AGRO-INDUSTRIAL WASTES: DRYING KINETICS

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ABSTRACT

The productive activities of Argentina, olive and wine industries, generate large amounts of agro-industrial waste which include the olive wet husk, the olive pits and grape stalks. These residues can be used as filler of polymeric composite materials. In order to prepare the residues for that use, a drying process is needed.
In this work the drying kinetics of agro-industrial waste was studied. It was carried out at three different temperatures: 60, 80 and 100 °C, for each material. The experimental results determined that the olive pit is the material which has higher moisture value (62%), followed by the grape stalks(45%)and finally by the olive wet husk(33%).
Six empirical mathematical models were selected to describe and compare the drying kinetics of the agro-industrial wastes. Among the tested models used to describe the drying kinetics of wastes, Logarithmic and Page models were those that presented the best fit. The moisture loss was described and the effective diffusivity was estimated on the basis of the obtained results, giving values in the range of $5x10^{-6}$ for the grape stalks, $4.09x10^{-7}$ for the olive wet husk and $5x10^{-6}\,m^2/s$ for the olive pits.
This study suggests that the olive wet husk shows better properties during drying process, followed by grape stalks and the olive pits, for their incorporation into polymeric composites.

Keywords: drying kinetics, olive wet husk, olive pits, grape stalks.

INTRODUCTION

Many of the productive activities of Argentina, specifically agriculture, generate large amounts of agro-industrial wastes. Olive wet husk, olive pits and grape stalks, from olive and wine industries respectively, are examples of this kind of wastes. The use of these wastes to obtain products of higher added value or energy has become a very important initiative in recent years. Besides, these have allowed a substantial reduction in the quantity of waste requiring final disposal.
The wastes resulting from the manufacturing process of olive oil are hazardous to the environment due to their high phenolic content. The mostly used manufacturing system for olive oil is the two-phase centrifugation also known as "ecologic method" by the lower water consumption in relation to the method of three phases. This system is called two-phase because two fractions are generated: a solid (namely in different ways: olive wet husk or wet pomace) and a liquid (olive oil) [1]. The olive wet husk is an aqueous sludge whose typical composition is: milled shell core (endocarp or pit wall, 42%), crushed seeds (3%), olive envelope (epicarp or skin) and pulp (mesocarp), 21%, water between 25% to 28% and a significant amount of residual oil (9 to 10%), [2].The large amount of water, together withglucidic chains andfine solids, givesto the waste a pasty consistency and makedifficult its transportation, storage and handling [3]. This characteristic together with its small particle size make it a material slightly porous, plastic and susceptible to compression [4- 5]. Olive wet husk constitutes more than 80% of the olives consumed in the production of oil and this percentage depends on the variety of olives and the extraction process [6].
Another waste of olive industries are olive pits, that are derived from the industrial extraction of olive oil and the manufacturing of pitless table olives [7].Currently they are used as combustion energy source. They are also used to produce activated carbon and other chemicals at laboratory scale. More recent applications consist of its incorporation into cosmetics industry [8], based on the exfoliating properties of powdered olive pits;and as reinforcing agents in polymeric compounds [9].
The industrialization of the grape is one of the main economic activities in the Cuyoregion, Argentina, producing wine, concentrated must, raisins, alcohol and oil seeds. As a result of this activity large volumes of waste are generated, mainly of stalks, which represent between 2.5 and 5.5% of the mature grape bunch. It is obtained from grapedestemming process, in which the grains are separated from the bunch. It is chemically composed of tissues experiencing a process of lignification along the progress of maturation.

The use of vegetable particles and fibers, as reinforcement agents in polymer matrix composite materials, has been reported since the introduction of plastics on the market, being used in diverse applications. The use of agro-industrial waste is an alternative technique of valorization. The drying of these wastes before the processing of the composites is an important factor because the water in the particle surface acts a separating agent in the particle-matrix interface.
Convection drying can be defined as the moisture removing process by simultaneous heat and mass transfer between the product and the drying air by means of evaporation, usually caused by the temperature difference and the velocity of the convective air [10]. The basic requirement for drying is the achievement of a dry product in a reasonable time with minimal operating costs. The process efficiency requires the optimization of the conditions, especially the temperature of the dry air. An important aspect of drying technology is the mathematical modeling of the process. This allows to define the most appropriate operating conditions, either in order to dimension and design the equipment or minimize drying times [11]. Drying kinetics can be described using transport properties, such as humidity diffusivity and dryingconstant, in relation with the operative conditions.
The main objective of this paper is to study the temperature effect on the drying kinetics of agro-waste materials as a previous stage of particle conditioning before their incorporation into the polymeric matrix, to form a composite.

MATERIALS AND METHODS

Materials
Wastes from the agro-industrial activity in the Cuyoregion, Argentina were used. The olive wet husk and olive pits from the manufacture of olive oil andcanned olives, provided by the company Frávega, Pocito, was used. The grape stalkswere provided by Bodegas Graffigna, San Juan.The olive wet husk was used as aslurry, such as received, with a moisture content of 70%.The fresh wastes employed were kept in cooler until use.
The samples were identified as GS (grape stalks), OP (olive pits) and OWH (olive wet husk).

