DRYING KINETICS OF NATURAL COFFEE FOR DIFFERENT TEMPERATURES AND LOW RELATIVE HUMIDITY

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(Recebido: 15 de março de 2012; aceito: 4 de julho de 2012)

ABSTRACT: Faced with the importance of the drying in the post-harvest phase of coffee and its influence in the final quality of the product, the current study had the aim of evaluating the kinetics of the drying in different temperatures of the drying air for a low temperature at dew point of fruits of arabic coffee (*Coffea arabica*) dry processed. The cherries were manually picked and submitted to hydraulic separation. After that, the fruits with initial water contents of 1.9 ± 0.1 kg.kg^{-1} (bs) were submitted to the drying process under three temperatures of dry bulb (35 °C, 40 °C e 45 °C) for the same temperature of dew point (2.6 °C) of the drying air. Seven mathematical models were adjusted to the experimental data to characterize the dry process of coffee cherries. Henderson and Pabis modified and Successive Residue models with two terms were the most adequate to describe the dry process, being the Henderson and Pabis modified model chosen, for being more simple. The elevation of the temperature of the dried bulb under the low temperature of dew point causes an increase of the effective diffusivity coefficient, the drying rate and reduces the time of drying. For the conditions which were studied, the effective diffusivity coefficient of water for coffee fruits varies between 1.908 e 3.721 x 10^{-11} m².s^{-1}. The activating energy for the liquid diffusion, described by the equation of Arrhenius, was of 52.89 kJ.mol^{-1}.

Index terms: Mathematical modeling, drying rate, *Coffea arabica* .

CINÉTICA DE SECAGEM DE CAFÉ NATURAL PARA DIFERENTES TEMPERATURAS E BAIXA UMIDADE RELATIVA

RESUMO: *Diante da importância da secagem na fase da pós-colheita do café e seu reflexo na qualidade final do produto, objetivou-se, neste trabalho, avaliar a cinética da secagem em diferentes temperaturas do ar de secagem, para uma baixa temperatura de ponto de orvalho de frutos de café arábica (Coffea arabica), processados via seca. Os frutos foram colhidos manualmente e submetidos à separação hidráulica. Para a secagem dos frutos, com teor de água inicial de* $1{,}9 \pm 0{,}1$ *kg.kg*$^{-1}$ *(bs), utilizou-se secador mecânico a três temperaturas de bulbo seco (35 °C, 40 °C e 45 °C) para a mesma temperatura de ponto de orvalho (2,6 °C) do ar de secagem. Sete modelos matemáticos foram ajustados aos dados experimentais para caracterizar o processo de secagem dos frutos do cafeeiro. Os modelos de Henderson e Pabis modificado e de Resíduos Sucessivos, com dois termo, foram os mais adequados para descrever o processo de secagem, sendo escolhido o de Henderson e Pabis modificado, pela maior simplicidade. A elevação da temperatura de bulbo seco, sob baixa temperatura de ponto de orvalho, provoca aumento no coeficiente de difusividade efetivo, na taxa de secagem e redução no tempo de secagem. Para as condições estudadas, o coeficiente de difusividade efetivo de água para os frutos do cafeeiro varia entre 1,908 e 3,721 x* 10^{-11} *m².s*$^{-1}$*. A energia de ativação para a difusão líquida, descrita pela equação de Arrhenius, foi de 52,89 kJ.mol*$^{-1}$*.*

Termos para indexação: *Modelagem matemática, taxa de secagem, Coffea arabica .*

1 INTRODUCTION

The freshly harvested coffee differs from other grains grown on a large scale, by presenting certain peculiarities, such as high water content, approximately 60% (wb) and unequal in relation to maturation (Resende et al., 2009). Therefore, the drying process is an essential step to prevent the attack of microorganisms and fermentation that will compromise the quality of the coffee. According Borém (2008), the drying step is important both from the aspect of energy consumption and the influence it has on the operation quality of the final product.

According to Resende, Almeida and Ferreira (2010), the mathematical simulation of the drying process is critical to the development and improvement of equipment used for drying grain.

