



Original Research Article

Mango Seeds Oil Extraction: Effects of Operating Variables, Kinetics and Thermodynamics Studies

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ABSTRACT

Kinetics and thermodynamics aspect of the extraction of oil from mango seeds using n-hexane as the extraction solvent were investigated in this study. The individual effects of operating variables such as temperature, extraction time, particle size and amount of solvent on the oil yield were also investigated. The actual experimental data obtained from the oil extraction process were analysed to ascertain the relative oil yields. The mass transfer kinetics power model and the laws of thermodynamics were applied to describe the kinetics and the thermodynamic parameters of the extraction process respectively. Maximum oil yield of 12.15 % was obtained at 80 °C for an extraction time of 210 minutes using 15 g of dried mango seeds of size 0.353 mm and 50 ml of n-hexane. Analysis of the experimental data showed that the extraction followed first-order kinetics with a rate constant largely influenced by temperature. The activation energy (E_a), enthalpy change (ΔH) and entropy change (ΔS) were estimated to be 45.640 kJ/mol, 32.781 kJ/mol and 0.109 kJ/mol respectively with negative values of Gibbs' free energy change ΔG at each prevailing temperature value. The positive value of enthalpy showed that mango seeds oil extraction process is endothermic and therefore required energy input.

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1. INTRODUCTION

Vegetable oils are known to be one of the oldest categories of chemical substances known to mankind (Willems, 2007). The view on oilseeds and oils, nowadays, spans beyond food and religious needs. The oils are now being used in making other products such as paint, cosmetics, soaps and detergent and more recently as renewable fuels, whose world market is growing very rapidly (Arisanu, 2013). World market for oil and fats is approaching 400 million metric tons of seed produced every year, resulting in a total amount of oil of around 100 million tons (Willems, 2007; Arisanu, 2013)

Mango seed kernel oil is one of the numerous vegetable oils which have many domestic uses. As a good source of phenolic compounds, mango seed kernel oil has found use in cosmetics industries as ingredients in soaps, shampoo and lotion (Soong and Barlow, 2004). The chemical properties of mango seed oil are amongst the most important properties of the oil. The major constituents of mango seed are starch, fat and protein. Mango seed contains about 9-13% oil by weight depending upon the variety (Nzikou et al., 2010). The oil of mango seed kernel consists of about 44-48% saturated fatty acids (majority being stearic) and 52-56% unsaturated fatty acids (Nzikou et al., 2010).

Large quantities of mango seed kernels are often generated as a result of industrial processes and human consumptions, creating environmental and disposal concerns (Puravankara et al., 2000; Kittiphoom, 2012; Osagiede et al., 2017). Utilization of mango seed kernels for the production of oil will assist in mitigating environmental challenges associated with its disposal.

In this study, kinetics and thermodynamic aspect of extraction of oil from mango seeds using n-hexane as the extraction solvent have been investigated. The individual effects of key operating variables such as temperature, extraction time, particle size and amount of solvent on the oil yield were also investigated.

2. MATERIALS AND METHODS

2.1. Material Collection and Preparation

n-hexane used in the extraction of mango kernel oil in this study was of analytical reagent grade and was used without further purification. Mango seeds (*Mangifera indica*) were collected from different locations in Benin City, Nigeria. The seeds were cracked to remove the kernels. The kernels were then ground in a grinder into different particle sizes as described by Kittiphoom and Sutasinee (2013). The ground seeds were placed in a metal tray after being cleaned and dried in an oven at a constant temperature of 60 °C for 24 hours in order to reduce its moisture content to the barest minimum (Osagiede et al., 2017).

2.2. Methods

In order to determine the individual effects of the operating variables, extraction temperature, extraction time, particle size and amount of solvent used were varied. The first set of experimental runs were carried out by varying the extraction temperature from 50 °C to 80 °C at interval of 5 °C while extraction time, particle size and volume of solvent were kept constant at 90 minutes, 0.353 mm and 50 ml respectively. The second set of the experimental runs were done by varying the extraction time from 60 minutes to 210 minutes at interval of 30 minutes while keeping extraction temperature, particle size, and volume of solvent constant at 60 °C, 0.353 mm and 50 ml respectively. The third set of experimental runs involved varying particle sizes in order to study the effect of particle size on oil yield from mango seed kernel. The particle sizes used were: 1.303 mm, 1.000 mm, 0.500 mm, 0.401 mm and 0.353 mm. Other variables remained constant for a period of 90 minutes, temperature of 60 °C and solvent volume of 50 ml. The effect of volume of solvent was investigated in the fourth set of experimental runs by varying the volume of solvent from 10 ml to 50 ml at interval of 10 ml while keeping extraction temperature, extraction time and particle size constant at 60 °C, 90 minutes and 0.353 mm respectively. In all the experimental runs, a fixed mass (15 g) of ground mango seed kernel was used and the percentage oil yield was calculated from Equation (1).

$$\text{Oil Yield, } Y(\%) = \frac{M_o}{M_s} \times 100 \quad (1)$$

Where: M_o = mass of pure oil extracted (g) and M_s = mass of the seed sample (g).

