} * 100 \tag{5}$$

$$R^2 = 1 - \frac{\sum(y_i - \hat{y})^2}{\sum(y_i - \bar{y})^2} \tag{6}$$

$$SSE = \frac{\sum_{i=0}^{n}(y_i - \hat{y})^2}{n} \tag{7}$$

$$Adj - R^2 = \frac{(1 - R^2)(N - 1)}{N - P_r - 1} \tag{8}$$

$$MPSED\% = \sqrt{\frac{\sum_{i=0}^{n}\left(\frac{y_i - \hat{y_i}}{y_i}\right)^2}{N - P_r}} * 100 \tag{9}$$

$$SEE = \sqrt{\frac{\sum(y_i - \hat{y})^2}{dt}} \tag{10}$$

$$SST = \frac{\sum_{i=0}^{n}(y_i - \bar{y}_i)^2}{n} \tag{11}$$

Where y_i is the experimental response values, $\hat{y}$ = predicted response values, $\bar{y_i}$" denotes the mean predicted response values, n number of sample runs or data points, P_r = number of predictors, N = Total sample size. Higher R^2 and adjusted- R^2, and lower RMSE, SSE, AARE, HYBRID%, SEE, MPSED%, SST and SD values, indicates a better goodness of fit [2, 28] and a fit that is more useful and convenient for prediction.

Thermodynamics of Jatropha oil extraction

In order to to investigate the feasibility and nature of the oil extraction process, the extraction thermodynamics parameters such as enthalpy, Gib's free energy and entropy were determined from the following equations (12) – (15).

$$\Delta G = -RT\ln K \tag{12}$$

$$In\ K = \frac{-\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{13}$$

Where, ΔG is Gibbs energy or free energy (KJ/mol), ΔH is change of enthalpy (KJ/mol), K is the equilibrium constant, ΔS is change in entropy (KJ/mol), T is the temperature (K), R is Universal gas constant (8.314KJ/Kmol) [14]

$$K = \frac{Y_{Te}}{Y_{Ue}} \tag{14}$$

Where, Y_{Te} is oil yield (%) at temperature, T and Y_{ue} is unextracted oil (%). Plot of lnk against 1/T gives will give -ΔH/R as slope and ΔS/R as intercept, hence ΔH and ΔS were determined. These values were used to compute ΔG* from the relation: (equation 8)

$$\Delta G = \Delta H - T\Delta S \tag{15}$$

RESULTS AND DISCUSSION

Influence of temperature and time on Jatropha seeds-oil extraction

The impact of temperature and time variation on oil extraction yield was investigated by carrying out experiments at different five extraction temperature levels of 32, 50, 55, 68, and 74oC and time intervals of 30, 60, 105, 150, and 180 minutes at a particle size of 0.1mm. The findings on the effect of temperature variation on the rate of oil extracted from jatropha seeds meal using petroleum ether as the solvent medium are presented in Fig. 1.

From Fig. 1, it is evident that the fraction of oil recovered increased with an increase in temperature and time. The oil extraction yield was observed to increase with an increase in temperature up to 68^{o}C, after which further increase in temperature resulted in an insignificant increase in the amount of oil recovered. The observed increase in oil yield with an increase in temperature is because temperature increase would result in enhanced mass transfer coefficient of extraction, reduced oil viscosity, increased diffusion, and improved oil extraction yield [22, 29-33]. Also, little temperature increase leads to a marginal fluid density reduction which in turn results in reduced solute solubility [22, 31, 34].

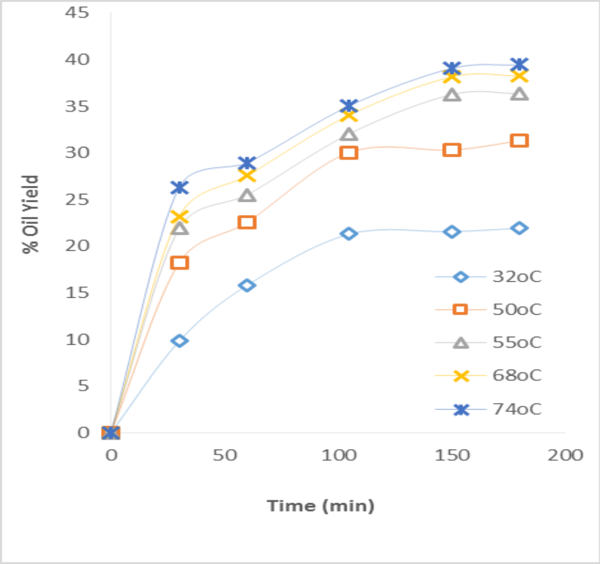
A rapid oil extraction process was observed at the beginning and later slowed down at about 100 – 180 minutes. This is similar to the findings of Menkiti et al. [22] in their report on oil extraction from the seeds of Terminalia catappa L using n-hexane. In this study, the initial rapid oil extraction process observed at the beginning is suggested to be due to the free oil disposed to fresh solvent at the surface of milled Jatropha seed. The vulnerability of the free oil at the surface of Jatropha seed particles caused the oil to be readily soluble in the solvent and thereby leading to fast oil extraction [12, 13, 22, 33, 35, 36]. Generally, the initial rapid rate and final slow rate yields observed with extraction could be explained by initial fast washing action and slow diffusion controlled regimes, respectively [2, 12, 13, 22, 36].

