Kinetics and Thermodynamics Study of Oil Extraction from Fluted Pumpkin Seed

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***Abstract*– The kinetics and thermodynamics of oil extraction from fluted pumpkin seed was studied. The influence of various parameters such as temperature, time, volume of solvent and particle size on oil yield was investigated. Oil yield increased with increase in temperature, time and volume of solvent but decreased with increase in particle size. Maximum oil yield of 46.98% was obtained at 100^{0}C for an extraction time of 40 minutes using 20g of grounded fluted pumpkin seed and 100 ml of n-hexane. The physicochemical analysis of the oil showed that the oil is edible oil with an acid value of 4.77 mg NaOH/g, saponification value of 162.69 mg KOH/g and iodine value of 123.83 mgI$_2$/100g. The oil has a viscosity of 119 cp, specific gravity of 0.9111, refractive index of 1.476, flash point of 168^{0}C, pour point of -7^{0}C, and pH of 5.9. The kinetics of the fluted pumpkin seed oil extraction was studied using the power model and it was found that the order of reaction was fourth order, and had a rate constant of 1.58x10^{-7} (dm^{-3}/mol) ^{3}s^{-1}. The thermodynamic study showed that the enthalpy change (ΔH) is positive, indicating that the extraction process is endothermic. The positive value of entropy change (ΔS) showed the randomness of the process while negative values of free energy change (ΔG) indicate that the process is feasible and spontaneous.**

***Keywords*–** Kinetics, Thermodynamics, Extraction and Fluted Pumpkin

I. INTRODUCTION

Fluted pumpkin, botanically known as Telfaina occidentalis, is a creeping vegetable shrub that spreads low across the ground with long twisting tendrils and large lobed leaves. It is grown mostly in Western and Eastern Africa because of the nutritional values derived from its part mostly from the leaves and seeds. In spite of the vast usage of the leaves of fluted pumpkin as nutritional supplement, the seed is found to contain majority of the nutrients (Levin, 2008). The seeds are power food rich in many nutrients including vitamin E, Zinc, vitamin A and precious omega (omega 3 and omega 6) also known as the essential fatty acids (Michael et al., 2000). Fluted pumpkin oil is reddish brown in colour and has a unique flavour (Roberts and Tanny, 2008). Pumpkin seed oil has many health benefits derived from its consumption. It contains essential fatty acids that help maintain healthy blood vessels, nerves and tissues (Levin, 2008). Pumpkin seed oil is known to alleviate and avert prostrate and bladder problems and are often prescribed to men over fifty years with prostrate problems.

Various techniques such as mechanical extraction, solvent extraction, traditional extraction and super critical fluid extraction are used to obtain the oil from the seeds. The solvent extraction has become the most popular method of extraction of oil because of its high percentage of oil recovery from seeds. Solvent extraction bridges the gap between mechanical extraction which produces oil with high turbidity metal and water content and supercritical fluid extraction which is very expensive to build and maintain its facilities. Hexane is often used as solvent for oil extraction 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 comparatively low toxicity when compared to other solvents.

Several parameters such as particle size, volume of solvent, operating temperature and extraction time has been found to affect the percentage yield of oil from seeds. Hence, the determination of the effects of these parameters on oil yields from seeds is important to minimize the loss of oil, the cost of extraction in general and the amount of energy expanded over time.

Liauw et al. (2008) studied the extraction of neem oil using n-hexane and ethanol. They observed that more yield of oil was obtained with the use of n-hexane than with ethanol and the extraction process followed first order kinetic. The thermodynamic parameters showed that the process of extraction of oil from neem seeds is endothermic, irreversible and spontaneous.

The present study is aimed at extracting oil from fluted pumpkin seeds using n-hexane, investigating the effects of temperature, time, solvent to solid ratio (volume of solvent) and particle size on the percentage of yield of oil and determining the kinetic and thermodynamics parameters of the oil extraction from fluted pumpkin seeds.

II. MATERIALS AND METHODS

A. Fluted pumpkin seed collection and preparation

Fluted pumpkin (Telifaria occidentalis) was bought from the local market in Awka, Anambra state, Nigeria. The shells were carefully cut open to expose the seeds which were embedded in an orange –yellow fibrous material. The seeds were removed from the fruit and thoroughly washed with distilled water to remove dirt and other impurities. After about two weeks, the seeds were then dehulled manually to remove the outer seed coat and subsequently dried in an electric oven at 60^{0}C until a constant weight was obtained (Topallar and Gecgel, 2000). After cooling the seeds were ground using a manual grinding machine and sieved through five different laboratory test sieves to obtain particle sizes of 2.0mm, 2.36mm, 3.35mm, 4.75mm and 7mm. The samples were stored in separate air tight containers and labeled adequately.