2.3. Kinetic Modelling

The mass transfer kinetics power model shown in Equation (2) was used to investigate the kinetics of the extraction process (Nwabanne, 2012).

$$\frac{dY}{dt} = kY^n \quad (2)$$

Where:

Y = percentage oil yield as calculated from Equation (1); t = time duration of extraction (minutes); k = extraction rate constant; n = order of the extraction and $\frac{dY}{dt}$ = Rate of change of oil yield (Y) with respect to time (t).

Linearization of Equation (2) produced Equation (3).

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

The values of n and k were obtained from slope and intercept respectively of the plot of $\ln\left(\frac{dY}{dt}\right)$ against $\ln Y$ (Topallar and Gecgel, 2000).

2.4. Thermodynamics Studies

The relationship between the rate constant (k) and temperature is described by the Arrhenius' equation given in Equation (4) (Truhlar et al., 1996). The linearized form of the equation is given in Equation (5). Equation (5) was used to determine the activation energy and the Arrhenius' constant. Change in enthalpy and change in entropy of the system were obtained using Equation (6) while Equation (7) was used to determine the Gibb's free energy change at various temperatures.

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

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

Where: k = reaction rate constant; A = Arrhenius' constant (frequency factor); E_a = Activation energy; R = Universal gas constant and T = absolute temperature.

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

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

3. RESULTS AND DISCUSSION

The result of the study showed that the amount of oil present in mango seed, as determined by exhaustive extraction (repeated extraction on the same sample until the entire oil was extracted), was found to be 14.64% of the total mass of the seeds. However, a maximum of 12.15% oil yield was obtained in a single-step extraction process at 80 °C for the duration of 210 minutes using 50 ml of n-hexane and 15 g of 0.353 mm particles of mango kernel seed

3.1. Effect of Operating Conditions on oil Yield

The effect of temperature on the extracted oil yield from mango seed kernel is shown in Figure 1. The percentage oil yield increased from 6.14% to 12.15% with increase in temperature from 323 K to 353 K. The increase occurred steadily over the temperature range used but a little increase was observed when the temperature increased from 348K to 353K. This could be attributed to the oil-bearing cell walls rupture that occurs as temperature increases leading to void formation that serves as migratory space for the contents of the oil bearing cells (Adeeko and Ajibola, 1990). Furthermore, yield is a function of temperature and higher extraction is achieved at higher temperature, which brings about reduction in the viscosity of the oil, thereby releasing oil from the intact cells and draws out moisture (Fellows, 1996; Nwabanne, 2012).

The effect of particle size on the percentage yield of oil extracted from mango seed kernel is shown in Figure 2. It was observed that oil yield increased as the particle size decreased. The oil yield increased from 6.3% to 8.64% as the particle size decreased from 1.303 mm to 0.353 mm. The highest oil yield was obtained with a particle size of 0.353 mm. The positive effect of particle size on oil yield could be attributed to the fact that smaller particles have larger amount of surface area coupled with increased number of ruptured cells resulting in a high oil concentration at the particle surface and low or little diffusion into the particles surface (Ebewele et al., 2010). In the investigation of oil extraction from *Jatropha* seed, Sayyar et al. (2009), suggested also that large particles have smaller amount of surface areas and are more resistant to diffusion of the oil into the solvent. This leads to the transfer of only a small quantity of the oil into the bulk of the solution.