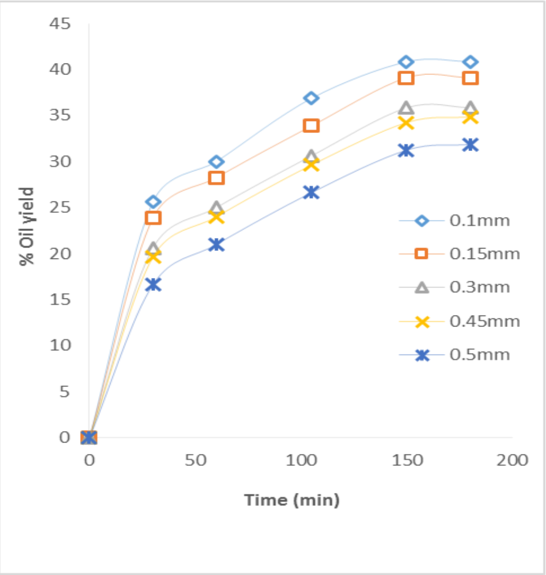
However, the oil extraction yield from Jatropha seed increased with an increase in temperature and time. The maximum percentage oil extraction of 39.5% was recorded at the temperature of 74ºC and time of 180 min.

Influence of particle size on Jatropha seeds-oil extraction

The characteristics of a starting material like the particle size, generally, influence the extraction process [33, 37, 22]. The particle size is relative to the surface area of reaction and thus a very important factor of interest in oil extraction study. Hence, the impact of particle size variation on oil extraction yield was investigated by conducting experiments at different Jatropha seed particle sizes of 0.1, 0.15, 0.3, 0.45, and 0.5mm and time intervals of 30, 60, 105, 150, and 180 minutes at the extraction temperature of 74ºC. The findings on the effect of particle size variation on the rate of oil extracted from milled Jatropha seeds using petroleum ether as the solvent medium is presented in Fig. 2. The Figure reveals that the percentage of oil extracted with time decreased as the particle size of the milled Jatropha seed was increased. It’s evident from the plot of results, that higher oil yield was achieved at smaller particle sizes, whereas lower oil yield was recorded at bigger particle sizes. The higher and lower oil yield achieved at smaller and bigger particle sizes, respectively, is attributed to the higher surface area possessed by the smaller particle sizes than the bigger particle sizes. The maximum oil extraction of 39.5% was achieved using the particle size of 0.1mm at 180 minutes.

Generally, an increase in oil yield with decreasing particle size is bound to a bigger interfacial area of the solid particles which results in lesser intraparticle diffusion resistance for the smaller particle sizes as a result of shorter diffusion path. The decrease in oil yield is pronounced in bigger particle sizes due to high intra-particle diffusion domicile in bigger particles. This was experimentally observed because not all the oil was extracted in the larger particle sizes owing to small contact surface area and minimal oil diffusion from the pores of the larger particles to the bulk of the solvent. On the other hand, greater milling increases the surface area of the resultant smaller particle sizes, thus, increasing the rate of oil extraction by freeing more oil from cells and getting them easily disposed to solvent for extraction. This phenomenon was observed in this study as the rate of extraction of oil from milled Jatropha seeds at smaller particle sizes were more rapid than the larger particles, due to reduced diffusion path, a higher rate of mass transfer, and a higher rate of oil dissolution in the solvent [22, 38, 39-41].





Kinetic parameters

The result of kinetic parameter values for the six kinetic models, namely; power law, parabolic diffusion models, hyperbolic, Elovich's, pseudo-first-order, and second-order models, respectively, studied at different temperature and particle size variation is presented in Table 2. It was observed that the parameters C1 and C2 for the hyperbolic model varied proportionally with increasing temperature but varied inversely with increasing particle size. The increase in C1 and C2 observed with an increase in temperature and decrease in particle size is associated with an increased yield of oil observed with increasing temperature and decreasing particle sizes, and the insignificant recorded differences between the models' predicted oil yields and the experimental values. Also, the observed trend of C1 and C2 observed across the temperature and particle size regimes signify a high initial rate and overall oil recovery at high temperatures and smaller particle sizes. A similar trend of the result was observed to be consistent for parabolic diffusion, power-law, and pseudo-first-order kinetic model parameters. The A1, Ao, K, B, and qe parameters for parabolic diffusion, power-law, and first-order kinetic models were found to maintain a consistent increase with increasing temperature and decreasing particle sizes. A similar pattern of results was observed in the study of Kitanovic et al. [2] and Menkiti et al. [20] for the solvent extraction of resinoid from the aerial part of Hypericum perforatum L using different solute to solvent ratios and Colocynthis vulgaris Shrad Seeds oil (CVSSO) extraction using solvent extraction method, respectively. The hyperbolic, parabolic, and Elovich parameter values of C1, Ao, and Eo were found to be higher than the corresponding parameter values of C2, A1, and E1, respectively.

