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## Pyrolysis kinetics of regional agro-industrial wastes using isoconversional methods

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### ABSTRACT

The thermochemical conversion, under inert atmosphere, at high heating rate of agro-industrial wastes was studied using thermogravimetric analysis. Two reaction mechanisms were supposed: (a) The thermal solid decomposition is carried out through a single reaction; or (b) this occurs through several independent parallel reactions based on its main components. Kinetic isoconversional methods were applied to both proposed mechanisms. The best fit was obtained for the single-reaction models. Nevertheless, to study the influence of pseudocomponent decomposition in the global process, the kinetic behavior of each of them was analyzed. The R2 and D3 models represent the thermal decomposition of biomass wastes and their pseudocomponents. The first model supposes that the reactions tend at first order, and the second assumes that the diffusion is the predominant phenomenon. In all cases, the model with the best fit for the cellulose decomposition is the same for the single global reaction model. The enthalpy variations are positive, indicating that the reactions are endothermic. The entropy variations have negative values, signifying that these processes are slow. The Gibbs free energy variations exhibited positive values, revealing that the total system energy increased at the approach of the reagents and the formation of the activated complex.

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### KEYWORDS

Thermochemical conversion; regional agro-industrial wastes; main components; kinetics; thermodynamic analysis

### Introduction

Biomass is known globally as a renewable and sustainable energy resource; it is considered a substitute for depleting fossil fuels [1]. On the other hand, agro-industry is very important in the Argentine economy, and generates very significant quantities of lignocellulosic wastes [2]. So, considering the wine industry, about 51,928 t year<sup>-1</sup> of stalk and grape are generated in just the Region of Cuyo, Argentina; and the peach canning and wood industries produce about 37,800 and 1,677,411 t year<sup>-1</sup>, respectively [3,4]. These wastes can be used as a source of energy due to their carbon content, transforming them into solid, liquid and gaseous products, utilizing different routes as thermal processes. The most commonly used of these processes are combustion, gasification and pyrolysis [5]. The quality and quantity of the obtained bioenergy depend on different characteristics, among which may be mentioned the chemical composition of the original biomass, and the reaction conditions.

Pyrolysis is an environmentally friendly method, and it is useful to transform biomass wastes into three kinds of products: char, liquid, and gas. It is also the first step in combustion and gasification reactions. Several researchers have investigated biomass pyrolysis, taking into account that it is composed of three main constituents: hemicellulose, cellulose and lignin. Therefore, Cai

et al. [6] studied the slow pyrolysis kinetics considering a three-parallel-distribution activation energy model (DAEM)-reaction model, concluding that the model is mainly influenced by the frequency factor and the mean value of the activation distribution for cellulose decomposition. Li et al. [7] researched the thermal decomposition at high heating rates of corn straw samples using thermogravimetric analysis (TG). These authors used two different three-pseudocomponent models to simulate the corn straw pyrolysis. Zhou et al. [8] studied the thermal behavior of five fruit vegetable biomasses using TG. They applied the thermogravimetric curve overlap ratio to evaluate the simulation of biomass by hemicellulose, cellulose and lignin. Their obtained results indicated that fruit vegetable biomass contained more hemicellulose and less lignin than wood biomass, and poplar wood contained the largest amount of cellulose. Pasangulapatie et al. [9] analyzed the effects of these biomass constituents on biomass thermal decomposition. These researchers considered the single-reaction model to describe the thermal decomposition and they applied the Arrhenius equation, solved using the multiple linear regression method.

There are several works about the kinetic behavior during thermal decomposition based on the main composition of the biomass with different points of view; however, this aspect has not yet been studied in

Argentina. It is significant to take into account the large quantities of the abovementioned lignocellulosic wastes produced in this country, the variability of their composition and the possibility of their use as source of bioenergy.

Taking into account these aspects, this paper analyzes the thermochemical conversion of four different regional agro-industrial wastes, during the pyrolytic stage at high heating rate, including the determination of thermodynamic parameters for non-isothermal analyses. This study was carried out using the Standard Test Method for Compositional Analysis by thermogravimetry (American Society of Testing Materials (ASTM) International standard-Designation: E1131-03).

Two kinetic models were proposed in order to describe the thermal decomposition mechanism: (a) The thermal solid decomposition is carried out through a single reaction; or (b) this occurs through several independent parallel reactions based on its main components. Kinetic isoconversional models were used to fit the experimental results of TG. The values of apparent activation energy ( $E_a$ ) and preexponential factor ( $A$ ) in the Arrhenius equation, as well as the changes of entropy ( $\Delta S$ ), enthalpy ( $\Delta H$ ) and free Gibbs energy ( $\Delta G$ ), were calculated.

## Methods

### Biomass characterization

The raw materials used in this work were: peach pits from canneries and jam factories, skin of the grape: marc and stalk from wineries, and sawdust from wood industry, all of them located in the South and West regions, Argentina. This material was ground and sieved, and the resulting 0.01–0.02-cm size fraction was used for the thermogravimetric tests. American Society of Agricultural Engineers (ASAE) Standard S319.3 was used to determine the size distribution of the grounds. The mass loss at 378 K, ash and organic matter content were determined according to ASTM standards (ASTM D3173-87, ASTM D3172-89 (02)). Elemental analysis of the samples was performed using a EuroEA3000 elemental analyzer. The results of elemental and proximate analysis are shown in Table 1.

In order to calculate the high heating value, the correlation proposed by Channiwala and Parikh [10] was used (Table 1):

$$\begin{aligned} \text{HHV [MJ / Kg]} = & 0.3491C + 1.1783H + 0.1005S \\ & - 0.1034O - 0.0151N - 0.0211A \end{aligned} \quad (1)$$

where  $C$ ,  $H$ ,  $S$ ,  $O$ ,  $N$  and  $A$  are the contents of carbon, hydrogen, sulfur, oxygen, nitrogen and ash in the biomass, respectively.

The lignin, cellulose and hemicellulose contents of different studied wastes were determined according to

**Table 1.** Results of proximate analysis, ultimate analysis. Contents of lignin, cellulose and hemicellulose determined by ASTM standard methods.

