Orbital: The Electronic Journal of Chemistry
journal homepage: www.orbital.ufms.br
e-ISSN 1984-6428

| Vol 11 | | No. 6 | | Special Issue November 2019 |

FULL PAPER

Evaluation of the Drying Kinetics of the Cake from Linseed Oil Extraction

Casi Santos dos Santos*, Amanda Heloize Rolim, Eliza Taborda Afonso, Marina Raquel Bento de Camargo, Rebeca Becker Miranda, Gracielle Johann, and Paula Fernandes Montanher[a]

Federal Technological University of Paraná, Estrada para Boa Esperança, Km 04, CEP 85660-00, Dois Vizinhos, PR, Brazil.

Article history: Received: 19 September 2018; revised: 16 October 2019; accepted: 17 October 2019. Available online: 21 November 2019. DOI: http://dx.doi.org/10.17807/orbital.v11i6.1247

Abstract:

Considering that drying is one of the oldest unit operations, and widely used in the preservation of biological products, the present study evaluated the drying kinetics of the cake obtained from linseed oil extraction. The samples were submitted to forced air circulation drying oven under temperatures of 40, 50, 60, 70 and 80 ± 1 °C. Simplified mathematical models were adjusted (Verna, Page, Newton, Henderson and Pabis, Two terms and Modified Page) to describe the drying kinetics of the by-product. It was observed that the drying time was dependent on both temperature and relative humidity of the drying air. The 'Two Terms' model was the best fit to the experimental temperature data measured, with highest range of coefficient of determination (0.97-0.99) and smaller range of root-mean-square error (between 1.96×10^{-4} and 5.69×10^{-4}). The standard error of prediction ranged from 1.86×10^{-2} to 7.94×10^{-2} and the average of relative standard deviation was the lowest observed (14.97). Thus, from the experimental data and adjusted parameters from the 'Two Terms' model, it is possible to predict the drying behavior in the temperature range studied.

Keywords: mathematical modeling; by-products; equilibrium moisture; water activity

1. Introduction

Linseed (*Linum usitatissimum* L.) is one of the most important cultivated plants concerning its linen and oil [1] and it is a rich source of linoleic acid (c18: 2n-6), linolenic acid (c18: 3n-3) and polyunsaturated fatty acids (n-6 e n-3). The cake from linseed oil extraction contains approximately 30% protein, a high content (23.59 g kg^{-1}) of polyunsaturated fatty acids (PUFA) and linoleic acid (c18: 2n-6) (5.52 g kg^{-1}) [2]. The linseed crop is commonly cultivated (468.0 thousand ha) in India, with a productivity of 349 kg/ha per year [3]. Linseed has attracted attention due to its antioxidant activity and estrogenic and antiestrogenic properties [4]. Estrela et al., [5] showed that agro-industrial residues are efficient adsorbents in the process of removal of pesticides containing carbofuran as the main active.

For the oil extraction, firstly the linseed seeds must go through the drying process, in order to prevent the chemical and biological decomposition of the raw material. Therefore, different drying methods influence differently, but significantly, the quality of oil extracted [6, 7]. The drying method is very important for linseed oil yield and its qualities. Zangh et al., [8] demonstrated that the linseed oils extracted from dried samples under different temperatures and drying methods contained more total phenolic and sterols content, but less chlorophyll and carotenoid pigment. Nevertheless, the effects of drying methods on the quality of the cake from linseed oil extraction have not yet been evaluated in the technical literature.

Thus, a simulation of the behavior of each material during the drying process is important for the development and improvement of equipment and processes, wherefore the

---

*Corresponding author. E-mail: casi.ufma@gmail.com

mathematical models are used to represent satisfactorily the drying kinetics [9]. Besides the descriptive function, the modeling has a comparative function. It is possible to analyze, comparing two models, the difference of behavior of the respective systems without previous experimental tests [10].

Mathematical modeling enables, through empirical and phenomenological models, to predict and simulate the behavior of determined parameters and processes. Although empirical models generally do not have theoretical basis, they are commonly simple and easy to apply due to these models are not based on experimental data, dimensional and statistical analyzes. On the other hand, phenomenological models are based on theories and laws. They are more complex and involve parameters that show the physical nature of the system [11].

Considering the importance of the study of the drying process of agricultural products, as well as their residues, the present work has the objective to experimentally investigate the drying kinetics of linseed cake and to adjust mathematical models in its description.

