Effect of temperature on the moisture adsorption process in brewers' spent grains

Efeito da temperatura sobre o processo de adsorção de água em bagaço de malte

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Luiz Eduardo Nochi Castro
Doutorando em Engenharia de Alimentos na Universidade Estadual de Campinas
Instituição: Universidade Estadual de Campinas
Endereço: Cidade Universitária Zeferino Vaz - Barão Geraldo, Campinas – SP
CEP: 13083-970
E-mail: luiz_nc@yahoo.com

Leda Maria Saragiotto Colpini
Doutora em Química pela Universidade Estadual de Maringá
Instituição: Universidade Estadual de Maringá
Endereço: Av. Colombo, 5790 - Zona 7, Maringá - PR, CEP: 87020-900
E-mail: ledasaracol@ufpr.br

ABSTRACT
In order to reduce the water activity of brewers' spent grains (BSG), drying processes are a viable alternative to this demand, since this residue has a high moisture content, which can contribute to deterioration processes to occur with more easiness. Thus, the objective of this work was to study the drying kinetics for BSG and optimize its dehydration process through mathematical models and statistical analysis. A 2^2 factorial design was used, where the factors of drying temperature and layer thickness were varied, in order to optimize the drying time at the lowest possible value. In addition, five drying kinetic models were used to determine model parameters. The kinetic model of Page was the one that best fit most of the data obtained in this study and through statistical analysis it was possible to conclude that the drying process occurs more efficiently when the process temperatures are higher, not depending on the thickness of the layer of material.

Keywords: biomass, drying kinetics, beer, factorial design, kinetics.

RESUMO
Com a intenção de diminuir a atividade de água do bagaço de malte, processos de secagem se mostram uma alternativa viável a essa demanda, uma vez que esse resíduo apresenta um elevado valor de umidade, o que pode contribuir para que processos de deterioração ocorram com mais facilidade. Assim, o objetivo deste trabalho foi realizar o estudo da cinética de secagem para o bagaço de malte e otimizar seu processo de desidratação através de modelos matemáticos e análise estatística. Foi utilizado um planejamento fatorial 2^2 onde variou-se os fatores de temperatura de secagem e espessura da camada de material, com o intuito de otimizar o tempo de secagem no menor valor possível. Além disso, foi utilizado 5 modelos de cinética de secagem para determinação de parâmetros do modelo. O modelo cinético de Page foi o que melhor se adequou a

maioria dos dados obtidos nesse estudo e através da análise estatística foi possível concluir que o processo de secagem ocorre de maneira mais eficiente quando as temperaturas de processo são mais elevadas, não dependendo da espessura da camada de material.

Palavras-chave: biomassa, cinética de secagem, cerveja, planejamento factorial, cinética.

1 INTRODUCTION

The main co-product generated during the malted barley industrialization process for beer production is brewers' spent grains (BSG) (Castro and Colpini, 2021; Sganzerla et al., 2021a). BSG is estimated to account for around 85% of all waste generated during the manufacturing of beer. For every 100 L of beer, approximately 20 kg of BSG is produced (Castro; Meurer; Colpini, 2021; Sganzerla et al., 2021b). According to the Ministry of Agriculture (MAPA), Brazil produced 14 billion liters of beer in 2018, resulting in around 3 million tons of BSG (Brasil, 2019). Beer was produced in roughly 190 billion liters over the world, with a by-product of around 40 million tons (Sganzerla et al., 2021c).

Currently, a substantial portion of this waste is destined for animal feed, which earns the business a minimal profit of roughly $40 per ton, and the rest is thrown as garbage in landfills (Castro; Matheus; Colpini, 2022). The high moisture content (80%) and rich amount of polysaccharides (14%) and proteins (5%), which renders this biomass prone to microbe growth and subsequent deterioration, are two of the challenges in processing this waste (Ozturk et al., 2002). Furthermore, because wet BSG has a higher density and takes up more space, transporting it is usually more expensive, causing industries to dispose of the waste to local providers, although in most situations, production exceeds demand (Silva et al., 2020).