Drying equipment
The drying tests were performed in a natural convection oven, Sybron Thermolyne, with electric heater and temperature stationary controller. This oven is connected to an analytical balance, Ohaus Adventure, by a hanger rod connected to a basket containing the sample. The basket is made of stainless steel Tyler mesh # 30, of circular section, of 3.7cmdiameter and 7cm height.

Drying
The drying tests were conducted at three different temperatures: 60, 80 and 100 °C, for each test material.The bed height of samples in basket were 2cm forolive wet huskand 7cm for olive pits and grape stalks, while the corresponding weights were 20 g, 55 g and 29g, respectively. Lower height was used in the bed of olive wet huskas it isa heaviermaterial [12]. Moisture loss was recorded at different time intervals: 1min for the first 180min, 2 min for the following 120 min, and 4 min until reaching equilibrium moisture content. Moisture was reported as dimensionless ratio (M_R) based on the initial (M_0) and final moisture (M) of sample through the following equation:

$$M_R = \frac{M - M_e}{M_0 - M_e} \quad (1)$$

The equilibrium moisture content (Me) was obtained using the dynamic method or drying until constant weight, where the final moisture content does not decrease significantly with increasing time [13].
The influence of air temperature was the parameter studied in this work, which is regarded by other authors as the main factor affecting the drying kinetics of biological materials [14-16]. Temperatures tested, between 60 and 100°C, were chosen considering the fact thatfor higher values protein denaturation processes may occur [10] or, in the case of olive wet husk, a superficialcaramelization of the material [17].

Mathematical modeling of drying kinetics
Generally, the drying kinetics depends on two set of parameters: operating conditions and material properties.
The water content of a material may be present as free or bound moisture. The free or interstitial humidity is the one that exceeds the content of equilibrium moisture and is relatively easy to evaporate. The bound moisture is adsorbed on the walls or inside the solid, and is not completely removed by evaporation; water is

bound to the surface of the particles by electrostatic forces. This moisture depends on the nature and particle size of each solid [18].

The drying process is divided into three periods: preheating, constant rate and falling rate. In the first one, free surface moisture is evaporated, reaching the maximum speed of drying. Then, the free moisture evaporates completely leaving water inside the capillaries. In the third period, there is a reduction of heat transfer in the bed of solids, water evaporates from within the capillaries; bound moisture is removed. The bed temperature increases continuously to reach the temperature of the surface exchange. This step also depends on the internal structure of the solid. Some moisture is present at the end of the drying cycle, is called Me.

The drying rate (D_R) could be expressed as g (water) g^{-1} (dry solids) min^{-1}:

$$D_R = \frac{M_1 - M_2}{t_2 - t_1} \quad (2)$$

Where t_1 and t_2 are different times in minutesduringthe dryingprocess; M_1 and M_2 are the moisture contents of each agricultural waste at time t_1 and t_2, respectively. The mechanism taking place during the drying of each residue was evaluated from the curves D_R versus time.

In general, the drying kinetics of agricultural residues can be described with three types of models: theoretical, semi-theoretical and empirical. Theoretical models are based on the process of diffusion (Fick's second law) or simultaneous equations of heat and mass transfer. The semi-theoretical models are derived from general simplifications of Fick's second law solution and are widely used for drying of agricultural products; for this reason they are used in this work [19].

All applied mathematical models dismiss the initial period and are more suitable for describing the period of falling rate. These were chosen considering that the thickness of the dried materials is small so that the temperature and humidity areexternallycontrolled [19].

Six of the most popular semi-theoretical models were selected from recent reports focused on drying of similar agricultural products [11, 14-15, 20-29]. Moisture dimensionless ratio (M_R), Eq. (1), was used for experimental data fitting.

The applied mathematical models are described below.

<u>Lewis or Exponential model</u>

It is the simplest model for adjustment of drying kinetics. It has been used to describe moisture transferred from agricultural equipment, biomaterial or food. It assumes negligible resistance in the movement of moisture from the inside to the surface of the material. The model can be written as it follows[10]:

$$M_R = \frac{M - M_e}{M_0 - M_e} = \exp(-kt) \quad (3)$$

Where k is a model constant and t is the time.

<u>Henderson and Pabis model</u>

It is the first term of a series of a general solution of Fick's second law; also known as two-parameter exponential model. The slope of this model, drying constant k, is related to the effective diffusivity when drying takes place only in the period of descending speed and is controlled by the diffusion process of the liquid [10].

$$MR = \frac{M - M_e}{M_0 - M_e} = \text{a} \exp(-kt) \quad (4)$$

Where a and k are constants model, and t is time.