There are three models of mathematical simulation of the process of thin layer drying, which aim to describe the drying kinetics of agricultural products. The theoretical model, which considers only the internal resistance to heat transfer between the product and water and warm

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air; semitheoretical and empirical models, which only consider the internal resistance, temperature and relative humidity of the drying air (Midilli; KUCUK; Yapar, 2002).

Numerous models have been proposed to describe the reduction rate of water during drying in a thin layer of biological materials (BURMESTER; Eggers 2010; DI SCALA; CRAPISTE, 2008; Erbay; icier, 2010; Hernández-Diaz et al. 2008; NILNONT et al., 2012, Oliveira et al., 2010; Putranto et al., 2011). An equation that describes the rate of drying of a thin layer is required for the drying simulation thick layer, as the simulation models are generally based on the assumption that the thick layer is composed of a series of thin layers (KASHANINEJAD et al ., 2007).

As conditions of the drying process, different models can be adjusted to adequately describe the kinetics of drying hair care products porous hygroscopic. Models Lewis, Page, Thompson, Midilli of Modified Verma, waste successive Henderson and modified Pabis have been adjusted frequently to predict the drying process seed and fruit (Akpınar, 2006; Andrade et al., 2006; Corrêa et al., 2010; CORRÊA; Resende; RIBEIRO, 2006; GONELI et al., 2009; KASHANINEJAD et al., 2007; MOHAPATRA; RAO, 2005).

Were not found in the scientific literature, information on models that describe the drying natural under different temperatures and low relative humidity. Thus, the aim of the present study was to evaluate the kinetics of drying at different drying air temperatures for a low dew point temperature of Arabica coffee fruits, processed dry.

2 MATERIALS AND METHODS

To conduct the experiment, we used ripe fruit coffee (*Coffea arabica* L. cv. Mundo Novo), collected manually with a water content of 1.9 ± 0.1, dry basis (db). After harvest, there was the hydraulic separation to remove fruits with smaller density followed by manual selection to remove unripe and overripe. Thereafter, drying was performed in mechanical dryers until fruits reach a water content of 0.50 ± 0.05 (bs). Then, interspersed by 14 hours of drying (8:00 h to 22:00 h) at intervals of 10 hours of rest (22:00 until 08:00 the next day), until they reach the fruit content water of approximately 0.14 (bs), which corresponded to the water content of processed coffee from 11 ± 0.5% (wb).

The moisture content of green coffee at the beginning and end of the mechanical drying was determined by the standard method ISO 6673 (International Organization for Standardization - ISO 2003). The monitoring of reduction of the water content of the fruit during the drying process was conducted by gravimetric (loss of weight), using an analytical balance with a precision of 0.01 g.

To evaluate whether the desired water content in the fruits of coffee has been reached, the study determined the rate of drying of the product, according to the following expression.

$$\text{Tx. Sec.} = \frac{U_{ant} - U_{at}}{\Delta t} \quad (1)$$

wherein:
Tx. Sec: Drying Rate (g. kg-1.h-1);
UPrev: Water content at the previous time (g. kg -1 (bs));
Uat: Water content current (g. kg -1 (bs)) and
Dt: time interval between weighings (hours);

Before the start of mechanical drying was calculated equivalent radius of the coffee fruit, defined as the radius of a sphere with a volume equivalent to the volume of the fruit. For the calculation of their volume taken up a sample of 100 fruits, which have been taken with length (a), width (b) and thickness (c) by using a caliper to an accuracy of 0.01 mm , and the volume of coffee fruits (V) calculated by Equation 2.

$$V = \frac{4}{3}\pi\, abc \quad (2)$$

wherein:
V: volume of fruit (m³);
a: length (m);
b: width (m) and
c: thickness (m).

The drying system consisted of an air conditioner attached to a fixed bed dryer (Figure 1). The characteristics of the air have been controlled by Air Conditioning System Laboratory (SCAL) as the model proposed by Fortes et al. (2006). The equipment allows precise control of flow, temperature (T) and relative humidity (RH) of the drying air. To obtain a dew point temperature (2.6 ° C) before the SCAL, the air is pre-conditioned by a cooling system comprised of three air-conditioning units.

