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Mathematical modelling of the drying of jatropha fruit: an empirical comparison¹

Modelagem matemática da secagem dos frutos de pinhão-mansão: uma comparação empírica

Valdiney Cambuy Siqueira^{2*}, Osvaldo Resende³ e Tarcísio Honório Chaves³

ABSTRACT - The jatropha has emerged on the world scene as a promising plant for the production of biodiesel. However, this crop still lacks the development of specific equipment for its processing, particularly post-harvest. Therefore, the aim of this work was to fit different mathematical models to experimental data obtained while drying jatropha fruits, and to recommend the one that best represents the facts. Jatropha fruit with a moisture content of 4.4 (kg moisture kg⁻¹ dry matter) were subjected to drying in a greenhouse with forced air-ventilation at five temperature conditions: 45; 60; 75; 90 and 10 °C and relative humidities of 14.5; 7.4; 3.8; 2.2 and 1.4%, respectively, until reaching a moisture content of 0.10 ± 0.005 (kg moisture kg⁻¹ dry matter), with three replications. Ten mathematical models, used to represent the drying of agricultural products, were adjusted to fit the experimental drying data. The models were analyzed using the coefficient of determination, chi-square, mean relative error, mean estimated error and residual distribution. It can be concluded that the Page model satisfactorily describes the kinetics of jatropha-fruit drying, at temperatures of 60; 75; 90 and 105 °C. However, drying at a temperature of 45 °C produced different behavior, making necessary the adjustment of a new model to describe the phenomenon.

Key words: Biodiesel. Drying temperatures. Mathematical models.

RESUMO - O pinhão-mansão tem se destacado no cenário mundial como planta promissora para a produção de biodiesel. No entanto, esta cultura ainda carece do desenvolvimento de equipamentos específicos para o seu processamento, principalmente na fase pós-colheita. Sendo assim, objetivou-se com o presente trabalho ajustar diferentes modelos matemáticos aos dados experimentais obtidos na secagem dos frutos de pinhão-mansão e recomendar aquele que melhor representa o fenômeno. Os frutos de pinhão-mansão com o teor de água de 4,40 (kg de água kg⁻¹ de matéria seca), foram submetidos à secagem em estufa com ventilação de ar forçada em cinco condições de temperatura: 45; 60; 75; 90 e 105 °C e umidades relativas de 14,5; 7,4; 3,8; 2,2 e 1,4%, respectivamente, até atingirem o teor de água de 0,10 ± 0,005 (kg de água kg⁻¹ de matéria seca) em três repetições. Aos dados experimentais da secagem foram ajustados dez modelos matemáticos utilizados para representação da secagem dos produtos agrícolas. Os modelos foram analisados por meio do coeficiente de determinação, do qui-quadrado, do erro médio relativo, do erro médio estimado e da distribuição de resíduos. Conclui-se que, o modelo de Page descreve satisfatoriamente a cinética de secagem dos frutos de pinhão-mansão nas temperaturas de 60; 75; 90 e 105 °C. No entanto, para a secagem na temperatura de 45 °C ocorreu um comportamento diferenciado sendo necessário um ajuste de um novo modelo para a descrição do fenômeno.

Palavras-chave: Biodiesel. Temperaturas de secagem. Modelos matemáticos.

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INTRODUCTION

According to Abreu *et al.* (2009), among the oilseed crops that have been presented as another means of diversification, and one that can be planted in order to increase the production of biodiesel, the jatropha (*Jatropha curcas* L.) stands out. Laviola and Day (2008) claim that depending on the spacing adopted when planting jatropha it is possible to achieve a productivity of over 2,000 kg oil ha⁻¹, and that with genetic improvements and changes to the production system, it is believed that the jatropha is capable of producing up to 4,000 kg oil ha⁻¹. This crop therefore becomes an extremely viable alternative for small, medium and large producers.

