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

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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 (*Deff*) 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

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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 (*Deff*) 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 *Deff*. 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 *Deff* 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 *Deff* as a temperature function with the complex optimization method, using TGA data.

In this work, the TGA was used in order to determine the *Deff* 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
Weigth 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