Some Thermodynamic Properties of White Yam (*Dioscorea rotundata*) Slices Dehydrated in a Refractance Window^{TM} Dryer

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Abstract- The objective of this study is to estimate the changes in Enthalpy, Entropy and Gibbs Free Energy of yam slices dehydrated at different temperatures using a Refractance Window^{TM} dryer. Dehydration of 1.5, 3.0 and 4.5 mm thick yam slices, was performed with water temperatures of 65, 75, 85 and 95^{o}C in the flume of a Refractance Window^{TM} dryer. During the dehydration operations, the moisture-content history data were recorded. For the process conditions considered, the moisture content history data was used to calculate the moisture diffusivity and the activation energy of dehydration of the samples. Subsequently, changes in Enthalpy, (ΔH), Entropy, (ΔS), and Gibbs Free Energy,(ΔG), were calculated. For the process conditions studied, the changes in, ΔH, ΔS, and,ΔG varied from 20,381.33 to 25,217.05 J.mol^{-1}., -140.69 to -122.29 J.mol^{-1}.K^{-1}.and 67,934.80 to 70,220.15 J.mol^{-1}, respectively. This study is essential as knowledge of these thermodynamic parameters are useful for the optimal design and sizing of preservation dryers for agro-products.

Keywords- Enthalpy; Entropy; Gibbs Free Energy; Refractance Window^{TM} Dryer; Yam

1 Introduction

Dehydration is becoming famous as a preservation method for agro-products and many foodstuffs in rural areas of developing countries. This is because in these regions, refrigeration, a food preservation method of first choice, rely on an undependable electric power supply. The studies of the thermodynamics involved in drying of food and agro-products are essential because these parameters are vital for the ideal design, correct operation and sizing of dryers. Therefore, understanding the thermodynamics and energy requirements for dryers is necessary. Research into food dehydration, food dryers and methods of removing moisture from foodstuff is growing, even though food dehydration operation has a long history. Dehydration kinetics are essential to designing dryers, and many researchers have been engaging in this study (Akinola *et al.*, 2016; Azizi *et al.*, 2017; Shende and Datta, 2018; Akinola *et al*., 2018a; 2018b.; Akinola and Ezeorah, 2019).

In designing dryers, it is important to know characteristics such as drying curve, drying rate curve, effective moisture diffusivity, and activation energy of dehydration of the dehydrated products, to perform design calculations and model the dryers. Literature provides extensive studies of these parameters (Akinola and Ezeorah, 2019; Akinola *et al*., 2018; Nindo and Tang, 2007; Krokida and Marinos-Kouris, 2003). Panagiotou *et al.* (2004), have compiled a list of moisture diffusivity for many foodstuffs used in drying studies. Flores-Andrade *et al.* (2018), Kaya and Kahyaoglu, (2006), McMinn and Magee, (2003), and Toğrul and Arslan, (2006) have studied the thermodynamic properties of moisture sorption of calcium–sucrose powders, sesame seed, rice, and potato, respectively. According to Nwakuba *et al.* (2018), the study of thermodynamic properties in the drying process of agricultural products aims to offer solutions to problems related to stability and optimization of process conditions (Jideani and Mpotokwana, 2009; Costa *et al.*, 2016).

Thermodynamic properties are necessary for optimal design and sizing of dryers and other devices in various processes of preservation of the products. These properties are also necessary for the proper understanding and provision of information on energy exchanges between one state of equilibrium to the other (Costa et al., 2016; de Oliveira et al., 2014). Therefore, this study engages in determining the changes in Enthalpy, ΔH, Entropy, ΔS, and Gibbs Free Energy, ΔG, of yam slices at varying drying temperatures.

The equipment used in this study is fabricated laboratory scale Refractance WindowTM Dryer. The Refractance Window Drying Technology was patented by Magoon (1986) and developed by MCD Technology Inc., Tacoma, WA, USA. The technology is emerging as a promising low-cost drying method appropriate for dehydrating agro-products (Ochoa-Martınez *et al.*, 2012). The dryer has been used extensively (Nindo and Tang, 2007; Azizi *et al.*, 2017; Akinola *et al.*, 2018b; Shende and Datta, 2019). The growing use of the Refractance Window™ drying technology is due to the fact at the 3 modes of heat transfer are employed to dehydrate the food sample, conduction from the plastic sheet, thermal radiation from the hot water through the plastic sheet and convection at the top surface of food material (Ortiz-Jerez *et al.*, 2015).

