

KINETICS AND THERMODYNAMICS OF OIL EXTRACTION FROM WATER-MELON SEEDS

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ABSTRACT

The kinetics of oil extraction is dependent on a number of factors, among which are temperature, duration of the extraction as well as the polarity of the solvent used. The solvent extraction of watermelon seed oil as reported in this paper was carried out between 313.15–343.15K in order to determine the kinetic and thermodynamic parameters of the extraction process. Three particle sizes of 500 μm , 1180 μm and 1700 μm were used to determine the optimum particle size for the process, which was found to be 1180 μm . The moisture content of the sample seed was 8.73% while the optimal n-hexane volume of 300ml was used to determine the percent oil yield at varying temperatures. The extraction process was found to obey first order kinetics. The activation energy, E_a for the oil extraction kinetics of watermelon seeds with n-hexane was found to be 13.92kJ/mol, and the activation thermodynamic parameters at 343.15K which was the optimum temperature were $\Delta H^\ddagger = 11.065 \text{ kJmol}^{-1}$, $\Delta S^\ddagger = -254.736 \text{ Jmol}^{-1}\text{K}^{-1}$ and $\Delta G^\ddagger = 98.48 \text{ kJmol}^{-1}$. The enthalpy value was $\Delta H = 7.83 \text{ kJmol}^{-1}$, and the other thermodynamic parameters at 343.15K were $\Delta S = 26.62 \text{ Jmol}^{-1}\text{K}^{-1}$ and $\Delta G = -1.305 \text{ kJmol}^{-1}$. Thus, the optimal extraction of watermelon seed oil is favoured at a temperature of 343.15K, a particle size of 1180 μm and an optimal n-hexane volume of 15ml/g sample.

KEYWORDS: Solvent Extraction, Watermelon Seed, Thermodynamic Parameters, Kinetics, Activation Energy, Enthalpy

INTRODUCTION

In Africa, watermelon seeds have been prized for their highly nutritive oil that they contain. Traditionally, the seeds are removed from the rind and then allowed to dry under the sun. Once dried, the seeds are then pressed to extract the beneficial oil (www.naturalsourcing.com). The seeds are 5 to 15mm in length and may be white with two black spots, cream-colored tipped with brown and stripped with brown at the edge, yellow with a black stripe around the margin and with black spots, sculptured or as if engraved with ornamental charters pink or red. The watermelon seed contain about 30% oil, the crude protein and fat contents of the oil is between 31–37% and 54–57%, depending on the variety, while the raw and fried defatted meals had between 69–78% and 1.1–2.7% respectively.

The removal of oil from seeds is of tremendous importance. In recent years, commercial grade hexane has become the solvent of choice for the extraction of oil from oil seeds, due to its low toxicity and boiling point [[Adriaans, 2006](#)]. The watermelon seed oil, also known as Ootanga or Kalahari oil, contains high amounts of calcium, phosphorus, magnesium, potassium, zinc and iron. The fat comprise of 52.3-57.9% linoleic acid, 13.6-21.7% oleic acid, 11.1-18.6% palmitic acid and 13.0-16.8% stearic acid. The oil is fairly unsaturated in nature owing to its high iodine value of between 113.1–118.7, and saponification number of 192.8–194.6 ([Hill, 1982](#)).

Studies have also shown that the physico-chemical properties of extracted vegetable oils increase with storage, (Abulude et al, 2007). Oyedeji and Oderinde, (2006) extracted oil from fourteen different vegetable seeds using isopropanol solvent. The characterization results showed that the oils extracted with isopropanol had deep colours and odours and higher percentage unsaponifiables than oil extracted with regular extraction solvents like hexane and petroleum ether. Ibemesi and Attah (1990) extracted the seeds of rubber and melon using different solvents at various temperatures and they determined the temperature coefficients and enthalpy changes accompanying the extraction process. The enthalpy values obtained was within the range of 4 – 13.5kJ/mol.