B. Solvent extraction

A determined quantity of n-hexane was delivered into the Soxhlet extractor. A certain amount of ground fluted pumkin on Whatman No 1 filter paper was placed in the thimble of the Soxhlet extractor. The heating mantle was set at a specified temperature for the experiment and the extraction was carried out for a given time. After the extraction with n-hexane, the set up (soxhlet extractor) was dismantled and the miscella (mixture of n-hexane and pumpkin seed oil) obtained was poured into the distillation flask and placed on the heating mantle. The heating mantle was set at 68^0C which is the boiling point of pure hexane. After distillation, the weight of the oil was determined

Effect of temperature on oil yield was tested by using 100ml of n-hexane, 20g of ground pumpkin seed of 2mm particle size, with the soxhlet extractor operated at a temperature of 80, 85, 90, 95 and100^{0}C for 40 minutes. Effect of particle size on oil yield was done by using 100ml of n-hexane, 20g of grounded pumpkin seed at a temperature of 100^{0}C for 40 minutes for particle sizes of 2.36mm, 3.35, 4.75mm and 7mm. Effect of time on oil yield was investigated using 100ml of n-hexane, 20g of grounded pumpkin seed of 2mm particle size at a temperature of 100^{0}C for 5, 10, 15, 20, 25, 30, 35, and 40 minutes. Effect of volume of solvent on oil yield was carried out using 20g of the 2mm ground pumpkin seeds for 75, 100, 125, 150 and 175ml of hexane.

The percentage oil yield was calculated using the expression below:

$$Y = \frac{W_o}{W} \times 100 \quad \text{-------------} \quad (1)$$

Where, Y is the oil yield (%), W_0 is the weight of pure oil extracted (g) and W_m is the weight of the sample of ground pumpkin seeds used in the experiment.

C. Characterization of the extracted pumpkin seed oil

Acid value, saponification value and iodine value were determined according to the methods prescribed by AOAC (1984). Specific gravity, viscosity, pH, refractive index, flash point, colour and pour point were determined according to the method of AOAC (1990).

D. Kinetics of Oil Extraction

Kinetic studies measure the speed or rate of a chemical reaction. The power model equation is given as:

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

Equation (2) can be expressed as

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

Where, Y is percentage oil yield (%), t is time of extraction (min), K is extraction constant and n is reaction order. A plot of ln(dy/dt) against lnY gives lnk as intercept and n as the slope (Topallar and Gecgel, 1999).

E. Thermodynamics of oil extraction

Thermodynamics parameters are determined from equation 4 (Liauw et al, 2008)

$$\ln k = \frac{-\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{------} \quad (4)$$

Where, k is equilibrium constant, ΔG is Gibbs energy or free energy (KJ/mol), ΔH is change of enthalpy (KJ/mol), ΔS is Change in entropy (KJ/mol.K), R is Universal gas constant (8.314KJ/Kmol), T is Temperature (K) and

$$k = \frac{Y_T}{Y_u} \quad \text{----------} \quad (5)$$

Where, Y_T = Percentage oil yield at temperature, T and Y_u = Percentage of unextracted oil. Plotting lnk against 1/T gives -ΔH/R as slope and ΔS/R as intercept, from where ΔH, ΔS and ΔG were determined.

III. RESULTS AND DISCUSSION

A. Physicochemical properties of extracted fluted pumpkin seed oil

The results for the physicochemical properties of extracted oil are presented in Table 1. The physical analysis of the oil obtained gave a pH of 5.9 which is almost acidic in nature. This value is close to the pH value (6.03) obtained by Olutoye and Garba, 2008 and indicates the presence of an unsaturated fatty acid in the oil. A value of 1.476 was obtained for the refractive index. The refractive index value obtained falls within the range reported by Eckey, 1954 for some fats in the nut family (1.45 – 1.49). The density/specific gravity of the oil was also obtained to be 0.911g/cm^3/0.9111 and these values are comparable with 0.82 and 0.84 reported for other oils (Ajayi and Oderinde, 2002). Refractive index of oils is a measure of how much a light ray is bent when it passes from air into the oil and it usually depends on the density of the oil. In general, the refractive index and relative density/specific gravity values of edible vegetable oils are physical measures of adulteration of vegetable oils, since different oils have characteristic density/specific gravity and refractive index (Olutoye and Garba, 2008). The oil was found to be yellow in colour and has non-offensive odour. The viscosity value of 119cp as determined reflects the resistance of the oil to shear stress. The value of the pour point is -70^{0}C. This is the temperature at which the oil ceases to flow. This is important as it gives an indication of the temperature above which the oil will perform best especially in mechanical applications. A high value of 168^{0}C was obtained as the flash point. This is the temperature at which the oil vapour formed will ignite when the oil is heated. The oil flash point is an important indication of the stability of the oil on heating as many vegetable oils are used for cooking purposes. The high value obtained implies high heat stability.

