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Research Article

Isothermal Drying Kinetic Study of Spent Coffee Grounds Using Thermogravimetric Analysis

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Drying coffee grounds involves high energy consumption and represents an important step in using coffee waste materials as green energy. This study analyzes the drying process using thermogravimetric analysis. The kinetics of the drying process of coffee grounds, containing equal proportions of Arabica and Robusta, were evaluated under isothermal conditions at various temperatures: 50, 60, 70, and 80°C, with sample layer thicknesses of 0.6, 1.2, 1.8, and 2.4 mm. The thermogravimetric curves obtained for the coffee grounds samples under conditions of constant temperature allowed the tracing of the drying curves (moisture content—drying time). The influence of the furnace air velocity on the drying and water evaporation process was analyzed. The drying rate has been established to be about 2.6 times slower than the rate of water evaporation under the same conditions; as a result the overall process is controlled by the effective water diffusion in the layer. This aspect is important in industrial practice for sizing tubular dryers. The activation energy was found to be influenced by the thickness of the coffee grounds layer subjected to the drying process and had values between 8.3 kJ/mol and 10.3 kJ/mol.

1. Introduction

The spent coffee grounds—a waste product—are used to obtain biodiesel, bioethanol, bio-oil, and also pellets [1, 2]. Drying spent coffee grounds represents an important step in its use as green energy and involves high energy consumption, approximately 5 MJ/kg of water when using convective dryers [3]. In the pellet industry, the moisture ratio of the final product must be below 10%. This is necessary both to ensure safe storage and to eliminate the possibility of microorganisms growth, especially molds [4]. Very few studies in the literature address the drying of spent coffee grounds using pilot-scale dryers [2–8]. Most of them are quite recent, demonstrating the growing interest of researchers in this subject due to the accelerated increase in coffee consumption in recent years and implicitly the amount of resulting spent coffee grounds, which is a valuable source of green energy. Osorio-Arias et al. [4] evaluated the convective drying of the spent coffee grounds in a tray-type convection dryer under the following conditions: temperature of 40, 50, and 60°C, air velocity from 1.0 up to 2.0 m/s, and the thickness of the coffee grounds layer between 10 mm and 20 mm. Their results indicated that the drying process was the most efficient at 60°C temperature, air velocity of 2.0 m/s, and layer thickness of 0.012 m. These drying conditions allow the separation of antioxidant compounds in spent coffee grounds and their use in the food, pharmaceutical, or beauty industries. Convective drying of spent coffee grounds was also analyzed by Gomez de la Cruz et al. [5] but at much higher temperatures, namely, 100, 150, 200, and 250°C, and spent coffee grounds layer thickness of 5, 10, 15, and 20 mm. The best results for modeling the time dependence of the moisture ratio (MR) were obtained with the two-term Gaussian model ($MR = a \cdot \exp[-(t - b/c)^2] + d \cdot \exp[-(t - e/fc)^2]$, where a, b, c, d, e, and f are parameters of the empirical equation). The two-term weighted Gaussian function is applied due to the similarity between the drying curve and the tail of the symmetrical Gaussian bell curve [9]. The drying time varied between 18 minutes for a layer thickness of 5 mm at 250°C and 3 hours for a thickness of 20 mm and a temperature of 100°C. The values of the effective moisture diffusivity varied between $1.79 \cdot 10^{-9}$ and $29.1 \cdot 10^{-9}\,m^2/s$. The effectiveness of other spent coffee grounds drying techniques was also analyzed. For instance, Burdo et al. [3] analyzed the infrared drying process, Solyom et al. [7] studied the same process using microwaves, and Tun et al. [8] tested the use of solar energy to dry spent coffee grounds. Tun et al. [8] compared the results obtained for drying using solar energy with drying in a convective heater at temperatures of 75°C, 90°C, and 105°C and with open-air drying. The experimental results indicated that the process of drying in the sun, in the open air, requires 10 hours to reach a final MR of 37%, while sun drying (at a temperature of 75°C) reached a MR of 10% in 10 hours, and drying in the heater at the same temperature reached a MR of 7% in 6 hours. Drying using solar energy has proven to be the most advantageous process in terms of energy but also in terms of the quality of the dry spent coffee grounds. The authors of the study showed that raising the temperature to 90°C or 105°C did not provide better drying conditions in the case of drying in a convective heater, especially for a thicker layer of spent coffee grounds. The performance of the microwave drying process of coffee grounds was recently analyzed by Fu and Chen [10]. They evaluated the influence of various power levels (119, 231, 385, 539, and 700 W) but also the presence of three mineral additives (10% sodium chloride, 10% sodium sulfate, and 10% lignite). A shorter drying time was observed by 38% in the case of the use of sodium sulfate and by 18% in the case of sodium chloride compared to the situation in which the drying of the spent coffee grounds was analyzed in the absence of the additive, the tests being conducted at 385 W. However, at the same power level, an increase in drying time was observed if lignite was used as an additive. The additives, sodium chloride and sodium sulfate, contributed to the efficiency of the drying process by improving the migration of moisture at higher power levels, respectively, 385, 539, and 700 W.

A few researchers reported in their works that other isothermal drying processes were applied to food materials. Kahyaoglu et al. tested the drying process of wheat using a spouted bed dryer [11], and Guzman-Meza and coauthors analyzed the isothermal drying of plant-based food material using a precision balance and UV light [12].