The kinetic and thermodynamic study of oil extraction from *Jatropha curcas* in aqueous acidic hexane solutions shows that the reaction order was found to be first-order kinetics. The activation energy and enthalpy values for the extraction at 333 K with 15% HCl were 26.6763kJ/mol and 0.1586kJ/mol respectively, (Amin et al, 2010). When a second order mechanism was assumed and the extraction conditions optimized, an activation energy value of 8.022 kJ/mol was found, (Sayyar et al., 2009). Physico-chemical analysis performed on various vegetable seed oil showed an interesting energy aspect. Actual evaluation of their energy parameters shows that fuels coming from oil extracted from *jatropha curcas* can be used for operating some thermal engines (Agboue and Yobou, 2007).

Topallar and Gecgel (2000) in their study on the kinetics and thermodynamics of oil extraction from sunflower seeds in the presence of aqueous acidic hexane solutions, obtained an enthalpy value of 11.2kJ/mol and found some other thermodynamic parameters of value. However, Roy et al (2006) studied the effect of temperature and pressure on the extraction yield of oil from sunflower seed with supercritical carbon dioxide for temperature range of 313-343K and pressure range of 20-40MPa. They found out that extraction rates increased with pressure at each temperature, but decreased with temperature increase up to about 28MPa. Akaranta and Anusiem (1996), discovered that feint, a bioresource solvent, could serve as an effective substitute solvent for commercial hexane in the extraction of castor oil intended for alkyd resin production. Microwave-assisted solvent extraction have also shown to give a better yield of oil extracted from vegetable seeds within very short times, and the technology could serve as a very effective alternative for the conventional solvent extraction, (Amarni and Kadi, 2010, Uquiche et al, 2008).

Supercritical fluid have also been used by several researchers in the extraction of oil from vegetable seed oil, and has shown a potentially higher yield at lesser time compare to the conventional solvent extraction processes (Papamichail et al, (2000), Gracia et al, (2009), Reverchon and Marrone, (2001), Perakis et al, (2005)). However, the process is expensive and requires more sophisticated equipment than is required in the conventional method.

In the present study, oil extraction from watermelon seeds with n-hexane was investigated with the aim of determining the kinetic and thermodynamic parameters of the oil extraction process, which could serve for the purpose of design and process optimization.

MATERIALS AND METHODS

Material Preparation

The watermelon seeds were purchased from local market (Samaru market), in Zaria, Nigeria in August 2009. Prior to use, the watermelon seeds were cleansed to remove dirt and other impurities, and subsequently dried in oven at 80°C until it reached constant moisture content (av. 8.73%). The watermelon seeds were grinded and sieved yielding three different particle sizes of 500µm, 1180µm and 1700µm.

The commercial grade n-Hexane (99%, 86.18g/mol, 0.66g/ml) used was obtained from the store of Chemical Engineering Department of Ahmadu Bello University, Zaria, Nigeria.

Extraction of Oil

About 20g of the different particle size of the grinded watermelon seeds was weighed and inserted into a thimble, fitted into the soxhlet apparatus. Commercial grade n-hexane was heated in the round-bottom flask of the soxhlet apparatus to effect the extraction of the oil from the grinded watermelon seeds. This was then used to determine the optimum particle size. The 1180 μm particle size was found to give the highest oil yield, and was hence used for the study as being the optimum particle size. This optimum particle size was in-turn used to determine the optimum conditions of temperature, extraction time and solvent volume. These optimum conditions were then used to study the oil extractability of the watermelon seed, for the purpose of establishing the kinetics and determining the thermodynamic parameters of the extraction process.

RESULTS AND DISCUSSIONS

Optimum Parameters of the Extraction Process

Figure 1 shows the effect of particle size on the percent oil yield of the watermelon seed oil for different runs of the extraction process.