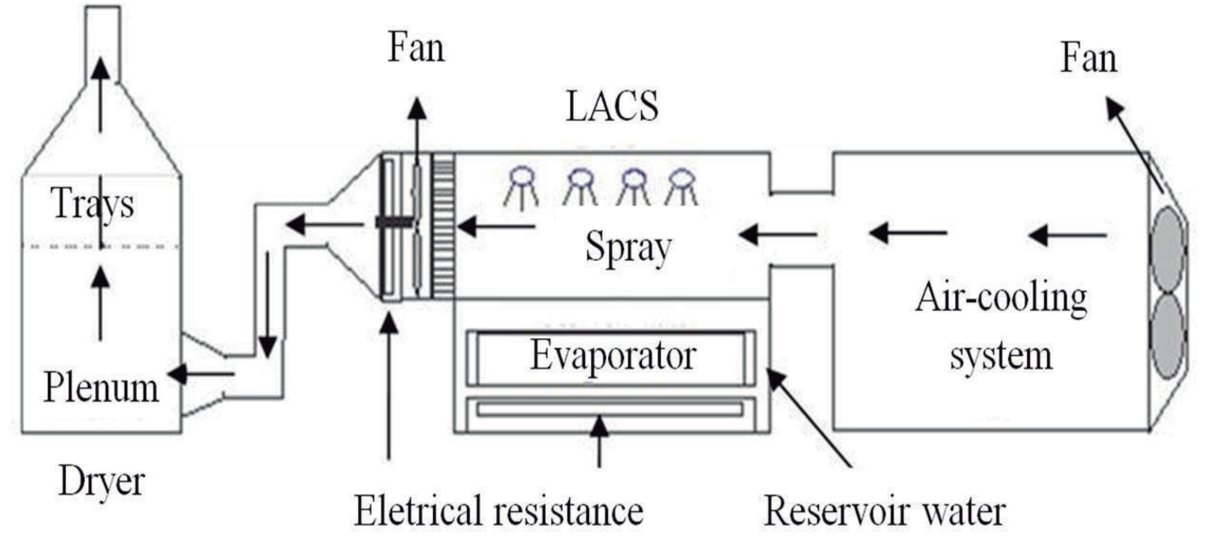

FIGURE1 - System for mechanical drying of coffee.

The dryer was composed of four removable trays with bottoms drilled square section with sides equal to 0.3 m depth of 0.1 m, located over a plenum for uniform air flow. To minimize possible temperature differences, made a 90 ° rotation of the position of the trays every hour.

The velocity of the drying air was monitored using an anemometer and vane for all treatments was held constant speed 0.33 ms-1, corresponding to the flow of 20 m^3. 1.m-2-min. We used three dry bulb temperatures (35, 40, and 45 ° C) and a dew point temperature (2.6 ° C), which was measured in the chamber of the SCAL and the temperature of the drying air, measured in the plenum . Depending on the combinations between the wet bulb temperature and dew point were obtained from different relative humidities (RH) of the air drying (Table 1). Each treatment was performed four replications.

Data analysis of the rate of drying moisture (RU) is essential for describing different models of the thin layer drying. The ratio of moisture during drying, depending on variables, was determined by Equation 3. For all the conditions tested, the values of the moisture ratio as a function of drying time are adjusted to the model used to describe the kinetics of drying the coffee fruit shown in Table 2.

$$RU = \frac{U - U_e}{U_i - U_e} \tag{3}$$

wherein:
RU: the moisture ratio (dimensionless);
U: the water content of the product at time t (decimal dry basis);
Ue: equilibrium water content of the product (decimal dry basis);
Ui: an initial moisture content of the product (decimal, dry basis).

TABLE 1 - Dry bulb temperature (Tb), dew point temperature (Tpo) and relative humidity of the drying air (RH).

Tbs (°C)	Tpo (°C)	UR (%)
35	2,6	13,1
40	2,6	10,0
45	2,6	7,7

TABLE 2 - Mathematical models used to predict the drying kinetics.

