

Drying kinetics of *Jatropha* seeds¹

Valdiney Cambuy Siqueira*² Osvaldo Resende³ Tarcísio Honório Chaves⁴

ABSTRACT

Given the necessity of developing *Jatropha* cultivation equipment, this work adjusted different mathematical models to experimental data obtained from the drying of *Jatropha* seeds submitted to different drying conditions and selected the best model to describe the drying process. The experiment was carried out at the Federal Institute of Goiás - Rio Verde Campus. Seeds with initial moisture content of approximately 0.50 (kg water/kg dry matter) were dried in a forced air-ventilated oven, at temperatures of 45, 60, 75, 90 and 105°C to moisture content of 0.10 ± 0.005 (kg water/kg dry matter). The experimental data were adjusted to 11 mathematical models to represent the drying process of agricultural products. The models were compared using the coefficient of determination, chi-square test, relative mean error, estimated mean error and residual distribution. It was found that the increase in the air temperature caused a reduction in the drying time of seeds. The models Midilli and Two Terms were suitable to represent the drying process of *Jatropha* seeds and between them the use of the Midilli model is recommended due to its greater simplicity.

Key words: drying, mathematical modeling, *Jatropha curcas* L., temperature, moisture content.

RESUMO

Cinética de secagem dos grãos de pinhão-mansô

Diante da necessidade de desenvolvimento de equipamentos para a cultura do pinhão-mansô, objetivou-se com este trabalho ajustar diferentes modelos matemáticos aos dados experimentais da secagem dos grãos de pinhão-mansô, submetidos a diferentes condições de secagem, e selecionar aquele que melhor representa o fenômeno. O experimento foi desenvolvido no Instituto Federal Goiano - *Campus* Rio Verde. Os grãos, com teor de água inicial de 0,50 (kg de água/kg de matéria seca), aproximadamente, foram submetidos à secagem em estufa, com circulação forçada de ar, nas temperaturas de 45, 60, 75, 90 e 105 °C, até atingirem o teor de água de $0,10 \pm 0,005$ (kg de água/kg de matéria seca). Aos dados experimentais, foram ajustados 11 modelos matemáticos utilizados para representação da secagem de 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 aumento da temperatura do ar promove redução no tempo de secagem dos grãos e que os modelos de Midilli e Dois Termos são adequados para a representação do fenômeno da secagem dos grãos de pinhão-mansô, e que, dentre estes, recomenda-se o modelo de Midilli para a descrição do fenômeno, por sua maior simplicidade.

Palavras-chave: secagem, modelagem matemática, *Jatropha curcas* L., temperatura, teor de água.

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² Agronomist, Master of Sciences. Doctoral student in Agricultural Engineering at Universidade Federal de Lavras - UFLA, Departamento de Engenharia/DEG, Programa de Pós-Graduação em Engenharia Agrícola, Caixa Postal 3037, 37200-000, Lavras, Minas Gerais, Brasil. vcambuy@yahoo.com

³ Agricultural Engineer, Doctor. IF Goiano - Campus Rio Verde, Rodovia Sul Goiana, km 01, Zona Rural, 75901-970, Rio Verde, Goiás, Brasil. osvresende@yahoo.com.br

⁴ Undergraduate student in Agronomy. IF Goiano - Campus Rio Verde, Rodovia Sul Goiana, km 01, Zona Rural, 75901-970, Rio Verde, Goiás, Brasil. tarcisio.chaves@hotmail.com

INTRODUCTION

The growing world's concern over environmental problems, along with the search for renewable energy sources has placed biodiesel in the spotlight of interest. Several countries, including Brazil, are pursuing the technological supremacy in biofuels, both in the agronomic and industrial sectors, which should have strong impacts on the national economy and social inclusion policies (Abdalla *et al.*, 2008).

Among the plants with potential for biodiesel production is *Jatropha* (*Jatropha curcas* L.). According to Santos *et al.* (2009), the oil produced from *jatropha* seeds has all the required qualities to be transformed into diesel oil. To meet the demand of the increasing production of *jatropha* seeds, new technologies must be adopted, aiming at the development of machinery used in the harvest and postharvest stages. Drying is one of the most important stages in post-harvest operations because it is directly related to quality of the final product. Resende *et al.* (2010) stated that product conservation through drying is based on the fact that the microorganisms or enzymes and all metabolic mechanisms depend on water for their activities.