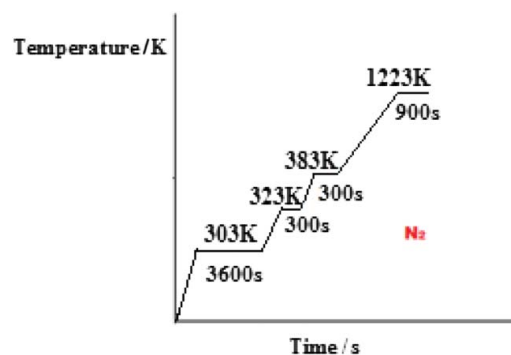
	Peach pit	Marc	Stalk	Sawdust
Volatile matter (db%)	84.8	69.21	66.77	86.31
Ash (db %)	1.30	8.81	10.16	1.90
Fixed Carbon (db %)	13.90	21.98	23.07	11.79
Moisture (tw %)	5.70	8.38	7.70	5.30
C (db %)	53.01	52.91	46.14	54.71
H (db %)	5.90	5.93	5.74	5.80
O* (db %)	36.89	30.41	37.54	33.01
N (%)	2.32	5.41	6.37	4.20
S (%)	1.88	5.34	4.21	2.28
$C_nH_mO_pN_qS_r$				
n	1.00	1.00	1.00	1.00
m	1.34	1.34	1.49	1.14
p	0.52	0.43	0.61	0.47
q	0.04	0.09	0.12	0.17
r	0.01	0.04	0.03	0.02
Hemicellulose (%)	21.02	4.96	5.78	19.99
Cellulose (%)	31.58	15.31	16.02	42.96
Lignin (%)	27.53	37.97	30.79	26.8
HHV (MJ kg <sup>-1</sup> )	21.77	22.58	19.10	22.65

\*By difference.

ASTM standards (ASTM D1106-56, ASTM D1103-60 and ASTM D1103-60, respectively). The hemicellulose content was determined by the difference between holo-cellulose and cellulose contents. These analyses were carried out by the laboratory of the Chemistry Section of Agro Products (EEAOC-Estación Experimental Agro-industrial Obispo Colombes) –Tucumán, Argentina. The analysis results are shown in Table 1.

### Thermogravimetric analysis

Thermogravimetric analysis was performed using a thermal analyzer DTG-60 simultaneous brand DTA-TG SHIMADZU; 40 mg of biomass wastes were evaluated. The experiments were carried out following the ASTM International Standard –Designation: E1131-03 Standard Test Method for Compositional Analysis by thermogravimetry. This test method is an empirical technique in which the mass of a substance, heated at a controlled rate in an appropriate environment, is recorded as a function of time or temperature. Mass loss over specific temperature ranges and in a specific



**Figure 1.** Temperature program used in thermogravimetric analysis (TG).

atmosphere provides a compositional analysis of the substance. Figure 1 shows the different stages of the methodology used. The flow rate of nitrogen was  $0.83 \text{ cm}^3 \text{ s}^{-1}$ .

Before starting the methodology, purging with nitrogen for 3600 s at constant temperature of 303 K is carried out in order to remove all traces of oxygen (Step 1). The method involves heating at  $5.38 \text{ K s}^{-1}$  to 323 K and an isothermal period at this temperature for 300 s. Subsequently, the sample is heated to 383 K, at the same heating rate, and held for 300 s. The temperature of the sample is raised to 1223 K at a heating rate of  $6.05 \text{ K s}^{-1}$ . Then, an isothermal period at this temperature is maintained; its duration was 900 s. All of these steps are carried out under a nitrogen atmosphere. After the mass remains constant, the system is closed. In this way, the TG and DTG curves (thermogravimetric and derivative thermogravimetric curves) are obtained for each studied agro-industrial waste. For each studied agro-industrial waste, three replications were performed. The reproducibility of the experiments was acceptable. The study was carried out working with the average values of these replications.

### Biomass waste decomposition during the pyrolytic stage

During the pyrolytic stage (between 383 and 1225 K) the cellulose, hemicellulose and lignin are decomposed. In order to describe the decomposition of each one, deconvolution of the DTG curves was carried out. Also from these peaks, separated by deconvolution, the contents of lignin, cellulose and hemicellulose were calculated. The DTG curve deconvolutions were carried out using the Origin 8.6 software. Figures 2 and 3 show the results of the deconvolution for stalk and sawdust.

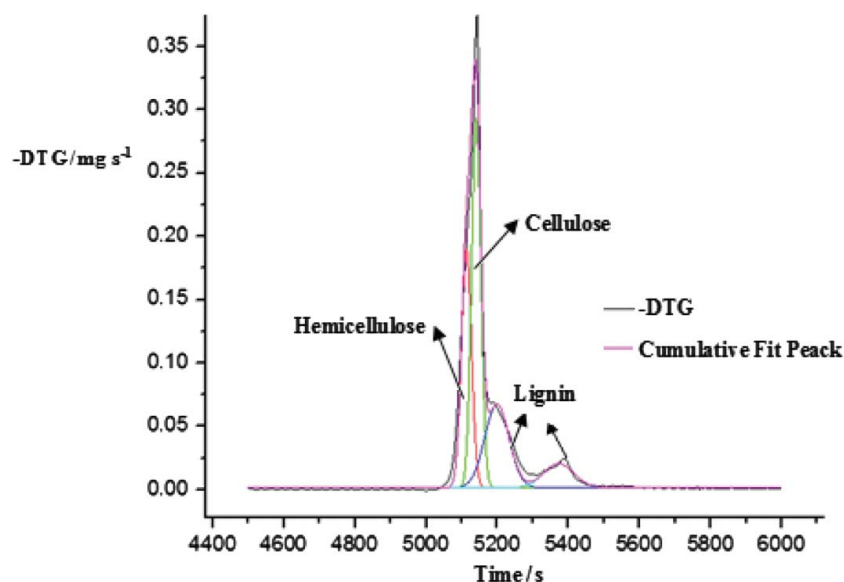


Figure 2. Deconvolution of the derivative thermo-gravimetric (DTG) curve corresponding to degradation of stalk.

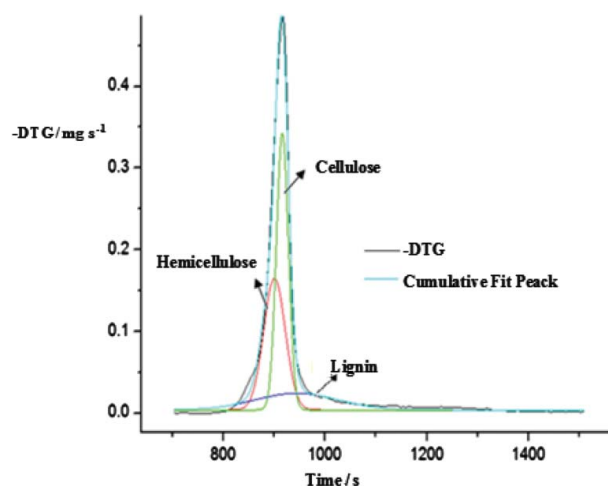


Figure 3. Deconvolution of the DTG curve corresponding to degradation of sawdust.

### Kinetic study

In order to determine the kinetic parameters, two different assumptions were analyzed:

1. The solid decomposition is carried out through a single reaction.
2. The agro-industrial wastes are composed of three pseudocomponents. They are decomposed by several independent parallel reactions.