As a result, this residue must be dried before it can be safely kept and sold without jeopardizing its integrity. Drying tries to lower a material's moisture content to extend its useful life, make storage easier, and minimize transportation costs by conserving water activity, which reduces the material's mass, volume, and thus the amount of space it takes up (Rasi; Bernardo; Pelloso, 2020).

It is vital to analyze the kinetics of the drying process, noting factors such as drying fluid speed, temperature, and humidity, to lower the costs of power and fuel to carry out the drying process as much as possible because it consumes a large amount of electrical energy (Castro et al., 2020).

Several mathematical models are cited in the literature to determine the dehydration behavior of lignocellulosic products; these models are useful in estimating the time required to reduce the moisture content of the sample under various drying conditions, assisting in decision making and increasing overall process efficiency (Mallen; Najdanovic-Visak, 2018).

The objective of this work was to evaluate the effect of temperature on the process of moisture adsorption in brewers' spent grains (BSG), through the study of water sorption isotherms.

2 MATERIALS AND METHODS

2.1 SAMPLE PREPARATION

The BSG samples (approximately 5 kg) were provided by a craft beer producer in the northern region of the state of Paraná, Brazil and immediately after collection were stored in a refrigerator at 4 ºC until use. The samples were placed on the bench and quartered, two quarters were separated for the experiment and the rest returned to storage, this process was repeated until there was a visual reduction of 80% of the initial mass. Then the samples were washed under running water until the residual liquid was colorless, after which the samples were placed in plastic bags, vacuum sealed and frozen until use.

2.2 EXPERIMENTAL PROCEDURE

The drying tests were carried out from a 2^2 factorial design with triplicate at the central point and the process variables are shown in Table 1.

Table 1 – Variables used in factorial design 2^2

Variable	Lower Level (-1)	Central point (0)	Upper level (+1)	Response variable
Layer thickness (cm)	1	2	3	Equilibrium time (min)
Drying temperature (°C)	40	60	80	

The tests were carried out in a natural ventilation oven (SolidSteel, SSDcr-110L), set at the experimental design temperatures. Approximately 30 g of sample was used per test and the layers were assembled with the aid of a caliper (Fortgpro, FG8331) until the desired thickness. Kinetics were collected every 15 minutes until the first hour and then every 30 minutes until the mass value was constant (± 0.1 g). In order to determine the equilibrium moisture, the samples were dried in an oven at 105 ºC for 24 hours. The moisture values were determined according to Equation 1 and from the moisture data the moisture ratio was determined using Equation 2.

$$U_t = \frac{(m_0 - m_t)\ 100}{m_0}$$

where: U_t it was the humidity in time t (%), m_0 the initial mass of the sample (g) and m_t the mass at time t (g).

$$MR = \frac{(U_t - U_e)}{(U_0 - U_e)}$$

where: MR was the humidity ratio (dimensionless), U_e the moisture in equilibrium (%) and U_0 the humidity at the beginning of the test (%).

To adjust the experimental kinetic data, five isothermal regression models were used: Page, Newton, Midilli-Kucuk, Logarithmic and Two terms, they are presented in Table 2. The difference between the experimental and theoretical data obtained by the models were evaluated a from the adjusted coefficient of determination (R^2_{adj}) and the root mean square deviation (RMSD) between the values.

Table 2 - Kinetic drying models.

Model	Equation
Page	$MR = \exp(-kt^n)$
Newton	$MR = \exp(-kt)$
Midilli-Kucuk	$MR = a \exp(-kt^n) + bt$
Logarithmic	$MR = a + b \exp(-kt)$
Two terms	$MR = a \exp(-k_1 t) + b \exp(-k_2 t)$

where: k, n, a, b, k_1 e k_2 (dimensionless) were the adjustable parameters of the models and t (min) the drying time.

