DRYING KINETICS STUDY OF PIMENTA-DE-MACACO (*Piper aduncum* L.) AERIAL PARTS

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Abstract. *The specie Piper aduncum L., popularly known as pimenta-de-macaco, is an aromatic plant of the Piperaceae family that occurs in the Amazon. This kind of study has great importance and economic exploitation due to the action of the essential oil present in the aerial parts of this plant over pathogens. The drying kinetics of its aerial parts is evaluated, based on experimental data obtained in a fixed bed convective dryer. Functional relationships are used between the moisture content of the biomass and the processing time, subjected to drying conditions in constant temperatures of 35, 45, 55 and 65 ° C, based on several kinetic models proposed in the literature. The Henderson and Pabis modified model proved to be suitable to describe the variation of the moisture content of the samples within the experimental domain assessed.*

Keywords*: drying kinetics, pimenta-de-macaco, fixed bed convective dryer.*

1. INTRODUCTION

The specie *Piper aduncum* L., popularly known as pimenta-de-macaco, is an aromatic plant of the Piperaceae family that occurs in the Amazon and, according to Silva (2004), has great potential for economic exploitation due to the high content of essential oil (2.5 to 4%) and its proven usefulness in agriculture and human health, for being rich in dilapiolle, one phenylpropanoid (Mota *et al*., 2002).

This specie has great importance both for study and economic exploitation due to the action of the essential oil present in the aerial parts of this plant over pathogens such as fungi, bacteria, mollusks, mites and larvae, in addition to its analgesic and anti-inflammatory effect with low levels of toxicity and with the advantage of being biodegradable (Gaia et al, 2004; Silva, 2004).

Pimenta-de-macaco emerges and begins to call attention from companies and farmers, mainly in the Amazon region, it presents high adaptability to soil and climatic conditions found in the region and represents an alternative in replacing highly toxic chemicals that are marketed both in Brazil and abroad (Lobato et al, 2007)

Drying is a complex unit operation to remove water by evaporation and it involves simultaneous heat and mass transfer. It must be conducted in a controlled manner, avoiding high temperature and moisture gradients within the material, once they may promote the loss of quality in the product. This unit operation is one of the oldest methods of food preservation and is a very important aspect in the processing of agroindustrial products. Products drying is designed to prolong the storage periods, reduce packaging and shipping costs as well as maximize the components of interest (Okos et al, 1992; Kadam et al, 2011.).

Drying kinetics analysis provides information on the behavior of the mass transfer between the product and the drying agent, usually atmospheric air, and is of fundamental importance for the design and simulation of dryers (Guedes and Faria, 2000).

In many agricultural products, the drying kinetics with industrial interest has been performed, aiming at describing the behavior of moisture removal, where experimental data are adjusted to different mathematical models.

Aiming at the promoting of technological applications for Amazonian plants with technological and industrial potential, there is the goal of contributing with the innovation processes of drying aerial parts of pimento-de-macaco. Based on this approach, this work has the objective of studying the kinetics of drying aerial parts of pimenta-de-macaco at temperatures of 35, 45, 55 and 65 °C, fitting different mathematical models at the experimental data obtained and analyze the quality of these adjustments.

2. METHOD

The work was performed at the Particle Drying and Covering Laboratory (LSRP), located at FEQ/UFPA, using *Piper aduncum* L. leaves and twigs collected in the CEASA area, city of Belém, and immediately brought to the laboratory, where the processing and the packaging in an environment with temperature control and relative humidity were done.

Biomaterial drying data were obtained in a fixed bed convection dryer in operating conditions, involving time, temperature and mass flow rate air inlet of the drying, and total solids loading, shown in Tab. 1.

Dry solid mass after drying processes needed to calculate the humidity content on a dry basis, were determined directly in an oven with forced air circulation at 105 ± 1 °C for 24 hours, according to standardized methodology.

Table 1. Drying operating conditions

Temp.(°C)	Time(min)	Flow(kg/h)	Loading(g)
35	265	11,856	60
45	255	11,535	
55	245	11,224	
65	195	10,892	

The drying process was performed in a fixed bed dryer designed, built and instrumented by Faria (1998). Basically it consists of a 25.4 cm square section duct, containing a centrifugal blower with speed control, able to move air into the bed of material. The dryer is also composed of two pairs of electrical resistances of 1kW and 2 kW each, distributed throughout the unit, providing air heating.