2 Methods and Materials

2.1 Drying Equipment

The fabricated laboratory-scale Refractance Window™ dryer used in this study is similar to that used by Akinola *et al.* (2018). A schematic diagram of the apparatus is shown in Figure. 1. The drying apparatus consisted of an electrically heated rectangular water tub 1.0 m in length, 0.5 m wide and a height of 75 mm. The water tub was covered with a 0.15 mm thick transparent polyethylene terephthalate (PET) Mylar plastic film, and the lower surface of the film was always in contact with the water during the drying process. A suction fan removed the moist air through a hood above the dryer. The suction fan was installed to ensure that the humid air above the dryer does not inhibit the drying process.

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2.2 Sample Preparation

Tubers of white yam (*Dioscorea rotundata*) bought from the local market in Lagos Nigeria are used for the study. The yam tubers were washed, peeled, and cut into 1.5, 3.0 and 4.5 mm thick slices using a Mandolin Slicer (Mueller, V-Pro 5 Blade, Cheyenne, WY, USA). The yam slices were further cut into squares of dimensions 2.5 cm.

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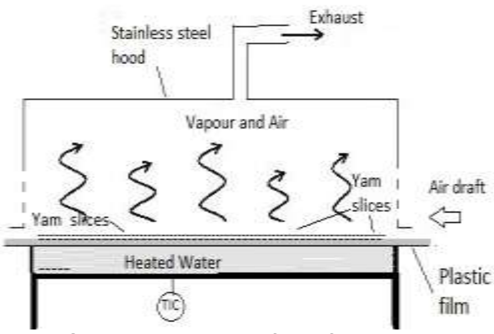

Fig. 1: A Schematic Diagram of a Refractance Window Dryer (Akinola et al., 2018)

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2.3 Experimental Procedure

The moisture content of yam slices was determined using a moisture analyser (OHAUS Corporation, MB45, Parsippany, NJ, USA). Twelve (12) sets of experiments were performed, in the Refractance Window™ dryer, with yam slices 1.5, 3.0 and 4.5 mm thick and at water temperatures of 65°C, 75°C, 85°C and 95 °C. The yam slices were placed in a thin-layer, on the transparent PET plastic on the dryer, and at pre-determined time intervals, some slices were removed and their moisture content determined. A moisture-content history dataset and subsequently a moisture-ratio history dataset was gathered. For each temperature and drying period, the experiments were performed in triplicate.

The moisture-ratio (MR), was obtained using Equation 1 (Akgun and Doymaz 2005; Sharifian *et al.*, 2012; Torki-Harchegani *et al.*, 2016).

$$MR = MC_t / MC_i \quad (1)$$

where

MC_t is the moisture content of the sample after drying for time t and,

MC_i is the initial moisture content of the fresh sample, all in the unit of grams of water removed/grams of solids.

2.4 Effective Moisture Diffusivity Estimation

Crank (1975), proposed a relationship between moisture ratio (MR) and effective moisture diffusivity, (D_{eff}), based on Fick's law second equation of diffusion. A simplified version of the relationship is presented in equation 2.

$$MR = \frac{8}{\pi^2} e^{-\frac{\pi^2 D_{eff} t}{4L^2}} \quad (2)$$

Linearize equation 2 to get equation 3

$$\ln(MR) = \ln\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 D_{eff} t}{4L^2} \quad (3)$$

where,

MR is the moisture ratio,

D_{eff} (m^2s^{-1}) is the effective moisture diffusivity,

L (m) is the sample thickness and,

t is the drying time (s).

Sharma *et al.* (2005), Jena and Das, (2007), and Taheri-Garavand *et al.* (2011) have discussed in detail the assumptions that equation 2 is based on. The assumptions are that the moisture content is initially uniformly distributed throughout the mass of a sample, equilibrium conditions exist between the surface moisture and the surrounding air, mass transfer resistance at the surface is insignificant compared to internal resistance of the sample, and the diffusion coefficient is constant.