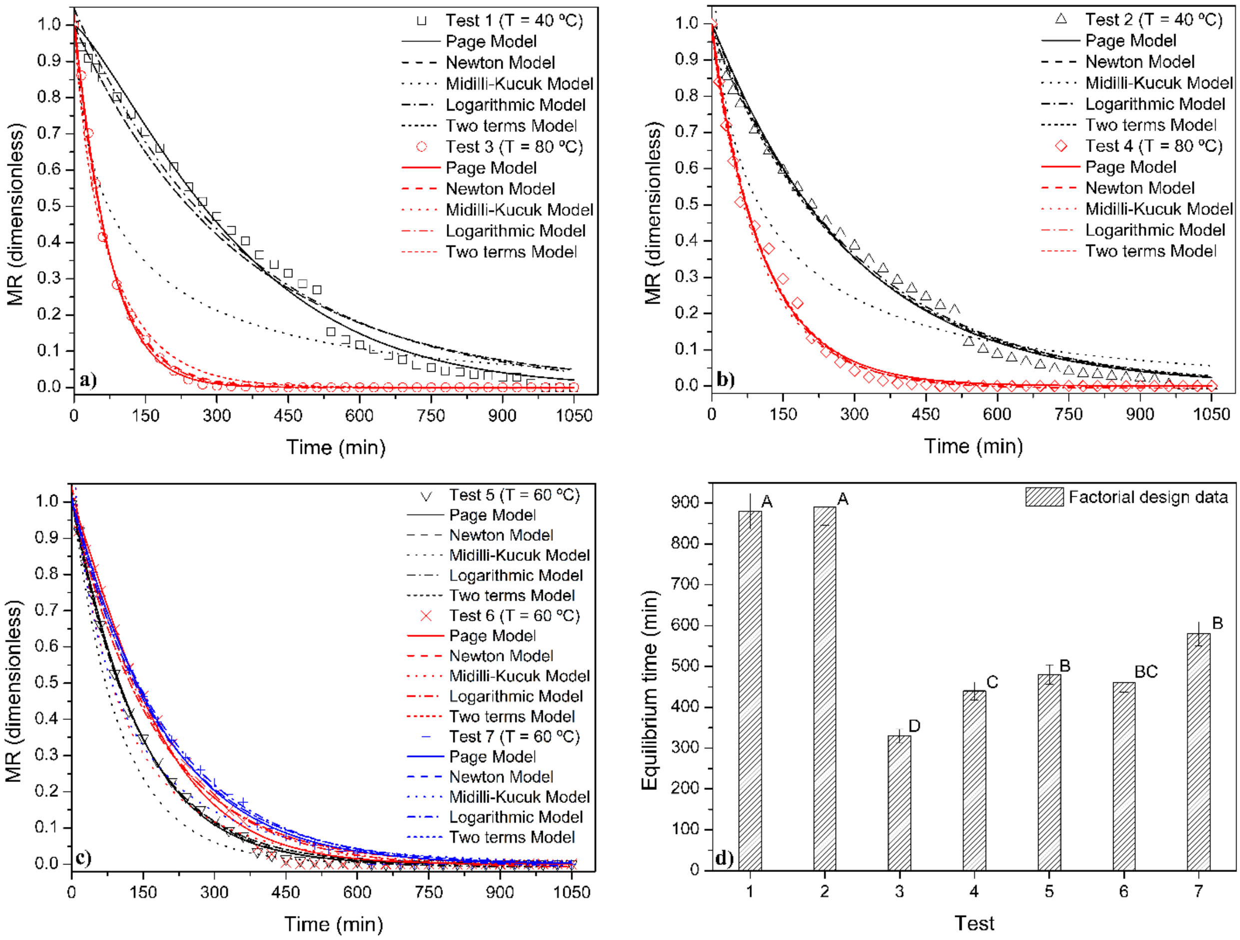
Results from all experiments were expressed as mean ± standard deviation. The statistical analysis of the factorial design was performed to assess the effect of the factors on the response variable and the interaction was statistically tested by ANOVA at a significance level of 0.05, and the Tukey test was used to compare means.