#### Single reaction kinetic

The kinetic of solid biomass decomposition can be expressed by the following equation:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (2)$$

where  $t$ ,  $\alpha$ ,  $d\alpha/dt$ ,  $f(\alpha)$  and  $K$  are time, conversion degree or extent of reaction, the process rate, conversion function, and rate constant, respectively. The conversion function represents the reaction model used

and depends on the controlling mechanism. The extent of reaction,  $\alpha$ , can be defined as the mass fraction of biomass substrate that has decomposed, and can be expressed as shown below:

$$\alpha = \frac{w_0 - w}{w_0 - w_f} \quad (3)$$

where  $w$ ,  $w_0$  and  $w_f$  are the mass present at any time  $t$ , the initial mass and the final mass of solids remaining after the reaction, respectively.

$K$  is the temperature function. The temperature dependence of the rate constant  $K$  for the process is described by the Arrhenius equation:

$$K(T) = A \exp\left(-\frac{Ea}{RT}\right) \quad (4)$$

where  $A$  is the pre-exponential factor,  $T$  is the absolute temperature,  $R$  is the universal gas constant and  $Ea$  is the apparent activation energy of the process.

If the temperature of the sample is changed by a controlled and constant heating rate,  $\beta = dT/dt$ , the variation in the conversion can be analyzed as a temperature function, the temperature being dependent on the heating time.

Relating Equations (2) and (4), the following expression is obtained:

$$\beta \frac{d\alpha}{dT} = A e^{-E/RT} f(\alpha) \quad (5)$$

Integrating Equation (5), the next expression is obtained:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_\alpha} e^{-E/RT} dT \quad (6)$$

Equation (6) can be integrated when the right-hand side is expanded into an asymptotic series and higher order terms are ignored:

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{Ea\beta} \left[ \frac{AEa}{Ea\beta} - \left(1 - \frac{2RT}{Ea}\right) \right] - \frac{Ea}{RT} \quad (7)$$

where  $g(\alpha)$  is an integral form of  $f(\alpha)$ . The most

common forms of  $f(\alpha)$  and the corresponding  $g(\alpha)$  are listed in Table 2. The term  $2RT/Ea$  can be neglected because it is much less than 1 in the thermal decomposition of lignocellulosic materials. Plotting  $\ln g(\alpha)/T^2$  versus  $1/T$ ,  $Ea$  and  $A$  can be obtained from the slope and intercept, respectively.

### Several independent parallel reactions kinetic

The studied agro-industrial wastes are composed of three or four pseudo-components (hemicellulose, cellulose and lignin, or lignins 1 and 2, according to the deconvolution results), and they react independently. The kinetic of solid biomass decomposition can be expressed by the following equations:

$$\frac{d\alpha}{dt} = \sum_{i=1}^3 c_i \frac{d\alpha_i}{dt} \quad (8)$$

$$\frac{d\alpha_i}{dt} = k_i(T) f_i(\alpha) \quad (9)$$

where  $c_i$  denotes the  $i$ th component contribution and  $i$  is the biomass principal pseudo-component: cellulose, hemicellulose and lignin. Curve deconvolution was performed in order to study the kinetic lignin, cellulose and hemicellulose decomposition. The DTG curve deconvolutions were carried out using the Origin 8.6 software. Afterward, the Coast Redfern and Sharp methods were applied in order to estimate the kinetic parameters [11–18].

### Model validation

In order to predict the active pyrolysis behavior of the studied agro-industrial wastes, the second stage of DTG curves was considered in all cases. The fitting of the experimental data of  $g(\alpha)$  and  $f(\alpha)$  versus temperature to the proposed models was performed and they were evaluated with adjustment coefficient  $R^2$ . The two proposed hypotheses are evaluated by the following expression:

**Table 2.** Expressions for the most common reaction mechanisms in solid-state reactions.

Reaction model	Symbol	$f(\alpha)$	$g(\alpha)$
Reaction order			
Zero order	R1	$(1 - \alpha)^n$	$\alpha$
First order	R2	$(1 - \alpha)^n$	$-\ln(1 - \alpha)$
$n$ th order	R3	$(1 - \alpha)^n$	$(n - 1)^{-1} (1 - \alpha)^{1-n}$
Diffusional			
One-dimensional diffusion	D1	$1/(2\alpha)$	$\alpha^2$
Two-dimensional diffusion	D2	$-1/\ln(1 - \alpha)$	$(1 - \alpha) \ln(1 - \alpha) + \alpha$
Three-dimensional diffusion (Jander)	D3	$3(1 - \alpha)^{2/3} / 2 [1 - (1 - \alpha)^{1/3}]$	$[1 - (1 - \alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstling–Brounstein)	D4	$3/2 [(1 - \alpha)^{-1/3} - 1]^{-1}$	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$
Nucleation			
Power law		$n(\alpha)^{(1-1/n)}$ ; $n = 2/3, 1, 2, 3, 4$	$\alpha^n$ ; $n = 3/2, 1, 1/2, 1/3, 1/4$
Exponential law		$\ln(\alpha)$	$\alpha$
Avrami–Erofeev	AE	$n(1 - \alpha)[- \ln(1 - \alpha)]^{(1-1/n)}$ ; $n = 1, 2, 3, 4$	$[- \ln(1 - \alpha)]^{(1/n)}$ ; $n = 1, 2, 3, 4$

$$\text{error\%} = \left/ \frac{(\frac{d\alpha}{dt})_{\text{experimental}} - (\frac{d\alpha}{dt})_{\text{predicted}}}{(\frac{d\alpha}{dt})_{\text{experimental}}} \right/ * 100 \quad (10)$$

### Thermodynamic properties

The thermodynamic properties as the variation of enthalpy ( $\Delta H$ ), free Gibbs energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) can be expressed by Equations (11), (12) and (13). This methodology has been used by [19,20]:

$$\Delta H = Ea - RT \quad (11)$$

$$\Delta G = Ea + R * Tm * \ln\left(\frac{Kb * Tm}{h * A}\right) \quad (12)$$

$$\Delta S = \frac{\Delta H - \Delta G}{Tm} \quad (13)$$

where  $Kb$  is the Boltzmann constant ( $1.38 * 10^{-23} \text{ JK}^{-1}$ );  $h$  is the Plank constant (equal to  $6.63 * 10^{34} \text{ Js}$ ) and  $Tm$  is the DTG peak temperature (temperature of the maximum mass loss rate).

The activation energy, pre-exponential factor and thermodynamic properties for each component were calculated with the best-fit model; also these parameters and properties were calculated for the global process in order to investigate the influence of these components on the overall kinetic process.