In this study, the drying process of spent coffee grounds is analyzed for the first time using thermogravimetric analysis. Previously, a thermogravimetric approach was carried out by Chen et al. to analyze the drying of powdered rice straw particles [13]. Thermal gravimetric analysis has also been applied by Liu et al. [14] to investigate the codrying kinetics of biomass with lignite. This method was chosen due to the high degree of accuracy in performing three measurements: mass change, temperature, and temperature change. The oven of the derivatograph Mettler Toledo TGA-SDTA851^e can be used to simulate conditions of industrial tubular dryers [15].

In this article, the kinetic study of the drying process of coffee grounds in conditions of constant temperature, different thicknesses of the layer of dough, and different rates of the air in the oven was performed. Based on the drying speed curves, the drying time, along with the time until reaching the humidity corresponding to the end of the drying period with decreasing linear speed, was also determined, which was correlated with the thickness of the coffee bean layer and the temperature. The evaporation rates of the water were also determined and then compared with the drying rates of the coffee grounds, determined under the same conditions. The observations obtained are important in industrial practice for sizing tubular dryers.

2. Materials and Methods

Spent coffee grounds can be collected from various coffee shops and represent the residue that generally comes from coffees containing blends of Arabica and Robusta in different proportions. For this reason, in this study, we have analyzed the kinetics of the drying process of spent coffee grounds, which contain equal proportions of Arabica and Robusta (Covim and Granbar), under isothermal conditions, at various temperatures of 50, 60, 70, and 80°C and sample layer thickness of 0.6, 1.2, 1.8, and 2.4 mm.

The analyzed spent coffee grounds resulted from a commercially available type of coffee, which, according to the manufacturers' specifications, contains 50% Arabica and 50% Robusta. A professional DeLonghi coffee machine was used and the following recipe for making coffee was followed to obtain comparable results: 12 g coffee and 40 ml water. Samples obtained under the same grinding conditions were used in all experimental determinations. Thus, particle size distribution did not change significantly. The samples also had the same composition, as they originated in the same source.

The moisture content of fresh spent coffee ground was determined using a Mettler Toledo HG63 Halogen humidity analyzer and a range of 38 to 48% moisture content has been identified.

The Scanning Electron Microscopy (SEM) technique was used to investigate the morphology of the spent coffee grounds samples. A scanning electronic microscope Quanta 200 was used, having a conventional source of wolfram electrons, which offers a resolution of 3.5 nm. The SEM studies were conducted on uncovered samples fixed on aluminum supports.

The determination of the particle size distribution of the spent coffee grounds was performed using the Anton Paar PSA 1190 analyzer in dry dispersion mode. Approximately 5 g of sample was analyzed under air pressure of 1600 mBar, vibrator frequency of 43 Hz, and 50% vibrator duty cycle [16].

The study of the water holding capacity for spent coffee grounds was performed under static conditions. Distilled water was used for each experiment, as well as 1 g of sample

Table 1: Experimental conditions in which the drying and evaporation processes, respectively, were analyzed.

Sample type	Mass of sample (mg)	Temperature (°C)	Air velocity (m/s)
Spent coffee grounds	10.48 ± 0.84	50 ± 0.01	0.003 ± 0.0003
	20.49 ± 0.78	60 ± 0.01	0.003 ± 0.0003
	30.09 ± 0.84	70 ± 0.01	0.003 ± 0.0003
	39.95 ± 0.83	80 ± 0.01	0.003 ± 0.0003
		70 ± 0.01	0.003 ± 0.0003
	39.95 ± 0.83	70 ± 0.01	0.009 ± 0.0009
		70 ± 0.01	0.018 ± 0.0018
Water		60 ± 0.01	0.003 ± 0.0003
	42.09 ± 4.11	70 ± 0.01	0.003 ± 0.0003
		80 ± 0.01	0.003 ± 0.0003
		70 ± 0.01	0.003 ± 0.0003
	38.80 ± 1.64	70 ± 0.01	0.009 ± 0.0009
		70 ± 0.01	0.018 ± 0.0018

coffee grounds. The water holding capacity (WHC) was expressed as g liquid/ g dry material.

The drying process, recording the thermogravimetric curves (TG) and the derivative thermogravimetric curves (DTG) under isothermal conditions at various temperatures: 50, 60, 70, and 80°C, was conducted using Mettler Toledo 851^e equipment. This equipment is characterized by a very good accuracy in measuring the change of the sample mass (1 μg) and controlling the temperature (0.01°C); therefore, we consider that it can be used to simulate the conditions in industrial tubular dryers. Sample amounts of moist spent coffee grounds with masses between 10 and 40 mg were used, and furnace air velocity was at 0.003 m/s, 0.009 m/s, and 0.018 m/s. A cylinder of synthetic air (Linde Gaz, Romania) was used, 20% oxygen, 80% nitrogen, impurities: hydrocarbons, max. 0.1 ppmV, and nitrogen oxides, max. 0.1 ppmV. Table 1 shows the experimental conditions in which the drying and evaporation process was analyzed in a Mettler Toledo 851^e device. The thickness of the material layer in the crucible was calculated considering sample mass and density (878 and 143 kg/m^3 for the spent coffee grounds) and crucible surface ($1.9625 \cdot 10^{-5}$ m^2).

The processing of the experimental data on the time dependence of the MR to obtain kinetic models of the spent coffee grounds drying process was performed with the SigmaPlot 11.2.

3. Results and Discussion

3.1. Characterization of Coffee Grounds' Particles. The SEM measurements allowed the investigation of the morphology of spent coffee grounds particles (Figure S1 Supplementary Information). Figure 1(a) shows an SEM micrograph at magnitude 100x. Its analysis indicates an inhomogeneous particle size distribution. The size value of the larger particle varied between 180 ± 1.80 and $690 \pm 6.90\,\mu$m, with an average value of $421 \pm 4.21\,\mu$m. This average size obtained is comparable to what Layao et al. reported, namely 413 μm, for dry spent coffee grounds particles, the determined value applying the evaluation of the particle size distribution by the sieving technique [17].