This is in agreement with the parameter values reported by [2, 20, 22, 42-44]. However, the C1 values recorded in this work were slightly (-0.1 or -0.2) lower than the C1 values reported by [44, 42, 22, 20], while the C2 values obtained in this study were (+0.1 or 0.2) higher than the C2 values reported by [20, 22, 42, 44]. On the other hand, the C1 and C2 values from this study across all temperature and particle size variations were found to be comparably approximate with the ones reported by Kadurumba et al. [45] on solvent extraction of oil from Colocynthis vulgaris Shrad (melon) seeds. The higher or lower values of C1 and C2 as reported by the various authors implies, higher or lower initial rapid oil extraction rate and final slow diffusion rate action, respectively, for oil extraction from different seeds studied. Hence, the variation in the initial rapid rate and final slow rate yields reported by the various authors could be explained by initial fast washing action and slow diffusion controlled regimes, respectively.

Also, the range of qe values (42 - 48) and (23.8 - 75) obtained in this work for pseudo-second-order and first-order model, respectively, were comparable with the qe values which ranged between 30.23 - 60.02 for the second-order model, as reported by Silmara et al. [14] on the kinetics of Jatropha seed oil extraction at different temperature and particle size variation. On the other hand, Sayyar et al. [12] reported slightly higher qe values which ranged between 84.03 - 90.91. However, the obtained qe values in this work were also incomparable agreement with the values of (45.25 – 74.63); (40.31-77.55), (40.65 – 75.19), (36.50 – 60.24), and (35.81 – 54.24) reported by [20, 22, 42, 44, 45], respectively, for pseudo-second-order model. The observed slight variation could be attributed to seed morphology, variation in extraction conditions, different extraction solvent, and technique.

On the other hand, generally, the elovich, pseudo-second-order, and power-law parameters: E1, Eo, α, β, qe, k, h, n, and B did not present any definite pattern across the different temperature and particle size variation studied. However, a consistent qe increase was observed for the second-order model while the second-order k increased inconsistently with an increase in temperature.

Similarly, the qe, k, h, and B for second-order and power-law presented an inconsistent increase with a decrease in particle size variation. Generally, the observed consistent kinetic parameter values increase with temperature is attributed to the prevalence and power of diffusion rate above the washing mechanism process, therefore, leads to better/greater oil extraction yield of in the models [20, 22, 46].