There are other attributes related to jatropha oil, as it is not edible and therefore cannot be diverted for human consumption (SATURNINO *et al.*, 2005), unlike soybean oil, which is considered as the reference for biodiesel production on an industrial scale, and is derived from raw material which is abundant in Brazil, with the technology for its production being readily available (SANTOS *et al.* 2009).

Given the characteristics of jatropha oil, this crop has been prominent on the world stage as one of the most promising for the production of biodiesel. However, the steps for processing the grains and fruit need to be studied in order to achieve more efficiency. Among the postharvest steps, drying is one of the most important as it is directly related to the end quality of the product, and as oil is the main product of the jatropha, it is necessary to develop drying techniques, which will give better yield and oil quality.

Mathematical modeling of the drying process of agricultural products allows predicting their behavior during the removal of water, reducing the time and costs involved in practical drying methods which are aimed at the development of suitable equipment. Among the models of thin-layer drying, the most used are: Exponential, Henderson and Pabis, Two-term, Lewis, Page, Thompson, and Wang and Sing (MOHAPATRA; RAO, 2005).

The process of thin-layer drying of agricultural products aims at determining the drying rate of the product by recording the weight losses which occur in any one sample during the removal of water (HILL *et al.* 2008). The drying curves of thin layers vary with the species, type, environmental conditions, and postharvest preparation methods, among other factors. In this regard, various mathematical models have been used to describe the drying process of agricultural products (RESENDE *et al.* 2008).

Empirical models are usually based on variables external to the product, such as temperature and the relative humidity of the air used for drying. However, they give no information about the phenomena of energy and

water transport inside the grains, and consider that the entire drying process occurs only in the falling-rate period (RESENDE *et al.*, 2009).

Given the above, the aim of the present work was to fit different mathematical models to experimental data obtained when drying jatropha fruit, and recommend the one that best represents the phenomenon.

MATERIAL AND METHODS

The experiment was developed in the Laboratory for the Postharvest of Vegetable Products at the Federal Institute of Education, Science and Technology of Goiás, Rio Verde Campus (IF Goiano). After manual harvesting, the jatropha fruit was left out in a laboratory environment for 30 hours in order to reduce and homogenise its moisture content to 4.40 (kg water kg⁻¹ dry matter), and then subjected to drying in a hothouse with forced air ventilation at five temperatures: 45; 60; 75; 90 and 105 °C, promoting the respective relative humidities: 14.5; 7.4; 3.8; 2.2 and 1.4%. The fruit was kept in the hothouse at 105 ± 1 °C for 24 hours until reaching a moisture content of 0.005 ± 0.10 (kg water kg⁻¹ dry matter). There were three replications (BRAZIL, 2009).

For the drying process, three aluminum trays each containing 250 g of jatropha fruit distributed in a single layer to an approximate height of 2.7 cm were left inside the hothouse until they reached the desired moisture content. During drying, in between weighings, the positions of the trays were rotated and the fruit turned.

The temperature of the air used for drying was monitored by a thermometer installed inside the hothouse. The relative humidity was obtained by employing the basic principles of psychrometrics, using the GRAPSI software (MELO; LOPES; CORREA, 2004). Equation 1 was used to determine the moisture-content ratios of jatropha fruit during drying.

$$RX = \frac{X - X_e}{X_i - X_e} \quad (1)$$

Where, RX: dimensionless moisture-content ratio of the product; X moisture content of the product (kg water kg⁻¹ dry matter); Xi: initial moisture content of the product (kg water kg⁻¹ dry matter); Xe: equilibrium moisture content of the product (kg water kg⁻¹ dry matter).

The equilibrium moisture content of jatropha fruit at each temperature was obtained experimentally. The trays with the samples stayed in the hothouse until the weight of the product had remained unchanged for three consecutive weighings.

The mathematical models frequently used to represent product drying were adjusted to the data from the drying process of the jatropha fruit, as shown in Table 1.