2. Results and Discussion

Figure 1 shows the drying kinetics behavior of the experimental data at 40, 50, 60, 70 and 80 °C.

The initial moisture values were 0.0761; 0.0707; 0.0689; 0.0751 and 0.0701 (d.b.) and the equilibrium moisture values were 0.0689; 0.0581; 0.0457; 0.0407 and 0.0236 (d.b.), respectively for the temperatures of 40, 50, 60, 70 and 80 °C. The moisture content decreases with increasing temperature, so the higher the temperature, the greater the amount of water removed. The gradient between the temperature at 40 °C and the ambient temperature is small promoting lower motive power, reaching the equilibrium faster. However, for higher temperatures, this gradient is higher, causing greater driving force and, consequently, greater removal of water from the material.

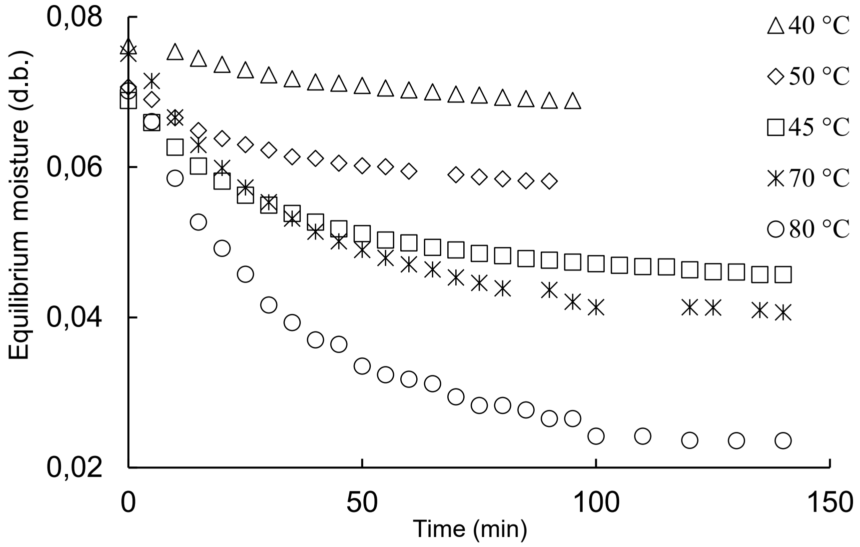

Figure 1. Drying curves.

Table 3 shows the coefficient of determination (R²), standard error of prediction (%SEP), root mean square error (RMSE) and relative standard deviation (RSD) for each of the mathematical models used for different drying temperatures. Table 3 shows that the model that best adjusted to the kinetics of drying data at 40 °C and 50 °C was the Verna model and for drying at 60, 70 and 80 °C the Two Terms model presented better results. However, mathematical modeling aims to predict and simulate the behavior of determined parameters and processes through a single model at different tested temperatures.

Table 1. Statistical evaluation of adjustments of simplified models to drying kinetics.

Model	T (°C)	R²	SEP (%)	RSD (%)	RMSE
Verna	40	0.9919	0.2863	3.27	2.03×10^{-4}
	50	0.9959	0.3321	6.00	2.35×10^{-4}
	60	0.9983	0.5538	13.80	2.71×10^{-4}
	70	0.9984	0.7375	16.01	3.50×10^{-4}
	80	0.9968	1.8543	42.56	6.00×10^{-4}
Two Terms	40	0.9790	0.4595	6.74	3.26×10^{-4}
	50	0.9943	0.3931	7.18	2.78×10^{-4}
	60	0.9990	0.4001	8.46	1.96×10^{-4}
	70	0.9983	0.7539	16.52	3.58×10^{-4}
	80	0.9971	1.7578	35.95	5.69×10^{-4}
Page Modified	40	0.9790	0.4596	6.75	3.26×10^{-4}
	50	0.9943	0.3931	7.18	2.39×10^{-4}
	60	0.9983	0.5298	13.22	2.59×10^{-4}
	70	0.9983	0.7539	16.52	3.58×10^{-4}
	80	0.9964	1.9576	42.62	6.33×10^{-4}
Page	40	0.9853	0.5637	8.15	4.00×10^{-4}
	50	0.9944	0.3970	7.08	2.81×10^{-4}
	60	0.9983	0.5538	13.80	2.71×10^{-4}
	70	0.9985	0.7877	15.95	3.74×10^{-4}
	80	0.9965	2.0720	42.92	6.70×10^{-4}
Henderson	40	0.9790	0.4595	6.74	3.26×10^{-4}
	50	0.9943	0.3931	7.18	2.78×10^{-4}
	60	0.9983	0.5298	13.22	2.59×10^{-4}
	70	0.9983	0.7539	16.52	3.58×10^{-4}
	80	0.9964	1.9576	42.62	6.33×10^{-4}