Reduction of seed moisture content is a complex process involving both heat and mass transfer, which can significantly modify product quality and physical properties depending on the method and conditions of drying (Resende *et al.*, 2008). It is, therefore, essential to better understand this process to obtain efficient drying from the technical and economic standpoint.

In the development and improvement of machinery for seed drying, simulation and gathering of theoretical information on the behavior of each product during reduction of moisture content become essential. For simulation, which is based on the principle of successive thin-layer drying, it is used a mathematical model that satisfactorily represents water loss during the drying process (Berbert *et al.*, 1995; Giner & Mascheroni, 2002).

Thin-layer drying aims at determining the rate of product drying, using data from the records of mass loss of a sample during water removal (Monte *et al.*, 2008). The drying curves in thin layers vary with the species, variety, environmental conditions, post-harvesting preparation methods, among other factors. Various mathematical models have, therefore, been used to describe the drying process of agricultural products (Resende *et al.*, 2008).

According to Midilli *et al.* (2002) there are three types of thin-layer drying models to describe the drying kinetics of agricultural products: the theoretical model that consider the internal resistance and transfer of heat and water between product and drying airflow; the semi-theoretical and empirical models that only consider the internal resistance, temperature and relative humidity of the drying airflow.

These models are generally based on external variables such as temperature and relative humidity of the drying airflow. However, there are no indicatives for the phenomena of energy and water transportation inside the seeds. These models also consider that the drying process takes place only during the decreasing rate (Resende *et al.*, 2009).

Considering the advantages of biodiesel production and the importance of the drying process, this work adjusted different mathematical models to experimental data of drying *jatropha* seeds under different air conditions and selected the model that best represents the process.

MATERIALS AND METHODS

The experiment was conducted at the Postharvest Laboratory at the Federal Institute of Education, Science and Technology of Goiás - Rio Verde *Campus* (IF Goiano - *Campus* Rio Verde).

Seeds with moisture content of 0.5 (kg water/kg dry matter) were manually extracted from the fruits after harvest. The seeds were then dried in a forced air-ventilated oven, with airflow of $48 \text{ m}^3 \text{ min}^{-1} \text{ m}^{-2}$ of drying area. Five temperature conditions were used: 45, 60, 75, 90 and 105°C and relative humidity of 15.6, 7.4, 4.0, 1.8 and 1.2% respectively to a moisture content of 0.10 ± 0.005 (kg water/kg dry matter) determined in an oven at $105 \pm 1^\circ\text{C}$, for 24 hours, with three replicates (Brazil, 2009).

The drying airflow temperature was monitored by a thermometer installed inside the dryer. The relative humidity inside the oven was calculated using a psychrometric chart, based on data from external environment conditions using the software GRAPSI (Melo *et al.*, 2004). The moisture content ratios of *jatropha* during drying were determined by the following equation:

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

where:

RX: moisture content ratio, dimensionless;

X: moisture content (kg water/kg dry matter);

X_i : initial moisture content (kg water/kg dry matter);

X_e : balanced moisture content (kg water/kg dry matter).

The balanced moisture content of *jatropha* seeds at each temperature was obtained experimentally. The trays containing the samples remained in the oven until constant mass was reached after three successive weighings.

The experimental data from drying of *jatropha* seeds were adjusted to the mathematical models most frequently used to represent the drying process of agricultural products (Table 1), where:

t = drying time, h

k, k₀, k₁: drying constants h⁻¹;

a, b, c, n: model coefficients.

The mathematical models were adjusted using nonlinear regression analysis with the Gauss-Newton method, using the software STATISTICA 7.0®. The models were selected considering: the magnitude of the coefficient of determination (R²), the chi-square test, the mean relative error and the estimate of the standard deviation. The behavior of the residual distribution was also verified. The relative mean error below 10% was considered as one of the criteria for model selection, as recommended by Mohapatra & Rao (2005).

The relative mean error, estimate of the standard deviation and the chi-square test for each model were calculated according to the following expressions:

$$P = \left[\frac{100}{n} \sum \left(\frac{Y - \hat{Y}}{Y} \right)^2 \right] \quad (13)$$

$$SE = \sqrt{\sum (Y - \hat{Y})^2 / FD} \quad (14)$$

$$\chi^2 = \left[\sum (Y - \hat{Y})^2 / FD \right] \quad (15)$$

where:

Y: Value observed in the experiment;

\hat{Y} : Value calculated by the model;

n: Number of experimental observations;

÷2: Chi-square;

SE: Standard deviation of the estimate

P: Mean relative error;

FD: Degrees of freedom of the model (the number of model parameters subtracted from the number of observations).