A simple linear regression analysis between –ln(MR) and drying time (t) gives a slope of k_d from which D_{eff} can be obtained according to the equation 4 and subsequently equation 5

$$k_d = \frac{\pi^2 D_{eff}}{4L^2} \quad (4)$$

$$D_{eff} = \frac{4L^2 k_d}{\pi^2} \quad (5)$$

2.5 Determination of the Activation Energy

The Arrhenius type equation in equation 6 is used to estimate the activation energy (Lopez *et al.*, 2000; Akpinar *et al.*, 2003):

$$D_{eff} = D_0 e^{\left(\frac{-E_a}{RT}\right)} \quad (6)$$

where

E_a is the energy of activation (J/mol),

R is universal gas constant (8.314 J/mol),

T is absolute air temperature (K), and

D_{eff} (m^2s^{-1}) is the effective moisture diffusivity, and

D_0 is the pre-exponential factor of the Arrhenius equation (m^2/s).

Linearizing equation 6 gives equation 7

$$\ln\left(D_{eff}\right) = ln(D_0) - \frac{E_a}{RT} \quad (7)$$

Using data for a given yam size thickness, the activation energy, E_a , and the pre-exponential factor of the Arrhenius equation, D_0, can be determined by performing a simple linear regression analysis between, *-ln*(D_{eff}) and 1/T. The slope of k_r of the regression analysis enables E_a to be estimated according to the Equation 6 and D_0, the pre-exponential factor of the Arrhenius equation is the intercept.

$$k_r = \frac{E_a}{R} \quad (8)$$

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2.6 Determination of the Thermodynamics Properties

The thermodynamic properties of the drying process were determined through the method described elsewhere (Jideani and Mpotokwana, 2009; Costa *et al.*, 2016; Nwakuba *et al.* 2018) and expressed as equations 9 to 11:

$$\Delta H = E_a - RT_a \quad (9)$$

$$\Delta S = R\left(\ln D_o - \ln\frac{K_B}{h_p} - \ln T_a\right) \quad (10)$$

$$\Delta G = \Delta H - \Delta T_a S \quad (11)$$

This study will be done at constant temperature, therefore equation 11 becomes equation 12

$$\Delta G = \Delta H - T_a \Delta S \quad (12)$$

where:

ΔH = enthalpy variation ($Jmol^{-1}$);

ΔS = entropy variation (Jmol^{-1}K^{-1});
ΔG = Gibbs free energy variation (Jmol^{-1});
R = 8.3145 J/mol·K.
K_B = Boltsmann constant (1.38 x 10^{-34} Js^{-1});
h_p = Planck constant (6.626 x 10^{-34} Js^{-1});
T_a = absolute temperature (°K).

3 Results and Discussions

3.1 Experimental Environment

The surface of the dryer was exposed to ambient air during the drying experiments. The temperature in the laboratory ranged between from 28 to 31°C and the humidity varied between 55 to 65% during experimentation.

3.2 Moisture Ratio History Relationship

The variations in moisture-content with drying time in the dehydration operation was recorded. The data was recorded at different temperatures for yam slices of varying sizes. The moisture content values were converted to moisture-ratio using equation 1. The initial moisture content of the yam slices was determined to be 194% dry basis, using a moisture analyser (OHAUS Corporation, MB45, Parsippany, NJ, USA).