Among the models evaluated, according to the data from Table 1, it was observed that the best statistical results were obtained for the Two Terms model in the studied temperatures, with the range of coefficient of determination (R^2) between 0.97 and 0.99. Moreover, the root mean square error (RSME) was the lowest value for most temperatures (between 1.96×10^{-4} and 5.69×10^{-4}), the standard prediction error (%SEP) ranged from 0.4595 to 1.7578 and the average of relative standard deviation was the lowest observed (14.97).

The behaviors of simplified models, for the drying kinetics, are shown in Figure 2 for the temperatures of 40, 50, 60, 70 and 80 °C.

Figure 2 illustrates that the Verna model showed the best fit for temperatures of 40 and 50 °C and the Two Terms model presented the best fit for higher experimental temperatures. Ghazanfari studied the Two Terms model for different drying temperatures of flax fiber (30, 50, 70 and 100 °C) and concluded that this model showed better results at temperatures from 70 to 100 ° C [12]. Corrêa et al., observed that in the drying of the berry coffee, the Verna model presented better results in the description of the experimental data at temperatures of 40, 50 and 60 °C [13].

3. Material and Methods

Approximately five kilograms of the cake from linseed oil extraction were donated by Pazze Industrial de Alimentos Ltda, located in Panambi city in the state of Rio Grande do Sul - Brazil. The samples was separated into 0.5 kg portions, packed in plastic bags and then stored at room temperature.

The drying kinetics experiments were carried in a forced circulation oven (Model SL-102/64) at 40, 50, 60, 70 and 80 ± 1 ° C. The mass of each sample was determined using an analytical balance (Even Ion Lab - precision: 0.0001 g), at every five minutes, until three consecutive weighing provided constant mass values.

Dry basis moisture content was determined by the ratio of weight of water (w_a) to the weight of the dry matter (w_d), as shown is equation 1:

$$U^* = \frac{m_a}{m_d} \qquad (1)$$

The dimensionless moisture ratio of linseed cake during the drying, under the different temperature conditions, was determined using the equation 2:

$$RU = \frac{U^* - U_e^*}{U_i^* - U_e^*} \qquad (2)$$

where:

RU – moisture ratio (dimensionless);

U^* – moisture at the time *t* (d.b.);

U_e^* – equilibrium moisture of the product (d.b.);

U_i^* – initial moisture of the product (d.b.).

Different models proposed in the literature were used to predict the drying kinetics of linseed cake. The mathematical models Verna [14], Page [15], Newton [16], Henderson and Pabis [17] Two terms [18] and Modified Page [19] (Table 1) were fitted to the experimental data through the Gauss Newton method in the *software* Statistica 7.0.

The best model was evaluated based on the statistical parameters: coefficient of determination *(R²)*, root mean square error (*RMSE*) standard error of prediction *(%SEP*) and relative standard deviation (*RSD*), as shown in Table 2.

The coefficient of determination (R²) shows the variation explained by linear regression, showing that the closer to the unit the more adjusted is the model. The root mean square error (RMSE), standard error prediction (%SEP) and relative standard deviation (RSD) represent a better adjustment of the models to the experimental data when their values approach zero [20].

Table 2. Mathematical models Verna, Page, Henderson and Pabis, Two Terms e Modified Page.

Model	Equation
Verna	$RU = a exp(-kt) + (1-a)\exp(-k_1 t)$
Page	$RU = \exp(-kt^n)$
Newton	$RU = \exp(-kt)$
Henderson and Pabis	$RU = a exp(-kt)$
Two Terms	$RU = a exp(-k_o t) + b exp(-k_1 t)$
Modified Page	$RU = a exp(-kt)^n$

Where *a*, k_o and k_1 are parameters of the models (dimensionless), *k* is the drying constant (min^{-1}) and *t* is the time (s).

Table 3. Statistical parameters for evaluation.