The body of the dryer bed is made in pyrex glass containing thermocouples which allow the measurement of the temperature at the inlet air. The device comprises a cylindrical grilled basket, in stainless steel, on which the pimenta-de-macaco leaves are deposited, subjected to drying. This basket, which consists of drying bed, has an internal diameter of 12.5 cm and height of 25.5 cm and a total volumetric capacity of 3.13 liters. During the experiment, it is suspended inside the cylindrical glass body, adapted to a Gehaka 8000 BG electronic weighing scale, sensitivity model with 0.01 g, which continuously indicates the decrease in weight of the material. A complete experimental arrangement draft is shown in Fig. 1.

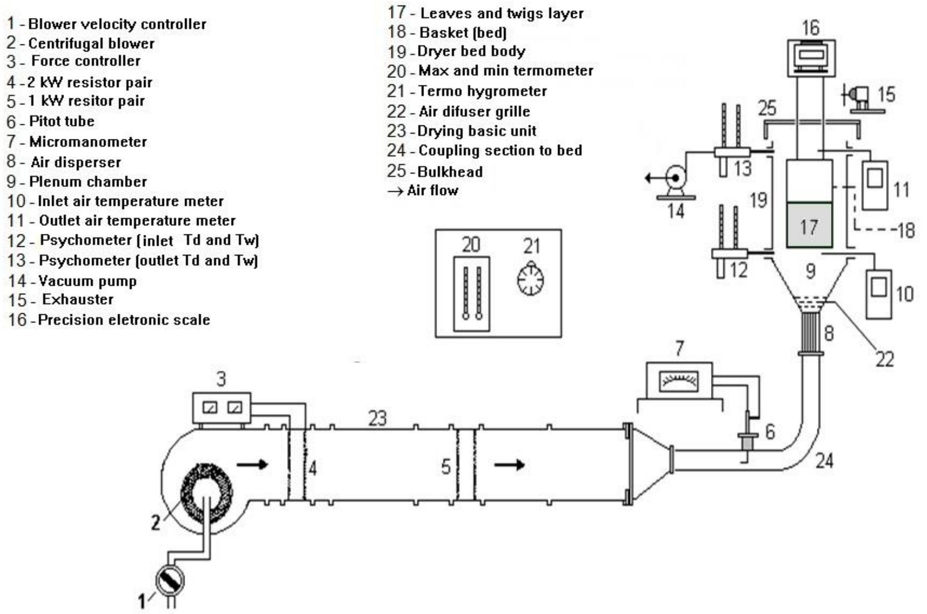

Figure 1. Schematic diagram of fixed bed convective dryer.

Calculation of the product moisture ratio (Xr) during the different experimental conditions was estimated by Eq. (1),

$$Xr = \frac{X_t - X_e}{X_o - X_e} \tag{1}$$

Where: Xr is the humidity ratio, dimensionless; Xt is the humidity content at time t, decimal b.s.; Xo denotes the initial humidity content of the product, decimal b.s. and Xe is the equilibrium humidity content, decimal b.s.

As the value of Xe is in many cases very small in relation to the Xo and Xt, the equilibrium humidity content (Xe) is usually neglected and the humidity ratio shall be represented in simplified form expressed by Eq. 2 (Doymaz , 2004; Goyal et al, 2007; Roberts et al, 2008; Kadam et al, 2011).

$$Xr = \frac{X_t}{X_o} \tag{2}$$

Xr values observed for each drying air temperature were evaluated by nine different mathematical models as summarized in Tab. 2, from non-linear regression using the Statistica 7.0 application.

The criteria used to measure the excellence of adjustments were the values of the coefficient of determination (R^2), the average relative deviation D (Eq. 3), standard error of estimative *e* (Eq. 4) and residue analysis.

$$D = \frac{100}{N} \sum \frac{|Y - Y'|}{Y} \tag{3}$$

$$e = \sqrt{\frac{\sum (Y - Y')^2}{df}} \quad (4)$$

In these equations, N represents the number of experiments; df degrees of freedom (number of experimental points obtained minus the number of constants in the model); Y and Y 'are the experimental values and those predicted by the model, respectively. According to Mohapatra (2005), mathematical adjustments by deviation values on average below 10% are generally considered satisfactory.

Table 2. Mathematical models used to evaluate pimenta-de-macaco drying.