<u>Page model</u>

It is an amendment of the empirical model of Lewis and corrects some deficiencies. The model uses two empirical constants; and it hasshown good fits to describe the dryingprocess of various agricultural products such as soybeans, green beans, corn nuts and pistachio [14, 20, 26, 30]. This is expressed as [10]:

$$M_R = \frac{M - M_e}{M_0 - M_e} = \exp(-kt^N) \quad (5)$$

Where k and N are the constants of the model.

Two-term exponential model

It is a part of the infinite negative exponential series derived from a general solution of the diffusion equation. It is applied regardless of the geometry of the particle and the boundary conditions, but assumes that the diffusivity is constant [10].

$$M_R = \frac{M - M_e}{M_0 - M_e} = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) \quad (6)$$

Where a_1, a_2, k_1, k_2 are the constants of the model.

Logarithmic

It is a modification of the model of Henderson and Pabis with an additional empirical constant (c). It has been successfully used to adjust the drying kinetics at different operating conditions for: Jatrophacurcas L. pits, green olives and pumpkin seeds [22, 24, 27]. Its expression is:

$$M_R = \frac{M - M_e}{M_0 - M_e} = \mathrm{a} \exp(-kt) + c \quad (7)$$

Where a, k and c are the constants of the model.

Diffusional approach or approximation of diffusion model

It is a modification of the two-term exponential model. Although it tends to despise the latter stages, it has a good fit between experimental and predicted values of M_R in the initial stage for different drying conditions [10].

$$M_R = \frac{M - M_e}{M_0 - M_e} = \mathrm{a} \exp(-kt) + (1 - \mathrm{a}) \exp(-kbt) \quad (8)$$

Where a, b and k are the constants of the model.

Drying constants and coefficients of all models were estimated using least squares nonlinear regression analysis, made throughMarguardt-Levenberg algorithm. The fit of the experimental data to the different models was performed by MATLAB software. The purpose of the adjustment is to determine the most suitable model describing the kinetics of drying.

Determination of the effective diffusivity

Fick's second law of diffusion can be used to interpret thedrying data, taking into account that moisture diffusion is one of the main transport phenomena that occur during drying. In this model the dependent variable is the moisture ratio (M_R) [11].

$$\frac{dM_R}{dt} = D_{eff} \frac{d^2 M_R}{dx^2} \quad (9)$$

D_{eff} is wet effective diffusivity (m^2s^{-1}), t is the drying time (s) and x is the spatial dimension (m).

The mathematical solution to Eq. (9), when the internal mass transfer is the controlling mechanism and the one-dimensional transport in an infinite plate is assumed, it is given by Eq. (10) developed by Crank (1975) [31]. This can be used for different regularly shaped bodies such as rectangular, cylindrical and spherical products. For total drying time, Eq. (10) can be simplified by considering only the first term. It can be rewritten exponential formas shown in Eq. (11) [10].

$$M_R = \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} exp\left[\frac{-(2i+1)^2 D_{eff} \pi^2 t}{4L^2}\right] \quad (10)$$

$$M_R = \frac{8}{\pi^2}\ exp\left[\frac{-D_{eff} \pi^2 t}{4L^2}\right] \quad (11)$$

Where L is the average thickness of the material (m) and i is a positive integer.

The uses of Eq. (11) assumes moisture migration by diffusion,constant diffusivity constant for each constant temperature and negligible contraction, which predicts a linear relationship between these variables [11].

Some authors have reported two or more periods of descending speed, and consequently, various effective diffusivity values were determined. However, only the first period of decreasing speed was considered useful to compare with data from similar reports [32-33].

RESULTS AND DISCUSSION

Analysis of the drying kinetics

The changes in experimental M_R versus drying time of GS, OWH and OP at different drying air temperatures (60 - 100 ° C) are shown in Fig. 1. To calculate M_R, the equilibrium moisture values (Me) (shown in Table 1) were employed. The drying time required to reduce the content of initial moisture to final moisture (equilibrium) is also shown in Table 1.

The moisture ratio is exponentially reduced as the drying time increases; this behavior is typical of some biological materials [15, 16, 20, 24, 28, 30, 35-37]. Drying kinetics shows that the drying of the three materials GS, OWH and OP completely occurs in the period of descent rate, suggesting that the material surface is no longer saturated with water and the drying rate is controlled by the internal diffusion phenomena, according to a mass transfer controlled process [14, 29].

Material	Air drying tem. (°C)	Me	Me average	S^2	t (min)
Grape stalks	60	13,81	13,26	0,29	516
	80	13,43			422
	100	12,53			326
Olive wet husk	60	7,22	6,85	0,08	458
	80	6,51			362
	100	6,81			340
Olive pits	60	35,4	34,36	0,56	648
	80	34,01			466
	100	33,67			480

Table1: Equilibrium moisture (Me) and drying time (t)for each material for each drying temperatures, being S^2 the standard deviation.