Model designation	Model	Equation
Lewis[1]	$RU = \exp(-kt)$	(4)
Page[2]	$RU = \exp(-kt^{n})$	(5)
Thompson[3]	$RU = \exp\{[-a-(-a^{2} + 4bt)^{0,5}](2b)^{-1}\}$	(6)
Midilli Modificado[4]	$RU = \exp(-kt^{c}) + bt$	(7)
Verma[5]	$RU = -a\exp(-kt) + (1-a)\exp(-k_{1}t)$	(8)
Resíduos Sucessivos[6]	$RU = a\exp\{-[b\exp(-c\,T^{-1})]\,t\}+d\exp\{-[e\exp(-f\,T^{-1})]t\}$	(9)
Henderson & Pabis Modificado[7] (KARATHANOS,1999)	$RU = a\exp(-kt) + b\exp(-k_{0}t) + c\exp(-k_{1}t)$	(10)

[1](LEWIS, 1921); [2](PAGE, 1949); [3](THOMPSON; PEARTT; FOSTER, 1968); [4](GHAZANFARI et al., 2006); [5](VERMA et al., 1985); [6](GLENN, 1978); [7](KARATHANOS, 1999).

wherein:
RU: Reason moisture;
t: drying time (h);
T: drying temperature (° C);
k, k0 and k1: constant drying, and
a, b, c, d, e, f and n: coefficients of the model.

To adjust the mathematical models, were analyzed by nonlinear regression Gauss-Newton method, using the software STATISTICA 5.0 ® (Statsoft, Tulsa, USA). The choice of the best model was based on statistical parameters: standard deviation of the estimate (SE), mean relative error (P), coefficient of determination (R2) and a tendency of the distribution of residuals. The standard deviation of the estimate and the mean relative error were calculated respectively by equations 4 and 5.

$$SE = \sqrt{\sum\left(Y - \hat{Y}\right)^{2} / GLR} \tag{4}$$

$$P = \left[\left(100/n\right)\sum\left(\left|Y - \hat{Y}\right| / Y\right)\right] \tag{5}$$

wherein:
SE: standard error of the estimate (decimal);
Y: value observed experimentally;
$\hat{Y}$: value calculated by the model;
GLR: degrees of freedom of the model;
P: mean relative error (%) and
n: number of observed data.

The effective diffusion coefficient for the drying conditions used in this work was calculated by adjusting a model based on diffusion theory liquid (Equação 6) to the observed data via nonlinear regression using the STATISTICA ® 5.0 (Statsoft, Tulsa, USA). This equation is the analytical solution to Fick's second law, considering the geometric shape of the product as spherical, disregarding the shrinkage of fruits and considering the boundary condition of the known water content in the product surface (Corrêa et al. 2010).

$$RU = \frac{U - Ue}{Ui - Ue} = \frac{6}{\pi^{2}}\sum_{n=1}^{\infty}\frac{1}{n^{2}}\exp\left[-\frac{n^{2}\,\pi^{2}\,D_{eff}}{R^{2}}t\right] \tag{6}$$

wherein:
Deff: effective diffusion coefficient (m². S-1);
R: equivalent radius of the coffee fruit (m);
n: number of terms, and
t: time (s).

To calculate the activation energy of drying kinetics of coffee fruits used the Arrhenius equation (Equation 7). This equation shows the relationship between the activation energy and the speed at which the reaction occurs.

$$D_{eff} = D_0 \exp\left(-\frac{Ea}{RTa}\right) \tag{7}$$

wherein:
D0: pre-exponential factor;
Ea: activation energy (kJ mol-1);
R: universal gas constant (8.134 J g mol-1 K-1) and
Ta: absolute temperature (K).

3 RESULTS AND DISCUSSION

As defined in the methodology, from the volume calculated by Equation (2), the equivalent radius of the coffee fruit calculated was 6.51 x 10-3 m.

Table 3 shows the drying times of the effective diffusion coefficients, the water content of the fruits of coffee, at the beginning and end of drying and mechanical drying rates mean and maximum, depending on the temperature of the drying air for dew point temperature of 2.6 º C. It is found that the increase in the dry-bulb temperature generally reduce the total time of drying and relative humidity values of the drying air. The temperature effect is evident in the diffusion coefficient and the average drying rates, maximum rise in temperature of the dry bulb provided an increase in the effective diffusion coefficient and the rate of drying.