Model	Equation
Newton	$Xr = \exp(-kt)$
Page	$Xr = \exp(-kt^n)$
Henderson e Pabis	$Xr = a.\exp(-kt)$
Logarithm	$Xr = a.\exp(-kt) + b$
Doistermos	$Xr = a.\exp(-k_o t) + b.\exp(-k_1 t)$
Midilli *et al.*	$Xr = a.\exp(-kt^n) + bt$
Verma *et al.*	$Xr = a.\exp(-kt) + (1 - a)\exp(-gt)$
Henderson e Pabis modified	$Xr = a.\exp(-kt) + b.\exp(-gt) + c.\exp(-ht)$
Page modified	$Xr = \exp(-kt)^n$

4. RESULTS

In Table 3 it´s summarized the values of the statistical parameters which assessed the description of the mathematical models used to describe the pimenta-de-macaco drying. They are: (R^2), (D), (e) and the behavior of the residues distribution analysis (DR) obtained by graphs of the difference between Y and Y ', compared to values Y '.

Table 3. Quality of the mathematical models adjustments evaluation.

Model	Temp.	R²(%)	e	D(%)	DR
Henderson and Pabis modified	35 °C	99,98	0,00313	0,4840	A
	45 °C	99,94	0,00541	0,8922	A
	55 °C	99,99	0,00259	0,4579	A
	65 °C	99,96	0,00446	0,4965	A
Logarithmic	35 °C	98,64	0,02181	2,9166	T
	45 °C	98,74	0,02282	4,3694	T
	55 °C	74,19	0,10576	17,390	T
	65 °C	99,84	0,00836	1,4312	T
Midilli *et al*.	35 °C	99,97	0,00323	0,4982	A
	45 °C	99,36	0,01657	2,9084	T
	55 °C	99,88	0,00730	0,9067	T
	65 °C	99,53	0,01454	2,3358	T
Henderson	35 °C	83,55	0,07412	11,000	T
	45 °C	82,06	0,08425	15,417	T
	55 °C	89,42	0,06640	12,173	T
	65 °C	77,22	0,09615	18,260	T
Page	35 °C	98,76	0,02035	3,2496	T
	45 °C	97,57	0,03097	5,2330	T
	55 °C	98,74	0,02299	4,0691	T
	65 °C	94,79	0,04598	8,5356	T
Page modified	35 °C	52,57	0,12588	22,133	T
	45 °C	60,13	0,12559	27,314	T
	55 °C	77,44	0,09694	20,395	T
	65 °C	62,92	0,12266	24,890	T

A: random distribution (desired); T: tendentious distribution (inadequate model)

Table 3. Quality of the mathematical models adjustments evaluation (continuation).

Model	Temp.	R^2(%)	e	D(%)	DR
Newton	35 °C	52,57	0,12311	22,133	T
	45 °C	60,13	0,12306	27,314	T
	55 °C	77,44	0,09513	20,395	T
	65 °C	62,92	0,11971	24,890	T
Two Term	35 °C	99,45	0,01427	1,9190	T
	45 °C	99,89	0,00680	1,2575	A
	55 °C	99,76	0,01046	2,0781	T
	65 °C	99,91	0,00624	1,0224	A
Verma	35 °C	99,23	0,01638	2,3868	T
	45 °C	99,89	0,00680	1,2703	A
	55 °C	99,72	0,01092	2,2500	T
	65 °C	99,91	0,00612	1,0444	A

A: random distribution (desired); T: tendentious distribution (inadequate model)

It is observed from the statistical parameters presented in Tab. 3 that the modified model of Henderson and Pabis is what best describes the drying of pimenta-de-macaco at temperatures of 35, 45, 55 and 65 ° C, by presenting values less than 1% relative to the average deviation, and coefficient of determination above 99% and completely random residual distribution, for all temperatures studied.

Residual distribution model to Henderson e Pabis modified at four temperatures (Figs. 3, 4, 5 and 6) demonstrates that mathematic model properly describes the experimental data, with no occurrence of contradictions between these and calculated values, once points are distributed randomly, ie. non-tendentious. A residual distribution is considered random if the residual values are near horizontal band around zero and does not form defined figures, indicating no results tendency. If it presents tendency distribution, the model is considered inappropriate to represent the phenomenon in question (Sousa et al., 2011).