Particle size distribution of spent coffee grounds particles (Figure S2 Supplementary Information) determined using the Anton Paar PSA 1190 analyzer was expressed in diameters D_{10}, D_{50}, and D_{90}, which means the corresponding particle size when the cumulative distribution percentage reaches 10%, 50%, and 90%, respectively. The obtained values were $23.33 \pm 1.16\,\mu$m, $115.88 \pm 5.79\,\mu$m, and $389.48 \pm 19.47\,\mu$m. The obtained results showed that most of the analyzed spent coffee grounds particles had the size of $389.48 \pm 19.47\,\mu$m, a value comparable to the particle size of spent coffee grounds obtained by other authors applying laser diffraction analysis: $341.11 \pm 21.37\,\mu$m [20].

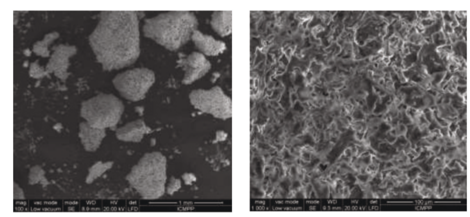

Figure 1: SEM images of dry spent coffee grounds particles. (b) The SEM image for spent coffee grounds particles registered at magnitude 1000x and indicates a "sponge-like" aspect. Based on this image, pore sizes were measured and found to vary between $8 \pm 0.08\,\mu$m and $17 \pm 0.17\,\mu$m, with an average value of $12.4 \pm 0.12\,\mu$m. Zein et al. have also reported in the literature pores with dimensions up to 30 μm for dry spent coffee grounds [18]. Le et al. also reported values for spent coffee grounds pore size not exceeding 30 μm [19].

Tests performed to assess the water sorption capacity of spent coffee grounds (Table S1 in Supplementary Materials) indicated that the maximum value of water sorption for spent coffee grounds samples is 3.77 ± 0.2 g water/g dry material and was close to the values obtained by other authors but under dynamic conditions: 3–7 g liquid/g dry material [21] and 5.73 ± 0.1 g liquid/g dry material [22]. The differences found could be due to the different granulation and sorts of coffee.

3.2. Kinetic Study of the Drying Process. The thermogravimetric curves obtained under isothermal conditions, namely, at 50, 60, 70, and 80°C and for different thicknesses of the sample layer of 0.6, 1.2, 1.8, and 2.4 mm, allowed tracing of the drying curves (material moisture-drying time)