The mathematical models were adjusted by nonlinear regression analysis using the Gauss-Newton method and the Statistica 7.0 software ®. The models were selected taking into account the magnitude of the coefficient of determination (R^2), the chi-square (χ^2), the mean relative error (P) and the standard error of estimate (SE), in addition to checking the behavior of residual distribution. Because it is a numeric value that indicates how much of the total observed variation in the experimental values is explained by the model, the closer it is to one or to 100% of the value of R^2 , the better the fit of the model. For evaluating the mean relative error, a value of less than 10% was considered as one of the criteria for selecting the models, according to Mohapatra and Rao (2005).

The mean relative error, the standard deviation of the estimate and chi-squared for each model were calculated according to the expressions 12; 13 and 14:

$$P = \frac{100}{N} \sum \frac{|Y - \hat{Y}|}{Y} \quad (12)$$

$$SE = \sqrt{\frac{\sum (Y - \hat{Y})^2}{GLR}} \quad (13)$$

$$\chi^2 = \frac{\sum (Y - \hat{Y})^2}{GLR} \quad (14)$$

Where, Y: observed experimental value; \hat{Y} : value calculated by the model; N: number of experimental observations; GLR: degrees of freedom of the model (number of observations less the number of model parameters).

RESULTS AND DISCUSSION

Table 2 shows the average ratio values for the moisture content of jatropha fruit when subjected to drying under different air conditions. It can be noted that the jatropha fruit reached a moisture content of 0.007 ± 0.10 (kg water kg^{-1} dry matter), with drying times of 10.28; 10.98; 15; 26; 21.83 and 38.62 hours at temperatures of 105; 90; 75; 60 and 45 °C respectively. Therefore, an increase in temperature decreased the drying time of jatropha fruit, showing an increase in the drying rate, a fact noted by various researchers for many agricultural products such as red pepper (AKPINAR; BICER; YILDIZ, 2003), parboiled wheat (MOHAPTRA; RAO, 2005), beans (RESENDE *et al.*, 2008), jatropha seeds (SIRISOMBOON; KITCHAIYA, 2009; ULLMANN *et al.*, 2010).

The reason drying takes place faster at higher temperatures is related to a greater difference between the vapour pressure of the air used in drying and that of the product, resulting in the water being removed faster. Thus, the higher the temperature, the greater the energy efficiency for drying time: this is beneficial, providing there is no morphological, physiological and/or biochemical damage to the product.

It can be further noted in Table 2 that the ratio of the moisture content of jatropha fruit was 0.12 at a temperature of 45 °C; 0.13 at 60 °C; 0.18 at 75 °C; 0.18 at 90 °C and 0.19 at 105 °C, there is therefore an increase in the moisture content ratio with an increase in the temperature of the air used in drying, due to the lower equilibrium-moisture content of the fruit under these drying conditions. Similar results were found for the turnip (SOUSA *et al.*, 2011), the crambe (COSTA *et al.*, 2011) and jatropha seeds (RESENDE *et al.*, 2011; ULLMANN *et al.*, 2010).

Table 1 - Mathematical models used to predict the drying of agricultural products

Model name	Model	
$RX = 1 + at + bt^2$	Wang e Sing	(2)
$RX = a \cdot \exp(-k \cdot t) + (1-a) \exp(-k_1 \cdot t)$	Verma	(3)
$RX = \exp [(-4 \cdot (a^2 + 4 \cdot b \cdot t)^{0.5}) / 2 \cdot b]$	Thompson	(4)
$RX = \exp(-k \cdot t^n)$	Page	(5)
$RX = \exp(-k \cdot t)$	Newton	(6)
$RX = a \cdot \exp(-k \cdot t^n) + b \cdot t$	Midilli	(7)
$RX = a \cdot \exp(-k \cdot t) + c$	Logarithmic	(8)
$RX = a \cdot \exp(-k \cdot t)$	Henderson e Pabis	(9)
$RX = a \cdot \exp(-k \cdot t) + (1-a) \exp(-k \cdot a \cdot t)$	Two-term exponential	(10)
$Rx = a \cdot \exp(-k_0 \cdot t) + b \cdot \exp(-k_1 \cdot t)$	Two-term	(11)