The temperature increase reduces the viscosity of water, directly influencing the resistance to fluid flow, the decrease of viscosity facilitates the diffusion of water molecules in capillaries of the product (Correa et al. 2010). Another factor that may be attributed to the increase in the effective diffusion coefficient, due to increases in the dry bulb temperature is that an increase in temperature allowed an increase in vibration level of the water molecules, which also contributes to a faster diffusion (GONELI et al. 2009).

The values of the effective diffusion coefficient obtained from the fruits of coffee subjected to thin layer drying are in agreement with the values obtained in other studies carried out on agricultural products, according Madamba, Buckle and Driscoll (1996), present in the range 10-9 to 10-11 m² s-1. Correa et al. (2010) studied the kinetics of drying coffee cherries at temperatures of 35 ° C, 45 ° C and 55 ° C to obtain diffusion coefficients between 2.39 and 5.98 x 10-11m ² s-1.

The relationship between the effective diffusion coefficient and the temperature of the drying air has been sufficiently described by the Arrhenius equation (Equação 8) (Correa et al. 2,010; GELY; Santalla, 2007; GONELI et al. 2,009; KASHANINEJAD et al. , 2007; Madamba; DRISCOLL, BUCKLE, 1996; MOHAPATRA; RAO, 2005).

Figure 2 shows graphically the values of ln (Deff) as a function of the inverse absolute temperature (1.K-1) obtained for the drying of coffee fruits.

The slope of the curve obtained by the Arrhenius equation (Equation 8) gives the relation Ea / R, while its intersection with the axis of ordinates indicates the value of D0. Equation 8 presents the coefficients of the fitted equations for the effective diffusion coefficient of the coffee fruit, previously calculated, according to Equação 8.

$$D_{eff} = 0,017223 \exp\left(-\frac{6866,99}{T_a}\right) \tag{8}$$

From Equation 8 the activation energy (Ea) calculated liquid diffusion of the coffee fruit is 52.89 kJ.mol-1. This value is within the range of activation energy for agricultural products, according Zogzas, Maroulis and Marinos-Kouris (1996) should be between 12.7 and 110 kJ.mol-1. Goneli et al. (2009) found values of activation energy of 55.40 kJ.mol-1 for coffee in parchment.

Figure 3 presents the drying rates as a function of water content in the fruits of coffee subjected to thorough drying in a dryer.

It can be seen in Figure 3, the rise in temperature gives higher rates of drying of coffee fruits for the same water content, and these different rates at different temperatures are higher at the beginning of drying, and as the fruits become drier, the differences decrease substantially.

TABLE 3 - Drying time, effective diffusion coefficient (Deff), water content of the initial and final drying rate average and maximum natural coffee, due to the dry bulb temperature (Tbs) and relative humidity of the drying air (RH).

Tbs (°C)	RH (%)	Drying time (h)	D_{eff} x 10^{11} ($m^2.s^{-1}$)	Water level ($kg.kg^{-1}bs$)		Drying rate ($g.kg^{-1}.h^{-1}$)	
				Initial	Final	Average	Maximum
35	13,1	104	1,908	1,882	0,143	16,72	97,31
40	10,0	78	2,456	1,890	0,145	22,37	106,08
45	7,7	52	3,721	2,021	0,132	36,33	145,36

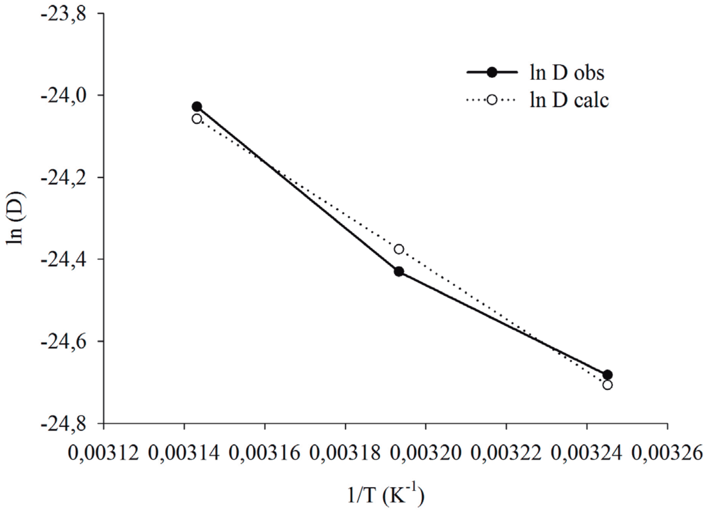

FIGURE 2 - Arrhenius representation of the effective diffusion coefficient, depending on the temperature of the drying air the fruits of coffee.

