

Determination of effective moisture diffusivity and thermodynamic properties variation of regional wastes under different atmospheres

Fernandez Anabel^a, Román Celia^a, Mazza Germán^b, Rodriguez Rosa^{a,*}

^a Instituto de Ingeniería Química - Facultad de Ingeniería (UNSJ), Argentina

^b Instituto de Investigación y Desarrollo en Ingeniería de Procesos, Biotecnología y Energías Alternativas PROBIEN (CONICET-UNCo), Argentina

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ABSTRACT

During the thermal process to transform lignocellulosic wastes in energy, the drying process is an important stage because it requires energy and decreases overall process yield. Considering this process, moisture diffusivity is an important factor that is considered essential to understand for design, analysis, and its optimization. In this work, this parameter was analyzed at non-isothermal condition and considering the process under inert and oxidative atmospheres. Lower diffusivities were obtained under low heating rates, due to the disfavoring the moisture diffusion in the particles. Higher effective diffusivity (D_{eff}) values were obtained when the drying is carried out under the atmosphere oxidative.

Moreover, the thermodynamic parameters and DTA curves were determined. ΔH values are positive in all cases, showing that the drying process is endothermic. ΔG are positive and ΔS negative, indicating that the process is non-spontaneous. DTA curves show that the drying process is endothermic, according with the calculated ΔH .

1. Introduction

The principal motive of the renewable energy sources use is due to reduce green-house gases emissions. Therefore, the use of this have been increasing in the world and it's more efficient as the investigation progresses. Many current energy policies stimulate research to increase the renewable energy sources utilization, in large part to help diminish environmental problems and improve the national energy security of countries dependent on the use of imported fossil fuels. Between renewable energy sources, biomass is currently one of the most popular options [1].

On the other hand, the agro-industry is one of the most important economic sectors in Argentina, it produces an important environmental impact due to the high quantities of generated wastes. In this country, approximately 140,000 t of peaches and plums are processed in the canning and jam industries, generating a solid biomass waste quantity of 79,800 tn/year. A quantity of marc and stalk equal to 51928.3 tn/year is generated by the wine industry. About 150,000 tn/year of olive oil is produced, generating 70,000 tn/year of olive pits. Finally, the wood industry produces approximately 7000 tn/year of sawdust [2].

A promising technology to transform these lignocellulosic wastes in energy are the thermochemical process. The most developed technologies are namely, pyrolysis, gasification, and combustion. During these processes, the biomass wastes drying is an important stage because it requires energy and decreases overall process yield. Several authors had analyzed pyrolysis and combustion processes and have used biomass dry base for the experimental research protocol and kinetic analysis [3–5]. However, it is important to consider the drying process in order to optimize an integrated process for energy recovery from agro-industrial solid waste, taking

* Corresponding author.

E-mail address: rrodri@unsj.edu.ar (R. Rosa).

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into account, principally, the pyrolysis (developed under inert atmosphere) and combustion (developed under oxidative atmosphere). Furthermore, drying process contributes to a cleaner production with a significant reduction in the cost of transport [6]. However, biomass is one of the most complex materials in natural form and the fundamental understanding of it drying has not been completely established [7]. The drying usually means moisture evaporation because simultaneous heat and mass transfers are produced [8].

Fernandez et al. [9], studied the non-isothermal drying kinetics of different biomass wastes, under inert and oxidative atmospheres, applying the Coats Redfern and Sharp methods. They concluded that the three-dimensional diffusion is the drying rate controlling step due to the best fitting for all experiments were showed by Jander's model. In the face of these results, the effective moisture diffusivity (D_{eff}) must be analyzed at non-isothermal condition and considering the process under inert and oxidative atmospheres, due to it is a significant parameter used to describe the drying mechanism, to optimize this process, to evaluate of the diffusive flow, to predicted of drying time and design the dehydrator [10]. Accurate simulation of different drying process also demands precise value of D_{eff} . This parameter varies due to numerous factors such as biomass properties and process parameters. The processing temperature, physical structure, moisture content and porosity influence the moisture distribution in the biomass [11].

In literature, several methods are presented to determine the D_{eff} such as, drying method [12], permeability method [13], sorption kinetics method [14], moisture profile method under non-isothermal condition, using thermogravimetric analysis (TGA) [15]. TGA to mass transfer mathematical modeling has a high level of drying process repeatability. Furthermore, TGA has a several advantages, such as precise measurement of temperature, time and weight. Li and Kobayashi [15] developed a non-isothermal (linearly increasing temperature) procedure (working with a heating rate constant) to determine the D_{eff} as a temperature function with the complex optimization method, using TGA data.

In this work, the TGA was used in order to determine the D_{eff} of different lignocellulosic wastes from regional agro-industry (plum and olive pits and sawdust) in non-isothermal condition, under inert and oxidative atmospheres. It is important to remark that the drying process is produced both during combustion and pyrolysis, however there are not studies about the diffusivity under inert atmosphere. Moreover, the changes of entropy (ΔS), enthalpy (ΔH) and free Gibbs energy (ΔG) into activated complex were calculated by DTG. These parameters permit to evaluate the drying process feasibility. On the other hand, differential thermal analysis (DTA) applied to drying was studied.