Where: t is the drying time in hours; k, k_0 , k_1 the drying constants h^{-1} ; and a, b, c, n, coefficients of the models

Table 2 - Ratio of moisture content of jatropha fruit over drying time (h) under five temperature conditions

-----45 °C-----		-----60 °C-----		-----75 °C-----		-----90 °C-----		-----105 °C-----	
RX	Time	RX	Time	RX	Time	RX	Time	RX	Time
1	0	1	0	1	0	1	0	1	0
0.633	8.93	0.623	4.73	0.648	2.60	0.644	2.10	0.614	1.85
0.443	14.01	0.443	7.47	0.442	4.20	0.449	3.36	0.444	2.78
0.317	17.59	0.316	9.10	0.323	5.05	0.318	4.21	0.318	3.63
0.228	20.59	0.231	11.06	0.234	6.43	0.241	4.81	0.235	4.98
0.170	22.57	0.163	12.32	0.178	8.03	0.177	5.54	0.174	5.48
0.120	24.72	0.122	13.40	0.127	8.84	0.129	6.17	0.124	6.01
0.081	26.93	0.084	14.68	0.088	9.77	0.089	7.05	0.088	6.72
0.054	29.08	0.050	16.66	0.060	11.00	0.060	8.00	0.059	7.50
0.027	32.91	0.027	19.12	0.030	12.63	0.036	9.23	0.032	8.68
0.012	38.62	0.013	21.83	0.018	15.26	0.018	10.98	0.019	10.28

Table 3 - Coefficients of determination (R^2 %), mean relative errors (P %) and mean estimated errors (SE, decimal) for the models analysed during drying of jatropha fruit under various temperature conditions (°C)

Model	-----45 °C-----			-----60 °C-----			-----75 °C-----			-----90 °C-----			-----105 °C-----		
	SE	P	R^2	SE	P	R^2	SE	P	R^2	SE	P	R^2	SE	P	R^2
2	0.019	23.8	99.6	0.014	9.8	99.8	0.028	31.2	99.2	0.019	23.8	99.6	0.024	24.0	99.4
3	0.125	33.0	86.5	0.018	16.9	99.7	0.025	18.3	99.4	0.033	30.6	99.0	0.018	16.5	99.7
4	0.064	86.1	95.9	0.055	67.1	97.0	0.036	32.7	98.7	0.017	18.2	99.7	0.031	32.5	99.0
5	0.015	13.5	99.8	0.012	7.1	99.8	0.014	6.9	99.8	0.007	7.7	99.9	0.014	9.4	99.7
6	0.061	86.2	95.9	0.052	67.1	97.0	0.034	32.7	98.7	0.046	40.5	97.6	0.03	32.6	99.0
7	0.014	17.7	99.8	0.013	11.3	99.9	0.015	5.9	99.8	0.008	2.5	99.9	0.016	11.0	99.8
8	0.034	54.2	98.9	0.032	43.5	99.1	0.026	20.4	99.4	0.034	32.3	98.9	0.019	18.7	99.7
9	0.062	82.1	96.3	0.053	63.6	97.2	0.034	30.2	98.8	0.046	37.5	97.8	0.03	30.7	99.1
10	0.064	86.2	95.9	0.055	67.1	97.0	0.037	33.6	98.6	0.049	40.9	97.6	0.032	33.6	98.9
11	0.075	82.1	96.3	0.06	63.6	97.2	0.014	9.4	99.8	0.034	29.2	99.1	0.202	68.9	68.6

Table 3 shows some statistical parameters employed to compare the ten models used to describe the drying kinetics of jatropha fruit. Note that the models tested had coefficients of determination (R^2) greater than 95%, which according Kashaninejad *et al.* (2007) indicates a satisfactory representation of the drying process. However, Madamba, Driscoll and Buckle (1996), claim that the coefficient of determination (R^2) alone is not a good criterion for selecting nonlinear models. The authors state that assessments are needed of other parameters such as the estimated mean error and the relative mean error, distribution of the residual values and the value of chi-squared.