## Results and discussion

### Biomass characterization

The proximate analysis results are shown in Table 1. The moisture contents were 5.70, 8.38, 7.70, and 5.30%, for peach pit, marc, stalk, and sawdust, respectively. High water content increases the energy requirements to carry out the thermal treatment, increases the residence time for drying and reduces the temperature, resulting in incomplete conversion of the hydrocarbons [21]. These aspects decrease the thermal process efficiency. In addition, the moisture increases microbial respiration and thereby reduces the physical quality of fuels, especially its durability. Considering the steam/air gasification process and the obtained results of moisture contents (less than 30%), these wastes can be converted to syngas without a previous drying process. The peach pit and sawdust showed a high volatile matter content, generally more than 70.00% (Table 1). High volatile matter levels promote ignition at lower temperatures, implying a high reactivity. The high volatile content improves the overall rate of the process due to high release of gases during the pyrolysis step (the gas-gas reaction rates are faster than gas-solid reactions) [22]. The ash contents are below 11.00%, which is considered low. This aspect has a significant impact

on the obtained amount of fly and bottom ash from the thermal process. A low percentage of ash content positively affects the high heating value (HHV) [7]. In addition, a fuel has a lower initial degradation temperature when the percentages of ash and impurities in its composition are elevated [23].

The higher volatile matter/fixed carbon ratio improves the contact of reactants and reduces the residence time for the thermal treatment processes, indicating a higher biomass reactivity degree [24]. This calculated ratio is 6.10, 3.14, 3.14, 2.89 and 7.32 for peach pit, marc, stalk and sawdust, respectively. According to the elemental analysis, the studied wastes are environmentally friendly, with only trace amounts of nitrogen and sulfur because their values are depreciable. Furthermore, these contents are much lower than those determined for fossil fuels. The peach pit has the highest carbon content. Considering the C and O contents in studied biomass, they vary in the range of 46.14–53.01% and 30.41–37.54%, respectively. These results are similar to the results obtained by Vasilev et al. [25].

Considering the lignin, cellulose and hemicellulose contents, Mckendry reported values of 40.00–50.00%, 20.00–40.00% and 10.00–40.00%, respectively [26]. This researcher worked with different biomass. Yang et al. determined hemicellulose, cellulose and lignin contents, which were about 20.00–40.00, 40.00–60.00, and 10.00–25.00 wt.%, respectively [27]. Considering the obtained results (Table 1), the highest hemicellulose and lignin contents are present in peach pit and marc, respectively. The sawdust has the highest cellulose content; equal to 42.96%. Agreeing with the obtained results by Gany and Narurse [28], the cellulose and lignin contents in the biomass qualitatively affect the reactivity. During pyrolysis, the overall reaction rate decreases with an increase of the lignin content. Nevertheless, during combustion, the lignin in the biomass controls the reaction rate [29]. Pasangulapati et al. [9] studied the pyrolysis of switch grass, wheat straw, red cedar, and dried distilled grains with soluble compounds; they observed that the lignin-rich biomass released a larger amount of methane, and the cellulose-rich biomass released larger amounts of CO and CO<sub>2</sub>. According to Fu et al. [30], cellulose may also produce higher CO due to secondary reactions of primary volatiles and scission of aldehyde groups (R-CHO). On the other hand, lignin decomposition has been correlated with methane formation due to cracking of methoxy groups of lignin molecules [31]. Lv et al. [32] studied pyrolysis and gasification of different biomasses (pine sawdust, sugar cane bagasse, rice-straw, rice-husk, cotton-stalk and corncob). The results obtained by these researchers showed that, through the entire temperature range, the main evolved product of cellulose decomposition is tar, with levoglucosan as the major component and including aldehydes,

ketones and organic acid, in addition to water and char. However, the lignin decomposition produces mainly char. On the other hand, Vassilev et al. [33] classified biomass into six different groups according to composition, denoted CHL, HCL, HLC, LHC, LCH and CLH. Each point is characterized by the consecutive decreasing amounts of the three components. For example, in the CHL sector, concentrations vary following the structural order cellulose > hemicellulose > lignin. These researchers suggest that a suitable process can be determined, according to the biomass composition, using this classification [33]. Considering Vassilev et al.'s classification [33], sawdust and peach pit are in the CHL area, while marc and stalk are in the LCH group sectors. Sawdust and peach pit have high cellulose contents, allowing the formation of volatile compounds conferring suitable conditions for biomass combustion. Stalk and marc have high lignin contents. The high content of benzene rings in the lignin explains the high char yield [25]. Consequently, for the production of a solid fuel, biomass with high lignin content is recommended. Moreover, due to the high stability of the benzene rings and of bonds between them, high molecular mass compounds are produced

during the lignin decomposition, contributing to tar production. Finally, the contents of cellulose, hemicellulose and lignin of sawdust, peach pit, stalk and marc are very similar to those obtained by other authors [33–35].

### TG analysis

The TG results were used to determine the lignin, cellulose and hemicellulose contents using a methodology based on DTG curve deconvolution. The hemicellulose contents were 22.22, 4.92, 6.18 and 19.52% for peach pit, marc, stalk and sawdust, respectively. Considering the cellulose percentage, the obtained results are: 30.80, 15.20, 16.14 and 42.40% for peach pit, marc, stalk and sawdust, respectively. Finally, the lignin contents are 27.46, 38.25, 28.11 and 22.75% for peach pit, marc, stalk and sawdust, respectively. The obtained results are similar to those shown in Table 1.

The hemicellulose, cellulose and lignin decomposition occurs in temperature ranges of 493–643, 573–723, and 450–1173 K, respectively [27]. The decomposition process depends on the contents of these principal components. Figures 4(a) and (b) show

