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Convectif drying and thermodynamic properties of three starch products (*Dioscorea cayenensis, Colocasia esculenta* and *Ipomoea batatas* Lam) usually consumed in Congo

BG Elongo, A Kimbonguila, L Matos, CH Hounounou Moutombo, M Mizere, SLH Djimi, JM Nzikou

CHAIRE UNESCO- ENSP, Laboratory Process Engineering, University Marien NGOUABI, Brazzaville, Congo

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Abstract

The objective of this work is to contribute to the study of starch products in particular *Dioscorea cayenensis*, *Colocasia esculenta* and *Ipomoea batatas* by the characterization of their kinetics of convectif drying to the drying oven and the determination their properties thermodynamic. The convectif drying of the samples of these three starch products of parallel epipedic form of thickness 4 and 14 mm was carried out at temperatures of 50, 60 and 70°C. The results obtained show that the kinetics of drying of *Dioscorea cayenensis*, *Colocasia esculenta* and *Ipomoea batatas* present two (02) phases. It is of the phase of temperature setting and the phase at decreasing speed. The temperature and the thickness of the product have significant effects on the duration of drying, effective diffusivity (D_{eff}), the energy of activation (E_a), the differential of enthalpy (ΔH^*) and the energy of Gibbs (ΔG^*) except for values of entropy (ΔS^*). A titrates illustrative, the reduction the thickness of the product from 14 to 4mm makes it possible to reduce the energy of action from 19.43 to 10.68kJ.mol^{-1}, 35.33 to 11.52kJ.mol^{-1} and from 11.08 to 5.77kJ.mol^{-1} respectively during the drying of *Dioscorea cayenensis*, of *Colocasia esculenta*.

***Corresponding Author:** Jean-Mathurin Nzikou ✉ nzikoumath@yahoo.com

Introduction

In sub-Saharan Africa, the roots and tubers constitute the most significant food cultures. These local roots and tubers are mainly the manioc (*Manihot esculenta*, the potato (*Solanum tuberosum*, the sweet potato (*Ipomoea batatas* the yam (*Dioscorea* and the taro (*Colocasia esculenta*. They are the subject of the particular studies for a valorization and diversification of the economies of the more share of the tropical and subtropical countries (Kouassi, 2009).

The industrial potential of the starch products was studied in under area because their very high contents of glucides (60-90% glucides in base dries mainly in the form of starch) (Nepa, 2006; Njintang, 2003; Payne *et al.,* 1941). It arises that the flours and the starches of these products can beings used as in alternative in agricultural processing industry and pharmaceutical industry (Dangui, 2015; Ahmed *et al.,* 2010; Kouassi, 2009). In Europe, South America and India for example, the made up flours are used primarily to reduce the incidence of the disease of intolerance to the gluten (coeliaque) and also recommended to the patients diabetic thanks to his regulating effect of the rate of blood glucose (Toufeili *et al.,* 1994).

The transformation of the roots and tubers into flours requires a process of drying inclusively. Drying is an operation having for goal water elimination impregnating the solid by evaporation by using like energy heat. Drying constitutes one of the complex processes where intervene of the phenomena of transfers of heat and matter in a simultaneous way. During drying, water is eliminated from the solid, reducing the growth potential of the micro-organisms and the undesirable chemical reactions, therefore increase in the lifespan of product (Gowen *et al.*, 2008).

The knowledge of properties of thermodynamics of product makes it possible to envisage activation and the evolution of drying in the course of time. In several studies of agricultural produce, the researchers used isotherms of sorption like a means to determine certain thermodynamic properties in order to describe the sorption of the material water and to define the energy needs implied in the process of drying (Oliveira *et al.*, 2014a; Koua *et al*, 2014; Smaniotto *et al.*, 2012).