2. Materials and method

2.1. Materials

In Cuyo Region, Argentina, one of the most important economic activities is the agro-industry. The raw material used in this work was peach and plum pits from canneries and jam factories, olive pits from oil industry, marc and stalk from wineries and pine sawdust from sawmills.

The material was dried, ground, sieved and the resulting 0.10–0.21 mm size fraction was used for the thermogravimetric tests. ASAE Standard S319.3 was used to determine the size distribution of the ground samples [16]. The weight loss at 378 K, ash and organic matter content were conducted according to ASTM standards [17,18]. Table 1 shows the analysis results.

2.2. Method

Thermogravimetric, derivative thermogravimetric and differential thermal analysis curves (TG, DTG and DTA curves. Figs. 1 and 2) of the powdered samples of different studied wastes were obtained using a TGA-50 Shimadzu microbalance, under nitrogen and air atmospheres, heated from room temperature to 423 K. The experiments were performed at three different heating rates of 5, 10, and 15 K/min for each sample. To diminish the difference of heat and mass transfer, the weight of all samples was kept around 12 mg. The inert gas used was nitrogen with a flow rate of 100 mL/min. For the experiment under oxidative atmosphere, air was used; its flow rate was of 100 mL/min. A computer connected to the TGA automatically recorded the mass loss and temperature and then, processed the data. Each experiment was repeated three times, and the average values were used. The reproducibility of the experiments was acceptable.

Table 1

Results of proximate and ultimate analysis (dry basis, weight percentage). High heating value (HHV).

	Plum pits	Olive pits	Sawdust	Peach pits	Marc	Stalk
C (%)	48.95	52.79	44.71	53.01	52.91	46.14
H (%)	1.38	2.57	1.48	5.90	5.93	5.74
N (%)	0.99	1.39	4.20	2.32	5.41	6.37
S (%)	0.27	0.50	0.28	1.88	5.34	4.21
O (%)	48.41	42.75	49.33	36.89	30.41	37.54
Ash (%)	0.73	2.33	1.19	1.30	8.81	10.16
Organic matter (%)	77.86	77.25	80.90	79.10	68.60	55.84
Weight loss at 378 K (%)	15.55	15.87	11.06	13.90	21.98	23.07
HHV (MJ/kg)	5.86	4.55	6.85	5.70	8.38	7.70