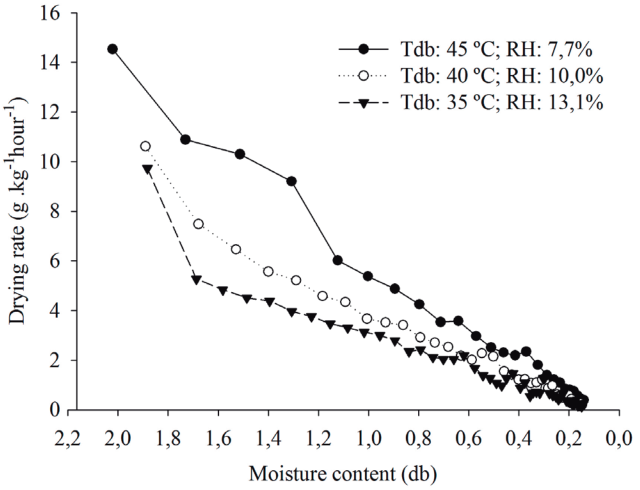

FIGURE 3 - Drying rate depending on the water content present in the fruits of coffee.

In the drying process, the removal of water from the fruit becomes more difficult due to the stronger bonding between the water and the other constituents of the grain, then drying rates for the three dry bulb temperatures, they tend to become equal or closer together at the end of the process.

Table 4 shows the statistical parameters for the models used in the description of the kinetics of drying coffee cherries, coefficients of determination (R^2), standard deviation of the estimate (SE), mean relative error (P) and the trend distribution of residues for the seven models used to describe the drying kinetics of coffee fruits, with initial average water content of 1.9 (bs), when subjected to different temperatures and dry bulb temperature dew point 2.6 ° C.

The analysis of a single parameter is not a good tool for the evaluation of nonlinear models, and will require an analysis of the parameters: coefficient of determination, standard error of the estimate and mean relative error. The ability of a model to describe faithfully given physical process is inversely proportional to the standard deviation of the estimate. As regards the mean relative error values below 10% are recommended (Madamba; DRISCOLL; BUCKLE, 1996; MOHAPATRA; RAO, 2005).

All models used in this experiment had coefficients of determination (R2) greater than 99.82%, which according Madamba, Driscoll and Buckle (1996) values are considered acceptable to describe the drying phenomena. When considering the mean relative error criterion (P) less than 10% for an acceptable fit, the results were similar, namely, all models showed on average errors less than 10% and the largest value was 6.95% to Thompson model for the dry bulb temperature of 45 ° C and the dew point temperature of 2.6 ° C.

TABLE 4 - Values of coefficients of determination (R^2), standard deviation of the estimate (SE), mean relative error (P) and trend distribution of residuals obtained for the models used to describe the drying kinetics of coffee fruits.

Model	Tbs (°C)	UR (%)	R^2(%)	P(%)	SE	Tendency
Lewis	35	13,1	99,84%	4,76	0,0742	Biased
	40	10,0	99,83%	5,23	0,0668	Biased
	45	7,7	99,83%	4,52	0,0582	Biased
Page	35	13,1	99,95%	3,03	0,0434	Biased
	40	10,0	100,00%	2,69	0,0327	Biased
	45	7,7	99,95%	5,54	0,0320	Biased
Thompson	35	13,1	99,90%	3,76	0,0576	Biased
	40	10,0	99,91%	3,32	0,0484	Biased
	45	7,7	99,91%	6,95	0,0420	Biased
Midilli modified	35	13,1	99,96%	3,19	0,0280	Biased
	40	10,0	99,97%	3,46	0,0196	Biased
	45	7,7	99,97%	2,84	0,0170	Biased
Verma	35	13,1	99,84%	4,72	0,0525	Biased
	40	10,0	99,84%	5,25	0,0472	Biased
	45	7,7	99,83%	4,47	0,0412	Biased
Successive residue	35	13,1	100,00%	1,69	0,0076	Random
	40	10,0	99,99%	2,01	0,0063	Random
	45	7,7	99,96%	4,15	0,0120	Biased
Henderson and Pabis modified	35	13,1	99,99%	1,52	0,0063	Random
	40	10,0	99,99%	2,01	0,0063	Random
	45	7,7	99,98%	2,94	0,0093	Random