The thermodynamic properties given in the process of drying are the latent heat of vaporization, the differential of entropy and enthalpy and the free energy of Gibbs (Oliveira *et al.,* 2014b; Ouedraogo, Raji and Owamah, 2013; Cladera-Olivera *et al.*, 2011; Rosa, Moraes and Pinto, 2010; Goneli *et al.,* 2010b; Goneli *et al.,* 2010a). It is accordingly that this work aims to characterize the kinetics of convectif drying of *Dioscorea cayenensis*, of *Colocasia esculenta* and *Ipomoea batatas* and to determine the coefficients of diffusion and the thermodynamic properties of each product under the various operating conditions.

Materiel and methods

1-sampling

The tubers of three starch-based were dimensioned in the parallelepipedic form (L×l×E = 40mm× 30mm × (4 or 14mm)). Dimensioning was carried out using an electric Slicer of mark RCL1. Exact dimensions were checked using a slide caliper and / or scale.

The samples were coded in the following way: X/Y/Z
With:
X: Code of starch product
Y: Code thickness (mm)
Z: Code temperature of drying (°C)

2-drying with the drying oven

The drying of the plates was carried out at temperatures of 50, 60 and 70°C. The sample of each starch product was placed at drying oven (INDELAB; 0-250°C), then weighed after each five minutes (5 min). Using a balance with precision of mark EXPLORER-PRO (0-210g, with E = 0.0001g), the mass of the each sample was followed in the course of time until this one does not vary any more between 3 successive measurements.

3-parameters of kinetics of drying

3-1- Water content

The determination of the water content was carried out according to method AOAC (1990) based to the measure of the loss in mass of the samples after stoving with 105 ± 2 °C until complete elimination of interstitial water and the volatile matters.

$X = [(m_h - m_s)/ m_h] \times 100$ (1)

X: water content;

m_h : mass wet sample (g);

m_s : mass dry sample (g);

3-2-Speed of drying

The instantaneous speed of drying at time T is determined by the formula hereafter:

$dX/dt = -[(X_{(t+ \Delta t)} - X_{(t)}) / \Delta t]\times 100$ (2)

With:

dX/dt: speed of drying ($g_{H2O}.g^{-1}.MS\ s^{-1}$)

X: water content in base dries ($g_{H2O}.g^{-1}.MS$)

Δt: variation of time in seconds (s)

4-Effective Diffusivity (D_{eff})

The transfer of matter during drying is controlled by internal diffusion. The second law of Fick of diffusion shown in equation (3) has been widely used to describe the drying process of most biologic products (Srikiatden *et al.*, 2008). The diffusion coefficient of three starch products layers has been determined from the analytic equation of the second Fick law, developed by Crank (1975). Supposing that transfers are one-dimensional, the tenor in water initially uniform in the product without contraction of the solid matter and a long time of diffusion. The analytic solution of Fick equation according to the geometric form of the sample (parallelepiped) is given by the following equation:

$X^* = (X_{(t)} - X_{eq}) / (X_o - X_{eq}) = 8/(\pi)^2 \exp [(\pi^2 \times D_{eff} / 4L^2) \times t]$ (3)

X*: water content reduced;

$X_{(t)}$:($g_{H2O}.g^{-1}.MS$) : water content instantaneous;

X_o :($g_{H2O}. g^{-1}.MS$) : water content initial;

X_{eq}: ($g_{H2O}.g^{-1}.MS$) : water content with balance;

D_{eff} (m^2s^{-1}): coefficient of effective diffusion;

L(m): half-thickness of the sample;

t(s): time of drying.

The water content reduced was simplified by the equation (Equation 4) because Xéq is relatively negligible compared to $X_{(t)}$ and X_O (Akmel *et al.,* 2009; Haoua, 2007).

or $(X^*)= X_{(t)} / X_o = \ln (8/\pi^2) -[(\pi^2 \times D_{eff} \times t) /4L^2]$ (4)

The coefficient of diffusion is thus calculated starting from the bearing graph in X-coordinate the time of drying and in ordinate lnX *.The slope of the straight regression line giving lnX* according to time makes it possible to calculate the coefficient of diffusion of moisture according to the following relation:

$(\pi^2 \times D_{eff})/4L^2 =K$ $D_{eff} = (4L^2 \times K)/\pi^2$ (4) ⟶

5 thermodynamic Properties

5 1-Energy of activation

The energy of activation it is the energy which it is necessary to start the mass phenomenon of diffusion in the agricultural produce (Sacilik, 2007).