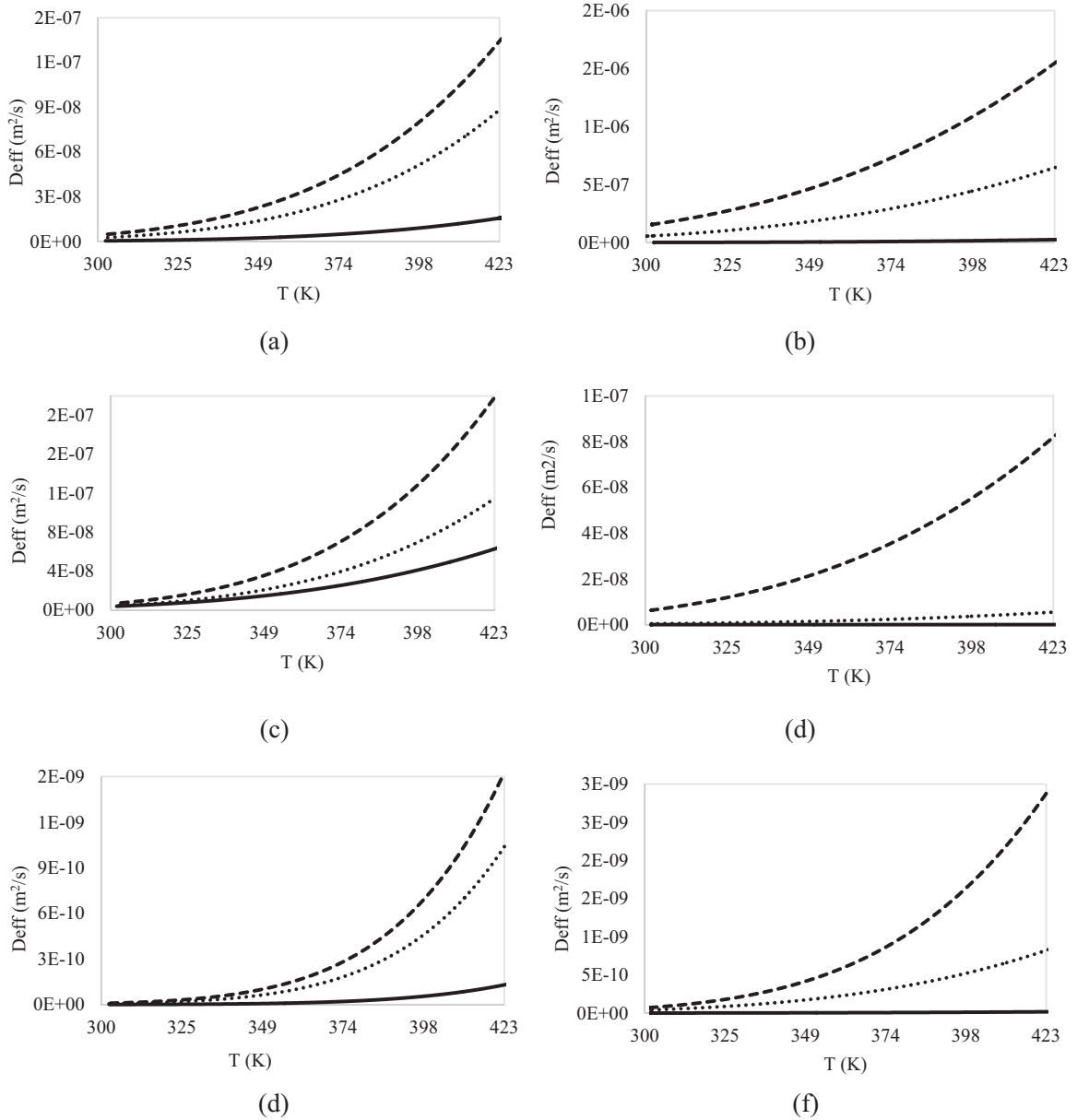


Fig. 1. Variation of D_{eff} with the temperature under oxidative atmosphere. (a) Olive pits, (b) peach pits. (c) plum pits, (d) stalk, (e) sawdust and (f) marc (– 15 K/min, . 10 K/min, – 5 K/min).

3. Effective diffusivity

Different mass transfer mode may occur at the same time in a system, considering the complex nature of lignocellulosic biomass. Nevertheless, at a certain time, one of them governs in the system. The diffusivity is usually utilized to describe drying kinetics and the driving force of diffusion is concentration gradient. It is accepted that the Fick's diffusion equation described this phenomenon and the mechanisms of moisture transport can be modeled mathematically with the following Eq.:

$$\frac{\partial MR}{\partial t} = \nabla[D_{eff}(\nabla MR)] \tag{1}$$

Where:

$$MR = \frac{(M_t - M_e)}{(M_0 - M_e)} \tag{2}$$

Where t is the time, MR is the moisture ratio of biomass; M_t is the moisture content at any time; M_0 is the initial moisture content and