Among the models used in the experiment to describe the process of drying coffee cherries, Waste Successive models with two terms, and Henderson Pabis modified and presented the best adjustments indicated by the values of coefficients of determination. These models had, on average, higher values of coefficients of determination (R 99.98%) and the lowest values of mean relative error and standard deviation of the estimate (P 4.16%, SE 0.012).

In Figure 4, presents the illustrations of the tendency of the distribution of residuals.

Trend analysis of residual distribution confirms the previous results. Although the seven models used have submitted coefficient of determination, standard deviation of the estimate and mean relative error as satisfactory, models and Henderson Pabis modified and Waste Successive two terms were more randomness in the distribution of residuals, indicating that these models are the most appropriate for describing the phenomenon of drying coffee fruits in conditions considered in this experiment.

According to Goneli et al. (2011), a model is considered that the random residuals meet near horizontal band around zero and does not form figures set, indicating no bias the results. If present biased distribution, the model is considered inappropriate to represent the phenomenon in question.

Due to the smaller number of parameters and, consequently, greater simplicity in relation to Waste Successive model with two terms, the model of Henderson and modified Pabis was selected to describe the drying kinetics of coffee fruits in this experiment.

Table 5 shows the coefficients of the model of Henderson and Pabis modified adjusted data observed kinetics of thin layer drying of coffee berries, the conditions considered in this experiment.

Figure 5 shows the comparison between observed and predicted values of the moisture ratio by the model and Henderson Pabis modified and Figure 6 shows the behavior of the moisture ratio of the fruits of coffee as a function of time during the drying layer thin, and the comparison between the observed and estimated values of the moisture ratio, the model of Henderson and Pabis modified. It is observed in these figures, the high correlation between the values of the moisture ratio observed experimentally and the values estimated by the model of Henderson and Pabis modified for all conditions studied, confirming the satisfactory fit of this model to describe the kinetics of drying of the coffee berries, the conditions studied.

In Figure 6 it can be seen that a temperature of 45 ° C afforded the shorter drying time and 35 ° C, a longer drying time. Note also that the drying took place only during the decreasing drying rate which can be characterized by a range in which the resistance to the transfer of water and energy are mainly inside the fruits, making the rate of evaporation surface markedly higher than the rate of replacement of water from the interior to the surface of the product.

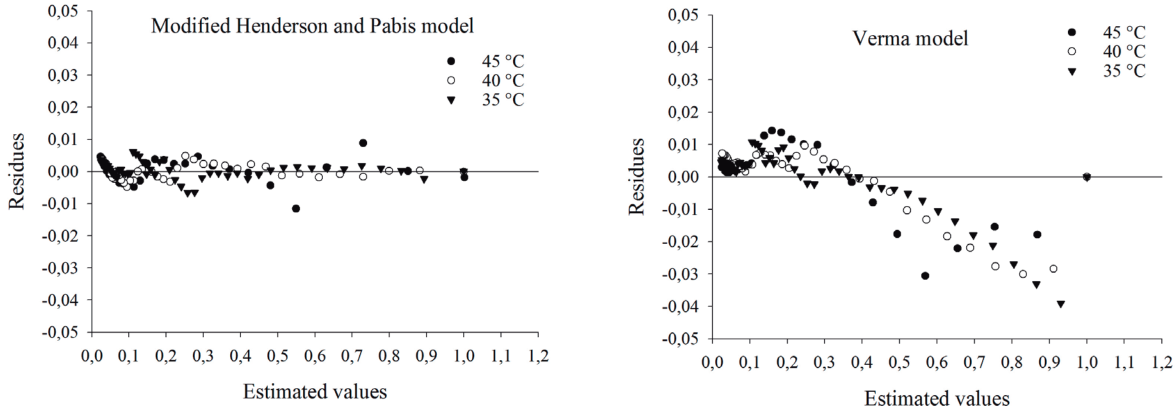

FIGURE 4 - Illustration of the distribution of residuals for the coffee fruits subjected to drying at three temperatures. A) Random model for Henderson and Pabis modified. B) biased to the model of Verma.