Of all those tested, the Page model (5) was that which most presented values of mean relative error (P) below 10%, the criterion adopted for using the proposed model. The values of the mean relative error (P) indicate the deviation of the observed values from the curve estimated by the model (KASHANINEJAD *et al.*, 2007). Thus the lower the value of P, less the deviations between the experimental values and those estimated by the model. However, the Page model showed satisfactory performance for only four of the drying conditions (60; 75; 90 and 105 °C). It is also noted in Table 3 that the Page model, as with the other models tested, did not satisfactorily represent the drying

of jatropha fruit at a temperature of 45 °C, indicating that under this condition the jatropha fruit have their moisture content reduced differentially.

Generally, the Page model and the Midilli model are those which present the lowest values of SE for most drying conditions. It is worth noting that the lower the value of SE, the better the quality of the adjustment of the model in relation to the experimental data (DRAPER; SMITH, 1998).

Table 4 shows the chi-squared values obtained for the different models adjusted to the drying curve of the jatropha fruit. All the models analysed were within the confidence interval of 99%. It can be noted that the Page model and the Midilli model were those with the lowest values for chi-squared. The lower the value of chi-squared, the better the adjustment of the model (AKPINAR;

BICER; YILDIZ, 2003; GÜNHAN *et al.*, 2005; MIDILLI; KUCUK, 2002). Therefore, even if the models show a satisfactory adjustment (for this parameter), the numerical value must be taken into account when choosing the model which will best fit the experimental values.

Table 5 shows the behavior of residual distribution for those models studied. It appears that the models of Page (5) and Midilli (7) were the two which more often represented the random distribution, confirming the analyses presented above, this parameter therefore, would be a good indicator for choosing the model. According to Goneli *et al.* (2011), a model is considered random when the residual values fall near the horizontal and are around zero, but do not form defined figures, indicating no bias in the results. If it

Table 4 - Values of chi-squared, calculated for the ten models used to represent the drying kinetics of jatropha fruit

Models	Temperature				
	45 °C	60 °C	75 °C	90 °C	105 °C
2	0.00037	0.00020	0.00079	0.00037	0.00062
3	0.01583	0.00033	0.00063	0.00110	0.00034
4	0.00419	0.00309	0.00136	0.00031	0.00100
5	0.00023	0.00016	0.00020	0.00006	0.00022
6	0.00377	0.00397	0.00175	0.00314	0.00129
7	0.00021	0.00018	0.00026	0.00007	0.00026
8	0.00118	0.00104	0.00070	0.00121	0.00039
9	0.00387	0.00284	0.00121	0.00220	0.00091
10	0.00419	0.00309	0.00139	0.00248	0.00103
11	0.00498	0.00365	0.00022	0.00117	0.04088

Table 5 - Residual distribution (A = random T = biased) for the ten models analysed when drying jatropha fruit under different air conditions

Models	Temperature (°C)				
	45	60	75	90	105
2	T	A	A	T	T
3	T	T	A	T	A
4	T	T	T	T	T
5	T	A	A	A	A
6	T	T	T	T	T
7	T	A	A	A	A
8	T	T	A	T	T
9	T	T	T	T	T
10	T	T	T	T	T
11	T	T	A	T	T

presents a biased distribution, the model is considered inappropriate to represent the phenomenon in question. For this reason most of the tested models could not be used to represent the drying process of jatropha fruit, as they all presented a biased distribution.

The traditional Page model has been consistently shown to represent the phenomenon of drying of various agricultural products: amaranth seeds (ABALONE *et al.*, 2006), tomato (DOYMAZ, 2007), apple pulp (WANG *et al.*, 2007), arabica (GONELI *et al.*, 2009), tarragon (ARABHOSSEINI *et al.*, 2009), coffee (RESENDE *et al.*, 2009), lemon grass (MARTINAZZO *et al.*, 2010), among others.