Parameter	Equation
Coefficient of Determination	$R^2 = \frac{(\sum(x_i - \bar{x})(y_i - \bar{y}))^2}{\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2}$
Root Mean Square Error	$RMSE = \sqrt{\frac{\sum(obs - pred)^2}{n}}$
Standard Error of Prediction	$\%SEP = \frac{100}{média\ obs}\sqrt{\frac{\sum(obs - pred)^2}{n}}$
Relative Standard Deviation	$RSD = \sum \frac{(pred - obs)}{obs} x100\%$

Where *pre* is the value predicted by the model and *obs* is the value observed by the experiment.

4. Conclusions

From the drying kinetics conducted in a forced circulation oven (Model SL-102/64) at temperatures of 40, 50, 60, 70 and 80 ± 1 ° C, it was observed that equilibrium moisture was dependent on both temperature and relative humidity of the drying air. The equilibrium moisture values decreased with increasing temperature. This means that for higher temperatures, the removal of water from the material was more efficient. Through the adjustments of mathematical models to the experimental data, it was noticed that the Two Terms model (1974) showed the best fit to describe the drying process of the linseed cake for the temperatures studied.

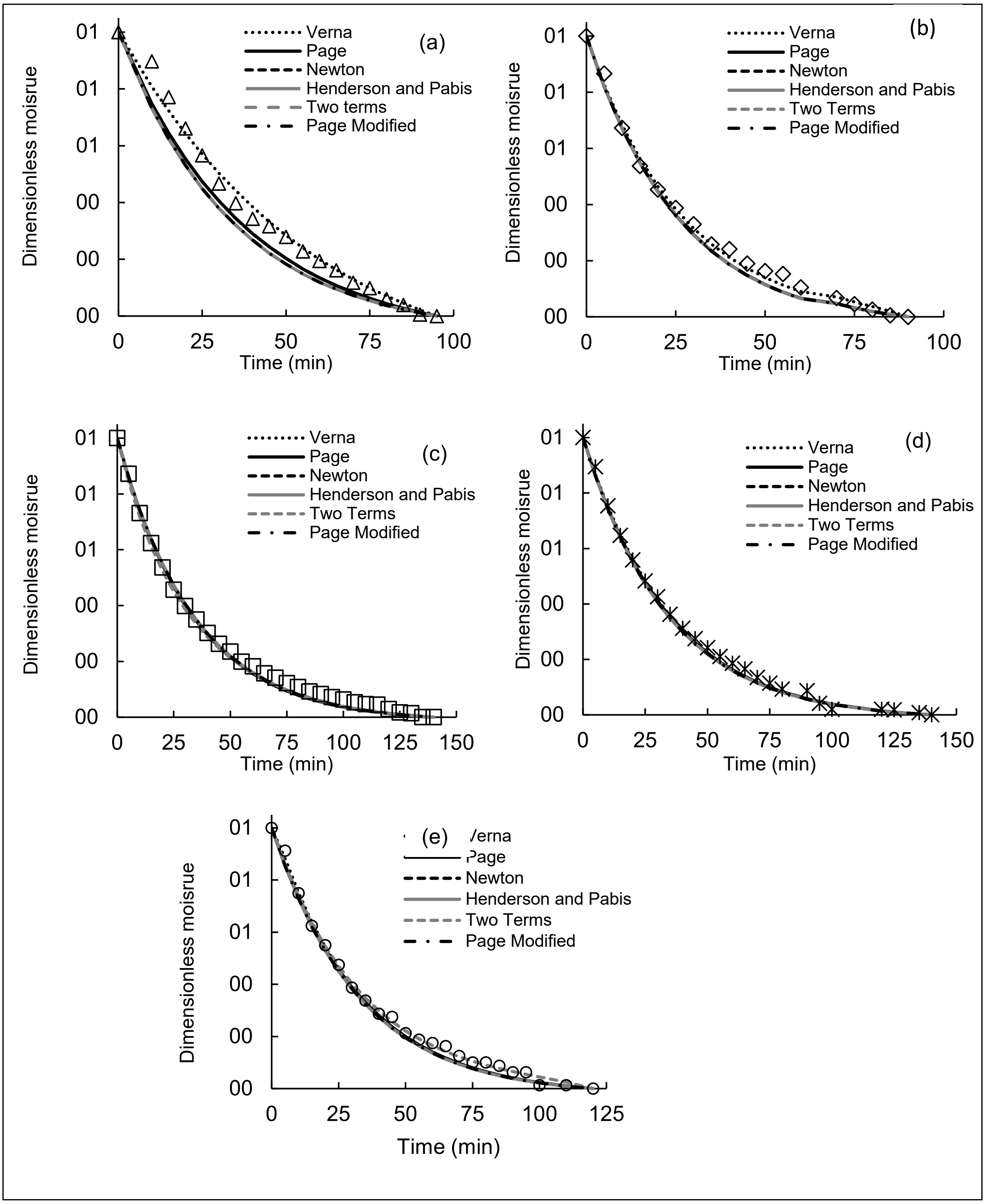

Figure 2. Adjustments of simplified models in the temperatures of 40 °C (a), 50°C (b), 60 °C (c), 70 °C (d) e 80 °C (e).