TABLE 5 - Henderson and Pabis model modified and adjusted to the experimental data of drying coffee fruits thin layer chromatography.

Tbs (°C)	Tpo (°C)	UR (%)	Henderson and Pabis model modified $RU = a \exp(-kt) + b \exp(-k_0 t) + c \exp(-k_1 t)$					
			A	b	c	K	k_0	k_1
35	2,6	13,1	0,0471	-9,899	10,852	1,3669	0,0416	0,0392
40	2,6	10,0	0,4472	0,5043	0,0485	0,0444	0,0444	0,7210
45	2,6	7,7	-1,932	0,1699	2,7639	0,0416	0,2182	0,0465

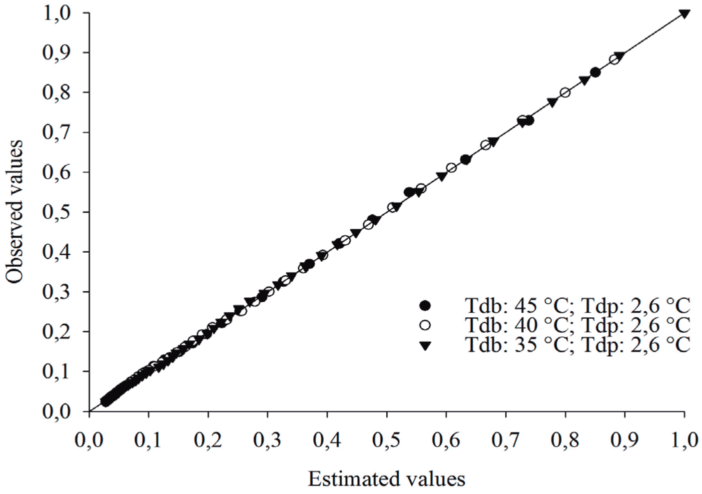

FIGURE 5 - Values of the moisture ratio (dimensionless) observed and predicted by the model of Henderson and Pabis modified for drying coffee cherries thin layer.

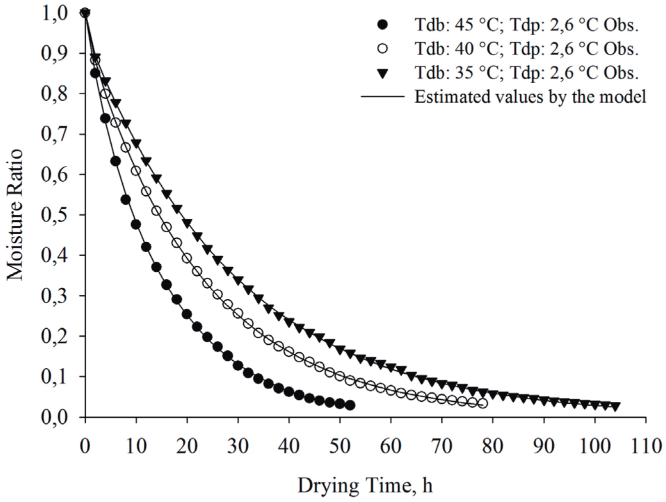

FIGURE 6 - Values of the moisture ratio observed and predicted by the model and Henderson Pabis modified for drying fruit thin layer of coffee as a function of time.

4 CONCLUSIONS

The conditions under which this work was developed, it was concluded that:

The Henderson and Pabis modified and Successive Residue models with two terms showed better adjustments to the experimental data.

The increased air temperature increases the rate of drying, the effective diffusivity coefficient, and reduces the drying time of the coffee berries.

The effective diffusivity coefficient of coffee berries varies between 1.91 and 3.72 x 10-11 m². S-1.

The activation energy for liquid diffusion during drying of coffee cherries is 52.89 kJ.mol-1.

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