Table.2 Kinetic parameters at different temperature and particle sizes

Temp(oC)	**32Oc**	**50oC**	**55oC**	**68oC**	**74oC**	**AVE**	**0.1mm**	**0.15mm**	**0.3mm**	**0.45mm**	**0.5mm**	**AVE**	**TOTAL AVE.**
HYPERBOLIC MODELS													
C1	0.4578	1.1628	1.4868	1.5918	2.1501	1.3699	1.8498	1.6753	1.3263	1.2375	0.9565	1.4091	1.3895
C2	0.0155	0.0316	0.0366	0.0369	0.0510	0.0343	0.0405	0.0385	0.0326	0.0313	0.0255	0.0337	0.0340
R2	0.8950	0.9674	0.9356	0.9558	0.8936	0.9295	0.9510	0.9478	0.9547	0.9679	0.9679	0.9579	0.9437
PARABOLIC MODEL													
A1	1.7225	1.7157	1.9784	2.0353	1.8068	1.8517	2.0683	2.0570	2.0558	2.0214	2.0214	2.0448	1.9483
Ao	0.3586	9.6255	10.9770	12.2450	16.0050	9.8422	14.5210	12.6360	9.3929	8.6114	5.6114	10.1545	9.9984
R2	0.8814	0.9195	0.9778	0.9787	0.9779	0.9471	0.9750	0.9833	0.9836	0.9904	0.9904	0.9845	0.9658
ELOVICH MODEL													
E1	7.7193	7.7662	8.7723	9.0626	7.9646	8.2570	9.2174	9.1150	9.1099	8.9580	8.9580	7.4125	7.8348
Eo	17.2250	8.2345	8.7991	8.2702	1.8465	8.8751	6.3625	7.9006	11.1320	11.5730	14.5730	10.3082	-9.5916
α	0.1295	0.1288	0.1140	0.1103	0.1256	0.1216	1.0849	0.1097	0.1098	0.1116	0.1116	0.3055	0.2136
β	0.8289	2.6898	3.2173	3.6386	6.3165	3.3382	0.0009	3.8311	2.6842	2.4612	1.7607	2.1476	2.7429
R2	0.8951	0.9527	0.9721	0.9811	0.9608	0.9524	0.9791	0.9763	0.9766	0.9835	0.9835	0.9798	0.9661
FIRST ORDER													
K	0.0036	0.0058	0.0104	0.0137	0.0164	0.0100	0.0362	0.0165	0.0101	0.0088	0.0069	0.0157	0.0128
qe	23.8081	25.1309	26.7999	28.1374	27.9635	28.3680	75.0009	31.5508	28.2304	28.1712	29.8505	38.5608	33.4644
R2	0.8406	0.8871	0.9708	0.9712	0.9712	0.9282	0.9197	0.9494	0.9673	0.9868	0.9860	0.9618	0.9450
SEDCOND ORDER													
qe	32.4675	37.3134	43.8596	45.6621	45.4545	40.9515	48.0769	46.7290	44.0529	42.9185	40.6504	44.4855	42.7185
K	0.0004	0.0008	0.0006	0.0006	0.0008	0.0007	0.0007	0.0006	0.0006	0.0006	0.0005	0.0006	0.0006
h	0.0127	0.0303	0.0277	0.0296	0.0358	0.0272	0.0326	0.0292	0.0249	0.0240	0.0200	0.0261	0.0267
R2	0.9155	0.9932	0.9925	0.9950	0.9936	0.9780	0.9955	0.9927	0.9911	0.9928	0.9913	0.9927	0.9853
POWER LAW MODEL													
N	0.5060	0.3186	0.3053	0.2985	0.2451	0.3347	0.2798	0.2928	0.3276	0.3357	0.3796	0.3231	0.3289
B	1.7023	6.2376	7.6187	8.3361	11.1418	7.0073	9.8139	8.7155	6.6912	6.2022	4.5317	7.1909	7.0991
R2	0.9101	0.9535	0.9816	0.9874	0.9706	0.9606	0.9847	0.9880	0.9890	0.9936	0.9942	0.9899	0.9753

Comparative statistical fitness degree for the kinetics models

The optimal criteria required for determination of the best fitness of the kinetic models (hyperbolic, parabolic diffusion, power law, Elovich's, pseudo-first-order and pseudo-second-order) to the experimental data were R2, Adj-R2, RMSE, SSE, AARE, SEE, HYBRID% SST, SD, and MPSED%. Usually, higher values of R2 and Adj-R2, and lower values of RMSE, SSE, AARE, SEE, HYBRID% SST, SD and MPSED% would indicate better model goodness of fit to the experimental data [2, 20, 22, 26, 28, 42]. The results of the statistical fitness degree for the six kinetic models studied were presented in Table 3 - 5. From the tables, the AARE, SSE, RSME, SD, HYBRID%, MPSED% and SEE were found to decrease with increasing temperature while the R2 and adjusted-R2 varied directly proportional with temperature for power law, elovich, parabolic and hyperbolic models whereas no definite variation pattern was observed for first order and seconder order models. The observed trend of the R2 and adjusted-R2 results illustrates the capability of the models to account for a greater proportion of total variation in the data about the average and that oil recovery increases with increasing temperature and decreasing particle sizes. That is, the lower or decreasing values of AARE, SSE, RSME, SD, HYBRID%, MPSED%, SEE, and higher values of R2 and adjusted-R2 at higher temperature regime and smaller particle sizes indicates higher oil yield at higher temperatures regime and smaller particle sizes. The observed trend of AARE, SSE, RSME, SD, HYBRID%, SST, MPSED%, and SEE for power-law, elovich, parabolic, and hyperbolic diffusion models is an indication of the models more usefulness and convenience for prediction. A similar result trend was reported by [20, 22, 42-45]. Generally, the values of AARE, SSE, RSME, SD, HYBRID%, MPSED% and SEE obtained in this work were comparable and in close agreement with the values obtained by [20, 22, 42-45], in their kinetic study of oil extraction from different seeds and nuts. Besides, the statistical error function values recorded in this report were slightly lower than the values reported by these authors. This implies that these empirical models could describe Jatropha oil extraction kinetics better than oil extraction from the various seeds studied by those authors, and hence, could be more useful for future prediction.