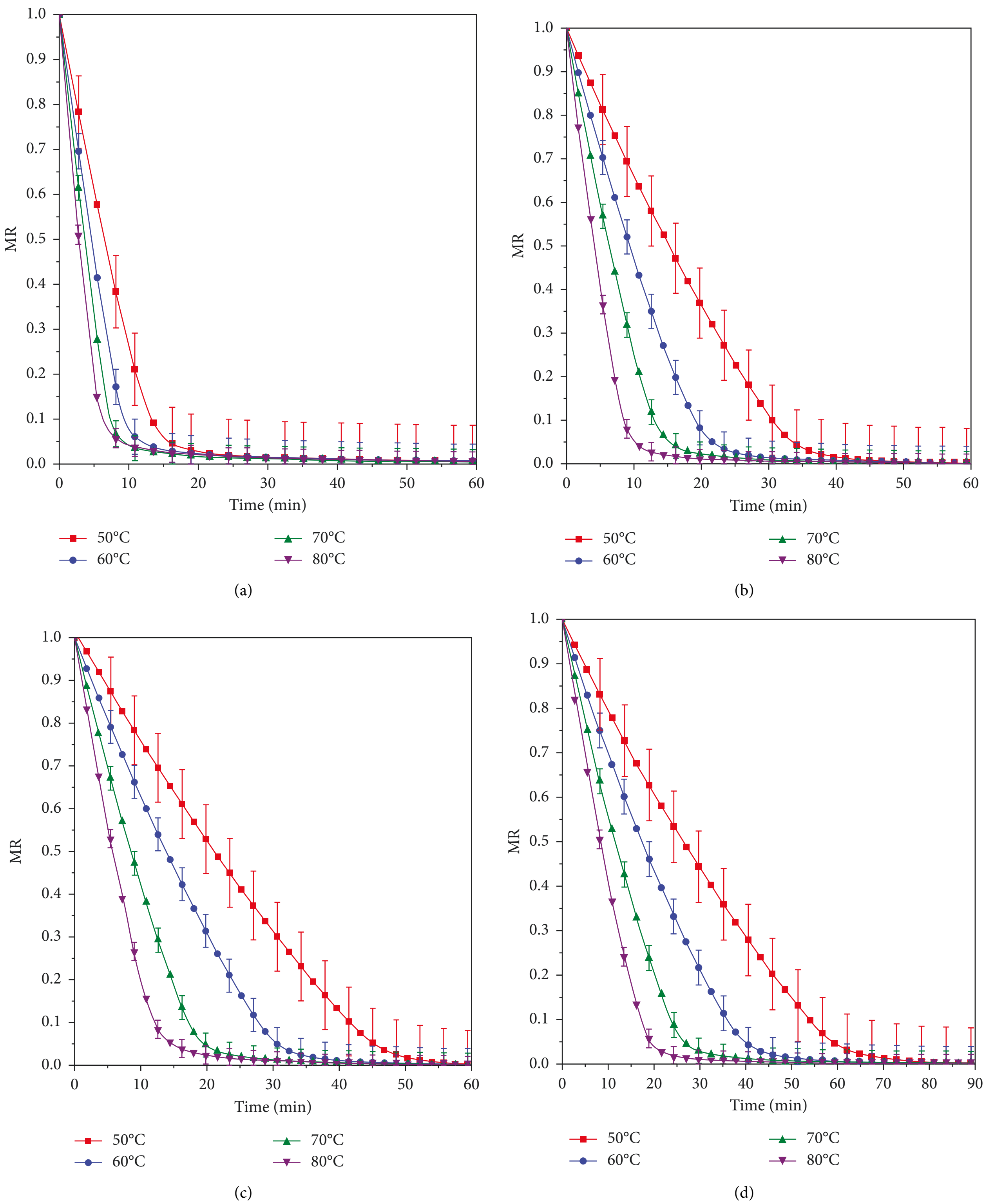

FIGURE 2: Drying curves (material moisture–drying time): (a) 0.6 mm; (b) 1.2 mm, (c) 1.8, and (d) 2.4 mm.

from Figure 2. The following relation was used to calculate the moisture ratio (MR) of the material:

$$MR = \frac{M(t) - M_e}{M_0 - M_e}, \quad (1)$$

where M_0 represents the initial MR of the spent coffee grounds, M_e represents the equilibrium MR determined from the drying curves at the moment when the mass of the sample does not change with increasing time, and $M(t)$ is the MR of the sample at any given time t [15].

Table 2: Mathematical modeling of food drying.

No.	Model equation	Model name
1.	$MR = a^* \exp(-kt)$	Henderson and pabis
2.	$MR = c + a^* \exp(-kt)$	Logarithmic
3.	$MR = a^* \exp(-k_1 t) + b^* \exp(-k_2 t)$	Two-term
4	$MR = c + a^* \exp(-k_1 t) + b^* \exp(-k_2 t)$	Modified two-term
5.	$MR = ca^* \exp(-kt) + b^* t$	Modified Henderson–Pabis

Using the program Sigma Plot 11.2, the experimental data MR = f (time) were processed to verify existing kinetic drying patterns in the literature [23] or modified by the authors of this study and presented in Table 2.

The best results for the process of drying the spent coffee grounds are obtained with a modified Henderson and Pabis model ($MR = c + a\exp(-kt) + bt$, where t is the time expressed in seconds and k is the drying rate constant). Table 3 presents the values of the coefficients a, b, c and the rate constant k, along with the performance of the models, respectively, the correlation coefficient (r^2) and standard deviation σ:

$$\sigma = \frac{\sqrt{\sum_{i=1}^{k}\left[\left(MR^E\right)_{\exp} - \left(MR^E\right)_{calc}\right]^2}}{(n-p)}, \quad (2)$$

where n represents the number of experimental data and p is the number of parameters [15].

The results presented in Table 3 show that for the temperature of 50°C and spent coffee grounds layer thicknesses of 1.2, 1.8, and 2.4 mm, the model that best correlates the experimental data was the logarithmic one $MR = c + a^* \exp(-kt)$.

Knowing the surface of the crucible accurately ($1.9625 \cdot 10^{-5}\,m^2$) in which the spent coffee grounds were introduced in layers of different thicknesses, the moisture removal rate at the four temperatures was calculated and represented graphically in Figure 3 according to the MR. As expected, an increase in temperature increases the drying rate. The drying stages at a constant rate (AB) and decreasing rate (BC and CD) are highlighted. Two drying stages with decreasing rates were identified in the study of the drying process of biomass and lignite, respectively, using mixtures in different proportions by Liu et al. [14].

The drying time was determined by means of relation (3) for the drying stage with a constant rate and by relation (4) for the drying stage with decreasing rate, based on the drying rate curves represented in Figure 3:

$$t_{AB} = \frac{m_i}{S \cdot w_{\max}} \cdot \left(u_i - u_f\right), \quad (3)$$