Figure 1 shows illustrations of the residual distribution: Random for the Page model and Biased for the Two-term model, when drying jatropha fruit at a temperature of 105 °C.

Considering that none of the models used, satisfactorily represented the drying of jatropha fruit at 45 °C, a computational analysis was carried out to adjust an equation that would meet all the statistical requirements necessary to validate any one model.

The process of drying the jatropha fruit at a temperature of 45°C was described by equation 15, which for purposes of identification was named Valcam.

$$RX = a + bt + ct^{1.5} + dt^2 \quad (15)$$

The statistical parameters used for selecting equation 15 are shown in Table 6. Note that the model presents a mean relative error of less than 10%, low chi-squared values and low standard deviation of the estimate, besides having a high coefficient of determination and random residual distribution (Figure 2).

Figure 2 shows the behavior of residual distribution when drying jatropha fruit at 45°C when using the Valcam model.

Table 7 shows the values of the coefficient values of the Page model at temperatures of 60; 75; 90 and 105 °C, and the Valcam model at 45 °C, to represent the drying of jatropha fruit.

It can be seen in Table 7 that the values of the drying-constant “k”, which according to Goneli *et al.* (2009) represents the effect of external drying-conditions,

Figure 1 - Illustration of residual distribution: A) Random for the Page model; B) Biased for the Two-Term model; when drying jatropha fruit at a temperature of 105 °C

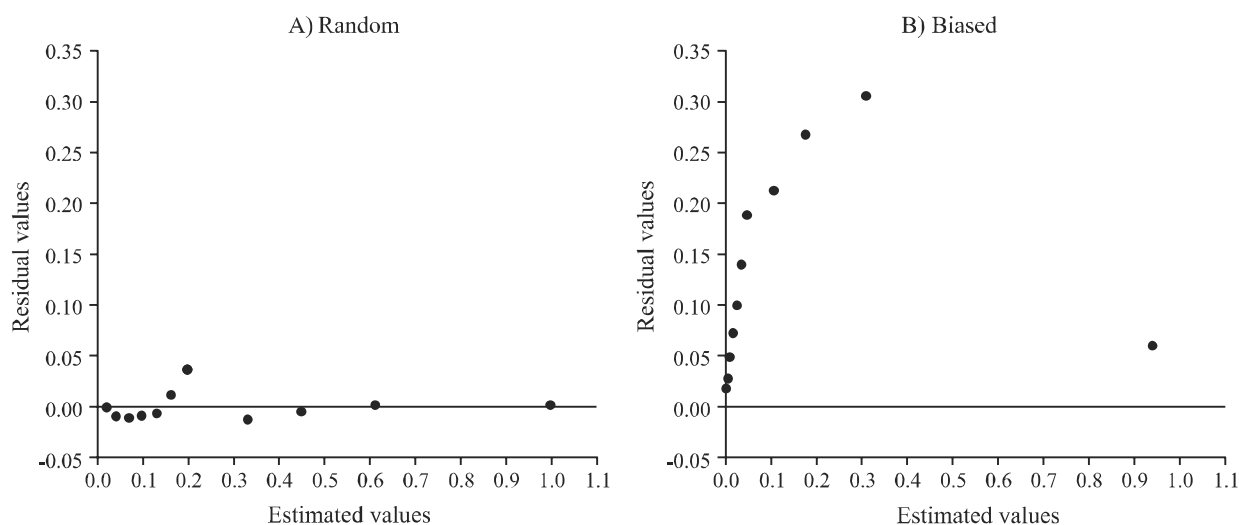
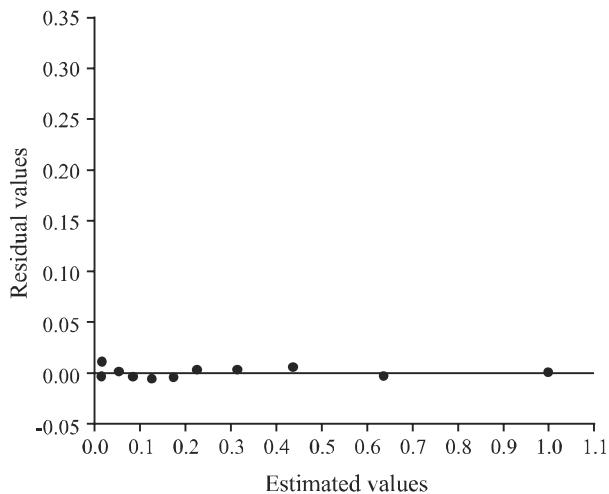