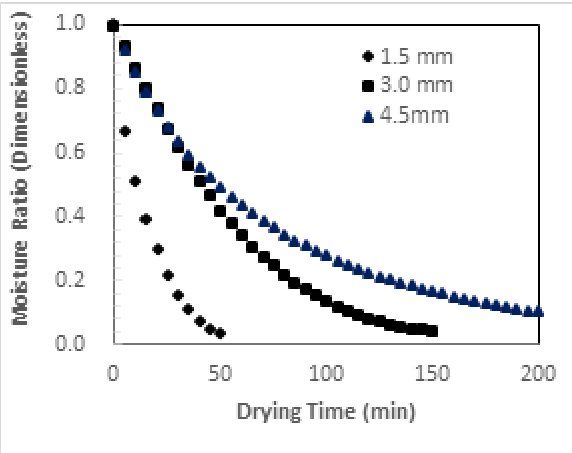

Fig. 2: Drying curves at 65°C

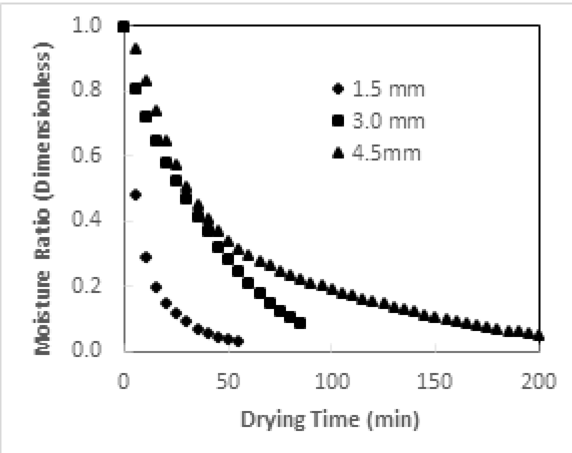

Fig. 3: Drying curves at 75°C

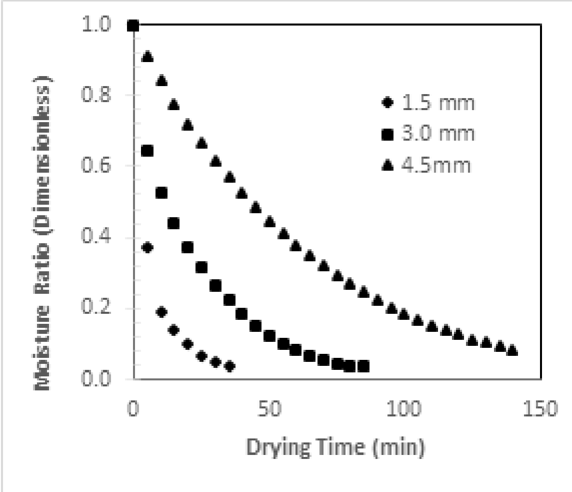

Fig. 4: Drying curves at 85°C

The variations of moisture-ratio with time is presented graphically in Figures 2, 3, 4 and 5. The graphs show that the moisture-ratio decreases exponentially with time. The drying times required to dehydrate the yam slices to 10% dry basis is observed to increase with increasing yam slice thickness for a given temperature. Also, as the drying temperature increases, the drying times decreased for a given yam slice size. Table 1 shows values of the drying times for different yam slice sizes at different temperatures.

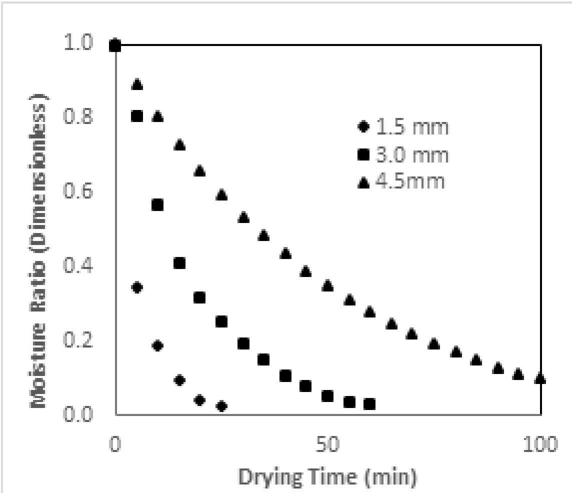

Fig. 5: Drying Curves at 95°C

Table 1. Drying Times for Different Sizes of Yam Slices at Different Temperatures to Dehydrate to 10% Dry Basis

	Temperature			
Size	65°C	75°C	85°C	95°C
1.5 mm	60 min.	45 min.	35 min.	25 min.
3.0 mm	200 min.	130 min.	90 min.	55 min.
4.5 mm	320 min.	240 min.	180 min.	160 min.

3.3 Estimation of the Effective Moisture Diffusivity

The effective moisture diffusivity, D_{eff}, was estimated using equation 3. The linear equations between –ln(MR) and the drying time (t), for the process condition considered are presented in Table 2. Table 2 also presents the correlation coefficients, R^2, obtained by performing the regression analysis between –ln(MR) and the drying time. The relationship between –ln(MR), and drying time, (t), have R^2, greater than 0.90. The implication is that there is a strong linear relationship between –ln(MR), and drying time. From the slope, k_d, obtained in each case, D_{eff}, is estimated. From the information presented in Table 2, for any given size, the moisture diffusivity increases with temperature. The values of effective moisture diffusivity are also presented in Table 2

Table 2. Moisture Diffusivities & Regression Coefficients, at Different Temperature for Different sizes of Yam Slices