However, it could be seen that the average values of AARE, SSE, RMSE, SD, HYBRID%, MPSED%, and SEE for hyperbolic, parabolic, elovich, and power-law models were all ≤ 1, while their SST values were ≤ 16.63 with R2 and Adj-R2 ≥ 93% ≤ 97%. The R^2 and Adj-R^2 values of the kinetic models in descending order were power law (96.8432, 96.4486), elovich (96.6070, 96.1828), parabolic (96.5795, 96.1520), hyperbolic (93.8043, 93.0298), second-order (67.2786, 63.1884), and first-order (29.9343, 46.3646). However, the first-order, and second-order kinetic models presented lower values of R^2 and Adj-R^2, and higher values of AARE, SSE, RMSE, SST, SD, HYBRID%, MPSED% and SEE.

For the values of average AARE, SSE, RMSE, SD, SST, R^2, ADJ-R^2, HYBRID%, MPSED% and SEE, the hyperbolic, parabolic, elovich, and power law, gave a good fit to the experimental data while the pseudo-first-order and second-order kinetic models gave poor fit to the experimental models. Based on the average AARE, SSE, RMSE, SD, SST, R^2, ADJ-R^2, HYBRID%, MPSED% and SEE values of the kinetic models investigated, their degree of fitness to the experimental data in ascending order is presented as given: First-order → Second-order → hyperbolic → parabolic → elovich → power-law. Power law and parabolic models having the highest and approximate R^2, adj-R^2, and lowest average AARE, SSE, RMSE, SD, SST, HYBRID%, MPSED% and SEE values were chosen simultaneously as the best extraction kinetic models that fit the experimental kinetics data investigated.

Hence, in ascending order, the ranks of the kinetic models that gave a good fit to the experimental data were hyperbolic → parabolic → elovich → power-law models.

Table 3. Statistical fitness degree for hyperbolic and parabolic diffusion kinetic models

HYPERBOLIC MODEL													
Temp(oC)	**32oC**	**50oC**	**55oC**	**68oC**	**74oC**	**Temp (Ave)**	**0.1mm**	**0.15mm**	**0.3mm**	**0.45mm**	**0.5mm**	**Part.Size (Ave.)**	**Total Average**
AARE	0.0027	0.0008	0.0009	0.0003	0.0002	0.0009	0.0001	0.0001	0.0012	0.0013	0.0003	0.0006	0.0007
SSE	1.5893	0.5641	1.0958	0.8246	1.4044	1.0957	0.9081	1.1191	1.0301	0.8388	0.6980	0.9188	1.0072
RMSE	0.0033	0.0004	0.0007	0.0004	0.0007	0.0011	0.0004	0.0005	0.0006	0.0005	0.0006	0.0005	0.0008
SD	4.1E-05	3.5E-06	5.0E-06	5.1E-07	3.1E-07	9.9E-06	3.5E-08	1.1E-07	7.6E-06	9.1E-06	6.8E-07	3.49E-06	6.7E-06
SST	14.2785	13.5049	16.8988	17.8572	14.0838	15.3246	18.5072	18.1536	18.1402	17.4171	17.4086	17.9253	16.6250
R2	88.8690	95.8230	93.5153	95.3820	90.0280	92.7235	95.0935	93.8353	94.3217	95.1842	95.9908	94.8851	93.8043
ADJ-R2	87.4776	95.3009	92.7047	94.8048	88.7815	91.8139	94.4801	93.0647	93.6119	94.5822	95.4896	94.2457	93.0298
HYBRID%	0.0386	0.0113	0.0135	0.0043	0.0034	0.0129	0.0011	0.0020	0.0167	0.0182	0.0050	0.0082	0.0105

MPSED%	0.4706	0.0598	0.0958	0.0634	0.1010	0.1581	0.0613	0.0751	0.0830	0.0749	0.0791	0.0747	0.1164
SEE	0.0441	0.0157	0.0304	0.0229	0.0390	0.0304	0.0252	0.0311	0.0286	0.0233	0.0194	0.0255	0.0280
PARABOLIC MODEL													
AARE	0.0069	0.0020	0.0005	0.0005	0.0003	0.0020	0.0005	0.0003	0.0004	0.0003	0.0004	0.0004	0.0012
SSE	1.6835	1.0860	0.3743	0.3810	0.3110	0.7672	0.4632	0.3024	0.2973	0.1677	0.1677	0.2796	0.5234
RMSE	0.0027	0.0007	0.0002	0.0001	0.0001	0.0008	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0004
SD	2.6E-04	2.3E-05	1.2E-06	1.4E-06	4.1E-07	5.7E-05	1.43E-06	5.5E-07	7.1E-07	4.5E-07	7.5E-07	7.72E-07	2.9E-05
SST	14.1950	13.4988	16.8799	17.8495	14.0769	15.3000	18.5024	18.1450	18.1199	17.3981	17.3981	17.9127	16.6064
R2	88.1400	91.9550	97.7825	97.8656	97.7907	94.7067	97.4966	98.3333	98.3593	99.0364	99.0364	98.4524	96.5795
ADJ-R2	86.6575	90.9493	97.5053	97.5988	97.5145	94.0451	97.1836	98.1249	98.1542	98.9159	98.9159	98.2589	96.1520
HYBRID%	0.0979	0.0290	0.0066	0.0072	0.0039	0.0289	0.0073	0.0044	0.0051	0.0041	0.0053	0.0052	0.0171
MPSED%	0.3896	0.0951	0.0249	0.0211	0.0201	0.1102	0.0225	0.0146	0.0172	0.0107	0.0130	0.0156	0.0629
SEE	0.0468	0.0302	0.0104	0.0106	0.0086	0.0213	0.0129	0.0084	0.0083	0.0047	0.0047	0.0078	0.0145