3 RESULTS AND DISCUSSION

Figure 1 shows the results of the drying curves for the samples and the result obtained for the factorial design.

It was possible to observe from both Figures 1 a) and 1 b) that the temperature had an influence on the curves of the drying kinetics, when the temperature was higher (T = 80 ºC) the equilibrium time, that is, the value at which the fraction of humidity remained unchanged, was much lower (t_{eq} = 330 min) than when the temperature was milder (T = 40 ºC), where the equilibrium time was t_{eq} = 880 min. Now observing Figure 1 c), for the temperature of T = 60 ºC, the equilibrium time was found in a range between t_{eq} = 460 and 580 min, values between those observed for temperatures of 40 and 80 ºC, which shows again that temperature and equilibrium time have an opposing relationship, that is, the higher the temperature, the shorter the equilibrium time.

Figure 1 – Brewers' spent grains drying kinetic isotherms for the thickness of: a) 1 cm; b) 3 cm; c) 2 cm and d) Diagram with the equilibrium times for the tests.



1: (e = 1 cm; T = 40 ºC); 2: (e = 3 cm; T = 40 ºC); 3: (e = 1 cm; T = 80 ºC); 4: (e = 3 cm; T = 80 ºC); 5, 6 and 7: (e = 2 cm; T = 60 ºC). Results are means of two replicates with respective standard deviation estimates. Equal capital letters do not differ between essays ($p \leq 0{,}05$) [ANOVA and Tukey test].

In fact, this phenomenon was expected to happen, since the drying of this biomass obeys the mechanisms of diffusion mass transfer, which in turn is governed by Fick's Law $\left(J = -D_{AB}\frac{dC_A}{dx}\right)$, where the diffusion coefficient (D_{AB}) tends to increase with the increasing of temperature, causing the water molecules present in the BSG to be transferred to the air present in the oven with a higher speed, since the concentration gradient favors this flow of mass, from the species with the highest water concentration (BSG) to the species with the lowest water concentration (air present in the oven), consequently reaching equilibrium more quickly (Mallen; Najdanovic-Visak, 2018).

From Figure 1 d), it was possible to observe that, in general, the equilibrium time for all assays was greater than 300 min, regardless of the different factors. Furthermore, between assays 1 and 2, assays 4 and 6 and between the triplicates of the central point (assays 5 to 7) there was no statistical difference between trials at a significance level of $\alpha = 0.05$.

Table 3 presents the parameter values determined through the drying kinetics models.

It was possible to observe from Table 3 that the Page model best fitted the drying kinetics data for most experiments (assays 1, 3, 5, 6 and 7) according to the high adjusted correlationcoefficient ($R^2_{adj} > 0.991$) and smallest root mean squared deviation (RMSD < 0.031). For assay 2, the logarithmic model was a better fit to the experimental data ($R^2_{adj} = 0.991$; RMSD = 0.029) and for assay 4, the two-term model was the best one, obtaining an $R^2_{adj} = 0.995$ and RMSD = 0.019.

Through the statistical analysis, it was possible to observe that the effect of the drying temperature significantly influenced the value of the equilibrium time of the process, since a value of $p < 0.05$ was obtained, as shown in Table 4. The residual error was $\sqrt{7500} = 86.6$ (see value in column 4, row 7 of Table 4).

Figure 2 presents the results obtained by the quadratic response surface model.