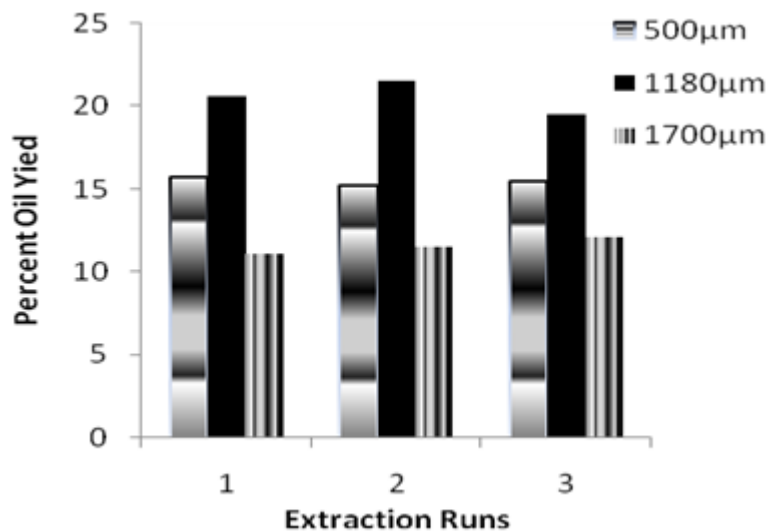


Figure 1: Percent Oil Yield for Different Particle Size of the Watermelon Seed

It could be seen that for the three different runs, the 1180 μm particle size gave the highest percent oil yield. It would have been expected that the 500 μm particle size would have given the highest yield, since it would have provided the largest surface area, but from the result it could be deduced that the particle size had become too fine and they end up being carried away in the process instead of providing the surface needed for extraction. The agglomeration of the fine particles thus reduces the effective surface area available for the free flow of solvent to solid as observed by [Sayyar, et al., \(2009\)](#). Thus the 1180 μm particle size could be seen to give the optimum yield.

Figure 2 shows the percent yield for different n-hexane volume. It could be seen that 300ml of the n-hexane gave the highest yield. Although the difference in yield compared to 350 and 400ml of the n-hexane solvent is quite negligible. Thus the 300ml will be the optimal solvent volume, as higher solvent volume will result into higher cost of extraction.

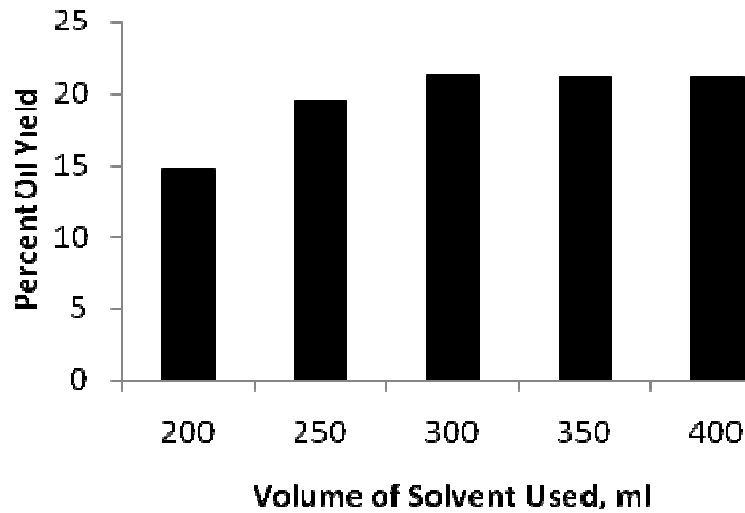


Figure 2: Volume of Solvent Used vs. Percent Oil Yield

Kinetic and Thermodynamic Parameters of the Extraction Process

The percent oil yield at various temperatures and extraction times are given in Table 1 for watermelon seed oil extraction.

Table 1: Percent Oil Yield at Various Extraction Temperatures and Time

t/ min	Oil Yield (%), Y _t			
	313.15K	323.15K	333.15K	343.15K
60	13.74	14.12	15.44	16.31
90	14.52	15.03	16.53	17.62
120	15.34	16.01	17.71	18.99
150	16.21	17.04	18.96	20.47
180	17.13	18.14	20.31	22.10

A reaction rate equation for oil extraction from watermelon seeds can be written as.

$$\frac{dY_t}{dt} = k Y_t^n \tag{1}$$

where Y_t is the percent oil yield, t is the time of extraction, k is the extraction constant and n is the reaction order. Since the percent oil yield increased in the course of time, the term dY_t/dt has a positive sign.