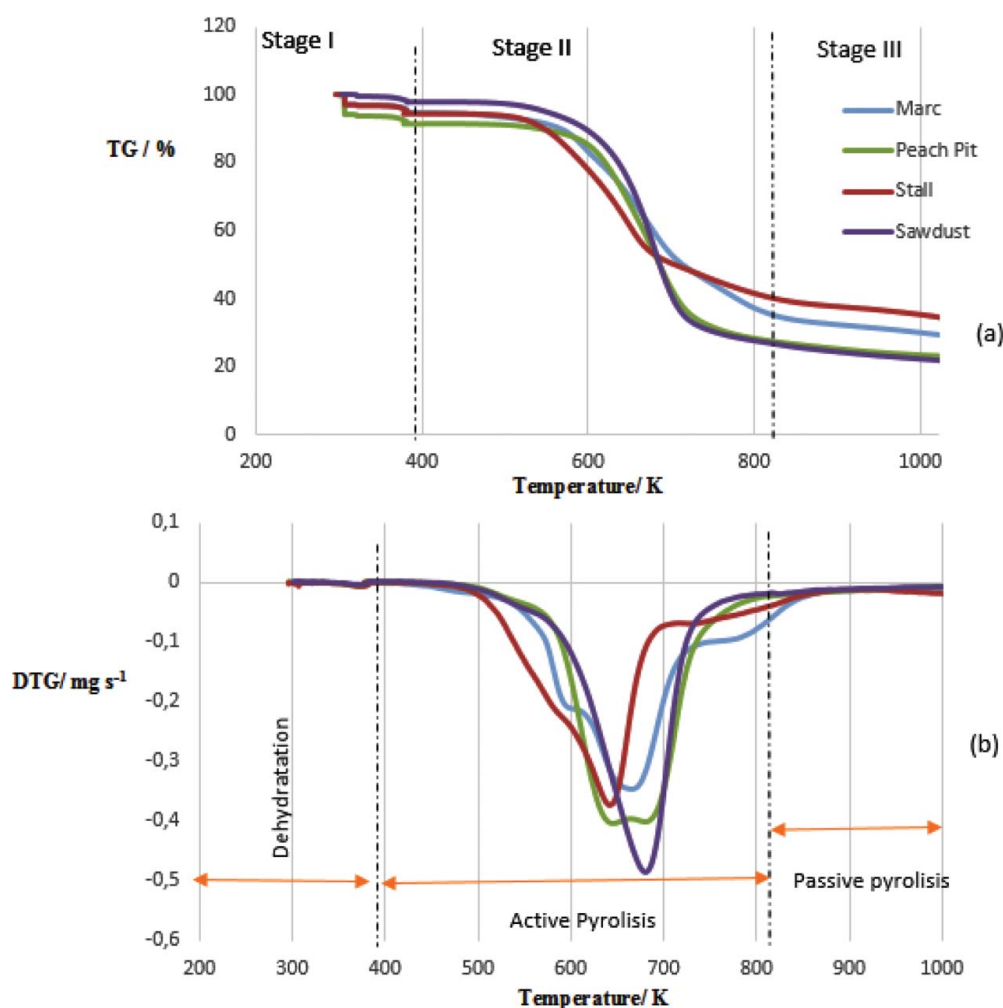


Figure 4. (a) Thermogravimetric analysis (TG) curves of four biomass wastes; (b) DTG curves of four biomass wastes.

TG and DTG curves obtained during the thermogravimetric experiments under nitrogen flows, at a constant heating rate [36]. According to the standard pyrolysis model [37], the peak resulting from the cellulose degradation is accompanied by a shoulder at low temperature, related to hemicellulose degradation, and a tail at high temperature associated with lignin volatilization. The first peak in DTG curves, ranging from 303 to 393 K, approximately, corresponds to the moisture loss and release of light volatile molecules. The mass loss at this stage ranges between 2.78% (sawdust) and 8.59% (peach pit), and this stage is called dehydration.

The second peak corresponds to the stage called active pyrolysis; it follows the usual shape for lignocellulosic materials [20]. During the second stage, several peaks are observed between 392 and 823 K; these could be attributed to hemicellulose and cellulose decomposition, and partial lignin decomposition. The analyzed wastes show small differences regarding temperature ranges. The initial and final temperatures of different stages for the four biomasses are different from each other. The discrepancies can be attributed to variations in hemicellulose, lignin and cellulose contents [27].

The DTG curve of peach pits exhibits a small shoulder between 490 and 563 K, associated mainly with hemicellulose decomposition. In addition, a prominent shoulder is shown in the temperature range 563–661 K, related mainly to cellulose decomposition. After 661 K, the DTG curves show a small shoulder, associated mostly with lignin decomposition. The maximum mass loss rate occurs at a temperature of about 638 K for all agro-industrial wastes.

Considering the stalk degradation under inert atmosphere, a small shoulder was observed between 546 and 600 K, where the hemicellulose decomposition is mainly carried out. In addition, the stalk DTG curve exhibits a larger shoulder in the temperature range 600–710 K, associated mainly with cellulose degradation. After 717 K, there is a small shoulder, associated mostly with lignin decomposition. The temperature of maximum mass loss rate is approximately 643 K.

The DTG curve of marc exhibits a small shoulder between 523 and 620 K, associated principally with hemicellulose decomposition. Additionally, a prominent shoulder is shown in the temperature range 620–731 K, corresponding to cellulose decomposition. After 650 K, there is a small shoulder, related mainly to lignin decomposition. The temperature of maximum mass loss rate is around 658 K.

The DTG curve of sawdust shows a small shoulder in the temperature range 493–578 K, associated principally with hemicellulose decomposition. A larger shoulder was observed between 493 and 823 K, related to cellulose and lignin degradation, due to fragmentation of the inter-unit linkages [36]. The temperature of maximum mass loss rate is about 685 K.

Considering stage II, the stalk and marcs start to degrade at lower temperatures than peach pits and sawdust do. This may be due to a higher concentration of low molecular weight compounds (oils and resins), because they are less stable and their degradation is faster, accelerating the decomposition of the following components [4].

On the other hand, the presence of inorganic species, such as K, usually present in the waste of the wine industry, catalyzes the lignin decomposition in a similar way as for holocellulose, accelerating mass loss, even to a greater extent than for cellulose and hemicellulose [38].

The DTG curve of peach pits exhibits the most prominent shoulder considering the DTG curves of stalk and marcs, due principally to the lower hemicellulose content [31]. The hemicellulose and cellulose are decomposed together forming this larger peak. The mass loss in this stage is between 51.72 and 66.59% for all studied wastes. The highest temperature for the maximum decomposition rate is about 679 K for sawdust sample, due, possibly, to a higher cellulose content [32].

Considering the third stage, a long tail of mass loss was observed above 823 K for all wastes. This stage is called passive pyrolysis and it is mainly attributed to lignin decomposition. The mass loss is small, so the reaction rate is minimal. During this stage, the lignin continues its decomposition without a characteristic peak [35,37] or a small shoulder can appear. This last phenomenon can be observed in DTG curves obtained for the studied agro-industrial wastes. The total mass losses during the complete pyrolysis process were between 54.35 and 70.32%.