Drying Temp	Slice Size	Relationship	R^2	D_{eff} (m²/s)
65°C	1.5 mm	-ln(MR65) = 0.0587t + 0.0959	0.9860	8.919E-10
	3.0 mm	-ln(MR65) = 0.0176t + 0.0667	0.9681	1.070E-09
	4.5 mm	-ln(MR65) = 0.0097t + 0.2276	0.9873	1.326E-09
75°C	1.5 mm	-ln(MR75) = 0.0604t + 0.4830	0.9543	9.177E-10
	3.0 mm	-ln(MR75) = 0.0265t + 0.0254	0.9840	1.611E-09
	4.5 mm	-ln(MR75) = 0.0131t + 0.2584	0.9831	1.791E-09
85°C	1.5 mm	-ln(MR85) = 0.0882t + 0.4570	0.9453	1.340E-09
	3.0 mm	-ln(MR85) = 0.0328t + 0.3271	0.9618	1.993E-09
	4.5 mm	-ln(MR85) = 0.0177t - 0.0295	0.9956	2.420E-09
95°C	1.5 mm	-ln(MR95) = 0.1097t + 0.4635	0.8963	1.667E-09
	3.0 mm	-ln(MR95) = 0.0378t - 0.0283	0.9848	2.297E-09
	4.5 mm	-ln(MR95) = 0.0218t + 0.0240	0.9810	2.981E-09

Comparing the results obtained, no documentation was found in the literature for the effective moisture diffusivity of yam slices in a Refractance Window™ dryer. However, the values of effective moisture diffusivities obtained for the process condition studied ranged from 8.919 x 10^{-10} to 2.981 x 10^{-09} m²s⁻¹, these are within the general range of 4.00 x 10^{-13} to 6.10 x 10^{-7} m²s⁻¹ for roots, fruits and vegetables (Panagiotou *et al.*, 2004).

3.4 Estimation of the Activation Energy

Thermodynamically, the activation energy E_a, is the ease with which moisture surpass the energy barrier during internal moisture diffusion from the yam structure (Costa *et al*, 2015; Resende *et al*., 2010). The activation energy, E_a, for a specific yam slice thickness was estimated by performing a linear regression analysis using Equation 7.

The natural log of effective moisture diffusivity, *ln(D_{eff})* and the inverse of the drying temperature (1/T) values were used in the analysis. Results of the regression analysis is presented in Table 3. As shown in Table 3, the correlation coefficient, R^2, values between *ln(D_{eff})* and the inverse of the drying temperature (1/T) is greater than 0.90; this implies that there is a strong relationship between the 2 parameters. From the slope, k_r, of the linear relationship, the activation energy, E_a, was obtained (Equation 9). The activation energy for the 1.5, 3.0 and 4.5 mm thick yam slices, was estimated to be 23.21 kJ/mol, 26.09 kJ/mol, and 28.30 kJ/mol respectively. The activation energy, E_a, is observed to increase with the yam slice thickness. D_0, the pre-exponential factor of the Arrhenius equation is obtained from the intercept of the linear relationship. D_0 values are 3.153E-06, 1.204E-05, and 3.139E-05 (m²/s) respectively for yam slices 1.5 mm, 3.0 mm, and 4.5 mm thick. Also, D_0, is observed to increase with the yam slice thickness.

Table 3. Activation Energy E_a, and Arrhenius Equation Pre-Exponential Factor D_o , for Yam Slices of Different Thickness

Slice Size	Relationship	R^2	D_o (m²/s)	E_a (kJ/mol)
1.5 mm	ln(D_{eff}) = -2789.3/T -10.369	0.9107	3.153E-06	23.21
3.0 mm	ln(D_{eff}) = -3135.1/T -11.327	0.9548	1.204E-05	26.09
4.5 mm	ln(D_{eff}) = -3400.9/T -12.667	0.9963	3.139E-05	28.30

3.5 Thermodynamics Considerations

Changes in Enthalpy, ΔH, Entropy, ΔS, and Gibbs Free Energy, ΔG was estimated for yam slices, 1.5, 3.0 and 4.0 mm thick at temperatures of 65, 75, 85, and 95°C respectively, using Equation 9 -12. Figure 4, 5, and 6 respectively present the results for ΔH, ΔS, and ΔG respectively.

Enthalpy change is a measure of how much energy is released or absorbed during a operation. A positive enthalpy change value, (i. e. ΔH > 0), indicates that the drying process is endothermic, and that heat energy needs to be supplied for dehydration to occur. A negative enthalpy change value, (i. e. ΔH < 0), indicates that the drying process is exothermic, and that heat energy is released to the environment.