Taking the natural logarithm as applicable in the differential method of analysis of reaction rate (Levenspiel,1999), Equation 1 yields

$$\ln \frac{dY_t}{dt} = \ln k + n \ln Y_t \tag{2}$$

Using the values in Table 1 and Equation 2, plots of ln dY_t/dt versus ln Y_t were drawn and were found to be linear as shown in Figure 3.

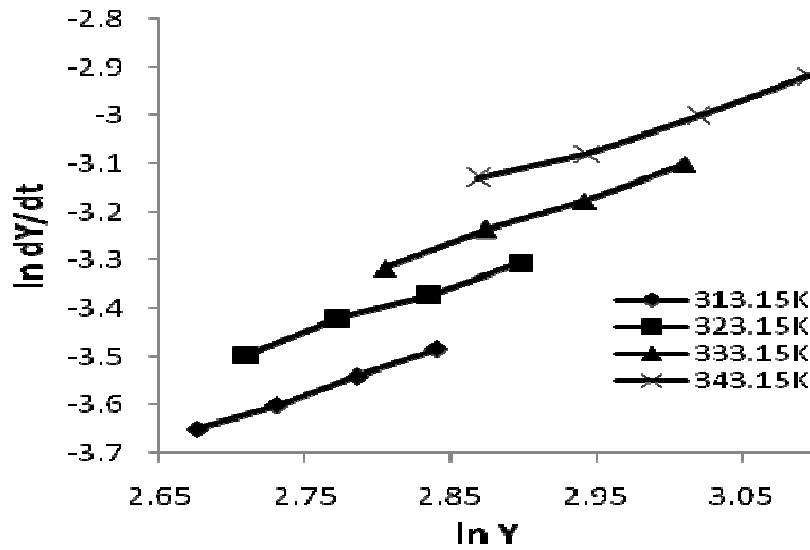


Figure 3: Plot of $\ln \frac{dY_t}{dt}$ Versus $\ln Y$ at Various Temperatures

A first-order kinetics was found from the values of n obtained from the slopes of the straight lines and the reaction rate constants were calculated from the slopes (Table 2).

Table 2: Values of the Order of Reaction and Reaction Rate Constants for Watermelon Seed Oil Extraction at Various Temperatures

T / K	n	k / min ⁻¹
313.15	1.014	0.001719
323.15	0.994	0.001864
333.15	1.026	0.002153
343.15	0.941	0.002629

The rate constant at 343.15K was the highest, which agrees with the trend in literature, that percent oil yield increases with increase in temperature (Ibemesi and Attah, 1990; Topallar and Gecgel, 2000). This is due to the fact that the pores of the seed are easily penetrated by the rising vapour of the solvent, and thus bring about a greater percent oil yield.

The oil extraction kinetics from the watermelon seeds can be described by Equation 3 obtained after the integration of Equation 1.

$$Y_t = Y_0 e^{kt} \tag{3}$$

where Y_t is the percent extracted oil content at time t, and Y_0 is the percent unextracted oil at time zero. This equation agrees with the general trend in literature as reported by Topallar and Gecgel, (2000).

The activation energy was calculated with the Arrhenius equation:

$$k = A e^{-E_a/RT} \tag{4}$$

where k is the reaction rate (extraction) constant, A is the Arrhenius constant or frequency factor, E_a is the activation energy, R is the universal gas constant and T, the absolute temperature.

A plot of $\ln k$ versus $1/T$ gives a straight line whose slope represents the activation energy of extraction, $-E_a/R$, and whose intercept is the Arrhenius constant, $\ln A$ (Figure 4).