References and Notes

[1] FAO (Food and Agriculture Organization of the United Nations): FAOSTAT, Domain ProdSTAT. Available from: http://faostat.fao.org/site/636/default.aspx#ancor. Access September, 2018.

[2] Ebrahimi, M.; Rajion, M. A.; Goh, Y. M.; Sazili, A. Q.; Schonewille, J. T. *BioMed Res. Int.* **2013**, *11*, 1. [Crossref]

[3] Mueller, K.; Eisner, P.; Yoshie-Stark, Y.; Nakada, R.; Kirchhoff, E. *J. Food Eng.* **2010**, *98,* 453. [Crossref]

[4] Hall III, C.; Tulbek, M.C.; Xu, Y. Flaxseed. In: Taylor, S. (Ed.), Advances in Food and Nutrition Research, vol. 51. Academic Press, San Diego, CA, USA, pp. 1–97, 2006, Chapter 1.

[5] Estrela, T. S.; Rodrigues, I. A.; Miranda, J. A; Braga, V. S. *Orbital: Electron. J. Chem.* **2016,** *8*, 36. [Crossref]

[6] Wanyo, P.; Meeso, N.; Kaewseejan, N.; Siriamornpun, S. *Drying Technol.* **2015**, *34*, 953. [Crossref]

[7] Qu, Q.; Yang X.; Fu, M.; Chen, Q.; Zhang, X.; He, Z.; Qiao, X. *Drying Technol.* **2016**, *34,* 822. [Crossref]

[8] Zhang, Z.; Lui, Y.; Che, L. *Rying Technol.* ***2018****, 36,* 1642. [Crossref]

[9] Berbert, P. A.; Queiroz, D. M.; Silva, J. S.; Pinheiro filho, J. B. *J. Agric. Eng. Res.* **1995**, *60,* 167. [Crossref]

[10] Tkach, V.; Cherkaoui, M.; Ojani, R.; Yagodynets, P. *Orbital: Electron. J. Chem.* **2016,** *8,* 154. [Crossref]

[11] Lisbôa, J. F.; Silva, J. N.; Cavalcanti, M. T.; Silva, E. M. C. A.; Gonçalves, M. C. *Revista Brasileira de Engenharia Agrícola e Ambiental* **2015**, *19*, 218. [Crossref]

[12] Ghazanfari, A.; Emami, S.; Tabil, L. G.; Panigrahi,S. *Drying Technol.* **2006**, *24*, 1637. [Crossref]

[13] Corrêa, P. C.; Resende, O.; Ribeiro, D. M. *Revista Brasileira de Produtos Agroindustriais* **2006**, *8*, 1. [Crossref]

[14] Verma, L. R.; Bucklin, R. A.; Endan, J. B.; Wratten, F. T. *Pap. - Am. Soc. Agric. Eng.* **1985**, *28*, 296. [Crossref]

[15] Page, G. E. Factors influencing the maximum rates of air drying shelled corn in thin layers. Indiana: Purdue University, 1949.

[16] O'Callaghan, J. R.; Menzies, D. J.; Bailey, P. H. *J. Agric. Eng. Res.* **1971**, *16*, 223.

[17] Henderson, S. M.; Pabis, S. *J. Agric. Eng. Res.* **1961**, *6*, 169.

[18] Henderson, S. M. *Trans. ASABE* **1974**, *17*, 1167. [Crossref]

[19] Overhults, D. D.; White, G. M.; Hamilton, M. E.; Ross, I. J. *Pap. - Am. Soc. Agric. Eng.* **1973**, *16*, 195.

[20] Vidotti, A. D. S. Cultivo heterotrófico axênico de Chlorella vulgaris: inibição por substrato. [Master' thesis.] Campinas, Brazil: Faculdade de Engenharia Química, Universidade Estadual de Campinas, 2012. [Link]