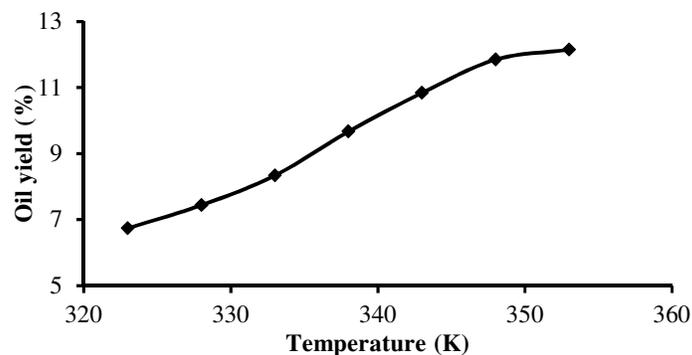


Figure 1: Effect of temperature on the yield of oil extracted from mango seed kernel

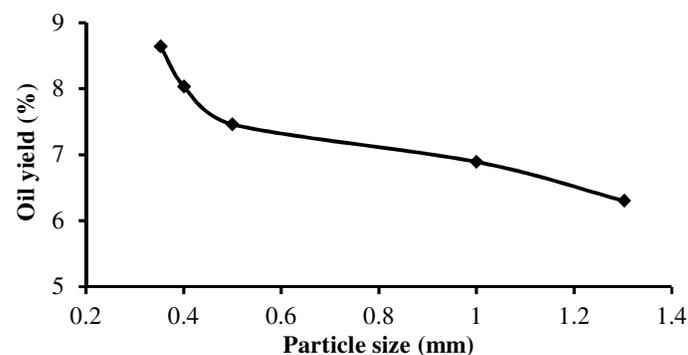


Figure 2: Effect of particle size on the yield of oil extracted from mango seed kernel

The effect of extraction time on the yield of oil extracted from mango seed kernel is shown in Figure 3. Oil yield increased as the extraction time increased. Similar trend was observed by Meziane et al. (2006) and Stanisavejeric et al. (2007). The oil yield rose steadily from 6.73% to 11.97% with time from 30 minutes up to 210 minutes. From Figure 3, it could be seen that equilibrium (a state where the concentration of oil in the seed was equal to the concentration of oil in the n-hexane) has almost been attained as there was very little increase in the oil yield when the time of extraction was increased from 180 to 210 minutes. The highest oil yield was thus obtained as 11.97% at 210 minutes.

The result obtained for the effect of the amount of solvent used on the oil yield is shown in Figure 4. It can be seen from the figure that the oil yield steadily increased as the amount of solvent increased from 10 to 50 ml. The highest percentage oil yield was obtained as 8.49% when 50 ml of solvent was used. Similar result was reported by Meziane and Hadi, (2008) who investigated kinetics and thermodynamics of oil extraction from olive cake. High volume of solvent increased the concentration gradient between the two phases, thereby increasing the rate of diffusion of the oil into the solvent medium. Moreover, the positive effect of solvent volume on the oil yield could also be attributed to the increased washing of the oil away from the surface of the particles by the solvent as a result of increased volume (Nwabanne, 2012). The increase in oil yield became lesser at a solvent volume of 50 ml when compared to initial increments, as it can be observed from Figure 4. At 50 ml of solvent, the increase in oil yield was small. This showed that the equilibrium yield was gradually being approached. The implication is that there wouldn't be any significant increase in the yield even at higher solvent volumes.

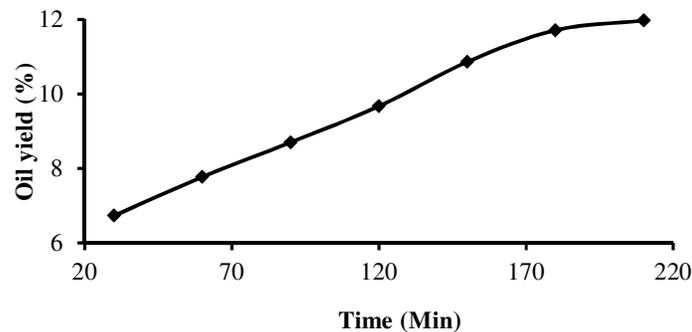


Figure 3: Effect of time on the yield of oil extracted from mango seed kernel

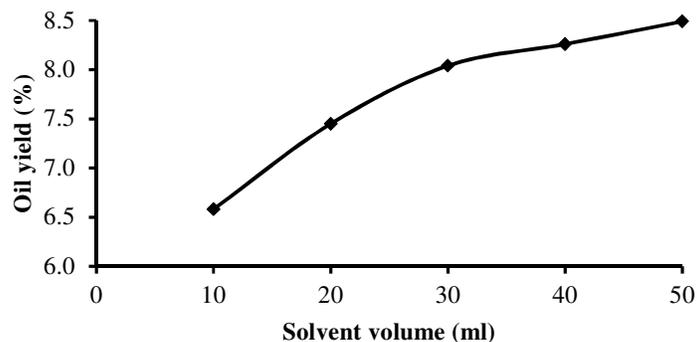


Figure 4: Effect of solvent volume on the yield of oil extracted from mango seed kernel

3.2. Kinetic and Thermodynamics Study

The linearized form of the n th power model given by Equation (3) was used to obtain a linear plot of $\ln(dY/dt)$ versus $\ln Y$. A first order kinetics was obtained from the slope of the straight lines. The extraction rate constants (k) were also determined from the intercepts of the plots as shown in Figure 5, with average R^2 value of 0.9502, and the values are shown in Table 1.