$$t_{BC} = \frac{m_i}{S} \cdot \int_{u_d}^{u_f} \frac{du}{w}, \quad (4)$$

where m_i is the initial mass of the spent coffee grounds sample, S is the surface of the spent coffee grounds layer that coincides with the inner surface of the crucible, $w_{\max}$ is the maximum drying rate, u_i is the initial MR, u_f is the MR at the end of the drying period at a constant rate (AB), and u_d is moisture ratio at the end of the drying period at a linear decreasing rate (BC) [15]. For the spent coffee grounds samples subjected to the drying process in this study, under the conditions mentioned, u_f had values between 0.32 and 0.53 kg moisture/kg initial sample and u_d varied between 0.072 and 0.10 kg moisture/kg initial sample. These values were determined from the charts in Figure 3, taking into account the drying rate decrease onset for u_d (coordinate on the X-axis of point B) and the change in the drying rate decrease slope for u_f (coordinate on the X-axis of point C). u_i is the initial moisture content of the material (coordinate on the X-axis of point A). Two tangents to the curve were drawn and the point of intersection was established. Total drying time ($t_{AB} + t_{BC}$) evaluated with the relations (3) and (4) for the four temperatures and thickness values of the spent coffee grounds layer are presented in Figure 4. The drying period at a constant rate, in which the diffusion process does not occur and the evaporation of moisture in the layer takes place only on the surface, was short, with the time between 2 and 5 minutes. The drying stages at a linear decreasing rate varied between 4 and 81 minutes, depending on the temperature and the thickness of the layer. Only the drying stage with the linear decreasing rate (BC) was taken into consideration because at the end of it, the humidity (u_d) is lower than 10% and, according to the literature, this value is sufficient both to ensure the safe storage of dry grounds and to eliminate the possibility of the growth of microorganisms, especially molds [3]. Figure 4 presents the variation of the total drying time until the moisture corresponding to the end of the drying period at a linear decreasing rate is reached (u_d), depending on the spent coffee grounds layer thickness at temperatures of 50, 60, 70, and 80°C. We noticed that the drying time decreased with increasing temperature: about 2 times with increasing temperature from 50 to 60°C, 1.4 times with increasing temperature from 60 to 70°C, and only 1.2 times with increasing temperature from 70 to 80°C. Drying agent parameters (temperature, speed, and moisture, if applicable) significantly influence the first stage of the drying process. The influence of internal moisture transfer and moisture transfer through the boundary layer is added to these parameters during the second drying stage. When temperature increases along with the increase in the effective diffusion coefficients, the thickness of the boundary layer decreases. However, internal moisture transfer is not accelerated to the same extent by the increase in temperature [24]. Taking into account the obtained results, where with the increase of the temperature from 70 to 80°C no major changes were observed, it could be considered that the optimal temperature for the drying process of spent coffee ground is around the value of 70°C. Other researchers have come to the same conclusion, analyzing the drying of spent coffee grounds at various temperatures. Tun et al. [8] evaluated the drying of spent coffee grounds in a convective heater at the following temperatures: 75°C, 90°C, and 105°C. The authors of the study showed that if the temperature increased from 75 to 90°C or 105°C respectively, better

Table 3: Values of the coefficient in the modified Henderson–Pabis model and its performance.

Nr.	Layer thicknesses, (mm)	Temperature, (°C)	Model	Model parameters	r^2	σ
1.	0.6 mm	50	Modified Henderson–Pabis	$a = 1.1674$ $b = 1.8260{*}10^{-6}$ $c = -0.0775$ $k = 0.0016$	0.9931	0.0287
		60	Modified Henderson–Pabis	$a = 1.1099$ $b = 4.8962{*}10^{-6}$ $c = -0.0161$ $k = 0.0030$	0.9917	0.0255
		70	Modified Henderson–Pabis	$a = 1.0798$ $b = 9.9879{*}10^{-7}$ $c = -0.0002$ $k = 0.0043$	0.9928	0.0208
		80	Modified Henderson–Pabis	$a = 1.0474$ $b = -2.0596{*}10^{-6}$ $c = 0.0126$ $k = 0.0053$	0.9954	0.0152
2	1.2 mm	50	Logarithmic	$a = 1.2073$ $c = -0.1297$ $k = 0.0008$	0.9925	0.0393
		60	Modified Henderson–Pabis	$a = 1.4671$ $b = 0.0001$ $c = -0.3951$ $k = 0.0011$	0.9948	0.0293
		70	Modified Henderson–Pabis	$a = 1.2249$ $b = 4.5332{*}10^{-5}$ $c = -0.1379$ $k = 0.0018$	0.9934	0.0300
		80	Modified Henderson–Pabis	$a = 1.1213$ $b = 1.1873{*}10^{-5}$ $c = -0.0303$ $k = 0.0035$	0.9931	0.0253
3.	1.8 mm	50	Logarithmic	$a = 1.4724$ $c = -0.4370$ $k = 0.0004$	0.9971	0.0243
		60	Modified Henderson–Pabis	$a = 12.7591$ $b = 0.0013$ $c = -11.7242$ $k = 0.0002$	0.9975	0.0222
		70	Modified Henderson–Pabis	$a = 1.3328$ $b = 7.7482{*}10^{-5}$ $c = -0.2558$ $k = 0.0013$	0.9942	0.0301
		80	Modified Henderson–Pabis	$a = 1.1483$ $b = 2.2764{*}10^{-6}$ $c = -0.0638$ $k = 0.0024$	0.9942	0.0262
4.	2.4 mm	50	Logarithmic	$a = 1.2662$ $c = -0.2151$ $k = 0.0004$	0.9950	0.0319
		60	Modified Henderson–Pabis	$a = 2.3774$ $b = 0.0002$ $c = -1.3318$ $k = 0.0004$	0.9968	0.0244
		70	Modified Henderson–Pabis	$a = 1.2807$ $b = 4.2844{*}10^{-5}$ $c = -0.2056$ $k = 0.0010$	0.9942	0.0290
		80	Modified Henderson–Pabis	$a = 1.1584$ $b = 1.7511{*}10^{-5}$ $c = -0.0747$ $k = 0.0017$	0.9934	0.0274