Figure 2 – Statistical analysis of the experiment: a) Level curves and b) Response Surface

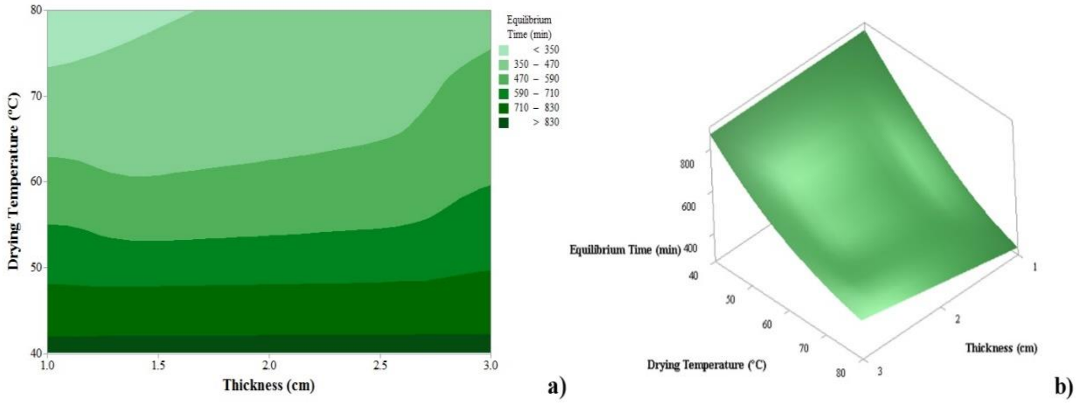


Table 3 – Parameters of drying kinetics models

Tests	Modelo																				
	Page				Newton			Midilli-Kucuk						Logarithmic					Two terms			
	k	n	R^2_{adj}	RMSD	k	R^2_{adj}	RMSD	a	b	k	n	R^2_{adj}	RMSD	-a	b	k	R^2_{adj}	RMSD	a	k	R^2_{adj}	RMSD
1	0.003	1.275	0.991	0.031	0.003	0.977	0.050	1.169	0	0.01	0.485	0.937	0.081	0.010	1.056	0.003	0.979	0.047	0.001	10	0.976	0.05
2	0.003	1.027	0.989	0.031	0.003	0.989	0.031	1.352	0	0.01	0.492	0.832	0.125	0.010	0.988	0.003	0.991	0.029	0.026	0.13	0.990	0.03
3	0.013	1.096	0.999	0.009	0.013	0.998	0.012	1.01	0	0.01	0.014	0.998	0.009	0.002	1.032	0.014	0.998	0.047	0.214	0.05	0.988	0.03
4	0.009	0.947	0.994	0.021	0.009	0.993	0.021	0.989	0	0.01	0.944	0.992	0.023	0.006	0.973	0.09	0.994	0.02	0.062	0.142	0.995	0.019
5	0.007	1.062	0.999	0.013	0.007	0.998	0.067	1.032	0	0.01	0.947	0.964	0.081	0.008	1.022	0.007	0.998	0.067	0.001	10	0.998	0.071
6	0.005	1.21	0.996	0.013	0.006	0.989	0.067	1.197	0	0.01	0.768	0.929	0.081	0.01	1.051	0.006	0.992	0.067	0.001	10	0.989	0.074
7	0.005	1.06	0.998	0.013	0.005	0.997	0.067	1.22	0	0.01	0.685	0.932	0.081	0.01	1.023	0.005	0.997	0.067	0.001	10	0.997	0.071

Table 4 –ANOVA results for the response surface quadratic model

Source	DF	Equilibrium time			
		Sum of squares	Medium square	F value	p-value
Thickness	1	5625	5625	0.75	0.478
Thickness ^{2}	1	25725	25725	3.43	0.205
Temperature	1	245025	245025	32.67	0.029
Thickness x Temperature	1	5625	5625	0.75	0.478
Error	2	15000	7500		
Total	6	297000			
		$R^2 = 0.949$	$R^2_{adj} = 0.848$		

It was possible to observe from Figures 2 a) and 2 b) that in fact the drying temperature was the only effect of the factorial design that actually influenced the equilibrium time, higher temperature values showed lower equilibrium time values. The optimal value fits in the temperature range between 75 and 80 ºC, since the intention was to obtain the shortest possible drying time so that the process could be optimized.

4 CONCLUSION

Therefore, it was possible to conclude that the dehydration process of malt bagasse occurs more efficiently at higher process temperatures and that the Page kinetics model was the one that best suited the drying kinetics data.

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