The coefficient of effective diffusion (D_{eff}) is corolla at the temperature of drying starting from the following equation of Arrhenius (Doymaz and Mehmet, 2002) Indeed, this function ln (D_{eff})= f (1/T) is linear whose slope is equal the opposite one of the energy of activation on the constant of perfect gases

$D_{eff} = D_o \exp (-E_a /RT)$ or $\ln (D_{eff}) = \ln(D_o) -(E_a /R)\times(1/T)$ (6)

The energy of activation is calculated starting from the slope of the graph ln(D_{eff}) according to (1/T); one obtains a line of equation Y' = $K_o' \times t + B'$

$K_o' = E_a /R$ $E_a = K_o' \times R$ (7) ⟶

D_{eff} : coefficient of diffusion ($m^2.s^{-1}$)

D_o : parameter of diffusion of Arrhenius ($m^2.s^{-2}$),

E_a : energy of activation or energy barrier to cross before evaporation is effective (J. mol^{-1})

T: temperature of drying (K)

R: constant of perfect gases (8.314 J.$mol^{-1}.K^{-1}$).

5 2- Enthalpy, entropy and the energy of Gibbs

The thermodynamic parameters such as enthalpy (ΔH^*), entropy (ΔS^*) and the energy of Gibbs (ΔG^*) during the drying of three starch-based were evaluated by the equations suggested by Sánchez *et al.*, (1992) and applied by Jideani and Mpotokwana (2009) and Guimaraes *et al.*, 2018.

$\Delta H^* = Ea - RT_{abs}$ (8)

$\Delta S^* = R(\ln k - \ln(k_b/h_p) - \ln T_{abs})$ (9)

$\Delta G^* = \Delta H^* - T_{abs} \Delta S^*$ (10)

ΔH^* : Enthalpy of activation (J mol^{-1});

ΔS^* : Entropy of activation (J mol^{-1} K^{-1});

ΔG^* : Energy of Gibbs (J mol^{-1});

k_b : Boltzmann Constant, (1.38×10^{-23} J K^{-1});

h_p: Planck's Constant (6.626×10^{-34} J s)

k: Constant speed (s^{-1}).

Results and discussion

1 Effect of the temperature on the kinetics of drying of three starch products

The effect of the temperature during convectif drying of 50 to 70°C of the samples of the parallelepipedic shape thickness E=14 mm of three starch products is presented on Fig.1a, Fig.1b and Fig.1c

For each product, the curves of kinetics decrease according to time and of the water content until stability. The curves take a decreasing exponential form (Fig.1a) The rise in the temperature to the drying oven increases the speed of water evaporation (Fig.1b and Fig.1c) They are evolve/move of 1.251×10^{-5} with 2.869×10^{-5} $g_{H2O}.g^{-1}MS.s^{-1}$ (DC), of 8.114×10^{-5} with 1.134×10^{-4} $g_{H2O}.g^{-1}MS.s^{-1}$ (CE) and of 4.1571×10^{-5} to 3.327×10^{-5} $g_{H2O}.g^{-1}MS.s^{-1}$ (IB) during the first 5 minutes when the temperature passes from 50°C to 70°C. The rise in the temperature of drying has by consequence the reduction of the time of drying of the samples (Fig. 1a). Thus, times necessary to reach a residual moisture of X* = 5% when the temperature increases by 50 to 70°C are 26 700 to 22 880 s, 21 900 to 14 400s and 21 000 to 14 700 s respectively for drying *Dioscorea cayenensis* (DC), *Colocasia esculenta* (CE) and *Ipomoea batatas* (IB). This reduction in the time of drying of about 14.61 % (DC), of 34.25 % (CE) and 30 % (IB).