Table 6 - Coefficient of determination (R^2 , %), mean relative error (P%) and mean estimated error (SE, decimal), chi-squared and residual distribution for the proposed model (Valcam) when describing the drying of jatropha fruit at a temperature of 45 °C

R^2	P	SE	χ^2	Residual Distribution
99,97	8,07	0,006115	0,000037	Random

Figure 2 - Illustration of residual distribution obtained by using the Valcam model, for drying jatropha fruit at 45 °C



increase with a rise in temperature of the air used in drying. According to Madamba, Driscoll and Buckle (1996) and Babalis and Belessiotis (2004), the drying constant “k” can be used as an approximation to characterize the effect of temperature, and is related to the effective diffusivity of the drying process for the falling-rate period, when liquid diffusion controls the process.

Normally, as the temperature of the air used in drying increases, the lower the value of “n” since there is a greater difference between the vapor pressure of the air and of the seed, which facilitates the removal of water. However, just as in the results obtained by

Goneli *et al.* (2009), for the drying kinetics of husked coffee beans in a thin layer, it was not possible to observe any clear behavior of the coefficient “n” with increasing temperature of the air.

In Figure 3, the drying curves are shown for the jatropha fruit as estimated by the Page model, at temperatures of 60; 75; 90 and 105 °C, and by the Valcam model for drying at 45 °C. Note that the models used, satisfactorily fit the phenomenon of drying the jatropha fruit.

Figure 3 - Estimated and experimental values of the moisture-content ratio when drying jatropha fruit under various conditions of temperature

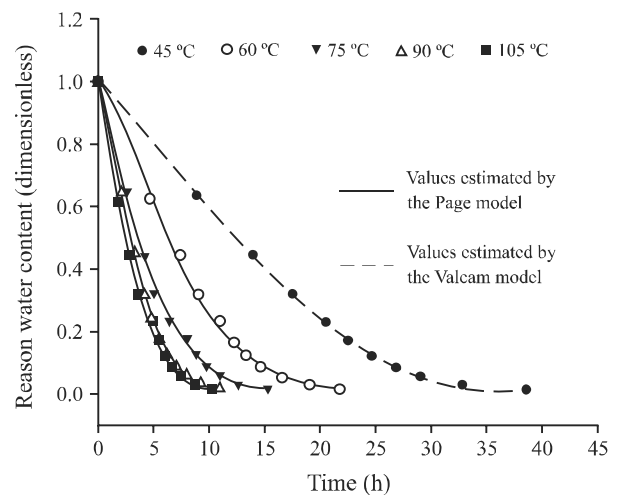


Table 7 - Model parameters, adjusted for the different drying-conditions of the jatropha fruit

Coefficients	Valcam Model	Page Model			
	45 °C	60 °C	75 °C	90 °C	105 °C
k	-	0.0443**	0.1354**	0.1485**	0.2321**
n	-	1.4758**	1.2613**	1.4247**	1.2072**
a	0.9998**	-	-	-	-
b	-0.0242**	-	-	-	-
c	-0.0103**	-	-	-	-
d	0.0016**	-	-	-	-

**Significant to 1% by the F test

CONCLUSION

Given the above it is concluded that the Page model showed the best adjustment when describing the drying kinetics of jatropha fruit at the higher temperatures (60; 75; 90 and 105 °C). When drying at 45 °C the behavior was different, and a new representative model (Valcam) was proposed.

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