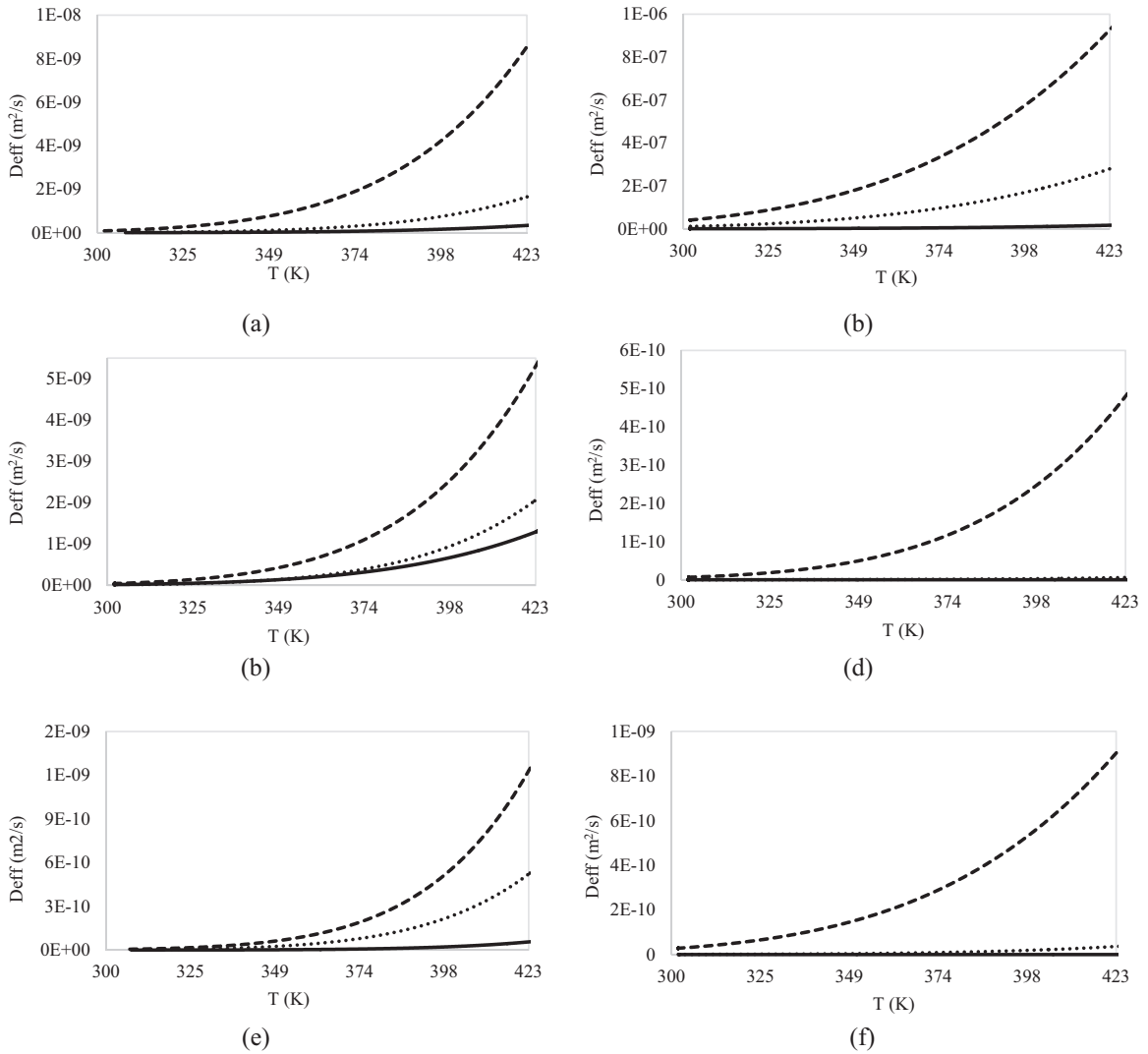


Fig. 2. Variation of D_{eff} with the temperature under inert atmosphere. (a) Olive pits, (b) peach pits. (c) plum pits, (d) stalk, (e) sawdust and (f) marc (-15 K/min , $.10\text{ K/min}$, -5 K/min).

M_e is the equilibrium moisture content. This equation provides an approximate method to present a comparison between different products in the aspect of moisture transfer due to it offers a description for diffusion coefficient in the drying process [19,20]. The solution of this equation is the following:

$$MR = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp\left(-\frac{(2n + 1)^2 \pi^2 D_{eff} t}{4L^2}\right) \tag{3}$$

Where n is a positive integer; t is the drying time and L is the half thickness of the sample. As indicated by previous studies [21]. The effective moisture determination using the Eq. (3) is appropriate if the initial moisture distribution is uniform and the shrinkage is negligible.

The diffusion depends on the temperature, and an Arrhenius type equation is used to calculate it:

$$D_{eff} = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

Where D_0 , E_a , R and T are the pre-exponential factor of the Arrhenius equation ($\text{m}^2\text{ s}^{-1}$), the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$), the perfect gas constant ($8.314\text{ J}\cdot\text{mol}^{-1}\text{ K}^{-1}$) and the temperature of the drying air (in K), respectively [22].

The Eqs. (1) and (4) describe the drying process under non-isothermal conditions, however, D_0 and E_a are the unknown parameters in Eq. (4). To solve these Eqs., it is necessary taking into account that the heating rate is constant and the temperature, at time t , can be expressed:

Table 2
Pre-exponential factor and activation energy obtained for all wastes.

Wastes	Atmosphere	β (K/min)	Kinetics parameters	
			A (1/s)	E (KJ/mol)
Sawdust	Oxidative	5	1123.62	49.91
		10	3982.61	47.01
		15	4125.24	45.76
	Inert	5	2365.10	50.56
		10	6289.84	51.09
		15	12362.72	50.44
Plum pits	Oxidative	5	423.21	24.42
		10	2562.28	28.69
		15	8253.56	30.56
	Inert	5	364.13	37.71
		10	4289.30	44.83
		15	5526.35	42.37
Olive pits	Oxidative	5	852.51	31.85
		10	3982.36	31.19
		15	4125.12	29.82
	Inert	5	364.84	42.51
		10	4289.37	45.63
		15	5526.05	30.67
Sawdust	Oxidative	5	1123.62	49.91
		10	3982.61	47.01
		15	4125.24	45.76
	Inert	5	2365.10	55.56
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		15	4125.12	29.82
	Inert	5	364.84	42.51
		10	4289.37	45.63
		15	5526.05	30.67

$$T = T_0 + \alpha t \tag{5}$$

Where T_0 is the initial temperature of the experiment and α is the heating rate.

Li and Kobayashi [15] rewritten the Eq. (4) in order to accelerate the convergence:

$$D_{\text{eff}} = \exp\left[\delta - \frac{E_a}{RT} \left(\frac{1}{T} - \beta\right)\right] \tag{6}$$

$$\delta = \ln(D_0) - \frac{E_a}{R} \beta \tag{7}$$

$$\beta = \frac{1}{t_\infty} \int_0^{t_\infty} \frac{dt}{T} = \frac{1}{\alpha t_\infty} \ln\left(\frac{T_0 + \alpha t_\infty}{T_0}\right) \tag{8}$$

Where δ is a dummy variable; β is the mean value of the reciprocal of temperature; t_∞ is the complete drying time. In this study, A (pre-exponential factor) and E_a were determined using the Jander’s model reported by Fernandez et al. [9] for stalk, marc and peach pits. Also, for the sawdust, plum and olive pits these parameters were obtained following the procedure proposed by these authors. Table 2 shows the obtained values of these parameters. D_0 was then calculated with them. The mathematical software, Matlab was used for this purpose.