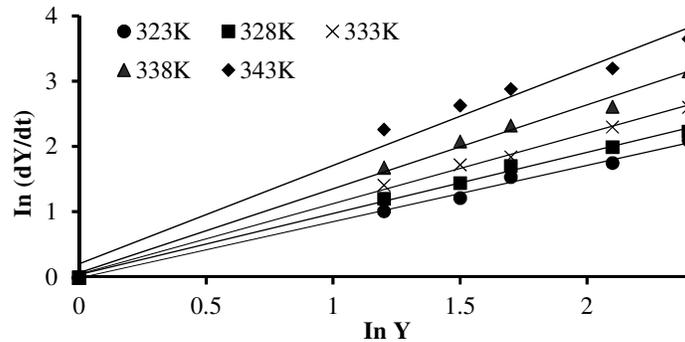


Figure 5: Variation of $\ln(dY/dt)$ with $\ln Y$ at various temperature

Table 1: Estimated values for Kinetic order n and rate constant k

Temperature (K)	Slope (n)	Intercept ($\ln k$)	K (min^{-1})	R^2
323	0.8014	0.168	0.846	0.9732
328	0.9127	0.149	1.161	0.9711
333	0.9415	0.283	1.328	0.9519
338	1.0011	0.515	1.674	0.9261
343	1.1386	0.892	2.439	0.9288

From the plot of $\ln k$ against $1/T$ shown in Figure 6, the activation energy (E_a), Arrhenius' constant (A), thermodynamic parameters (enthalpy change (ΔH), entropy change (ΔS)) of the extraction process were determined from the slope and intercept using Equation 5 and 6. The result is presented in Table 2. The Gibbs' free energy change ΔG of the extraction process, at each temper value, was also calculated from Equation (7) and the results are shown in Table 3.

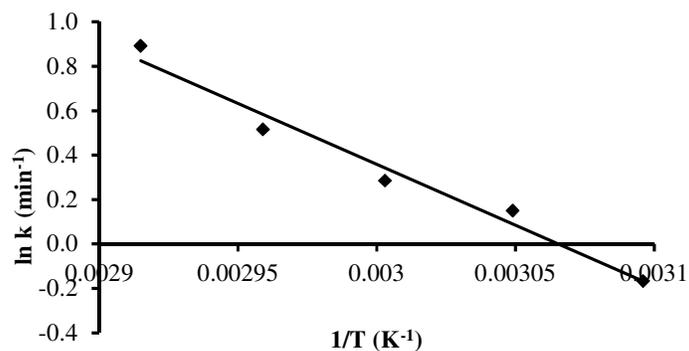


Figure 6: Variation of $\ln k$ with $1/T$

Table 2: Estimated values of thermodynamic parameters

E_a (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol.K)	A (min ⁻¹)
45.64	32.78	0.108	2.03 x 10 ⁷

Table 3: Estimated values of change in Gibb's free energy at various temperatures

Temp. (K)	323	328	333	338	343
ΔG (kJ/mol)	-2.3512	-2.8951	-3.4389	-3.9828	-4.5266

This result compares favourably with the result obtained by Liauw et al. (2008) who obtained values of 31.02 J/mol, and 0.11 J/mol for the change in enthalpy and entropy respectively, under similar conditions while studying the extraction of neem seed oil using n-hexane. The increase in entropy indicates the randomness of the process. The negative values of Gibb's free energy shown in Table 3 indicate there is a decrease in the free energy, which implies that, the extraction is a spontaneous process which agrees with previous investigations (Topallar and Gecgel, 2000; Khraisha, 2000; Liauw et al., 2008). It also indicates that the process is thermodynamically feasible (Nwabanne, 2012).

4. CONCLUSION

From this study, it has been shown that mango (*Mangifera indica*) seeds are low content oil seeds with only about 14.64% total oil content. The operating parameters such as temperature, particle size, extraction time and amount of solvent used on the extraction process have been shown to influence the yield of the extracted oil. The estimation of the kinetic and thermodynamic parameters showed that the mango seed oil extraction data were well described by a first order kinetics with a rate constant largely affected by the temperature of extraction. The positive value of enthalpy indicates that the extraction process is endothermic and therefore requires energy input.

5. ACKNOWLEDGMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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