The chemical analysis showed that the oil obtained has an acid value of 4.77 mg NaOH/g, saponification value of 162.69 mgKOH/g and iodine value of 123.83 mg/100g. The acid value gives an indication of the amount of free fatty acids present in the oil at the time of the test. It is an indicator for edibility and suitability for its use in industry like soap production. Akubugwo et al (2008) obtained a value of 3.97meqk^{-1} for fluted pumpkin seed oil. The fluted pumkin oil could therefore be used as edible oil. Akubugwo et al (2008) obtained saponification value of 158.40 ± 3.40mgKOH/g. The high saponification value recorded for the oil is indicative that they have potential for use in the industry (Amoo et al, 2004). It can be used for soap production and in making other cosmetic products such as shampoo.

Iodine value of 123.83mgI$_2$/100g was obtained. Iodine value measures the degree of unsaturation of a particular vegetable oil. Studies have shown that as the degree of of unsaturation increases, iodine value increases and the liability of the vegetable oil to become rancid by oxidation increases (Eka, 1980). This result is comparable to a value of 124-139gI$_2$/100g reported for soyabean oil (Ebewele et al., 2010). Iodine value is useful in predicting the drying properties of oils and the value for fluted pumpkin seed oil suggests that it is a semi-drying oil. The oil will not be used in paints and coating industries unless it is dehydrated before use (Abayeh et al., 1998).

Table 1: Physicochemical properties of fluted pumpkin seed oil

Property	Value
PH	5.9 at 29.1^{0}C
Refractive index	1.476
Specific gravity	0.9111
Density	0.9111g/cm^3
Colour	Yellow
Odour	Agreeable
Viscosity`	119CP
Pour point	-7^{0}C
Flash point	168^{0}C
Acid value	4.77mgNaOH/g
Saponification value	162.69mgKOH/g
Iodine value	123.83mgI$_2$/100g

B. Effect of temperature on fluted pumpkin seed oil yield

From Figure 1, it can be seen that oil yield increased as temperature increased. The oil yield increased from 38.45 to 45.98% as the temperature increased from 80 to 100^{0}C. The highest oil yield was obtained at100^{0}C. Hickox (1953) also reported increase in oil yield with increase in temperature for cotton seed oil.

The positive effect of temperature on oil yield is as a result of rupturing of oil cell walls which now create a void which serves as migratory space for the contents of the oil bearing cells (Adeeko and Ajibola, 1990). Temperature influences oil yield and higher extraction is achieved by increasing the temperature, which lowers the viscosity of the oil, releases oil from the intact cells and draws out moisture (Fellows, 1996).

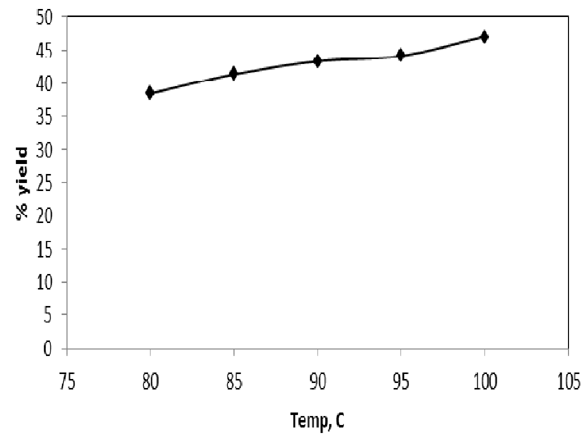

Fig. 1: Effect of temperature on yield of fluted pumpkin seed oil

C. Effect of particle size on fluted pumpkin seed oil yield

The effect of particle size on fluted pumpkin seed oil yield is shown in Figure 2. It can be observed that the oil yield increased as the particle size decreased. The oil yield increased from 20 to 41% as the particle size decreased from 7 to 2mm. The highest oil yield was obtained with a particle size of 2mm. Similar result was obtained by Goodrum and Kilgo (1987) while extracting oil from peanut.