4. Thermodynamic parameters calculation

The follow study was based on Transition State Theory (TST), which explains the reaction rates. The theory assumes a special type of chemical equilibrium (quasi-equilibrium) between reactants and activated transition state complexes. This theory was developed in 1935 by Henry Eyring [23,24].

TST is used primarily to understand qualitatively how chemical reactions take place. TST has been less successful in its original

goal of calculating absolute reaction rate constants because the calculation of absolute reaction rates requires precise knowledge of potential energy surfaces, but it has been successful in calculating the enthalpy of activation (ΔH), the entropy of activation (ΔS), and the Gibbs energy of activation (ΔG) for a particular reaction if its rate constant has been experimentally determined [25].

The thermodynamic properties, were calculated according the methodology proposed by Kim et al. [26]:

$$\Delta H = E_a - RT_m \tag{9}$$

$$\Delta G = E_a + RT_m \ln \left(\frac{k_b T_m}{h^* A} \right) \tag{10}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \tag{11}$$

Where K_b is Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$); h is Plank constant (equal to $6.63 \times 10^{-34} \text{ J s}$) and T_m is DTG peak temperature (temperature of the maximum mass loss rate), A is the pre-exponential factor.

5. Results and discussion

5.1. Effective moisture diffusivity

During the drying, an apparent water loss peaks was observed at 332.72–365.16 K and 331.89 K – 369.15 K under inert and oxidative atmospheres, respectively, for all solid wastes.

According to Chen et al. [27] the moisture evaporation can separate to growing rate stage and dropping rate stage. Due to the variation in water loss rate is associated to the bonding force between water and solid, water can be classified into free water (adhering to the grain surface of materials and existing in pores of diameters greater than 10 – 5 cm) and bound water (coagulated, adsorbed, or penetrating into the pores and cells inside the grains of biomass). The first vapours before the temperature reaching 363 K and the second, would be completely separated only at the temperature above 393 K.

The De_{eff} values were calculated using drying data reported in Table 2. Figs. 1 and 2 show the De_{eff} variation with the temperature (under inert and oxidative atmospheres) at different heating rate and the Table 3 show the maximum and minimum value for the studied wastes.

When the drying is carried out under oxidative atmosphere, the De_{eff} values are higher than the drying is performed under inert atmosphere. This can be due to the presence of oxygen produce oxidation reactions during the drying stage, generating the release of light volatile compounds [28]. Therefore, it is important to note that, during dry under oxidative atmosphere, the carboxyl and carbonyl groups increase gradually with the oxidation temperature up to 423 K. This phenomenon does not occur with drying under a nitrogen atmosphere [29].

Increasing the heating rate, the values De_{eff} values and its variation with the temperature also increase. According to Li and Kobayashi [15], when a the biomass is exposed to the environment of higher temperature, the moisture evaporation rate at the surface layer is higher than the moisture migration rate from the internal to the surface so that a crust is formed due to the transition. This phenomenon produces a drying due to the hardcover leads to higher resistance to moisture diffusion. However, in this case, the lignocellulosic wastes present a different behavior due to the particle size studied is very small compared to the bean size, preventing

Table 3
 De_{eff} ($\text{m}^2 \text{ s}^{-1}$) values maximum and minimum for all wastes.

Wastes	β (K/min)	Oxidative atmosphere		Inert atmosphere	
		Min	Max	Min	Max
Plum pits	5	4.01×10^{-09}	6.23×10^{-08}	1.86×10^{-11}	1.25×10^{-09}
	10	4.67×10^{-09}	1.12×10^{-07}	2.09×10^{-11}	1.99×10^{-09}
	15	7.36×10^{-09}	2.18×10^{-07}	4.52×10^{-11}	5.24×10^{-09}
Olive pits	5	4.41×10^{-10}	1.58×10^{-08}	3.91×10^{-12}	3.44×10^{-10}
	10	2.74×10^{-10}	8.88×10^{-08}	1.55×10^{-11}	1.69×10^{-09}
	15	4.86×10^{-09}	1.33×10^{-07}	8.80×10^{-11}	8.72×10^{-09}
Sawdust	5	4.87×10^{-13}	1.32×10^{-10}	1.57×10^{-13}	5.77×10^{-11}
	10	5.35×10^{-12}	9.95×10^{-10}	3.36×10^{-12}	1.32×10^{-10}
	15	9.31×10^{-12}	1.49×10^{-09}	5.79×10^{-12}	1.20×10^{-09}
Peach pits	5	1.25×10^{-09}	2.61×10^{-08}	3.90×10^{-10}	1.67×10^{-08}
	10	5.79×10^{-08}	6.35×10^{-07}	1.07×10^{-08}	2.77×10^{-07}
	15	1.56×10^{-07}	1.54×10^{-06}	4.10×10^{-08}	9.22×10^{-07}
Marc	5	1.01×10^{-12}	1.77×10^{-11}	8.64×10^{-16}	4.67×10^{-14}
	10	4.23×10^{-11}	8.16×10^{-10}	4.69×10^{-13}	3.58×10^{-11}
	15	7.32×10^{-12}	2.82×10^{-09}	2.79×10^{-11}	2.07×10^{-09}
Stalk	5	6.67×10^{-16}	4.20×10^{-14}	1.60×10^{-17}	1.67×10^{-15}
	10	4.64×10^{-10}	5.55×10^{-09}	4.99×10^{-14}	5.99×10^{-12}
	15	6.33×10^{-09}	8.29×10^{-08}	6.54×10^{-12}	1.72×10^{-09}

Table 4
Variations of enthalpy, free Gibbs energy and entropy obtained for all wastes.