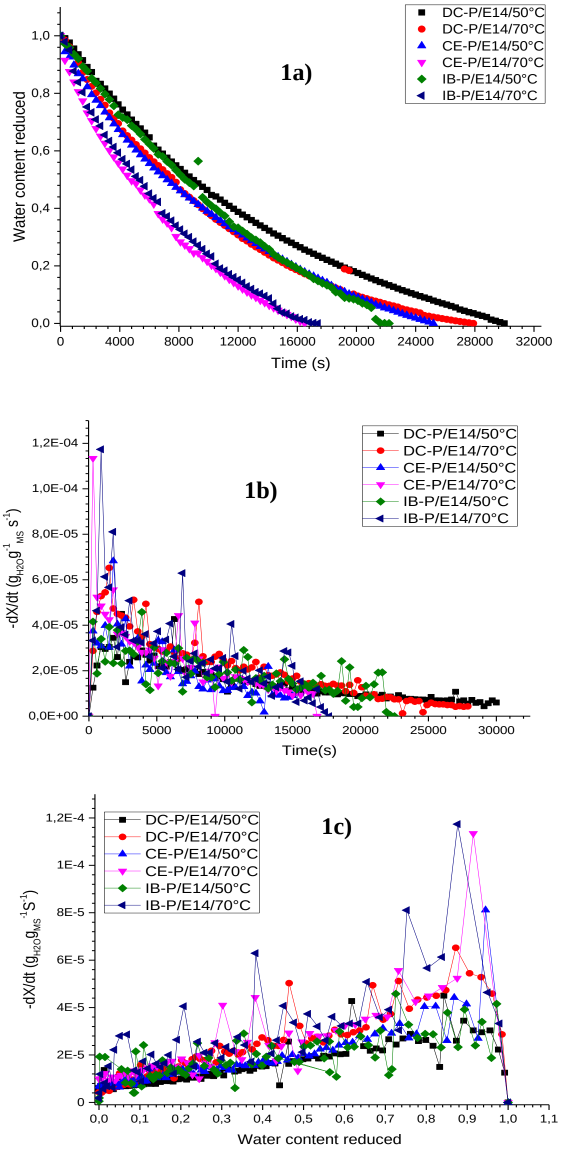

Fig. 1 (a, b, c). Influence temperature on the kinetics of convectif drying of three starch-based (E=14mm).

Indeed, this influence of the temperature on the speed of evaporation is due to the contribution of heat to the product, which believes with the rise in the temperature. The reduction speed according to time (Fig. 1b) and water content reduced (Fig. 1c) is primarily due to the instantaneous reduction in the availability out of water. Therefore the exchanges are done with difficulty.

The kinetics of drying of three products proceeds in two (02) phases. It is acted of a phase of temperature setting relatively short, of a phase at constant speed

and as end of a phase at decreasing speed (Fig. 1b; Fig. 1c)
The phase at constant speed is not always identifiable, same for the crop product with strong water content initial by the fact of the absence of an interstitial water film because of the cellular walls which disturb the migration of moisture. (Bonnazi and Bimbenet, 2003).

The absence of the phase at constant speed during drying was also highlighted by several authors for foodstuffs and biological at the time convectif drying (Mujumdar, 2006; Bonazzi and Bimbenet, 2003; Van Brakel, 1980).

The effect of the temperature on the kinetics of drying was deferred by several authors in the literature (Menasra and Fahloul, 2015; Arslan and Musa Ozcan, 2007; Locin, 1961). These authors noted that the time of drying decreases with the increase in the temperature.

Effective diffusivity

The influence thickness of the samples and the temperature of drying on the coefficient of effective diffusion of three starch-based is presented on Table 1.

Table 1. Effective diffusivity of three starch-based.