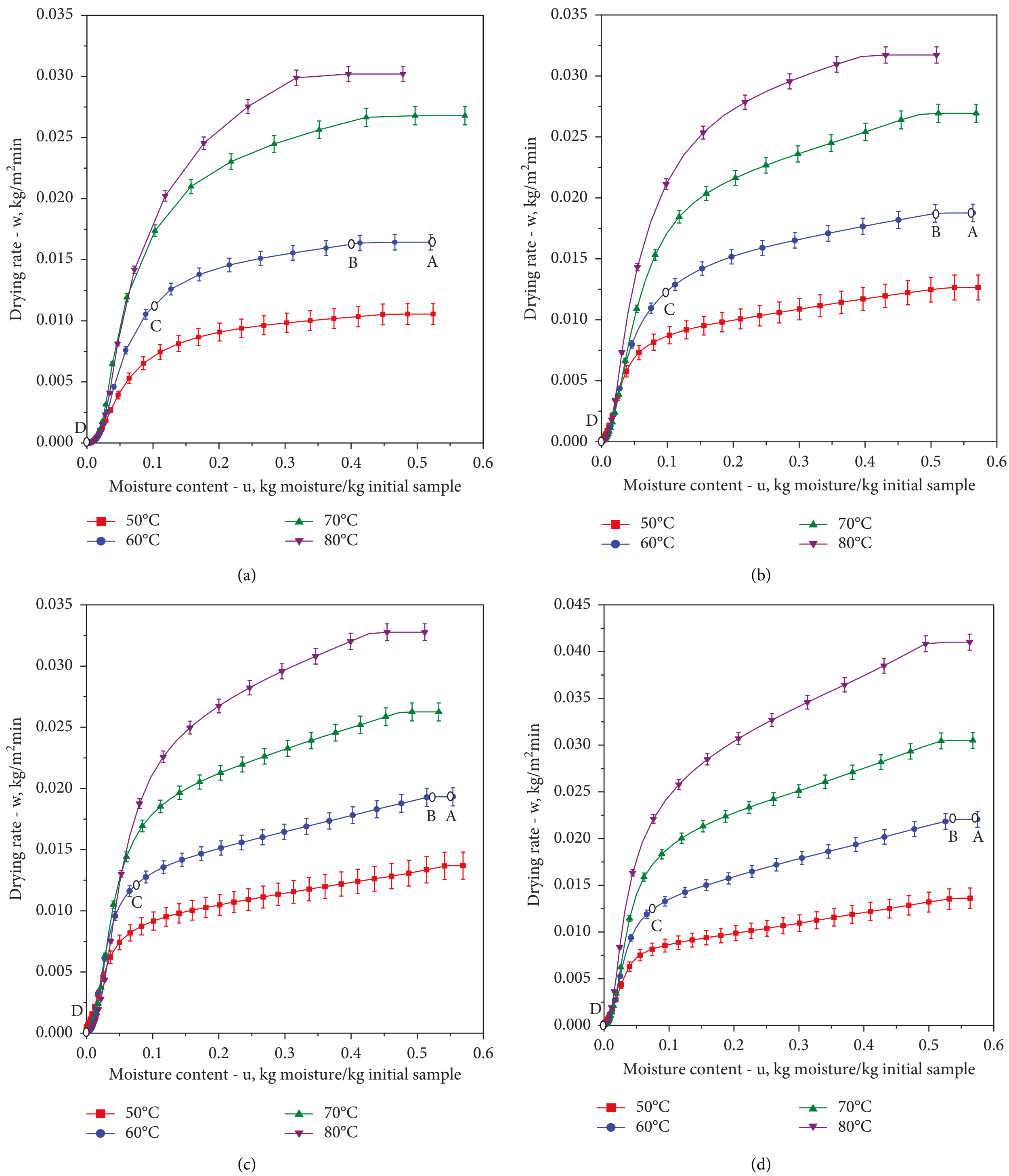

Figure 3: Variation of drying rate depending on humidity: (a) 0.6 mm; (b) 1.2 mm; (c) 1.8 mm; (d) 2.4 mm.

drying conditions were not obtained, especially for a thicker layer of spent coffee grounds. The study conducted by Tun et al. [8] identified that the optimal drying process for removing moisture from spent coffee grounds without any changes in its composition due to drying that took place at temperatures around the value of 75°C, so that dry spent coffee grounds qualify as a source of renewable energy.

Experimental data obtained for the total drying time and the time until the moisture corresponding to the end of the drying period at a linear decreasing rate were reached (u_d), depending on temperature and the thickness of the layer (Figure 4), and were processed with SigmaPlot 11 and the model given by the following equation was obtained:

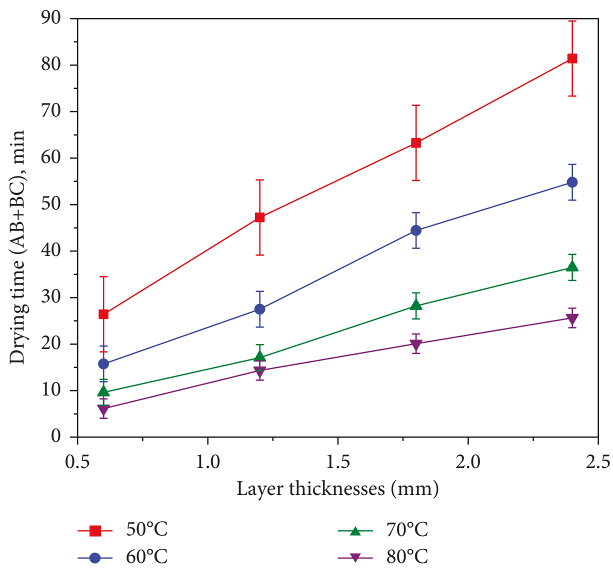

Figure 4: Variation of drying time with the thickness of the spent coffee grounds layer.

$$\ln(t) = 10.6111 + 0.85625 \cdot \ln(\delta) - 0.10325 \cdot (T)^{0.5} \cdot \ln(T), \quad (5)$$

where t is the time in seconds, δ is the layer thicknesses in mm, and T is the temperature in °C.

The correlation coefficient obtained was $r^2 = 0.9949$. Figure 5 compares the experimental values and those calculated with the model given by equation (5). The model given by equation (5) was also applied to data recently published in the literature by Osorio-Arias et al. [4]. Thus, for temperatures of 60°C and spent coffee grounds thickness of 10 and 15 mm, the drying time calculated with the model proposed in this study was 184 and 260 minutes, respectively, compared to the experimental values of 180 and 250 minutes [4].