Wastes	Atmosphere	β (K/min)	DTG peak temperature (K)	Thermodynamic parameters		
				ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (KJ/mol K)
Sawdust	Oxidative	5	335.23	47.12	112.76	-0.20
		10	345.32	44.14	108.20	-0.19
		15	352.02	42.83	108.09	-0.19
	Inert	5	336.96	47.76	111.66	-0.19
		10	343.7	48.23	110.68	-0.18
		15	351.53	47.52	109.47	-0.18
Plum pits	Oxidative	5	340.16	21.59	90.99	-0.20
		10	351.95	25.76	92.40	-0.19
		15	364.48	27.53	93.10	-0.18
	Inert	5	333.65	34.94	103.37	-0.21
		10	355.07	41.88	107.61	-0.19
		15	358.34	39.39	105.00	-0.18
Olive pits	Oxidative	5	331.89	29.09	94.81	-0.20
		10	343.33	28.34	92.01	-0.19
		15	360.07	26.83	93.65	-0.19
	Inert	5	332.72	39.74	107.98	-0.21
		10	347.2	42.74	106.96	-0.18
		15	356.07	27.71	92.89	-0.18
Peach pits	Oxidative	5	342.55	44.20	114.53	-0.21
		10	346.36	18.51	84.97	-0.19
		15	369.15	17.24	86.52	-0.19
	Inert	5	340.66	30.56	96.67	-0.19
		10	345.82	26.04	88.72	-0.18
		15	363.11	24.68	88.05	-0.17
Marc	Oxidative	5	337.63	32.54	101.64	-0.20
		10	345.85	23.43	92.00	-0.20
		15	364.84	35.54	100.83	-0.18
	Inert	5	345.12	22.45	96.99	-0.22
		10	362.43	39.50	104.28	-0.18
		15	365.16	27.77	98.78	-0.19
Stalk	Oxidative	5	350.21	33.65	103.82	-0.20
		10	362.64	20.11	90.78	-0.19
		15	365.17	19.68	86.83	-0.18
	Inert	5	342.43	38.18	108.42	-0.21
		10	363.48	39.39	104.53	-0.18
		15	369.15	35.15	99.81	-0.18

the hard surface formation and favoring the moisture diffusion when the heating rate increases. Consequently, high heating rate is suitable for the non-isothermal procedure. These results are similar to those obtained by Chen et al. [30]. The highest De_{eff} values are predicted when the olive pits are dried under oxidative atmosphere and, the lowest values are calculated when the sawdust is dried under inert atmosphere.

5.2. Thermodynamic properties and DTA curves

The thermodynamic parameters, ΔH , ΔG and ΔS , were calculated at the temperature of the maximum weight loss rate is produced (Table 4) [26]. The results are showed in Table 4.

The Gibbs free energy, also known as free enthalpy, a function extensive, expresses the equilibrium condition and spontaneity of a process (at constant pressure and temperature). The obtained ΔG values are positives in all cases, showing the total system energy growth at the activated complex formation. It is a widespread analysis of the heat flow and disorder change. A higher ΔG value shows lower process favorability. It is important to consider that the water is present in a solid as free and bound water, at a comparatively low drying temperature, the removed moisture is usually considered to be the free water, however to higher temperatures the removed moisture is the bound water. So, higher ΔG values indicate the bound water presence in the wastes.

Enthalpy is a measurement of energy in a thermodynamic system. Enthalpy is defined as a state function and it depends only on the prevailing equilibrium state identified by the internal energy, pressure, and volume. ΔH , under such conditions, is the heat absorbed (or released) by the material through a chemical reaction or by external heat transfer. Considering that the obtained ΔH values are positives in all cases, these values means that an external energy source is necessary to increase the biomass energy level to their transition state, showing that the drying process were all endothermic. [31,32].

All obtained ΔS values related with the formation of complex activated species are negative showed the drying process was developed from disordered-state to ordered-state. When $\Delta S < 0$, the process can be characterized as “slow”, the material has just passed through some kind of physical or chemical aging process, bringing it to a state near its own thermodynamic equilibrium. In this situation, the material shows little reactivity [33].