Dioscorea cayenensis		*Colocasia esculenta*		*Ipomoea batatas*	
Samples	D_{eff} (10^{-10}. m^2s^{-1})	Samples	D_{eff} (10^{-8}. m^2s^{-1})	Samples	D_{eff} (10^{-8}. m^2s^{-1})
DC/E04/50°C	4.75	CE/E04/50°C	3.41	IB/E04/50°C	8.92
DC/E14/50°C	24.2	CE/E14/50°C	21.90	IB/E14/50°C	83.40
DC/E04/60°C	5.15	CE/E04/60°C	3.73	IB/E04/60°C	10.69
DC/E14/60°C	29.60	CE/E14/60°C	25.84	IB/E14/60°C	91.35
DC/E04/70°C	8.02	CE/E04/70°C	4.38	IB/E04/70°C	12.90
DC/E14/70°C	31.40	CE/E14/70°C	27.83	IB/E14/70°C	95.32

The results obtained show that the variation the thickness of the samples of three starch-based from 4 to 14 mm and of the temperature of convectif drying of 50 to 70°C, has an effect on the increase of the coefficient of diffusion. The coefficients of diffusion respectively vary from 4.75×10^{-10} with $3.14\times10^{-9} m^2.s^{-1}$ for *Dioscorea cayenensis* (DC), from 3.41×10^{-8} with 2.78×10^{-7} $m^2.s^{-1}$ for *Colocasia esculenta* (CE) and from 8.92×10^{-8} with $9.53\times10^{-7} m^2.s^{-1}$ for *Ipomoea batatas* (IB). It is also noted that the increase thickness of the samples generates an increase in diffusivity. The effect the thickness would be due to the increase in the heat-transferring surface between the product and the environment of drying.

The coefficients of effective diffusion vary from one product to another. At illustrative title, the samples thickness E = 4mm, dried with 70°C respectively present the coefficients of 8.02 $\times10^{10} m^2.s^{-1}$ (DC) of $4.38\times10^{-8} m^2.s^{-1}$ (CE) and $1.29\times10^{-7} m^2.s^{-1}$ (IB).

The variation of diffusion coefficient, between the two thicknesses (4 and 14mm) for each product is primarily related to the side diffusion. Indeed, for the thick samples, the side diffusion is taken into account. These results are in agreement with those found in the literature (Boughali *et al.*, 2008; Nguyen and Price 2007; Doymaz, 2004a).

The effect of the temperature of drying on the coefficient of diffusion on the one hand and the thickness of cutting in plates on the other hand are in agreement with those obtained by Messaoudi *et al.,* (2015), Zielinska and Markowski (2010), Aghfir *et al.* (2008) and Park *et al.,* (2002).

Activation energy

Energies of activation of the various samples from the three starch-based ones were graphically given starting from the equation of Arrhenius (Fig. 2). Energies of activation of the reaction of evaporation during the drying of *Dioscorea cayenensis, Colocasia esculenta* and *Ipomoea batatas* are presented in Table 2.

They are about 11.52 to 35.33kJ.mol^{-1} from 10.68 to 19.43kJ.mol^{-1} and 5.77 to 11.08 kJ.mol^{-1} of for and respectively for the drying of *Dioscorea cayenensis, Colocasia esculenta* and *Ipomoea batatas*. It is also noted that the values of energy of activation strongly depend with the matrix on the product to dry.

Table 2. Activation energy of three starch-based.

Products	Samples	Energy of activation ($KJ.mol^{-1}$)	References
Dioscorea cayenensis	DC / E04	10.68	Present work
Dioscorea cayenensis	DC / E14	19.43	Present work
Colocasia esculenta	CE / E04	11.52	Present work
Colocasia esculenta	CE / E14	35.33	Present work
Ipomoea batatas	IB / E04	5.77	Present work
Ipomoea batatas	IB / E14	11.08	Present work
Mint	/	84.79	Aghfir *et al.* (2008)
Round mint	/	62.96	Doymaz (2006)
Spearmint	/	82.93	Park *et al.* (2002)
Carrots	/	28.36	Doymaz (2006)
Red pepper	/	42.80	Kaymak-Ertekin (2002)
Green pepper	/	24.70	Simal *et al.* (1996)
Black tea	/	406.02	Panchariya *et al.*(2002)

For each product, one notes that the energy of activation believes with the increase thickness of the samples. The larger the sample is, the more the quantity of energy necessary to start the reaction of evaporation is large.