In order to evaluate the influence of the furnace air velocity on the drying process, tests were performed at 70°C, moist spent coffee grounds layer thickness of 2.4 mm, and air velocity of 0.009 m/s and 0.018 m/s. The results obtained are presented in comparison with those previously obtained for an air velocity of 0.003 m/s in Figure 6. It is obvious that the drying rate increased with the increase of the air velocity. Under the same experimental conditions, the rate of water evaporation expressed in kg/m^{2}s was also determined. This was compared in Figure 7 with the drying rate of spent coffee grounds in the drying stages at a constant rate (AB) and the first drying period at a linear decreasing rate (BC). Water evaporation rates at various temperatures were also determined at 50, 60, and 70°C and the same air velocity of 0.003 m/s, which were compared in Figure 8 with the drying rates of the spent coffee grounds determined under the same conditions in the drying stages (AB and BC). It has been established that in all the situations analyzed in Figures 7 and 8, the drying rate was approximately 2.6 times lower than the water evaporation rate under the same conditions. This aspect is important in industrial practice for sizing tubular dryers.

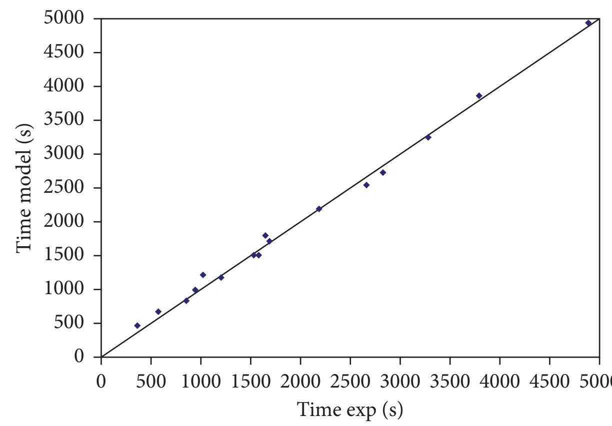

Figure 5: Experimentally determined drying time compared to the time calculated with equation (5).

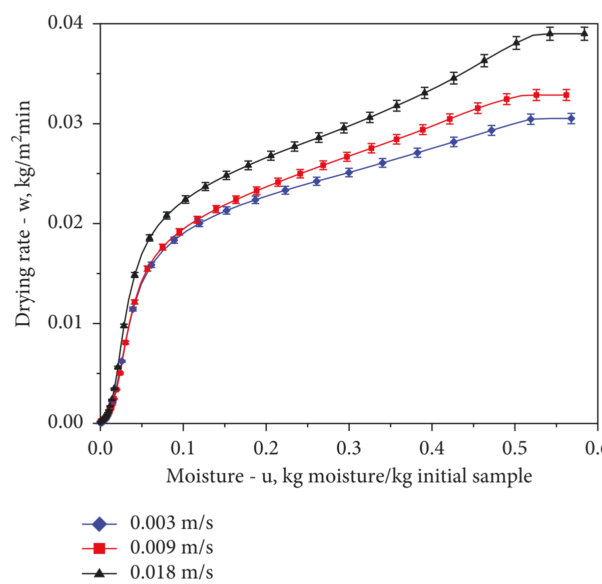

Figure 6: Influence of furnace air velocity on drying rate for 2.4 mm thick layer of spent coffee ground.

If we consider that the transport of moisture from the spent coffee grounds layer takes place by diffusion, and the layer thickness, temperature, and diffusion coefficients have a constant value, we can determine the effective moisture diffusivity (D_{eff}), taking into account the equation that describes the variation of the water ratio in the time given by Crank [25].

$$MR = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 \pi^2 D_{eff} t}{\delta^2} \right], \quad (6)$$

where δ is the thickness of the spent coffee grounds layer, t is the time [s], and D_{eff} is the effective diffusion coefficient [m^2/s]. If we consider only the first term of the series in equation (6), we should obtain the following:

$$MR = \frac{8}{\pi^2} \cdot e^{-D_{eff} t (\pi/\delta)^2}. \quad (7)$$

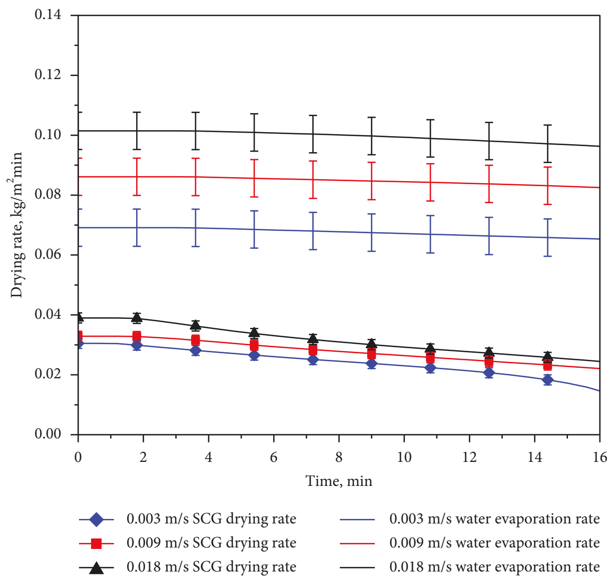

Figure 7: Comparison between the drying rate of spent coffee grounds and the water evaporation rate at 70°C and furnace air velocities of 0.003, 0.009, and 0.018 m/s.