As it can be seen in Fig.1 the olive pits are more difficult to dry, relatively to the other two, i.e., longer drying time is needed for each of the three considered temperatures. Such behavior could be attributed to the different nature and composition of the three wastes. Grape stalks present a woody structure with high porosity, which eases the removal of water from inside. The same happens with olive wet husk, since it is aslurry with free water added. On the other hand, olive pit has important oil content and a compact structure. It is concluded that the sequence of materials according to their drying facility is OWH, GS and OP.

Analysis of the drying rate curves

The amount of removed water versus time is represented by the drying rate (D_R) given in Fig. 2 for each material at different temperatures. It can be observed that the olive wet husk has a different behavior when the slope of the curve is considered; such difference can be attributed to its heterogeneous composition (slurry with particles of pulp and olive pits).

As expected, D_R decreases continuously as the material dries. Also, when the air temperature increases, D_R also increases since the drying rate is directly proportional to the temperature gradient between the material surface and the air. Similar results have been reported in several studies for biological materials [16, 37-40].

Mathematical modeling of drying kinetics

The statistical validity of the models was evaluated and compared using the regression coefficient R^2. In order to select the best model, that factor was used as the main selection criterion, additionally the goodness of fit is determined using statistical parameters such as the chi-square (χ^2) test, the mean relative percent deviation (EMD), the root mean square error (ERMS) and the residue. For a good fit, R^2 value should be the highest and values of χ^2, EMD, ERMS should be the lowest, and the residue the closest to zero.

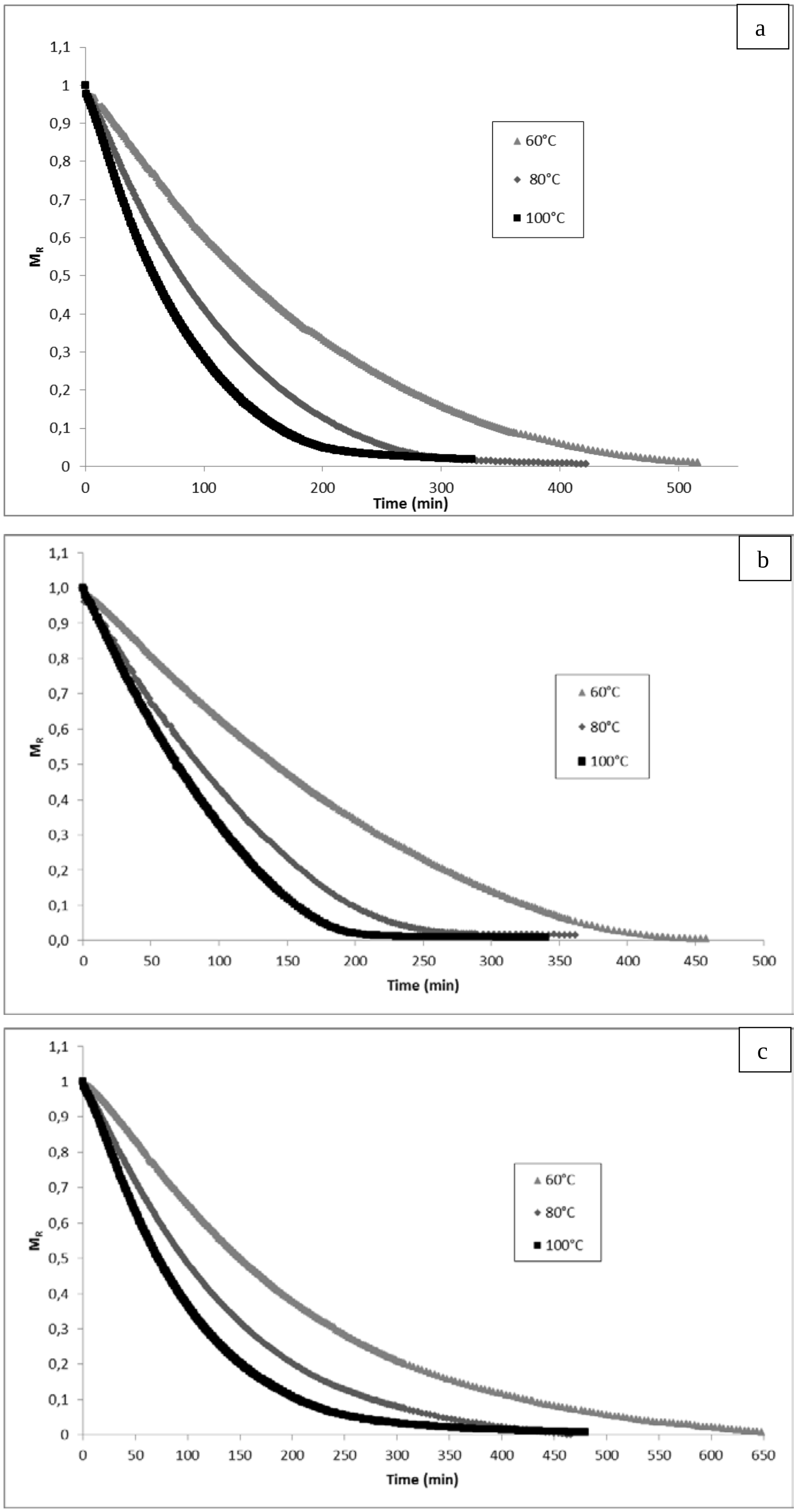

Fig1 Experimental moisture ratio (M_R) as a function of drying time for different temperatures forGS (a), OWH (b) and OP (c).