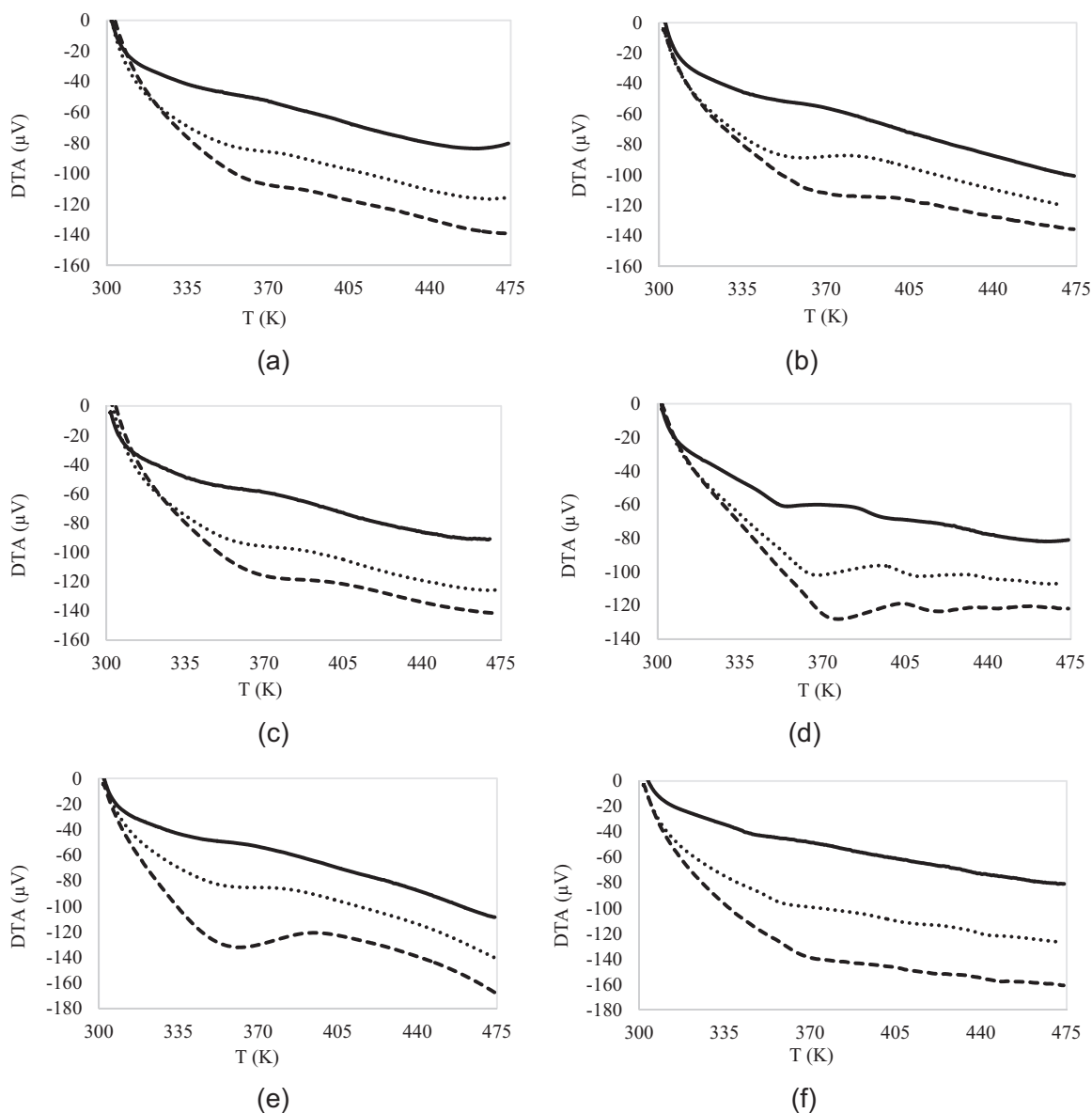


Fig. 3. DTA curves under oxidative atmosphere. (a) Olive pits, (b) peach pits. (c) plum pits, (d) stalk, (e) sawdust and (f) marc (-15 K/min, $.10$ K/min, -5 K/min).

DTA curves show that the drying process is endothermic (Figs. 3 and 4). The heating rate also has an obvious influence on DTA of biomass particles. When the heating rate increases, the temperature of the biomass particle drops more abruptly, showing greater energy absorption. It is due to that this phenomenon is mainly affected by heat transfer. So, it would take a longer time of the heat conduction from the particle external to the interior as the heating rate increased [34].

When the heating rate is equal to 10 and 15 K/min, under both atmospheres, for the sawdust, about 370 K, the sample temperature falls, then it rises to later fall to lower values. This behavior is not notable during drying process of plum and olive pits.

Considering the atmosphere influence on the DTA curves of the drying process, there is not notable effect on the temperature of the biomass particle. This is related to the heat transfer limitation. At higher heating rates, this limitation is higher because stronger thermal shock is being acquired over a short time and there is greater temperature gradient between the inside and outside; this aspect does not favor the release of volatile matter [35].

Taking into account the nature of lignocellulosic wastes, the sawdust shows the maximum temperature drop under inert atmosphere.

The calculated ΔH values do not reveal a notable influence of the atmosphere under which the drying process is carried out, excepting the plum pits, coinciding with the DTA curves conclusions.