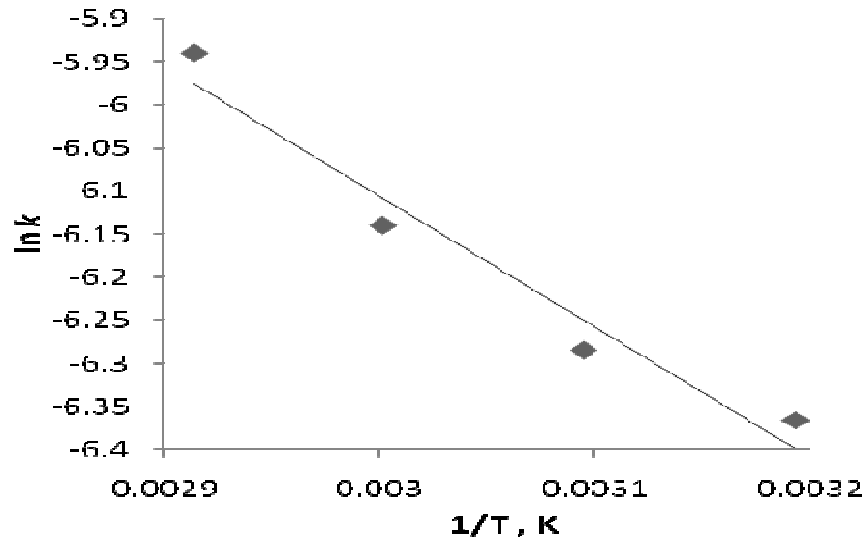


Figure 4: A Plot of $\ln k$ Versus $1/T$ for Watermelon Seed Oil Extraction

Thus, the activation energy and the Arrhenius constant were calculated. These were $E_a = 12.6$ kJ/mol and $A = 3.51 \times 10^{-3} \text{ s}^{-1}$ respectively. The activation thermodynamic parameters were calculated as in the following equations according to the transition state theory, (Wright, 2004):

$$A = \frac{RT}{Nh} e^{\Delta S^\ddagger/R} \tag{5}$$

$$\Delta H^\ddagger = E_a - RT \tag{6}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \tag{7}$$

where N is the Avogadro constant; h is the Planck constant; ΔS^\ddagger is the activation entropy; ΔH^\ddagger is the activation enthalpy; and ΔG^\ddagger is the activation free energy or Gibb’s energy. These activation thermodynamic parameters are shown in Table 3 for each temperature.

Table 3: The Activation Thermodynamic Parameters for Watermelon Seed Oil Extraction at Different Temperature

T /K	$\Delta S^\ddagger / \text{Jmol}^{-1}\text{K}^{-1}$	$\Delta H^\ddagger / \text{kJmol}^{-1}$	$\Delta G^\ddagger / \text{kJmol}^{-1}$
313.15	-253.976	10.000	89.533
323.15	-254.237	9.917	92.074
333.15	-254.49	9.834	94.618
343.15	-254.736	9.751	97.164

The thermodynamic parameters for watermelon seed oil extraction were determined using the Van’t Hoff type of expressions (Akaranta and Anusiem, 1996, Topallar and Gecgel, 2000).

$$K = \frac{Y_T}{Y_U} \tag{8}$$

$$\ln K = \frac{\Delta G}{R} \frac{1}{T} = -\frac{\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R} \tag{9}$$

where K is the equilibrium constant; Y_T is the percent oil yield at temperature T; Y_U is the percent unextracted oil; ΔH is the enthalpy change; ΔS is the entropy change ; and ΔG is the free energy or Gibb’s energy.

From the plot of $\ln Y_T$ vs $1/T$, it can be seen that the plot gives a straight line whose slope represents the enthalpy change of extraction, $-\Delta H/R$. Thus the enthalpy was calculated to be $\Delta H = 7.83 \text{ kJmol}^{-1}$ for watermelon seed oil extraction (Figure 5).

The ΔH value obtained was in agreement with the range 4 – 13.5 kJmol^{-1} in literature. Other thermodynamic parameters (ΔG and ΔS) and the equilibrium constant values for watermelon seed oil extraction are given in Table 4 for each temperature.