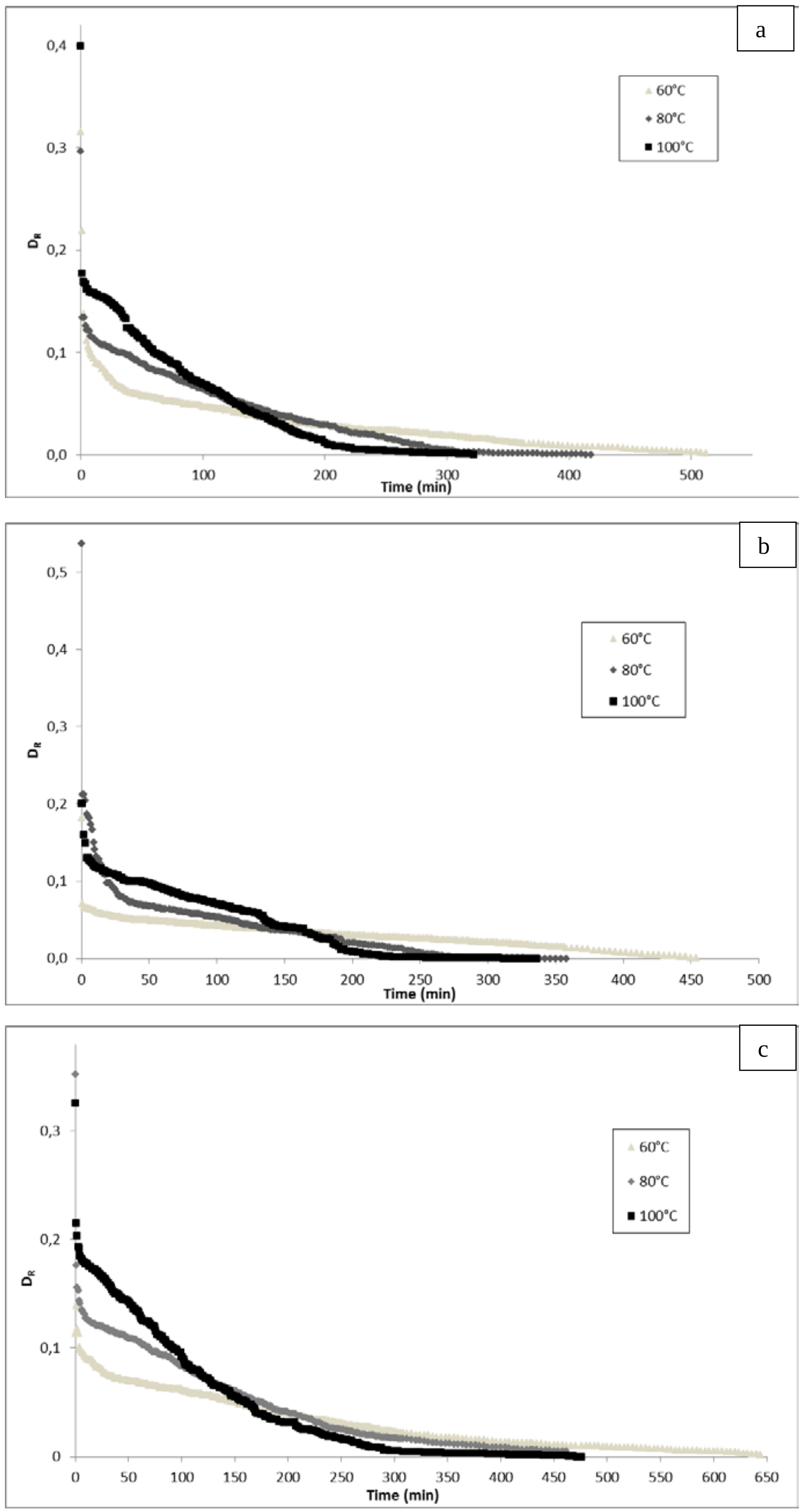

Fig2 Drying rate curves (D_R) at different temperatures for grape stalks (a), olive wet husk (b) and olive pits (c).

The parameters were calculated using the following expressions:

$$E_{MD} = \frac{100}{N}\sum_{i=1}^{N}\frac{\left|M_{R,ex,i} - M_{R,pre,i}\right|}{M_{R,ex,i}} \quad (12)$$

$$E_{RMS} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(M_{R,ex,i} - M_{R,pre,i}\right)\right]^{1/2} \quad (13)$$

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(M_{R,ex,i} - M_{R,pre,i}\right)^2}{N - z} \quad (14)$$

$$Residue = \sum_{i=1}^{N}\left(M_{R,ex,i} - M_{R,pre,i}\right) \quad (15)$$

Where $M_{R,ex,i}$ is the ith experimental dimensionless ratio of moisture; $M_{R,pre,i}$the ith predicted moisture dimensionless ratio; N is the number of observations; z is the number of constants [10].