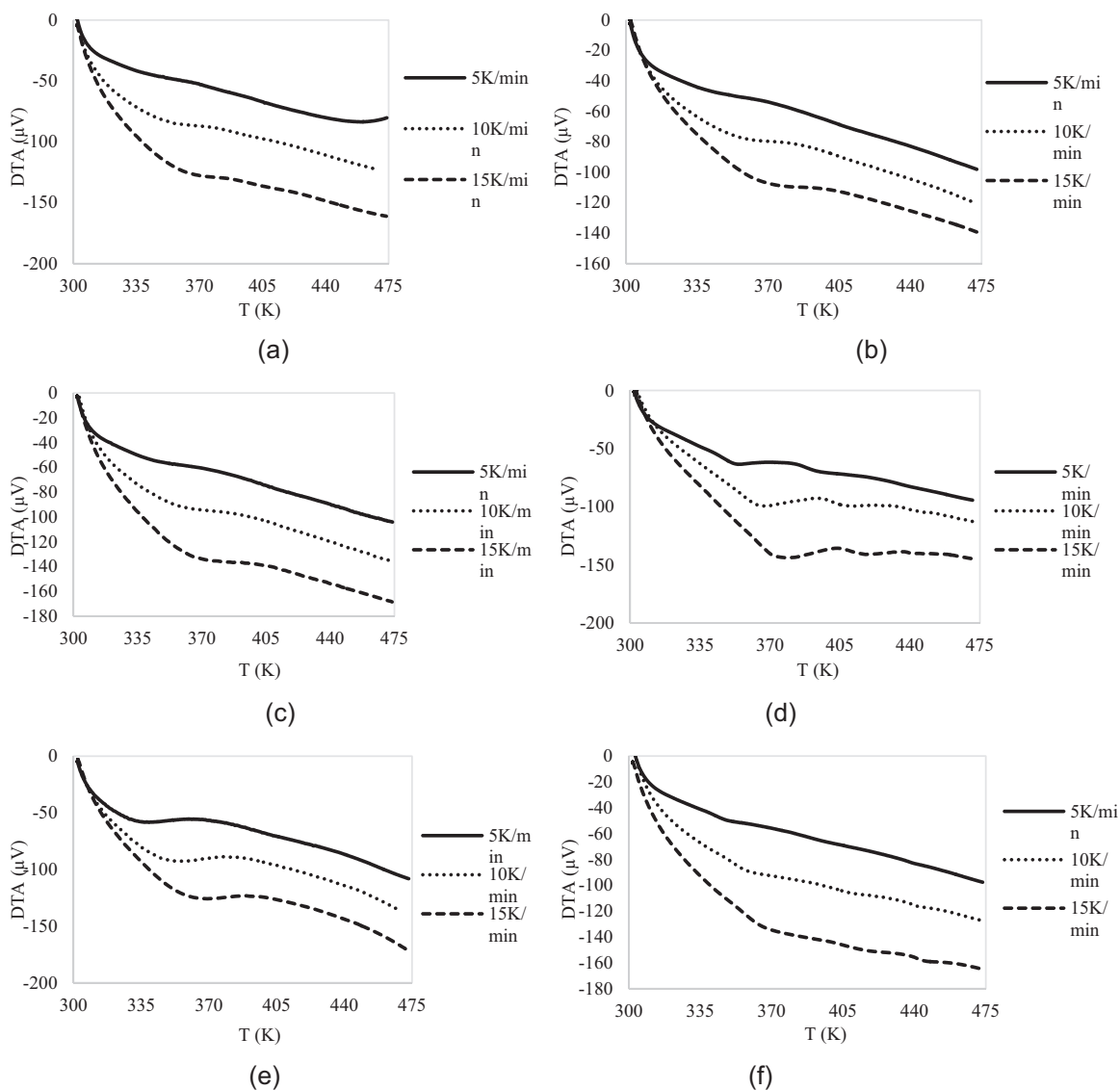


Fig. 4. DTA curves under inert atmosphere. (a) Olive pits, (b) peach pits. (c) plum pits, (d) stalk, (e) sawdust and (f) marc (– 15 K/min, . 10 K/min, – 5 K/min).

6. Conclusions

Moisture diffusivity of different lignocellulosic wastes was determined using TGA, applying a non-isothermal technique. Lower diffusivities were obtained under low heating rates, disfavoring the moisture diffusion. Due to the particle size studied is very small, the hard surface is not formed and the high heating rate favors the moisture diffusion.

Under oxidative atmosphere, the $Deff$ values increase with respect to the obtained values under inert atmosphere. The presence of oxygen could produce oxidation reactions during the drying stage, generating the release of light volatile compounds.

The thermodynamic parameters values show that the lignocellulosic wastes drying under oxidative and inert atmospheres have a low favourability.

DTA curves show that the drying process is endothermic. With the heating rate augmentation, the biomass particle temperature drops more abruptly, showing greater energy absorption. This limitation is higher because stronger thermal shock is being acquired over a short time and there is greater temperature gradient between the inside and outside. There is not notable atmosphere influence on the DTA curves of the drying process.

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