RESULTS AND DISCUSSION

It was found that the time needed for the jatropha seeds to reach the moisture content of 0.10 ± 0.005 (kg water/kg dry matter) was 7.11, 3.90, 2.60; 1.79 and 1.26 h for the drying temperatures of 45, 60, 75, 90 and 105°C, respectively (Table 2). Therefore, the increase in temperature reduced the drying time of the seeds.

The difference between the vapor pressure of the drying air and that of the product increases with the temperature, promoting greater and faster water removal. This was observed by several authors in a number of products (Lahsasni *et al.*, 2004; Mohapatra & Rao, 2005; Santalla & Gely, 2007; Sirisomboon & Kitchaiya, 2009; Miranda *et al.*, 2009; Vega-Gálvez *et al.*, 2011), as it is shown in Table 2.

Table 2 also shows that the moisture content ratio of jatropha seeds was 0.14 at 45°C, 0.16 at 60°C, 0.17 at 75°C,

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

Model designation	Model	
RX = 1 + at + bt ²	Wang & Sing (Wang e Sing, 1978)	(2)
RX = a . exp(-k . t) + (1 - a) exp(-k ₁ . t)	Verma (Verma <i>et al.</i> , 1985)	(3)
RX = exp [[-a - (a ² + 4 . b . t) ^{0.5}] / 2 . b]	Thompson (Thompson <i>et al.</i> , 1968)	(4)
RX = exp(-k . t ⁿ)	Page (Page, 1949)	(5)
RX = exp(-k . t)	Newton (Lewis, 1921)	(6)
RX = a . exp(-k . t ⁿ) + b . t	Midilli (Midilli <i>et al.</i> , 2002)	(7)
RX = a . exp(-k . t) + c	Logaritmico (Yagcioglu <i>et al.</i> , 1999)	(8)
RX = a . exp(-k . t)	Henderson & Pabis (Henderson & Pabis, 1961)	(9)
RX = a . exp(-k . t) + b . exp(-k ₀ . t) + c . exp(-k ₁ . t)	Henderson & Pabis modificado (Karathanos, 1999)	(10)
RX = a . exp(-k . t) + (1 - a) exp(-k . a . t)	Two exponential terms (Sharaf-Eldeen <i>et al.</i> , 1980)	(11)
RX = a . exp(-k ₀ . t) + b . exp(-k ₁ . t)	Two terms (Henderson, 1974)	(12)

Table 2. Water content ratio of the grains of Jatropha over time (h) in five drying conditions of temperature

		Temperature (°C)									
		45		60		75		90		105	
RX	Time	RX	Time	RX	Time	RX	Time	RX	Time	RX	Time
1.000	0.00	1.000	0.00	1.000	0.00	1.000	0.00	1.000	0.00	1.000	0.00
0.813	0.40	0.784	0.25	0.805	0.16	0.792	0.08	0.817	0.05	0.817	0.05
0.637	1.15	0.667	0.53	0.623	0.41	0.651	0.24	0.679	0.18	0.679	0.18
0.498	1.78	0.512	0.93	0.527	0.66	0.530	0.49	0.543	0.36	0.543	0.36
0.368	3.13	0.393	1.66	0.408	1.11	0.414	0.81	0.410	0.63	0.410	0.63
0.255	4.76	0.284	2.49	0.291	1.70	0.301	1.21	0.288	0.95	0.288	0.95
0.140	7.11	0.164	3.90	0.175	2.60	0.185	1.79	0.191	1.26	0.191	1.26

0.18 at 90°C and 0.19 at 105°C. Thus, there is an increase in the moisture content ratio with the temperature of the drying air, due to the lower balance moisture content in the seeds in such drying conditions.

It was found that only the mathematical models Wang and Singh (2) and Newton (6) showed correlation coefficients (R^2) below 95%, indicating a satisfactory representation of the drying process (Table 3) as reported by Madamba *et al.* (1996) and Kashaninejad *et al.* (2007). The models of Wang and Singh (2), Newton (6), Verma (3) and Two Terms (11) provided mean relative errors above 10% for at least one condition analyzed. The mean relative errors (P) indicate the deviation of the observed data from the curve estimated by the model (Kashaninejad *et al.*, 2007), whereas, according to Mohapatra & Rao (2005), values below 10% are recommended for selection of models. Madamba *et al.* (1996) reported that when the coefficient of determination (R^2) is used alone, it is not a good criterion for the selection of nonlinear models. Thus, the models described above do not represent satisfactorily the drying process of *Jatropha* seeds (Table 3).