The kinetic study is essential to describe the drying of waste in terms of M_R versus time (Fig.1). The detailed results of the statistical analysis for the six models are presented in Table 2. For all models, R^2 values greater than or equal to 0.97 were accepted. It can be seen that the logarithmic model and Page model had the highest values of R^2. On the other hand the model of Lewis and diffusional approach presented the lowest values of R^2.

The EMD (%) parameter indicates the difference between the experimental and predicted data; values less than10% are recommended for selecting good models [10].

The diffusional approachmodel showed the lowest values of EMD for all drying temperatures tested and all materials. M_R values estimated from diffusional approach and Lewis models tend to be higher in the early experimental stages and lower in the later stages of drying, for all temperatures. Furthermore both models showed less adjustment than Logarithmic and Page models.

ERMS analysis showed that Page and Logarithmic models give superior fitting to the experimental data in all cases. Additionally they provided the lowest values of χ^2.

Regarding to residues, Page and Logarithmic models at low temperatures (60 to 80 ° C), gave the lowest values. At high temperatures (100 ° C), the residues were close to zero but not the lowest.

According to the analysis of all statistical parameters, Page and Logarithmic models showed the best prediction for all materials and temperatures tested. Similar findings have been reported by Demir [22] for green olives.

Specifically, it can be said that Page is the best representative model of the drying behavior for olive pitsfor the three temperatures, for olive wet husk only at high temperatures (80 to 100 ° C) and forgrape stalks only at 100 ° C. The logarithmic model, turned out to be a good fit for low temperatures (60 to 80 ° C) in the case of the grape stalks and 60 ° C for olive wet husk. However, the difference in regression coefficients between the two models is very small. Further, the EMD parameter for Page model has the lowest value of all the models, for each of the materials and temperature values. For this reason, the Page model is selected for the studyof all materials and temperatures, considering in addition, the simplicity of its application.

In general, it can be concluded that there is a direct relationship between the coefficient k of the model and the drying air temperature. The values of the coefficients k are related to the wet effective diffusivity when the drying process takes place only during the period of decrease in speed [20]. Therefore, the coefficient k may be associated with the ease of moisture removing.

Material	Temperature(°C)	Model	Constants		R^2	Residue	$\chi 2$	E_{RMS}	$E_{MD\ (\%)}$
Grape stalkss	60	Lewis	K:	0,005497	0,9885	0,01	9,68E-04	3,11E-02	31,40
		Henderson y Pabis	a: K:	1,053 0,005863	0,9928	-1,57	6,11E-04	2,46E-02	25,52
		Page	K: N:	0,002105 1,187	0,9988	-0,94	1,04E-04	1,02E-02	11,47
		Two-termexponential	a1: K1: a2: K2:	0,5267 0,005863 0,5267 0,005863	0,9927	-1,57	6,15E-04	2,46E-02	25,52
		Logarithmic	a: K: c:	1,145 0,004569 -0,124242	0,9991	0,07	7,47E-05	8,60E-03	8,10
		Diffusionalapproach	a: K: b:	0,0002475 0,00557 0,9868	0,9884	0,00	-2,75E-01	3,11E-02	0,10
	80	Lewis	K:	0,009262	0,9910	-0,49	7,30E-04	2,70E-02	32,43
		Henderson y Pabis	a: K:	1,051 0,009778	0,9942	-1,37	4,71E-04	2,16E-02	26,58
		Page	K: N:	0,004268 1,163	0,9987	-0,82	1,02E-04	1,01E-02	12,69
		Two-termexponential	a1: K1: a2: K2:	0,5254 0,009775 0,5254 0,009771	0,9941	-1,39	4,75E-04	2,16E-02	26,64
		Logarithmic	a: K: c:	1,108 0,008026 -0,0867	0,9992	-0,04	6,10E-05	7,76E-03	9,80
		Diffusionalapproach	a: K: b:	0,01364 0,009262 1	0,9909	-0,49	-2,90E-01	1,19E+01	0,07
	100	Lewis	K:	0,01269	0,9949	-0,37	4,01E-04	2,00E-02	16,35
		Henderson y Pabis	a: K:	1,045 0,01327	0,9969	-0,89	2,41E-04	1,55E-02	12,34
		Page	K: N:	0,007152 1,127	0,9995	-0,27	4,11E-05	6,39E-03	7,10
		Two-termexponential	a1: K1: a2: K2:	0,3304 0,01327 0,7142 0,01327	0,9969	-0,48	1,59E-04	1,55E-02	12,33
		Logarithmic	a: K: c:	1,059 0,01225 -0,0295	0,9982	0,04	1,39E-04	1,17E-02	14,71
		Diffusionalapproach	a: K: b:	5,096 0,008651 0,9123	0,9984	0,52	1,29E-04	1,13E-02	15,06
	60	Lewis	K:	0,005356	0,9734	0,37	2,29E-03	4,78E-02	77,75
		Henderson y Pabis	a: K:	0,005855 0,005855	0,9820	-2,09	1,55E-03	3,93E-02	65,15
		Page	K: N:	0,001177 1,295	0,9960	-1,58	3,42E-04	1,84E-02	31,40
		Two-termexponential	a1: K1: a2: K2:	0,334483 0,005855 0,739858 0,005855	0,9820	-2,13	1,56E-03	3,93E-02	65,17
		Logarithmic	a: K: c:	1,32 0,003571 -0,3	0,9988	0,11	9,94E-05	9,92E-03	22,67
		Diffusionalapproach	a: K: b:	5,096 0,008651 0,9123	0,9984	69,11	6,64E-02	2,56E-01	76,83