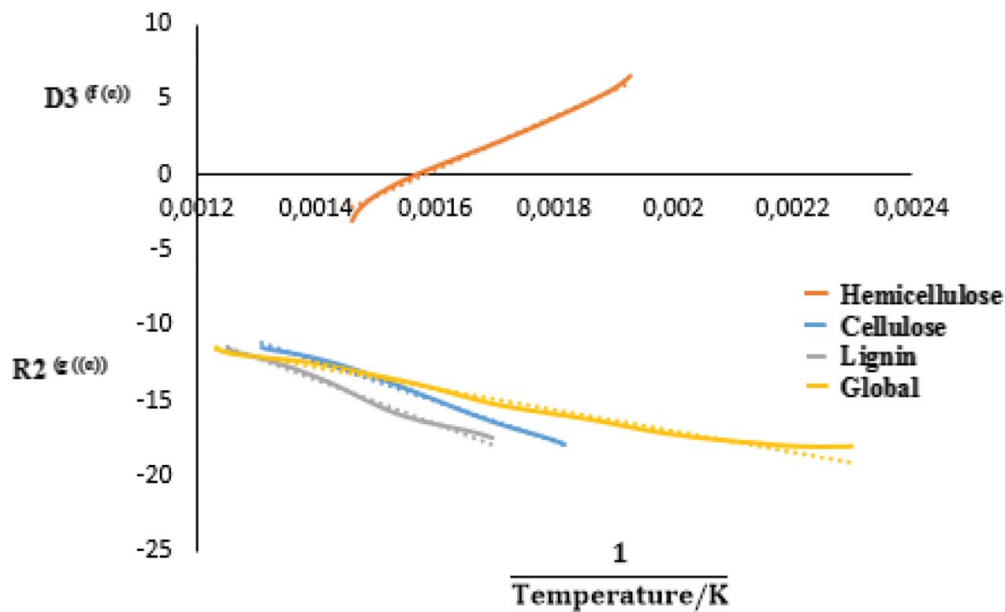
### **Kinetic study**

The kinetic analysis of the agro-industrial waste pyrolysis was carried out for the active pyrolysis stage because that is where the highest mass loss is produced. Two kinetic mechanisms were considered: a single reaction, and three independent parallel reactions.

#### **Single-reaction kinetic results**

In order to determine the different kinetic parameters, the isoconversional methods described above were used (Table 2). Figure 5 shows a comparison between the experimental data and the model results for peach pits. The D3 model (three-dimensional) shows the best fit for the global decomposition of the stalk and sawdust, producing similar results to those of Mian Hu et al. [39]. This model shows that the process is governed by the mechanism of the internal diffusion, indicating a low porosity of the solid after the dehydration stage.





**Figure 5.** The experimental data vs fitting models for peach pits.

Considering the marc and peach pits, the best fit is obtained for the R2 model, indicating the reaction is considered a first-order reaction [40].

The representative model, the obtained values for the activation energies and pre-exponential factors, and  $R^2$  values are shown in Table 3 for each agro-industrial solid waste.

Fernandez et al. [41] studied peach pit, marc and stalk decomposition under an inert atmosphere at low heating rates. They considered that the single reaction model describes their thermal decomposition, particularly the contraction geometry model. Comparing

these results with those obtained in this work, an important influence of heating rate can be observed, particularly in the case of marc and peach pit decomposition. At a low heating rate, the reaction interface progress toward the center of the solid controls the reaction rate, but at a high heating rate the reactions are considered first-order reactions.

The obtained values of activation energy vary between 58.25 and 173.52  $\text{kJ mol}^{-1}$  for all studied agro-industrial wastes. A lower value of energy activation was predicted for peach pits. The observed activation energy values are similar to the values obtained

**Table 3.** Kinetic parameters and thermodynamic properties.

		Zone II: active pyrolysis				
Waste		Hemicellulose	Cellulose	Lignin 1	Lignin 2	Global
Marcs	model	$D_3^{(f(\alpha))}$	$R_2^{(g(\alpha))}$	$R_2^{(g(\alpha))}$	$R_2^{(g(\alpha))}$	$R_2^{(g(\alpha))}$
	Ea ( $\text{kJ mol}^{-1}$ )	173.52	107.02	68.52	71.28	173.52
	A ( $\text{s}^{-1}$ )	$1.84 \times 10^{13}$	$1.02 \times 10^7$	$2.05 \times 10^5$	$1.00 \times 10^3$	$1.84 \times 10^{13}$
	$R^2$	0.97	0.99	0.99	0.99	0.99
	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	167.93	101.36	62.87	62.82	167.70
	$\Delta G$ ( $\text{kJ mol}^{-1}$ )	172.23	187.20	170.80	269.78	172.41
Peach pit	model	$D_3^{(f(\alpha))}$	$R_2^{(g(\alpha))}$	$R_2^{(g(\alpha))}$	$R_2^{(g(\alpha))}$	$R_2^{(g(\alpha))}$
	Ea ( $\text{kJ mol}^{-1}$ )	149.09	110.44	121.27	–	58.25
	A ( $\text{s}^{-1}$ )	$2.64 \times 10^{10}$	$3.41 \times 10^8$	$7.08 \times 10^8$	–	$1.81 \times 10^4$
	$R^2$	0.99	0.99	0.99	–	0.98
	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	140.62	104.79	115.62	–	52.68
	$\Delta G$ ( $\text{kJ mol}^{-1}$ )	206.05	170.80	177.50	–	172.47
Sawdust	model	$D_3^{(f(\alpha))}$	$D_3^{(f(\alpha))}$	$D_3^{(f(\alpha))}$	–	$D_3^{(f(\alpha))}$
	Ea ( $\text{kJ mol}^{-1}$ )	138.98	248.36	24.35	–	105.39
	A ( $\text{s}^{-1}$ )	$3.67 \times 10^{08}$	$3.95 \times 10^{16}$	9.09	–	$7.34 \times 10^{06}$
	$R^2$	0.99	0.99	0.99	–	0.98
	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	133.56	242.65	18.63	–	99.67
	$\Delta G$ ( $\text{kJ mol}^{-1}$ )	196.22	203.33	185.05	–	188.38
Stalk	model	$R_2^{(g(\alpha))}$	$D_3^{(f(\alpha))}$	$R_2^{(g(\alpha))}$	$R_2^{(g(\alpha))}$	$D_3^{(f(\alpha))}$
	Ea ( $\text{kJ mol}^{-1}$ )	58.32	209.62	72.00	115.92	73.30
	A ( $\text{s}^{-1}$ )	$6.02 \times 10^5$	$4.48 \times 10^{14}$	$5.17 \times 10^4$	$4.17 \times 10^5$	$4.24 \times 10^2$
	$R^2$	0.98	0.99	0.99	0.99	0.99
	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	53.54	204.29	65.76	107.36	68.50
	$\Delta G$ ( $\text{kJ mol}^{-1}$ )	138.87	191.10	194.02	268.34	203.10
	$\Delta S$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )	–0.15	0.02	–0.17	–0.16	–0.21

by Li et al. [42] using the DAEM method. The activation energy represents the minimum energy requirement to start a reaction (energy barrier). Due to this, a higher value of activation energy means that reaction rates are low and the reaction has difficulty starting. The values of pre-exponential factors vary between  $1.84 \times 10^{13} \text{ s}^{-1}$  and  $4.24 \times 10^2 \text{ s}^{-1}$ . Similar values were found by Biney et al. [40].