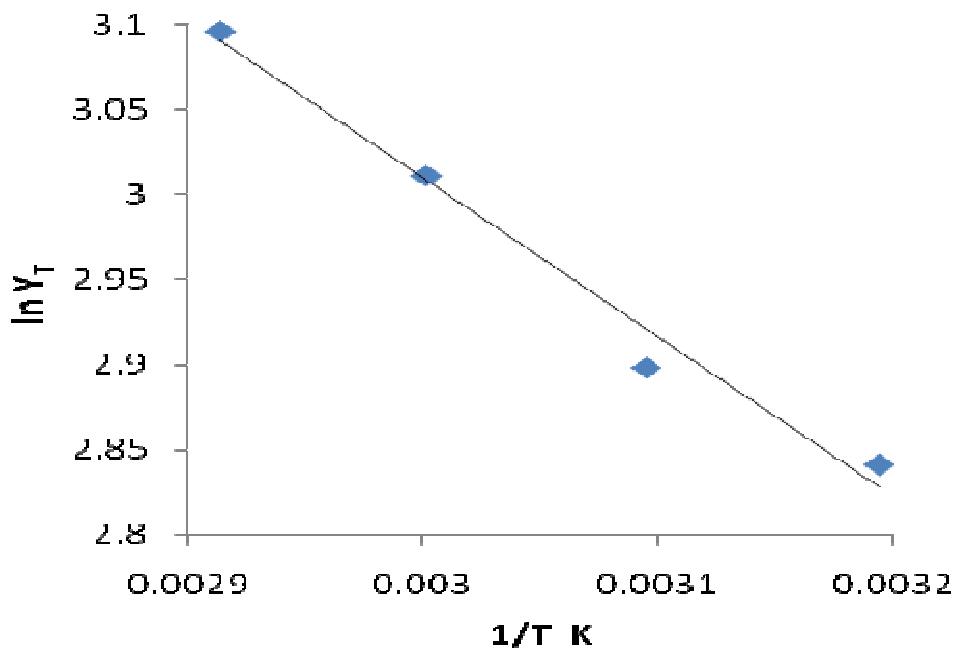


Figure 5: A Plot of $\ln Y_T$ Versus $1/T$ for Watermelon Seed Oil Extraction

Table 4: The Equilibrium Constant (K) and the Thermodynamic Parameters (ΔG and ΔS) for Watermelon Seed Oil at Various Temperatures

T /K	K	ΔG /Jmol ⁻¹	ΔS /Jmol ⁻¹ K ⁻¹
313.15	1.39	-857.352	27.74
323.15	1.45	-998.268	27.32
333.15	1.51	-1141.47	26.93
343.15	1.58	-1305.01	26.62

According to these results, the fact that ΔH is positive for watermelon seed oil extraction shows that the process is endothermic. In addition, $\Delta S > 0$ and $\Delta G < 0$ indicate that there is an increase in the entropy change and a decrease in the free energy, that is the process is spontaneously forward.

The reaction system initially consists of ground watermelon seeds and n-hexane, whereas the oil molecules are extracted from the watermelon seeds during the extraction process and therefore, the entropy of the mixture increases in the course of the extraction and therefore the entropy change has a positive value. It could also be seen from Table 5 that ΔS decrease with increase temperature, which implies that the process is gradually attaining equilibrium. $\Delta S = 0$ at equilibrium and this condition will correspond to the state at which no more oil is extracted from the seed. This thus agrees with literature, in which the extraction (reaction) curve reaches a maximum and remains constant over a wide range of extraction time, before decline. At this point it could be postulated that ΔS value will be zero.

CONCLUSIONS

The watermelon seed oil extraction has a first-order kinetics. The activation energy was $E_a = 12.6$ kJ/mol and the activation thermodynamic parameters at 343.15K were $\Delta H^\ddagger = 9.751$ kJmol⁻¹, $\Delta S^\ddagger = -254.736$ Jmol⁻¹K⁻¹ and $\Delta G^\ddagger = 97.164$ kJmol⁻¹. The enthalpy value was $\Delta H = 7.83$ kJmol⁻¹, and the other thermodynamic parameters at 343.15K were calculated to be $\Delta S = 26.62$ Jmol⁻¹K⁻¹ and $\Delta G = -1.305$ kJmol⁻¹.

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