Olive wethusk	80	Lewis	K:	0,009144	0,9791	-0,83	1,96E-03	4,42E-02	61,50
		Henderson y Pabis	a:	1,065	0,9841	-2,06	1,49E-03	3,84E-02	51,25
			K:	0,009811					
		Page	K:	0,002548	0,9959	-1,59	3,86E-04	1,96E-02	19,66
			N:	1,27					
		Two-termexponential	a1:	0,5321	0,9839	-2,07	1,50E-03	3,84E-02	51,43
			K1:	0,009799					
			a2:	0,5321					
			K2:	0,0098					
		Logarithmic	a:	1,153	0,9944	-0,03	5,26E-04	2,28E-02	33,30
			K:	0,007508					
			c:	-0,1257					
		Diffusionalapproach	a:	0,1842	0,9789	-0,84	-5,61E-01	4,42E-02	0,20
			K:	0,009143					
			b:	1					
	100	Lewis	K:	0,01149	0,9756	-0,91	2,32E-03	4,80E-02	104,22
		Henderson y Pabis	a:	1,089	0,9834	-2,23	1,58E-03	3,95E-02	0,16
			K:	0,01256					
		Page	K:	0,002672	0,9964	-1,19	3,42E-04	1,84E-02	30,57
			N:	1,321					
		Two-termexponential	a1:	0,591191	0,9835	-2,25	1,59E-03	3,95E-02	83,12
			K1:	0,012557					
			a2:	0,497831					
			K2:	0,012557					
		Logarithmic	a:	1,144	0,9917	-0,02	7,90E-04	2,79E-02	69,48
			K:	0,0103					
			c:	-0,0872					
		Diffusionalapproach	a:	0,85559264	0,9756	-0,90	2,34E-03	4,80E-02	104,16
			K:	0,0114922					
			b:	1,00000321					
Olive pits	60	Lewis	K:	0,004747	0,9896	-3,20	4,62E-04	2,15E-02	25,42
		Henderson y Pabis	a:	1,068	0,9961	-1,56	1,84E-04	1,35E-02	0,02
			K:	0,005174					
		Page	K:	0,001707	0,9999	-0,16	9,12E-06	3,01E-03	4,23
			N:	1,196					
		Two-termexponential	a1:	0,5336	0,9960	-1,54	1,86E-04	1,36E-02	17,55
			K1:	0,005171					
			a2:	0,5336					
			K2:	0,005172					
		Logarithmic	a:	1,11	0,9986	-0,34	4,08E-05	6,36E-03	6,28
			K:	0,004526					
			c:	-0,06					
		Diffusionalapproach	a:	1	0,9896	-3,20	4,65E-04	2,15E-02	25,42
			K:	0,004747					
			b:	1					
	80	Lewis	K:	0,007527	0,9940	-0,10	4,98E-04	2,23E-02	46,92
		Henderson y Pabis	a:	1,049	0,9970	-1,14	2,52E-04	1,58E-02	37,88
			K:	0,007952					
		Page	K:	0,003747	0,9998	-0,19	1,43E-05	3,77E-03	16,89
			N:	1,143					
		Two-termexponential	a1:	0,5191	0,9969	-1,09	2,53E-04	1,58E-02	37,91
			K1:	0,00795					
			a2:	0,5291					
			K2:	0,007948					
		Logarithmic	a:	1,08	0,9991	0,04	7,46E-05	8,59E-03	15,47
			K:	0,007087					
			c:	-0,04962					
		Diffusionalapproach	a:	0,8519	0,9939	-0,10	5,02E-04	2,23E-02	46,91
			K:	0,007548					
			b:	0,9819					

	100	Lewis	K:	0,01014	0,9948	-0,07	4,32E-04	2,08E-02	14,73
		Henderson y Pabis	a: K:	1,056 0,01103599	0,9978	-0,73	1,67E-04	1,29E-02	8,71
		Page	K: N:	0,005215 1,142	0,9999	0,15	8,47E-06	2,90E-03	7,24
		Two-termexponential	a1: K1: a2: K2:	0,4990333 0,01075024 0,55690772 0,01075023	0,9989	-0,73	1,68E-04	1,29E-02	8,71
		Logarithmic	a: K: c:	1,064 0,01028 -0,01669	0,9984	0,06	1,26E-04	1,12E-02	18,76
		Diffusionalapproach	a: K: b:	0,02467 1 0,01014	0,9947	2,12	7,63E-04	2,75E-02	13,86

Table 2: Statistical data obtained from the selection of six drying models and the corresponding parameters estimated forgrape stalks,olive pits and olive wet huskwaste.