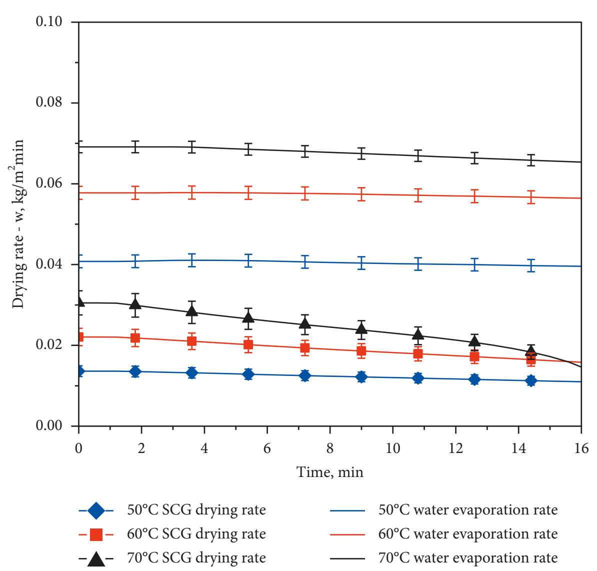

Figure 8: Comparison between the drying rate of spent coffee grounds and the water evaporation rate at a furnace air velocity of 0.003 m/s and the following temperatures of 50, 60, and 70°C.

By logarithmizing the relation (7), we should be able to obtain a linear dependence that allows us to evaluate the effective diffusion coefficient:

$$\ln(MR) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D_{eff}}{(\pi/\delta)^2}\cdot t. \quad (8)$$

The graphic representation $\ln(MR) = f(t)$ for the first drying period at a linear decreasing rate (BC) determined lines with a negative slope and correlation coefficients greater than 0.855. The values of the effective moisture diffusivity were found to increase with increasing temperature and varied between 0.37 $10^{-10}$and 9.99 10^{-10} m^2/s.

Table 4: The values of the kinetic parameters of the spent coffee grounds drying process.

No.	Layer thicknesses δ (mm)	$\ln D_0$	Ea (kJ/mol)	r^2
1.	0.6	−20.92	8.2894	0.9805
2.	1.2	−18.36	8.7411	0.9634
3.	1.8	−18.02	9.0668	0.9685
4.	2.4	−17.27	10.2612	0.8753

The temperatures dependence of the effective diffusion coefficient can be expressed by an Arrhenius-type equation (4):

$$D_{eff} = D_0 \cdot e^{(-Ea/RT)}, \quad (9)$$

where D_0 is the preexponential factor, R is the universal gas constant, T is the temperature expressed K, and Ea is the activation energy. By logarithmizing equation (9), a linear dependence is found to be obtained between ln (D eff) and 1/T, which allows the evaluation of the activation energy and the preexponential factor for the first drying period at a linear decreasing rate (BC).

$$\ln\left(D_{eff}\right) = \ln(D_0) - \frac{Ea}{R}\cdot\frac{1}{T}. \quad (10)$$

The values obtained for the kinetic parameters of the spent coffee grounds drying process are presented in Table 4. The value of the activation energy was found to increase with the increase of the thickness of the spent coffee grounds layer, varying between 8.3 and 10.3 kJ/mol. Gómez-de la Cruz et al. obtained activation energies between 12.3 and 16.9 kJ/mol for drying spent coffee grounds in a conventional convective heater, in which the thickness of the drying layer was 5, 10, 15, and 20 mm and the working temperatures were 100, 150, 200, and 250°C [2].

4. Conclusions

The kinetic study of the drying process of spent coffee grounds under conditions of constant temperature and various thicknesses of the layer of spent coffee grounds, performed for the first time in Mettler Toledo TGA-SDTA851^e equipment, which can be used to simulate conditions in industrial tubular dryers, allowed to determine the time dependence of the moisture ratio (MR), of the effective moisture diffusivity, and kinetic parameters (activation energy and preexponential factor).

Out of the models in the literature that describe the drying process of some food products, it was found that, in general, the best results for drying spent coffee grounds can be obtained with a modified Henderson–Pabis model ($MR = a + b\exp(-kt) + ct$, where t is time expressed in seconds and k is the drying rate constant). The rate of the drying process increased with increasing temperature. For drying at constant rate drying, values were between 0.011 kg/m^2·min ($\delta = 0.6$ mm, at a temperature of 50°C) and 0.041 kg/m^2·min ($\delta = 2.4$ mm, at a temperature of 80°C). The water evaporation rates at various temperatures of 50, 60, and 70°C and the same air velocity of 0.003 m/s, and at a temperature of 70°C and air velocity of 0.009 and 0.018 m/s were also determined. It has been established that the drying rate was approximately 2.6 times lower than the water evaporation rate under the same conditions; thus, the overall process was controlled by the effective diffusion in the layer. The study shows that removing moisture from spent coffee grounds is a fairly easy process. Basically, a decrease in humidity up to about 10%, a convenient value for the recovery of spent coffee grounds, may be achieved in a short time in the drying area at a constant rate and linear decreasing rate. The water removed in this area is surface moisture and moisture in the large pores of the material. The effective moisture diffusivity varied between $0.37\ 10^{-10}$and $9.99{\cdot}10^{-10}\ m^2/s$. The activation energy was influenced by the thickness of the coffee grounds layer subjected to the drying process and had values between 8.3 kJ/mol and 10.3 kJ/mol.

Data Availability

The drying kinetic data used to support the findings of this study are included within the article. The SEM, particle size distribution, and water holding capacity data used to support the findings of this study are included within the supplementary information file. The thermogravimetric data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Supplementary Materials

In the supplementary materials, SEM images of dry coffee grounds particles (2000x and 5000x), the particle size distribution, and the water holding capacity data are presented. (*Supplementary Materials*)

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