Table 4 shows that, for a given yam slice size, the enthalpy change, ΔH, while positive, decreases by about 1% as the temperature increase from 65°C to 95°C. The 1% change in Enthalpy over the temperature range 65 – 95°C is insignificant., the implications are that there is no change in energy requirement for drying sliced yam at higher drying temperatures to drying at lower temperatures. However, for a given temperature, Enthalpy change increases with slice size, suggesting a there is a higher energy requirement for drying of larger sliced yam. The positive enthalpy change values, (i. e. ΔH > 0), presented in Table 4, indicates that the drying process is endothermic, and that heat energy needs to be supplied for dehydration to occur.

Table 4. Change in Enthalpy for Yam Slices at different Temperatures

	1.5 mm	3.0 mm	4.5 mm
Temperature	**Enthalpy (Jmol⁻¹)**		
65°C	20,381.33	23,256.49	25,466.48
75 °C	20,298.19	23,173.34	25,383.34
85 °C	20,215.04	23,090.20	25,300.19
95 °C	20,131.90	23,007.05	25,217.05

Table 5 presents the changes in Entropy, ΔS, for different sizes of yam slices at different temperatures. For any given slice size, the change in entropy increases with temperature. Also, for a set temperature, a decrease in Entropy change is observed as the yam slice increase, indicating increase in the order of the system.

Table 5. Changes in Entropy for Yam Slices at different Temperatures

	1.5 mm	3.0 mm	4.5 mm
Temperature	Entropy ($Jmol^{-1}K^{-1}$);		
65°C	-140.69	-129.55	-121.58
75 °C	-140.93	-129.79	-121.83
85 °C	-141.17	-130.03	-122.06
95 °C	-141.40	-130.26	-122.29

Table 6 presents the changes in Gibbs Free Energy, (ΔG), for different sizes of yam slices at different temperatures. The changes in Gibbs Free Energy (ΔG), of a drying process, is the energy that is available for or required for modifying the cell structure of the dehydrating product. By examining the free energy change that occurs during dehydration, a drying operation that will proceed (favourable) and one that will not (unfavourable) can be determined. Favourable operations have negative ΔG values and are known as exergonic processes, while unfavourable operations have positive ΔG values, and are known as endergonic processed. As indicated in Table 6, the ΔG values are all positive and are known as endergonic processes. The implication is that the operations are all unfavourable. Therefore, energy in the form of heat is required for them to proceed.

For any given slice size, the change in Gibbs Free Energy increases with temperature. Also, for a given temperature the change is Gibbs Free Energy decreases. The positive values for Gibbs Free Energy (i.e. $\Delta G > 0$) mean that the dehydration process requires energy from the environment; this energy is in the form of heat.

Table 6. Change in Gibbs Free Energy for Yam Slices at different Temperatures

	1.5 mm	3.0 mm	4.5 mm
Temperature	Gibbs Free Energy ($Jmol^{-1}$)		
65°C	67,934.80	67,044.15	66,561.87
75 °C	69,342.92	68,340.86	67,778.93
85 °C	70,753.44	69,639.96	68,998.38
95 °C	72,166.27	70,941.38	70,220.15

4 Conclusion

A laboratory-scale Refractance Window™ dryer was used to dehydrate, white yam slices, 1.5, 3.0 and 4.0 mm thick at temperatures of 65, 75, 85, and 95°C respectively. During dehydration, variations in moisture content with dehydration time of the yam slices were recorded. The following conclusions were deduced from the estimated changes in ΔH, ΔS, and, ΔG.

For the temperature range of 65 to 95°C, the Enthalpy change for any given yam slice size increased slightly with dehydration temperature. However, for any given temperature, there is about 20% change in the energy requirement in drying yam slices in the range 1.5 mm to 4.5 mm. The Enthalpy change for the process conditions studied varied from 20,381.33 to 25,217.05 J/mol. Also, the Entropy change for any given yam slice increased by less than 1% with dehydration temperature, indicating that changes in Entropy during dehydration of yam slices in the temperature range of 65 to 95°C is small. However, for any given temperature, there is about a 16% change in the entropy change in drying yam slices in the range 1.5 mm to 4.5 mm. The Entropy change for the process conditions studied vary from -140.69 to -122.29 $J.mol^{-1}.K^{-1}$.

Finally, the change in Gibbs Free Energy for any given slices varied by about 5% with a dehydration temperature range of 65 to 95°C, and for any given temperature, there is about 2% change in the change in Gibbs Free Energy during the drying of yam slices in the range 1.5 mm to 4.5 mm. The change in Gibbs free energy for the process conditions studied varies from 67,934.80 to 70,220.15 $J.mol^{-1}$.

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