They found that total oil recovery was increased from 36 to 82% when the particle size range was decreased from (3.35 – 4.75 to 0.86 – 1.19mm). The negative 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). Sayyar et al (2009), while investigating the extraction of oil from Jatropha seed, suggested also that large particles have smaller amount of surface areas and are more resistant to intrusion of solvent and oil diffusion. Therefore, small amount of oil will be carried from inside the large particles to the surrounding solution.

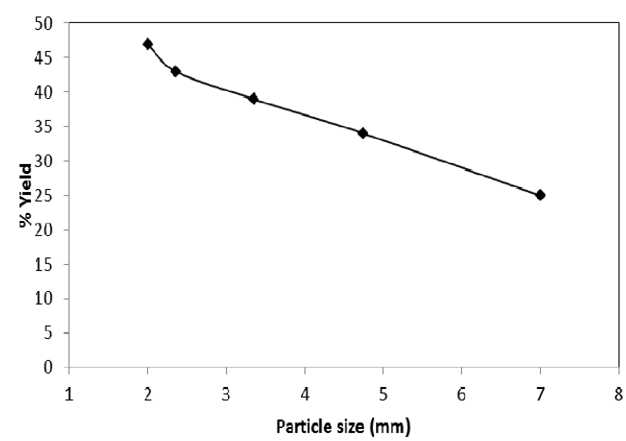

Fig. 2: Effect of particle size on yield of fluted pumpkin seed oil

D. Effect of time on fluted pumpkin seed oil yield

Oil yield increased as the extraction time increased (Fig. 3). The same trend was reported by Meziane et al (2006) and Stanisarejevic et al (2007). The oil yield rose rapidly with time (up to 20 minutes) at first and thereafter the yield of oil was not very significant. At 20 minutes, the oil in the seeds was almost exhausted hence the negligible oil yields. Oil yield increased from 38.55 to 46.98% as time increased from 5 to 40minutes.The highest percentage oil yield is obtained at 40minutes.

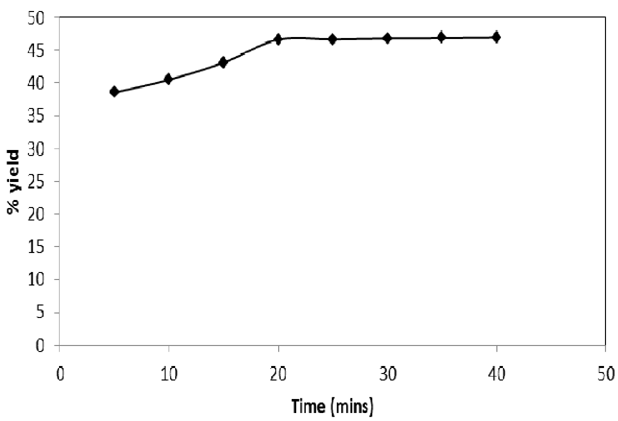

Fig. 3: Effect of time on fluted pumpkin seed oil yield

E. Effect of volume of solvent on fluted pumpkin seed oil yield

The result obtained for the effect of volume of solvent on the oil yield is shown in Figure 4. It can be seen from Fig. 4 that the oil yield increased as the volume of solvent increased from 75 to 175ml. The oil yield rose rapidly with volume of solvent (up to 125ml), then less and less quickly as extraction progressed. The highest percentage oil yield was obtained when 175ml of solvent was used. This is in accordance with the result obtained by Meziance and Kadi (2008) that studied kinetics and thermodynamics of oil extraction from olive cake. They reported that the positive effect of volume of solvent on oil yield was as a result of increase in the concentration driving force as volume of solvent increases. It was also as a result of increased washing of the oil extracted, away from the particle surface by the solvent as a result of increased volume. The increase in oil yield became less significant at 125ml because 125ml hexane was sufficient to bring the oil solute to equilibrium.

F. Kinetic study on extraction of fluted pumpkin seed oil

A plot of ln(dY/dt) versus lnY was found to be linear. A fourth order kinetics was obtained from the slope of the straight line as shown in Figure 5. The reaction rate constant was determined from the intercept as 1.58 x 10^{-7} $(dm^3/mol)^3S^{-1}$.