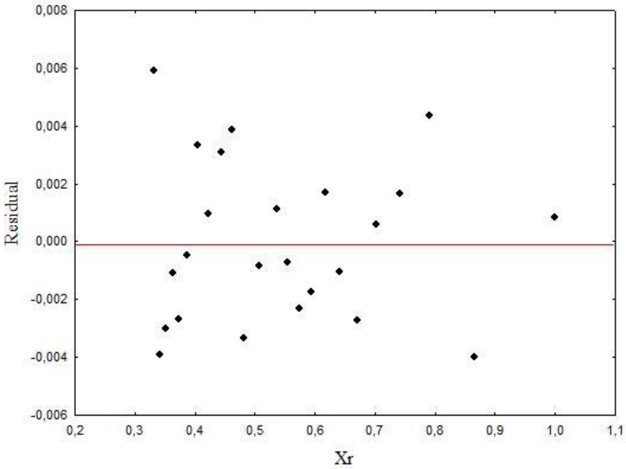

Figure 3. Residual distribution to Henderson e Pabis model at 35 °C.

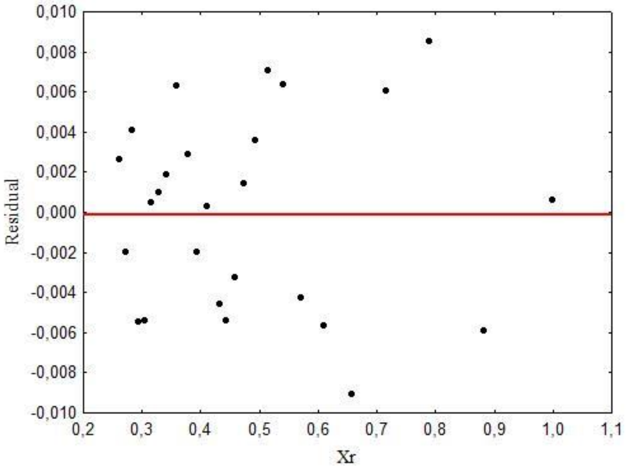

Figure 4. Residual distribution to Henderson e Pabis model at 45 °C.

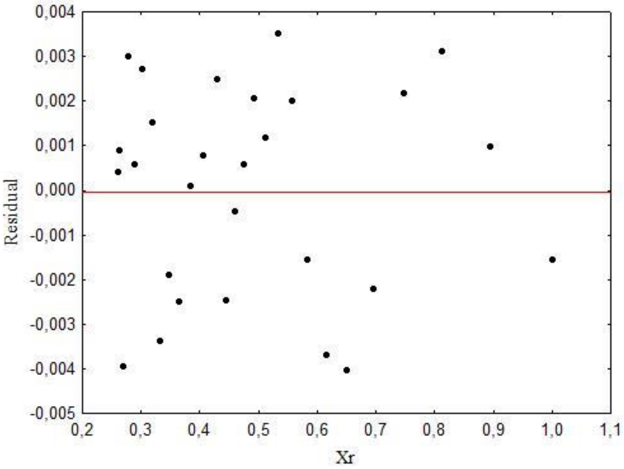

Figure 5. Residual distribution to Henderson e Pabis model at 55 °C.

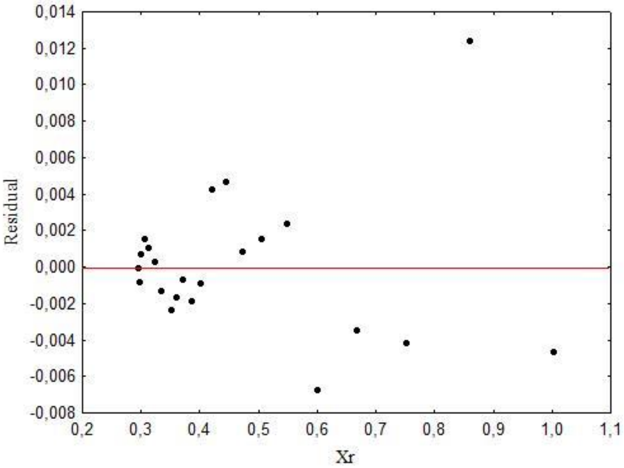

Figure 6. Residual distribution to Henderson e Pabis model at 65 °C.

The values to parameters of models adjusted to experimental data of drying kinetics, to the different studied temperatures, are described in Tab. 4.

Table 4. Predicted parameters to mathematical models in function of temperature.