The models of Thompson (4), Page (5), Midilli (7), Logarithmic (8), Henderson and Pabis (9), Henderson and Pabis Modified (10) and Two Terms (12) provided mean relative errors below 10% in all tested conditions. Among the models assessed, they showed the lowest standard deviation of estimate or estimated mean error (SE) (Table 3). It is worth noting that the smaller the SE, the better the fit of the model to experimental data.

The Wang and Singh model (2) was the only one to show biased distribution at the five temperatures. According to Goneli *et al.* (2011), a model is considered random if the residuals are scattered in a horizontal band around zero, not taking defined shapes and not indicating biased results (Table 4). If it presents biased distribution, the model is considered unsuitable to represent the phenomenon in question.

Only three models showed random distribution at the higher temperatures (90 and 105°C), probably because of the lower drying time, which lightens the exponential curve. This is typical in the drying process of agricultural products and can be used as a parameter for all the models used, except the Wang and Singh model (Table 4).

The eleven assessed models showed a confidence interval of 99%. However, the models of Thompson (4), Page (5), Midilli (7), Henderson and Pabis (9) and Two Terms (12) showed the lowest chi-square values (Table 5). The lower the chi-square values, the better the fit of the model (Akpınar *et al.*, 2003; Midilli & Kucuk, 2003; Günhan *et al.*, 2005).

The analysis of the statistical parameters showed that the Midilli (7) and the Two Terms (12) models can be used to represent the drying kinetics of *jatropha* seeds.

Table 3. Coefficients of determination (R^2 , %), average relative errors (P, %) and estimated (SE, decimal) for the models analysed, during the drying of grain of *jatropha* in various conditions of temperature (°C)

Model	Temperature (°C)														
	45			60			75			90			105		
	SE	P	R^2	SE	P	R^2	SE	P	R^2	SE	P	R^2	SE	P	R^2
2	0.067	13.8	96.0	0.076	13.7	94.5	0.070	12.2	95.2	0.086	12.9	92.4	0.074	11.4	94.6
3	0.013	1.8	99.8	0.012	1.4	99.9	0.010	0.7	99.9	0.090	13.2	93.3	0.078	10.7	95.2
4	0.015	3.8	99.8	0.014	3.2	99.8	0.010	2.8	99.8	0.028	5.5	99.2	0.033	6.0	98.9
5	0.012	2.4	99.8	0.012	2.0	99.9	0.010	1.8	99.9	0.019	3.6	99.6	0.022	3.9	99.5
6	0.048	12.2	97.6	0.060	14.0	95.8	0.060	12.6	96.1	0.073	13.2	93.3	0.063	10.7	95.2
7	0.015	2.0	99.9	0.015	1.7	99.9	0.010	1.5	99.9	0.004	0.6	99.9	0.006	0.8	99.9
8	0.029	6.1	99.4	0.034	6.6	99.1	0.030	5.8	99.1	0.051	7.3	97.8	0.045	6.0	98.4
9	0.042	9.2	98.4	0.052	10.0	97.4	0.050	9.2	97.5	0.058	8.3	96.6	0.049	6.5	97.6
10	0.025	1.2	99.9	0.024	1.2	99.9	0.010	0.7	99.9	0.003	0.3	99.9	0.011	1.0	99.9
11	0.021	4.2	99.6	0.032	6.6	99.0	0.030	5.6	99.2	0.050	7.34	97.4	0.069	10.7	95.2
12	0.015	1.9	99.9	0.014	1.4	99.9	0.010	0.7	99.9	0.002	0.3	99.9	0.006	1.0	99.9

However, the Midilli model was selected to represent the drying process of *jatropha* seeds for its less complexity. Several researchers have recommended this model to predict the drying process of different agricultural products: red bean (Corrêa *et al.*, 2007), leaves of bushy lippia (Barbosa *et al.*, 2007), leaves of lemon grass (Martinazzo *et al.*, 2007), chopped sugarcane (Goyalde *et al.*, 2009), leaves of sage (Radünz *et al.*, 2010), yellow lantern chili (Reis *et al.*, 2011), among others.

In Table 6, the coefficients of the Midilli model adjusted to the drying kinetics data of *jatropha* seeds at different temperatures show that the magnitude of the drying constant “k”, which represents the effect of the external

drying conditions (Goneli *et al.*, 2009), tends to increase with increasing temperature of the drying air, although it was significantly lower at a temperature of 90 °C relative to 75 °C. According to Madamba *et al.* (1996) and Babalis & Belessiotis (2004), the drying constant “k” can be used as an approach to characterize the effect of temperature and is related to the effective diffusivity in the drying process for the decreasing period, indicating that the drying rate increases with temperature.