For the various products, the energy of activation varies from one product to another with the operating conditions. The reduction in the energy of activation with the thickness of the product was also made by Messaoudi and Fahloul (2015). By comparing the results obtained with those of the literature (Table 2), one notes that energies of activation of *Ipomoea batatas* weak, are followed those of *Dioscorea cayenensis* and at the end *of Colosasia esculenta*. This difference can be explained by the fact that the starch products are very rich in interstitial water, consequently, they require a weak energy necessary to start evaporation the water molecules which are there.

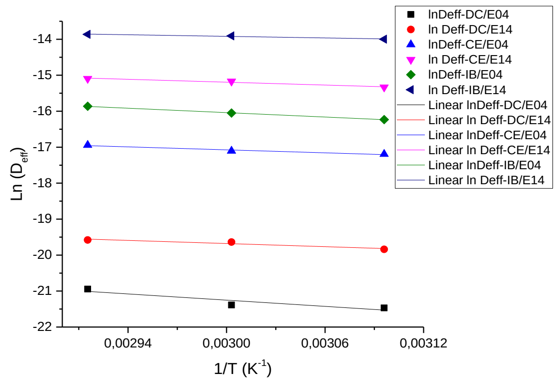

Fig. 2. Law of Arrhenius applied to the drying of the three starch-based ones.

Thermodynamic properties

The thermodynamic parameters of three starch products under the various conditions of drying are presented in Table 3.

Table 3. Thermodynamic properties of three starch-based.

Products	Samples	$k(s^{-1})$	ln(k)	R^2	ΔH* ($KJ\ mol^{-1}$)	ΔS* ($J.mol^{-1}\ K^{-1}$)	ΔG* ($KJ.mol^{-1}$)
Dioscorea cayenensis	DC /E04/50°C	0.01111	-4.49991	0.97293	7.9946	-245.4797	87.2845
	DC /E14/50°C	0.00500	-5.29832	0.98526	16.7446	-245.5305	96.0509
	DC /E04/60°C	0.01095	-4.51442	0.96412	7.9114	-245.7345	89.7410
	DC /E14/60°C	0.00619	-5,08482	0.98671	16.6614	-245.7741	98.5042
	DC /E04/70°C	0.01673	- 4.09055	0.98694	7.8283	-245.9324	92.1831
	DC /E14/70°C	0.00622	- 5.07999	0.9808	16.5783	-246.0198	100.9631
Colocasia esculenta	CE /E04/50°C	0.00972	- 4.63357	0.98548	8.8346	-284.0955	100.5974
	CE /E14/50°C	0.00162	- 4.71630	0.96549	32.6446	-298.9922	105.4091
	CE /E04/60°C	0.01021	-4.58439	0.98681	8.7514	-283.9401	103.3035
	CE /E14/60°C	0.01600	-4.13517	0.97579	32.5614	-280.2053	125.8698
	CE /E04/70°C	0.01609	-4.12956	0.99469	8.6683	-280.4047	104.8471
	CE /E14/70°C	0.01873	- 3.97763	0.97579	32.4783	-279.1415	128.2238
Ipomoea batatas	IB /E04/50°C	0.00763	- 4.87567	0.98775	3.0876	-286.1083	95.5006
	IB /E14/50°C	0.00567	- 5.17257	0.96779	8.3986	-288.5768	101.6089
	IB /E04/60°C	0.00869	-4.74558	0.93654	3.0044	-285.2803	98.0028
	IB /E14/60°C	0.00751	-4.89152	0.99923	8.3154	-286.4936	103.7178

IB /E04/70°C	0.00986	-4.61927	0.96754	2.9213	-284.4761	100.4966
IB /E14/70°C	0.00886	-4.72621	0.98082	8.2323	-285.3652	106.1126