Model	T(°C)	Parameters		
		k		
Newton	40	0,0041		
	50	0,0067		
	60	0,0096		
		k	n	
Page	40	0,0091	0,8477	
	50	0,0225	0,7600	
	60	0,0409	0,6936	
		a	k	
Henderson e Pabis	40	0,9443	0,0037	
	50	0,8816	0,0056	
	60	0,8357	0,0076	
		a	k	b
Logarithmic	40	- 68,35	0,0000	0,0069
	50	0,8630	0,0061	0,0279
	60	0,8166	0,0087	0,0404

Table 4. Predicted parameters to mathematic models in function of temperature (continuation).

Model	T(°C)	Parameters					
		a	k_o	b	k_1		
Two terms	40	0,1239	0,0265	0,8769	0,0034		
	50	0,1774	0,0816	0,8225	0,0052		
	60	0,2887	0,0720	0,7143	0,0063		
		a	k	N	b		
Midilli *et al.*	40	1,0081	0,0113	0,7996	-0,0001		
	50	1,0029	0,0362	0,6348	-0,0003		
	60	1,0164	0,0631	0,5852	-0,0002		
		a	k	g			
Verma *et al.*	40	-0,0878	0,0041	0,0040			
	50	-0,1612	0,0067	0,0067			
	60	0,2861	0,0711	0,0063			
		a	k	b	k_o	c	k_1
Henderson e Pabis modified	40	-0,4691	0,0024	0,1348	0,0242	1,3341	0,0030
	50	0,7985	0,0048	-0,0017	-0,0067	0,1996	0,0654
	60	0,3576	0,0063	0,3566	0,0063	0,2888	0,0719
		k	n				
Page modified	40	0,0638	0,0635				
	50	0,0818	0,0818				
	60	0,0979	0,0979				

It is seen at the Tab. 4 that the drying coefficient K to the modified model of Henderson and Pabis raised within temperature, indicating been linked with effective diffusivity on drying process in the decreasing period (Brooker et al., 1992; Madamba et al., 1996).

Figure 2 illustrates the fixed bed drying curves at all temperatures and adjusted to the modified model of Henderson and Pabis. It is observed that the thermodynamic equilibrium between the material and the atmospheric air was achieved within our experimental conditions. The time needed to achieve equilibrium humidity content in all experiments was between 195 and 265 min. It also seems that humidity decreases continuously along the drying time and increasing air temperature, thus agreeing with drying theory fundamentals (Strumillo and Kudra, 1986).

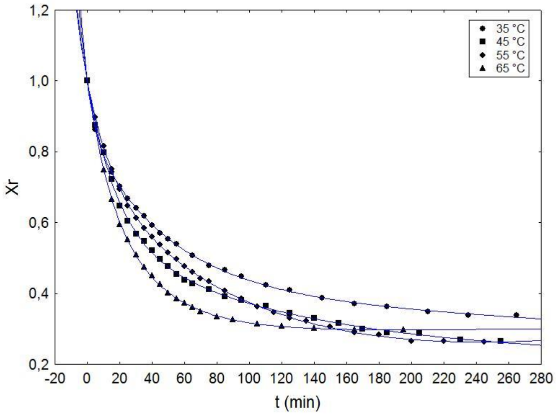

Figure 2. Drying curves corresponding to the dehydration of pimenta-de-macaco leaves at various temperatures adjusted by Henderson and Pabis modified model.

It is also observed the significant effect of temperature on the drying curves, in other words, increasing temperature generates higher rate of water removal from the material, a fact found by various researchers for the drying of many agricultural products, in particular sheets and twigs of plants (Martinazzo et al., 2007; Silva et al, 2008; Zanoelo et al., 2007; Radünz et al., 2010; Kadam et al., 2011).

Although the drying kinetics was temperature-dependent, the differences decreased as the system reached equilibrium. Further, an exponential tendency was noted in the drying curves, which was validated using the Henderson and Pabis modified model to simulate the drying of the product.

4. CONCLUSIONS

Air drying is a process where heat and mass transfer occur simultaneously. The experimental results of this study showed that the drying kinetics of pimenta-de-macaco leaves is a direct function of drying air temperature. The modified model of Henderson and Pabis was the best to describe the experimental data of drying of pimenta-de-macaco. The thermodynamic equilibrium between the material and the atmospheric air was achieved in the experimental conditions evaluated in a fixed bed convection dryer.

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