Table 4. Statistical fitness degree for elovich and power law kinetic models

ELOVICH MODDEL													
AARE	0.0053	0.0010	0.0003	0.0002	0.0004	0.0014	0.0002	0.0001	0.0001	0.0000	0.0001	0.0001	0.0008
SSE	1.4895	0.6385	0.4716	0.3373	0.5511	0.6976	0.3867	0.4296	0.4243	0.2879	0.2879	0.3633	0.5304
RMSE	0.0035	0.0004	0.0003	0.0002	0.0003	0.0010	0.0002	0.0002	0.0003	0.0002	0.0003	0.0002	0.0006
SD	1.6E-04	5.4E-06	4.8E-07	1.6E-07	7.2E-07	3.3E-05	2.25E-07	1.2E-07	8.7E-08	2.1E-10	2.3E-08	8.99E-08	1.6E-05
SST	14.1950	13.4988	16.8799	17.8495	14.0769	15.3000	18.5024	18.1450	18.1199	17.3981	17.3981	17.9127	16.6064
R2	89.5067	95.2699	97.2062	98.1103	96.0848	95.2356	97.9098	97.6323	97.6587	98.3454	98.3454	97.9783	96.6070
ADJ-R2	88.1951	94.6787	96.8570	97.8741	95.5954	94.6401	97.6486	97.3363	97.3660	98.1386	98.1386	97.7256	96.1828
HYBRID%	0.0756	0.0141	0.0042	0.0024	0.0052	0.0203	0.0029	0.0021	0.0018	0.0001	0.0009	0.0012	0.0107
MPSED%	0.5036	0.0562	0.0471	0.0272	0.0451	0.1358	0.0263	0.0313	0.0391	0.0324	0.0424	0.0343	0.0851
SEE	0.0414	0.0177	0.0131	0.0094	0.0153	0.0194	0.0107	0.0119	0.0118	0.0080	0.0080	0.0101	0.0147
POWER LAW MODEL													
AARE	0.0027	0.0004	0.0002	0.0002	0.0002	0.0008	0.0002	0.0002	0.0002	0.0000	0.0001	0.0001	0.0004
SSE	1.7016	0.8872	0.3445	0.2920	0.3759	0.7202	0.3530	0.2840	0.2749	0.1456	0.1456	0.2406	0.4804
RMSE	0.0026	0.0005	0.0002	0.0001	0.0002	0.0007	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0004
SD	4.1E-05	3.5E-06	5.0E-06	5.1E-07	3.1E-07	9.9E-06	3.46E-08	1.1E-07	7.6E-06	9.1E-06	6.8E-07	3.49E-06	6.72E-06
SST	14.1983	13.4990	16.8800	17.8495	14.0770	15.3007	18.5024	18.1450	18.1200	17.3982	17.3982	17.9127	16.6067
R2	88.0157	93.4276	97.9591	98.3642	97.3298	95.0193	98.0922	98.4347	98.4828	99.1630	99.1633	98.6672	96.8432
ADJ-R2	86.5177	92.6060	97.7040	98.1597	96.9960	94.3967	97.8537	98.2390	98.2931	99.0584	99.0587	98.5006	96.4486
HYBRID%	0.0383	0.0064	0.0027	0.0035	0.0034	0.0109	0.0028	0.0023	0.0022	0.0004	0.0007	0.0017	0.0063
MPSED%	0.3734	0.0710	0.0270	0.0175	0.0283	0.1034	0.0187	0.0157	0.0179	0.0110	0.0127	0.0152	0.0593
SEE	0.0473	0.0246	0.0096	0.0081	0.0104	0.0200	0.0098	0.0079	0.0076	0.0040	0.0040	0.0067	0.0133

Table 5. Statistical fitness degree for first order and second order kinetic model