G. Thermodynamic study on extraction of fluted pumpkin seed oil

Fig. 6 shows the plot of lnk vs 1/T using the values from Table 3. An intercept of 28.17 was obtained from where the entropy change was calculated to be 0.234 KJ/mol.K. This is comparable with that of Liauw et al (2008) who obtained values of 0.13, 0.11 and 0.09KJ/mol.K while studying the extraction of neem oil using n-hexane. The increase in entropy indicates the randomness of the process. From the slope, the value of enthalpy change (ΔH) was calculated as 78.84 KJ/mol. This is close to the value obtained by Liauw et al (2008) for the extraction of neem oil. The positive value of enthalpy change indicates that the process is endothermic and required energy during process.

The Gibbs free energy at different temperature is calculated using the formula blow:

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

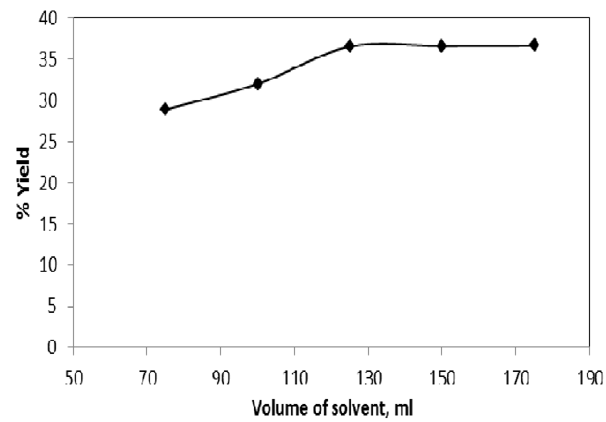

Fig. 4: Effect of volume of solvent on fluted pumpkin seed oil yield

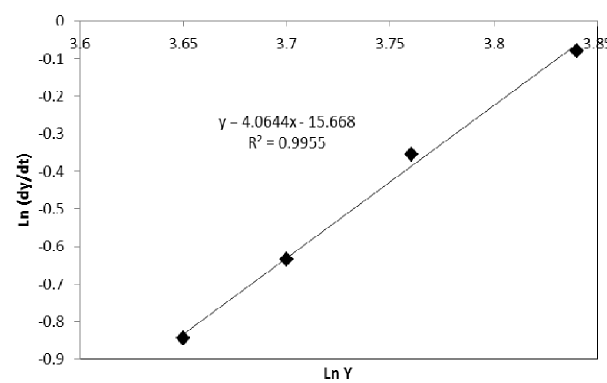

Fig. 5: A plot of ln(dY/dt) versus lnY

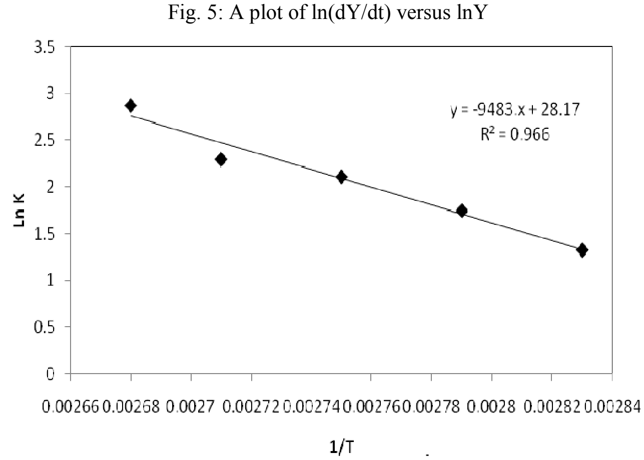

Fig. 6: A plot of lnk versus 1/T

The values of Gibbs free energy change obtained are shown in Table 2. The negative values indicate the feasibility and spontaneous nature of the process.

Table 2: Thermodynamic Data for extraction of fluted pumpkin seed oil

T(K)	K	ΔG(10^{-3}) (KJ/mol.K)
353	3.78	-3.902
358	5.67	-5.211
363	8.28	-6.379
368	9.95	-7.029
373	17.69	-8.909

IV. CONCLUSION

This study has shown that fluted pumpkin seeds are high yielding oil seeds and can serve as a commercially rich source of vegetable oil. Parameters such as temperature, time and volume of solvent and particle size affect the oil yield. The oil has the qualities are suitable for the production of soap, margarine and also for consumption. The oil is semi-drying and its relatively low free fatty acid value is a good attribute for the oil to be used in the food industry as ingredient in food manufacturing. Because of the low degree of unsaturation and acid value of the oil, it can be stored in plastic container but not for long period as the high iodine value indicates a high degree of unsaturation and a high tendency to deteriorate with time. Fluted pumpkin seed oil extraction followed 4th order kinetics. It was also found that ΔH is positive, ΔS is positive, and ΔG is negative indicating that this process is endothermic, irreversible and spontaneous.

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