From a kinetic point of view, it is important to consider that the approximation of the thermal decomposition reaction as a one-step reaction is discussed because it is governed by multiple complex reactions affected by the interactions between biomass components. Due to this, thermal decomposition based in three parallel reactions will be analyzed in the next section. The kinetic study of the lignocellulosic materials and their fractions (cellulose, hemicellulose and lignin) could reveal the correlations between their behavior when isolated and when forming part of the raw material.

### Three independent parallel reactions kinetic results

The curve deconvolution was performed in order to study the kinetic decomposition of lignin, cellulose and hemicellulose contained in different wastes. The kinetic parameters were calculated for the decomposition of each component during the active pyrolysis stage.

The R2 model shows the best fit considering the experimental data for cellulose and lignin contained in marc and peach pits, and lignin and hemicellulose contained in the stalk. These are similar to those obtained by other authors [43]. Additionally, Varhegiet et al. [44] evaluated kinetic models of parallel independent reactions, competitive reactions and successive reactions, and determined that the cellulose decomposition under an inert atmosphere is well described by first-order reactions. However, the decomposition of the three main components of sawdust, cellulose contained in stalk, hemicellulose in marc and peach pits are represented by the three-dimensional model (D3), giving the best fit. Considering these results and the hypothesis of Shafizadeh and Mc Ginnis [45], the distinction between models can only be made by chemical considerations.

Hong et al. [46], in the main temperature range of pyrolysis decomposition, found activation energy values between 27.00 and 48.00  $\text{kJ mol}^{-1}$ , and for the pre-exponential factor between 25.99 and 3711.20  $\text{min}^{-1}$ , for hemicellulose presented in bamboo. They extracted it via different methods. Damartzis et al. [47] studied the kinetics of cardoon pyrolysis using TG and found that the activation energy varied in the range of 51.90–180.00  $\text{kJ mol}^{-1}$ , and the pre-exponential factor between 16.67 and  $7.34 \times 10^{10} \text{ s}^{-1}$  for hemicellulose. Considering cellulose decomposition under an inert atmosphere, these researchers found the activation

energy and pre-exponential factors values varied in the ranges of 72.70–92.40  $\text{kJ mol}^{-1}$ , and  $5.33 \times 10^3$ – $16.66 \times 10^6 \text{ s}^{-1}$ , respectively. For lignin pyrolysis, the Arrhenius parameters varied between 29.00 and 49.50  $\text{kJ mol}^{-1}$  (energy activation) and between 0.30 and 2.00  $\text{s}^{-1}$  (pre-exponential factor) [38]. The activation energy values of cellulose decomposition, under an inert atmosphere, from different sources, reported by Negandar et al. [48], oscillates in a range of 105.00–188.00  $\text{kJ mol}^{-1}$ . The results obtained in this study are similar to the data in the literature for other biomasses. The smallest obtained value of activation energy corresponds to the decomposition of lignin contained in sawdust, and the highest value of this kinetic parameter was obtained for the decomposition of the cellulose contained in the sawdust. The peach pits and sawdust show similar activation energy values for the hemicellulose reaction.

The sawdust and stalk presented the highest activation energy value for cellulose decomposition. The peach pits and marc exhibit the highest activation energy value for the hemicellulose reaction. The peach pits and sawdust have only one peak for the lignin decomposition; this agrees with previous studies [48]. In contrast, the marc and stalk presented two peaks for this reaction. The smallest value of activation energy corresponds to the decomposition of lignin contained in sawdust, and the highest value was obtained for the decomposition of lignin contained in the peach pits. In the case of stalks and marcs, two peaks describe the degradation of this component. This behavior may be because lignin pyrolysis takes place over several stages. According to Anca-Couce [49], there are two different temperature ranges of lignin decomposition under an inert atmosphere, corresponding to softwood and hardwood lignin [50]. On the other hand, Faravelli et al. [51] proposed that the lignin is made up of three different components: LIG-C, LIG-H and LIG-O, richer in carbon, hydrogen and oxygen, respectively. The softwood lignin is richer in LIG-C; therefore, it reacts at higher temperatures and produces a higher char yield.

The pre-exponential factor values are directly related to the material structure [52], while the reactivity of samples is determined by the activation energy [33]. Pre-exponential factor values of less than 109  $\text{s}^{-1}$  indicate mainly a surface reaction or the existence of a closed complex; however, values greater than or equal to 109  $\text{s}^{-1}$  indicate a simple complex [52,53]. All cases studied showed greater activation energy at a greater pre-exponential factor. The lowest values in  $A$  and  $Ea$  indicate a faster and easier decomposition effect of this biomass for the respective degrees of conversion [34]. Three products are obtained during thermal processes: gas, liquid and solid. Usually, solid residues contain two kind of matter: char and ash, and metal oxides (this can prevent the formation of stable chemical hydrocarbon structures, and speed up the degradation

of hydrocarbon). The main decomposition products of hemicellulose are acetic acid, furfural 1-hydroxy-2-propanone, CO<sub>2</sub>, CO and H<sub>2</sub>O [51]. Di Blasi et al. [52] pointed out that hydroxyl-methyl-furfural is a main product in softwood hemicellulose (mainly composed of hexoses) pyrolysis, but is not produced from hardwood hemicellulose (mainly composed of pentoses) [54]. The yields of the different products of cellulose pyrolysis are greatly affected by the pyrolysis conditions [55]. During cellulose pyrolysis, the fragmentation of sugar units, accompanied by other reactions such as dehydration, produces a variety of carbonyl and alkene compounds as well as water, CO, CO<sub>2</sub> and char. Patwardhan et al. [56] concluded that the presence of alkali and alkaline earth metals reduced the sugar yield, increasing the char and CO<sub>2</sub> yields.

Lignin pyrolysis produces large amounts of solid, liquid and gaseous products (phenolic compounds, water vapor, carbonyls and alcohols, and permanent gases, including CO and CO<sub>2</sub>). In addition, methane and methanol are produced in high quantities due to the scission of methoxyl groups [57]. Phenolics are the most distinctive group of volatile products resulting from lignin pyrolysis. In softwood lignin, the extra methoxy group increases the CO<sub>2</sub>, CH<sub>4</sub> and char yields [58].

The composition of produced char depends mainly on the final pyrolysis temperature and the initial biomass material. The char carbon content increases at higher pyrolysis temperatures. The ash content of char depends mainly on the initial inorganic biomass composition. Inorganic elements such as Mg, Ca, Si, Fe, Al, or Ti are almost completely retained due to their characteristic non-volatility [59].