FIRST ORDER MODEL													
AARE	0.1607	0.1849	0.1055	0.0735	0.0601	0.1170	0.0359	0.0467	0.1010	0.1168	0.1323	0.0722	0.0946
SSE	14.2422	43.9512	20.2040	12.2884	12.3028	20.5977	5.2701	7.0605	17.0568	20.0708	19.1404	13.7197	17.1587
RMSE	0.0322	0.0419	0.0174	0.0101	0.0086	0.0220	0.0028	0.0059	0.0162	0.0201	0.0239	0.0138	0.0179
SD	1.4E-01	1.9E-01	6.2E-02	3.0E-02	2.0E-02	8.9E-02	7.2E-03	1.2E-02	5.7E-02	7.6E-02	9.7E-02	4.98E-02	6.94E-02
SST	26.3936	53.5280	32.2815	25.7628	19.9699	31.5871	20.9694	21.1593	31.1150	33.8500	34.3139	28.2815	29.9343
R2	46.0393	17.8912	37.4131	52.3017	38.3934	38.4077	74.8676	66.6319	45.1816	40.7065	44.2197	54.3215	46.3646
ADJ-R2	39.2942	7.6276	29.5898	46.3394	30.6925	30.7087	71.7260	62.4609	38.3293	33.2948	37.2471	48.6117	39.6602
HYBRID%	2.2960	2.6418	1.5074	1.0496	0.8591	1.6708	0.5124	0.6674	1.4432	1.6687	1.8894	1.0313	1.3510
MPSED%	4.5953	5.9866	2.4916	1.4425	1.2261	3.1484	0.3975	0.8427	2.3187	2.8694	3.4162	1.9689	2.5587
SEE	0.3956	1.2209	0.5612	0.3413	0.3417	0.5722	0.1464	0.1961	0.4738	0.5575	0.5317	0.3811	0.4766
SECOND ORDER MODEL													
AARE	0.2009	0.0650	0.0441	0.0671	0.0639	0.0182	0.0945	0.0801	0.0473	0.0311	0.0035	0.0499	0.0158
SSE	22.9993	6.1146	4.0548	9.3814	9.8409	10.4782	21.3693	13.7474	4.2344	1.8937	0.5177	8.3525	9.4153
RMSE	0.0471	0.0048	0.0026	0.0050	0.0049	0.0129	0.0094	0.0070	0.0029	0.0016	0.0006	0.0043	0.0086
SD	2.2E-01	2.4E-02	1.1E-02	2.5E-02	2.3E-02	6.1E-02	5.0E-02	3.6E-02	1.2E-02	5.4E-03	7.0E-05	2.06E-02	4.09E-02
SST	35.0578	19.0238	20.1924	26.6779	22.8633	24.7630	39.2258	31.1598	21.6910	18.7652	17.4294	25.6543	25.2086
R2	34.3962	67.8584	79.9191	64.8345	56.9577	60.7932	45.5222	55.8811	80.4785	89.9085	97.0295	73.7640	67.2786
ADJ-R2	26.1958	63.8407	77.4089	60.4388	51.5774	55.8923	38.7125	50.3662	78.0383	88.6471	96.6582	70.4845	63.1884
HYBRID%	2.8706	0.9285	0.6294	0.9589	0.9122	0.2597	1.3499	1.1436	0.6753	0.4440	0.0506	0.7124	0.2264
MPSED%	6.7299	0.6858	0.3777	0.7141	0.6981	1.8411	1.3454	1.0060	0.4117	0.2232	0.0862	0.6145	1.2278
SEE	0.6389	0.1698	0.1126	0.2606	0.2734	0.2911	0.5936	0.3819	0.1176	0.0526	0.0144	0.2320	0.2615

Thermodynamics parameters

The thermodynamics parameters and the equilibrium constant for Jatropha seeds oil extraction are shown in Table 6. Also, the plots of Ln K against 1/T for the different particle sizes (0.1, 0.3, and 0.45 mm) used for the determination of the thermodynamics parameters values were presented in Figure 2. The estimated enthalpy values for the oil extraction process ranged between 29.67 – 45.79 kJ/mol for the different particle sizes. The enthalpy results obtained in this work are slightly higher than (14.27 – 18.60 KJ/mol) reported by Silmara et al. [14], for oil extraction from Jatropha curcas L. using ethanol as a solvent. Also, Meziane et al. [30] reported a lower enthalpy value of (4 - 13.5 kJ/mol) for olive cake oil. This may be explained by the morphology of the different seed which could affect the extraction of oil. The positive enthalpy value is an indication that oil extraction is an endothermic process. Therefore, external energy input is needed for an efficient extraction process [13, 14, 33]. However, the obtained enthalpy results are incomparable agreement with the values reported by Amin et al. [13] and Rodrigues et al. [47] for Jatropha Curcas oil extraction in aqueous acidic hexane solutions and soybean oil extraction process using a renewable solvent.