The coefficient “n”, which reflects the product internal resistance to drying (Goneli *et al.*, 2009), tended to decrease with the increasing temperature of the drying airflow. This occurred because of the greater difference between the vapor pressure of drying airflow and the seeds at higher temperatures, facilitating water removal which also increase the drying rate (Table 6). It was also verified that the coefficients “a” and “b” had different behavior at temperature ranges of 45-75°C and 90-105°C, particularly coefficient “b”, which was significant only at temperatures 90-105 °C. This confirms the hypothesis that a different drying curve is produced when *Jatropha* seeds are subjected to drying at higher temperatures.

The Midilli model is a semi-empirical model derived from a simplification of the Fick’s theoretical model (Lima *et al.*, 2007). However, the behavior of the empirical coefficients reveals the empirical characteristics of the model and complicates the equation of the coefficients as a function of the temperature, which is a disadvantage of the model. According to Keey (1972, *as cited in* Martinazzo *et al.*, 2007), empirical models omit the fundamentals of

Table 4. Distribution of residues (R = random; B = biased) for the 11 models analysed during the drying of grain of *Jatropha* in various temperature conditions

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

Table 5. Chi-square values calculated for the 11 models used to represent the drying kinetics of grain of *jatropha*

Models	Temperature (°C)				
	45	60	75	90	105
2	0.004487	0.005728	0.004780	0.007382	0.005487
3	0.000175	0.000147	0.000027	0.008152	0.006074
4	0.000239	0.000211	0.000166	0.000800	0.001104
5	0.000146	0.000138	0.000106	0.000379	0.000514
6	0.002288	0.003635	0.003240	0.005435	0.004049
7	0.000238	0.000226	0.000167	0.000019	0.000041
8	0.000852	0.001195	0.001076	0.002640	0.002076
9	0.000646	0.000565	0.000105	0.000010	0.000124
10	0.001820	0.002723	0.002498	0.003340	0.002369
11	0.000424	0.001007	0.000790	0.002510	0.004859
12	0.000232	0.000195	0.000035	0.000003	0.000041

Table 6. Parameters of models of Midilli adjusted for different conditions of drying the grain of *jatropha*

Coefficients	Temperature (°C)				
	45	60	75	90	105
a	1.0013*	1.00113*	1.00238*	0.99971*	0.99914*
b	0.7568 ^{ns}	0.70866 ^{ns}	0.70867 ^{ns}	0.51149*	0.50871*
k	0.4203*	0.65689*	0.83281*	0.80931*	0.84700*
n	-0.0016 ^{ns}	-0.0029 ^{ns}	-0.0062 ^{ns}	-0.08490*	-0.15491*

¹Significativo a 5% pelo teste F.

the drying process and its parameters have no physical significance.

The statistical comparison of the moisture content ratio between the experimental and the estimated values indicates a satisfactory adjustment of the Midilli model for the drying process of *Jatropha* seeds at the different temperatures (Figure 1).

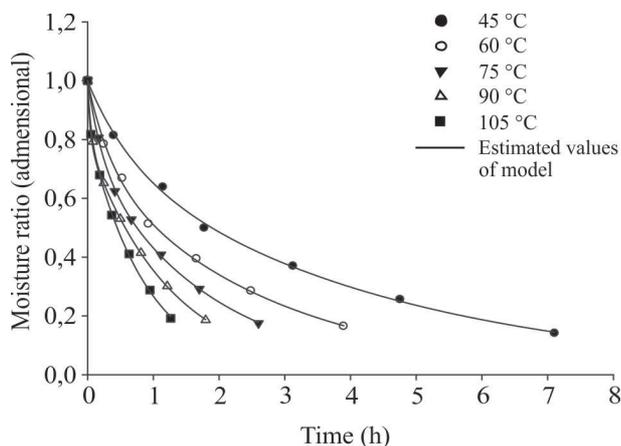


Figure 1. Experimental and estimated values by the Midilli model for the moisture content ratio of *jatropha* seeds drying at different temperatures

CONCLUSION

It was found that the increase in the airflow temperature causes a reduction in the drying time of the seeds. The Midilli and the Two Terms models are suitable to represent the drying process of *jatropha* seeds. Between them, The Midilli model was selected for best describing the *jatropha* seeds drying process for its greater simplicity.

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