Wet effective diffusivity (Deff)

As mentioned previously, complete drying takes place in the period of descending speed and moisture transfer is controlled by internal diffusion. Also, it is known that the effective diffusivity of different materials varies with its surface temperature and moisture content. It has been accepted that the period of decreasing velocity can be expressed by Fick diffusion equation. Thus, the effective diffusivity for each temperature was calculated by plotting ln (M_R) versus time and D_{eff} is obtained from the slope of the line.

D_{eff} for the wastes is shown in Table 3. These values are generally within a range of 10^{-6} to 10^{-7} m^2s^{-1}. It can be seen that while there is a small increase with temperature, it is not very significant in the studied temperature range. In addition the results obtained in this study are consistent with those reported by other authors for different wastes (Table 4).

Material	Temperature (°C)	D_{eff}
Grape stalks	60	5,004E-06
	80	5,029E-06
	100	5,036E-06
Olive wethusk	60	4,090E-07
	80	4,109E-07
	100	4,126E-07
Olive pits	60	4,996E-06
	80	5,016E-06
	100	5,020E-06

Table3: Coefficient values for effective diffusivity for different drying air temperature.

Material	Effective diffusivity (m2/s)	Dryingconditions	Reference
Grape stalks	$5,00 \times 10^{-6}$ – $5,04 \times 10^{-6}$	Convectivedrying (60-100°C)	Presentwork
Olive wethusk	$4,09 \times 10^{-7}$ – $4,13 \times 10^{-7}$	Convectivedrying (60-100°C)	
Olive pits	$4,99 \times 10^{-6}$ – $5,02 \times 10^{-6}$	Convectivedrying (60-100°C)	
Olive pomace	$1,84 \times 10^{-7}$ – $3,94 \times 10^{-7}$	Convective drying (1,5m/s, 60-80°C)	[33]
Olive pomace	$0,68 \times 10^{-7}$ – $2,15 \times 10^{-7}$	Fluidized bed dryer (1 m/s,50-80°C)	[41]
Olive pits of olive wet husk	$3,98 \times 10^{-9}$ – $5,97 \times 10^{-8}$	Drying tunnel (1 m/s, 100 - 250°C)	[42]
Olive pits of olive pomace	$1,17 \times 10^{-7}$ – $2,92 \times 10^{-7}$	Convective drying (50 - 150°C, 0,683 m/s)	[43]
Grape pomace	$11,01 \times 10^{-9}$ – $26,05 \times 10^{-9}$	Infrareddryer(100 - 160°C)	[44]

Seed grape	$5,39 \times 10^{-10} - 2,09 \times 10^{-11}$	Infrareddryer(50 - 80°C)	[45]
Poplarsawdust	$9,38 \times 10^{-10} - 1,38 \times 10^{-9}$	Thermogravimetricmethod (60- 90°C)	[46]

Table 4: Effective diffusivity values of several wastes in different drying conditions.

CONCLUSION

Drying of the different agro-wastes (GS, OWH and OP) was studied. The results indicated that the moisture transferred during drying is controlled mainly by internal diffusion. Page and Logarithmic models showed the best fit for the kinetics of drying at different temperatures and for different materials, compared with the other semi-theoretical models tested. The difference in regression coefficients between the two models is very small, however, and considering its simplicity, Page model can be chosen for all cases.

The effect of drying air temperature was studies in the range of 60-100 ° C for GS, OWH and OP. D_{eff} and D_R increased both with the increasing of drying temperature, and consequently the drying time decreased. The D_{eff} value ranged from 5.10^{-6} m^2s^{-1} to $5,04.10^{-6}$ m^2s^{-1} for GS, from $4,09.10^{-7}$ m^2s^{-1} to $4,13.10^{-7}$ m^2s^{-1} for OWH and from $4,99.10^{-6}$ m^2s^{-1} to $5,02,10^{-6}$ m^2s^{-1} for OP. This suggests that at high temperatures the water diffusion phenomena into the material are significant and depend on the internal structure of the material.

The results of this work suggest that OP is the material having greater difficulty to be dried, preserving higher residual humidity, followed by the grape stalks and olive wet husk. Taking into account that the presence of water on the particle surface avoids a good interaction with the polymer matrices, it could be presupposed that,after a convenient drying process, the olive wet husk could have better adhesion to the polymer in the composite, followed by the olive stalks and olive pits.

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