Furthermore, in all cases, the values of differential entropy were observed to be positive. This is an indication of the irreversibility of the process and a rise in the molecular disorder degree during the extraction process. The increase in disorder of the extraction process is attributed to the mixing of two different matters/substances [14, 48]. Other researchers like [12-14, 18, 30, 33, 49-51] reported similar observations in their experiments for extraction of oil processes from different oilseed raw materials, irrespective of the extraction solvent employed.

On the other hand, the entropy values for Jatropha oil extraction using petroleum ether range between 0.10 and 0.15 kJ/mol. This is in close agreement with the entropy values reported by [14, 30, 50]. The values of mixture entropy were all positive in all cases and varied inversely with an increase in the particle size, due to oil molecules extraction. This indicates the irreversibility of the oil extraction process. This is consistent with the observations of different authors such as [13, 14, 20, 22, 30, 33, 50].

The Gibb's free energy change ($\Delta G\circ$) values recorded for the oil extraction were found to be negative, indicating the feasibility and spontaneity of the extraction process under the experimental conditions studied. The comparatively high negative values of Gibb's free energy change suggest that the oil extraction process was highly spontaneous [14, 20, 22, 33]. Conclusively, it is evident from the thermodynamic study results, that the energy necessary to destroy the solid-solid and liquid-liquid bonds and interactions were smaller than the energy released in solid-liquid interaction [14, 33]. Hence, the larger the particle sizes the further the process is from spontaneity [14].

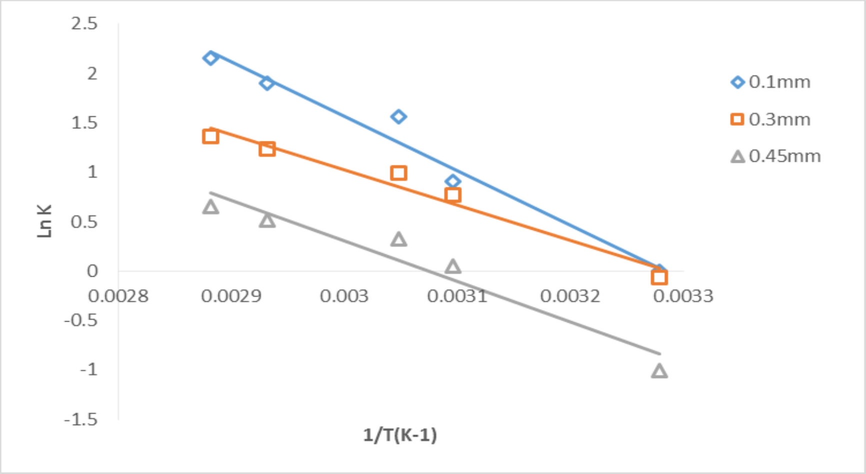


Fig. 3 Plot of Ln K (equilibrium constant) vs. 1/T (temperature, K^{-1}) for different particle sizes

Table 6 Thermodynamic parameters for the extraction of Jatropha seeds oil using petroleum ether

	0.1MM				0.3MM				0.45MM			
											ΔH	ΔS
(K)	(KJ/mol)	K	(KJ/mol)	(KJ/mol)	(KJ/mol)	K	(KJ/mol)	(KJ/mol)	(KJ/mol)	K	(KJ/mol)	(KJ/mol)
305	-0.07	0.99	45.79	0.15	-0.08	0.94	34.17	0.11	2.14	0.37	29.67	0.10
323	-2.78	2.47			-1.84	2.16			0.24	1.05		
328	-3.53	4.76			-2.33	2.69			-0.28	1.38		
341	-5.49	6.67			-3.60	3.43			-1.65	1.68		
347	-6.39	8.64			-4.18	3.92			-2.28	1.92		

CONCLUSION

It could be conclusively stated from this work that the kinetics of Jatropha seeds oil extraction has been ascertained to proceed through the initial fast washing action and final slow diffusion phase as seen in the kinetic analysis. The oil yield increased with an increase in temperature and time but decreased with an increase in particle size. The maximum oil yield of 39.5% was recorded at 74 °C, 0.1mm, and 150 min. The comparative statistical degree of fitness for the six extraction kinetics models showed that power law, elovich, parabolic and hyperbolic models gave the best fit to the experimental data, as revealed by their high average values of R2 and adjusted-R2, and low average values of RMSE, SSE, AARE, SEE, MPSED%, SST, SD, and HYBRID%. However, the pseudo-first-order and pseudo-second-order model failed to give adequate fit to experimental kinetic data. Also, the best fitted kinetic models could dish up as significant and valuable base equations for plant and process design drives. Conclusively, the obtained thermodynamics parameters values of Gib's free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS) at the different extraction process conditions signify the irreversibility, spontaneity, and endothermic nature of the oil extraction process.

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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