### Comparisons and validations of the models

The D3 model represents the overall process for the sawdust and the decomposition of individual components (cellulose, hemicellulose and lignin) under an inert atmosphere. The overall decomposition of the marc and peach pits and their cellulose and lignin were fitted by the R2 model; their hemicellulose thermal degradation was well represented by the D3 model. Considering the stalk, the overall process and the cellulose decomposition are well represented by the D3 model; however, the decomposition of the other two components was fitted accurately by the R2 model. These results suggest that the overall process follows the kinetic models of cellulose thermal degradation; in other words, the global process is more influenced by this component.

The calculated errors, considering the model of single reaction and using three parallel independent reactions, are 2.37 and 3.90%, respectively.

According to Mian Hu et al. [39], the one-step reaction is unsuitable to study slow pyrolysis kinetics of lignocellulosic biomass (pine wood, rice husk and

bamboo) because the variation of apparent activation energy with the conversion is complex. They evaluated the pyrolysis process of lignocellulosic biomass using the Fraser–Suzuki deconvolution and concluded that deconvolution of lignocellulosic biomass using three Fraser–Suzuki functions showed even better fit to the experimental data than DAEM did.

### Thermodynamic properties

The thermodynamic parameters,  $\Delta H$ ,  $\Delta G$  and  $\Delta S$ , were calculated at the temperature that the maximum mass loss rate is produced [16]. Enthalpy is a measurement of the 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. It is an extensive quantity. If  $\Delta H$  is positive, the reaction is endothermic. The exothermic processes exhibit a negative value of this variation.  $\Delta H$  is equal to the change in the internal energy of the system, plus the pressure–volume work that the system has done on its surroundings.  $\Delta H$ , under such conditions, is the heat absorbed (or released) by the material through a chemical reaction or by external heat transfer. The activation  $\Delta H$  also shows the energy differences between the activated complex and the reagents. If this difference is small, the formation of an activated complex is favored, because the potential energy barrier is low [60].

Calculated  $\Delta H$  values are shown in Table 3. Considering the decomposition of different biomass components,  $\Delta H$  values varied between 18.68 and 242.64 kJ mol<sup>-1</sup>, presenting the lowest value for the decomposition of lignin contained in the sawdust and the highest value for the degradation of cellulose contained in the same waste. The cellulose decomposition shows the highest  $\Delta H$  values, excepting the marc and peach pit cases, where the hemicellulose and lignin degradations, respectively exhibit the highest  $\Delta H$ . Xu and Chen [20] determined the  $\Delta H$  of pyrolysis of several wastes. For the decomposition of hemicellulose, present in rice straw and chicken manure,  $\Delta H$  was 162.23 and 165.45 kJ mol<sup>-1</sup>, respectively. For the cellulose and hemicellulose present in the rice bran,  $\Delta H$  values were 111.03 and 173.30 kJ mol<sup>-1</sup>, respectively.

The Gibbs free energy, also known as free enthalpy, an extensive function, expresses the equilibrium condition and spontaneity of a chemical reaction (at constant pressure and temperature).  $\Delta G$  shows the total energy increase of the system at the approach of the reagents and the formation of the activated complex [20,61–62]. Considering the decomposition of each pseudocomponent,  $\Delta G$  varied between 138.87 and 269.78 kJ mol<sup>-1</sup>, showing the lowest value for the decomposition of hemicellulose present in the stalk, and the the highest value for the degradation of lignin 2, contained in the marcs. Xu and Chen [20] studied

the kinetics for rice and determined that  $\Delta G$  was 141.61 and 180.14 kJ mol<sup>-1</sup> for hemicellulose and cellulose decomposition, respectively.

Considering the  $\Delta S$  values obtained during degradation of the different components present in all of the studied solid wastes, negative values were obtained for most components, except for those contained in the sawdust and stalk (Table 3). The  $\Delta S$  values varied between  $-0.24$  and  $0.06$  kJ mol<sup>-1</sup> K<sup>-1</sup>, presenting the lowest value for the decomposition of the lignin in the sawdust, and the highest value for the degradation of cellulose contained in the same waste.  $\Delta S < 0$  indicates that the formed activated complex is more structured or 'organized' than the initial molecules, so its formation is accompanied by a decrease in the entropy of activation. 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, increasing the time taken to form the activated complex.

By contrast, when  $\Delta S > 0$ , there are a fair number of dissociative reactions of the complex molecules to the simpler fragments (smaller molecules or radicals). If  $\Delta S > 0$ , the process can be characterized as 'fast'; the material is far from its own thermodynamic equilibrium. In this case, the reactivity is high and the system can react faster to produce the activated complex, resulting in short reaction times [63].

## Conclusion

The behavior of different agro-industrial wastes during thermal treatment was studied. They present low ash contents, positively affecting the high heating value. They have trace nitrogen and sulfur contents, converting them to environmental friendly wastes in the thermal process.

Sawdust and peach pit allow the formation of volatile compounds, conferring suitable conditions for combustion due to their high cellulose contents. The high volatile content improves the overall rate of the process due to the high release of gases during the pyrolysis step. Stalk and marc have high lignin contents and they produce high char and tar yields.

Taking into account the obtained TG and DTG curves, the pyrolysis has different characteristics depending on the origin and composition of the studied wastes. So, the marcs and stalk show the presence of lignins 1 and 2.

Two reaction mechanisms for the pyrolysis were supposed: several independent parallel reactions, and single-reaction models. Kinetic isoconversional methods were applied to both proposed mechanisms.

Taking into account the single-reaction model and the influence of heating rate on the kinetic behavior of thermal decomposition under an inert atmosphere, an important influence was observed, particularly in the case of marc and peach pit decompositions. At a low heating rate, the reaction interface progress toward the center of the solid controls the reaction rate, but at a high heating rate the reactions are considered first-order reactions.

Considering the pyrolysis data of all the studied agro-industrial wastes, the best fit was obtained for the single-reaction models, although the errors of both proposed mechanisms are small and close. Nevertheless, in order to study the influence of the decomposition of pseudocomponents in the global process, it is important to analyze the kinetic behavior of each of them.

The R2 and D3 models represent the thermal decomposition of biomass wastes and their pseudocomponents. The first model supposes that the reactions tend to be first-order (marc and peach pit pyrolysis), and the second (stalk and sawdust pyrolysis) assumes that diffusion is the predominant phenomenon. In all cases, the model with the best fit for the cellulose decomposition is the same as for the single global reaction model, suggesting that the decomposition of this mean component is the controlling step of the whole pyrolysis phenomenon.

On the other hand, the biomass wastes exhibited different thermodynamics characteristics. Thereby,  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  values varied between 52.68 and 167.70 kJ mol<sup>-1</sup>, 172.41 and 203.10 kJ mol<sup>-1</sup> and  $-0.01$  and  $-0.21$  kJ mol<sup>-1</sup> K<sup>-1</sup>, respectively, considering the single-reaction model.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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