The results obtained show that each parameter varies from one product to another with the operating conditions. The values of enthalpy vary from 7.83 to 16.75KJ.mol^{-1} from 8.67 to 32.6KJ.mol^{-1} and from 2.92 to 8.40KJ.mol^{-1} respectively for the convectif drying of *Dioscorea cayenensis* (DC) *Colocasia esculenta,* (CE) and *Ipomoea batatas* (IB). The free energy of Gibbs varies from 8.28 to 100.96KJmol^{-1} for (DC), from 100.59 to 128.22KJ.mol^{-1} for the drying from (CE) and 95.50 to 106.11KJmol^{-1} for (IB).

However, one notes light variation of entropy with the temperature and the thickness of the product. The values entropy are about -246.02 to -245.48J.mol^{-1}.K^{-1} from -298.99 to -279.14J.mol^{-1}.K^{-1} and from -288.57 to -284.48J.mol^{-1}.K^{-1} during the convectif drying of *Dioscorea cayenensis* (DC) *Colocasia esculenta* (CE) and *Ipomoea batatas* (IB) when the temperature of drying and the thickness of the product vary from 50 to 70°C and from 4 to 14 mm. One also notes a light variation of entropy between the three products.

The values of enthalpy (ΔH^*) and free energy of Gibbs (ΔG^*) increase with the temperature and the thickness of the product.

The increase in the enthalpy and the free energy with the rise the thickness of the product is primarily correlated with the increase in the energy of activation. The positive values of enthalpy ($\Delta H^* > 0$) and of the free energy ($\Delta G^* > 0$) show that the separation of the water molecules contained in these three starch products is not spontaneous. The variation of these various thermodynamic parameters is in conformity with that noted by Guimaraes *et al.,* (2018), Oliveira *et al.,* (2014b), Oliveira *et al.,* (2013), Correa *et al.,* (2010), Goneli *et al.,* (2010 b) in their studies on seeds of jatropha, "okara", gombo, coconut, cherries and of coffee respectively. The values of the variation of entropy obtained for the three starch products are higher than those obtained by Guimaraes *et al.,* (2018) during drying of "okara" at same temperatures.

Conclusion

Drying remains one of the unit operations which necessarily intervene in the transformation of the roots and tubers.
It makes it possible to preserve the foodstuffs by the water elimination per evaporation by using like energy heat. The reduction in the water content of the product during drying makes it possible to reduce the growth potential of the micro-organisms and the undesirable chemical reactions during the storage of this one while increasing its lifespan.

This study was undertaken on the convectif drying of plates of *Dioscorea cayenensis Colocasia esculenta* and *Ipomoea batatas* of thickness 4 and 14 mm at temperatures of 50, 60 and 70°C.

The results show that the kinetics of convectif drying of these three starch products proceed in two (02) phases in particular the phase of temperature setting and the phase at decreasing speed in absence of the phase at constant speed. The temperature of convectif drying, to the drying oven and the thickness of the product, have effects on the duration of drying, effective diffusivity and the thermodynamic properties. The coefficients of diffusion are of 4.75×10^{-10} with 3.14×10^{-9}m^2.s^{-1} for *Dioscorea cayenensis* of 3.41×10^{-8} with 2.78×10^{-7}m^2.s^{-1} for *Colocasia esculenta* and of 8.92×10^{-8} with 9.53×10^{-7}m^2.s^{-1} for *Ipomoea batatas*. The values of entropy are not very variable with the operating conditions. They are -246.02 to -245.48J.mol^{-1}.K^{-1} -298.99 to -279.14J.mol^{-1}.K^{-1} and -288.57 to -284.48J.mol^{-1}.K^{-1} during the convectif drying of *Dioscorea cayenensis, Colocasia esculenta* and *Ipomoea batatas* respectively. The reduction thickness of the product makes it possible to reduce the energy of activation and to increase the molecular agitation from one product to another and consequently the reduction of their times of drying.

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