



Research Paper

Kinetic study of regional agro-industrial wastes pyrolysis using non-isothermal TGA analysis

Anabel Fernandez^a, Alejandra Saffe^a, Regina Pereyra^c, Germán Mazza^b, Rosa Rodríguez^{a,*}^a Instituto de Ing. Química, Fac. de Ingeniería, Univ. Nac. de San Juan, Libertador 1109 (O), Argentina^b Instituto de Investigación y Desarrollo en Ingeniería de Procesos, Biotecnología y Energías Alternativas, CONICET-Universidad Nacional del Comahue, Neuquén, Argentina^c Universidade Federal de Santa Catarina, Laboratório de Emergência y Meio Ambiente – LEMA, Brazil

HIGHLIGHTS

- The pyrolysis of regional agro-industrial wastes were studied using TGA analysis.
- The contraction geometry's model describe the active pyrolysis stage.
- The calculated activation energy values are between 38.96 and 68.99 kJ/mol.
- The kinetic rate is controlled by the physical transformation.

ARTICLE INFO

Article history:

Received 31 March 2016

Revised 6 June 2016

Accepted 14 June 2016

Available online 15 June 2016

Keywords:

Thermogravimetry analysis

Agro-industrial wastes

Inert atmosphere

Kinetic models

ABSTRACT

Pyrolysis characteristics and kinetic study of six regional lignocellulosic wastes (sawdust, marcs, stalks, peach plum and olive pits) at different heating rates was investigated using thermogravimetric analysis. The pyrolysis could be divided into three stages, drying, active and passive pyrolysis. The specific location where the thermal degradation reaction are occurring is called active pyrolysis zone. The samples have the highest residual weight equal to 35–40% at 603 K, approximately during this stage.

To describe the active pyrolysis behavior, the Coats Redfern and Sharp methods were used. The contraction geometry's model describe this phenomenon, indicating that the degradation rate is controlled by the resulting reaction interface progress toward the center of the solid.

The activation energy values for the active pyrolysis stage are between 38.96 and 68.99 kJ/mol for all studied agro-industrial wastes. This parameter increases with the heating rate. This variation can be due to the kinetic rate of active pyrolysis is controlled by the occurrence of physical transformation the temperature-dependent which is not mass dependent. The calculated values of pre-exponential factor were about 2.01×10^7 and $2.51 \times 10^{10} \text{ s}^{-1}$. These parameters indicate that the pyrolysis of the studied wastes similar to other lignocellulosic materials, proving the feasibility of their valorization by pyrolysis.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Most of the world's energy resources are based on non-renewable and depleting fossil fuels. This has resulted in increasing worldwide interest in exploring alternative and renewable fuels, out of long - term economic, environmental and national security concerns [1].

From all available energy sources, biomass is gaining importance due to its abundance and low price. One of the most promising alternatives for energy from biomass is by conversion to useful

fuels, which can be done either through pyrolysis or gasification processes [2].

Considering the Cuyo Region, Argentina, one of the most important economic activities is the agro-industry, highlighting the wine, olive, wood and seasonal fruits industries such as peaches and plum. This sector produces a significant environmental impact in specific geographical areas because these residues are totally wasted.

The energy production from biomass can contribute to the reduction of CO₂ emissions, because the same amount of CO₂ is extracted from the atmosphere during the growth period of the plants as is released by combustion (CO₂ balance). On the other hand, generally, the biomass contents lower nitrogen and sulfur concentrations comparing with the fossil fuels, contributing to

* Corresponding author.

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

smaller pollutant emissions, products of these elements reactions during the thermal conversion.

Pyrolysis is a fundamental thermochemical conversion process that can be used to transform biomass directly into gaseous and liquid fuels. This phenomenon is also an important step in combustion and gasification processes. Thereby, a thorough understanding of pyrolysis kinetics is vital to the assessment of items including the feasibility, design, and scaling of industrial biomass conversion applications [3,4].

In addition, this process can be source of various chemical products [5]. Therefore, research on the pyrolysis process of a lignocellulosic waste, would be beneficial for a better understanding of the pyrolytic-cracking mechanism and to improve its transformation and application as bio-fuels, chemical products and biomaterials. Pyrolysis technologies represents an excellent way of utilizing lignocellulosic biomass which makes them highly attractive especially when concerning environmental issues during energy production. There are various studies on pyrolysis analysis of different biomass but their properties can significantly influence both heat transfer and reaction rates such that the optimal operating conditions are highly variable [6].

Knowledge of the chemical composition, the thermal behavior and the reactivity of these biomass fuels during pyrolysis, is very important for the effective design and operation of the thermochemical conversion units, given that solid devolatilization is always a fundamental step. Thermoanalytical techniques, in particular thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG), allow to obtain this information in a simple and straight forward manner. Thermogravimetric analysis (TGA) is one of the commonly used techniques to study thermal events during the pyrolysis process of fuel [7–12]. Detailed weight loss profile during biomass thermal decomposition can be obtained from this analysis. Non-isothermal methods are generally used due to it is less difficult to keep a constant heating rate than to keep an environment at a constant temperature, particularly when exothermic reactions are involved [6,7].

The pyrolysis of wastes biomass is a chemically complex process. Because of this complexity, a large number of papers from the literature assume different approaches to describe the thermal degradation using TGA analysis and non-isothermal methods [10–13].

The isoconversional integral and differential models are equations widely used because they are able to estimate the activation energy requiring only a mathematical approximation for the temperature dependency [13]. However, when the pre-exponential factor and reaction order are to be estimated, it is mandatory to use an approximation for the composition dependency [14]. These methods have the ability to reveal complexity of the process in the form of a functional dependence of the activation energy on the extent of conversion. Application of model-free methods was highly recommended in order to obtain a reliable kinetic description of the investigated process. The basic assumption of these models are that the reaction rate for a constant extent of conversion depends only on the temperature [15]. These models do not require previous knowledge of the reaction mechanism for biomass thermal degradation. Another advantage of isoconversional approaches is that the systematic error resulting from the kinetic analysis during the estimation of the Arrhenius parameters is eliminated [16]. They can follow either a differential or an integral approach to the treatment of TGA data [17,18]. Coast Redfern, FWO, Vyazovkin and Kissinger–Akahira–Sunose (KAS) methods are classified like integral isoconversional methods. Friedman, Sharp and Friedman-Reich-Levi models are differential methods [19]. Differential isoconversional methods are extremely susceptible to data noise and can result in important scatter in the resulting derivative curves. Extensive use of differential techniques has been inhibited because

of the discouraging calculations involved [20,21]. Vyazovkin and Lesnikovich [22] proposed a methodology wherein a linear relation that exists between the Arrhenius parameters is used to extract the frequency factor for a given isoconversional value of E_a [23]. When E_a depends on α , however, it was found that the integral isoconversional methods use leads to systematic errors [22]. E_a is overestimated, generally, due to error introduced by the truncation of the additional higher-order terms in Doyle's approximations [24]. Vyazovkin [25] proposed a modification for his isoconversional method that accounts for the variation in apparent activation energy with increasing the conversion. However, this modification is an artifact that in reality conceals the true differential character of the method [26]. Isoconversional methods are unsuitable for those reaction schemes containing competing reactions, where the net rate of reaction depends on changes in temperature, or concurrent reactions that switch which reaction is rate-limiting over the experimental temperature range [27]. Thereby, in heterogeneous reactions, it is possible that the kinetic rate-controlling event may be the occurrence of the temperature-dependent physical transformation which is not mass dependent [28], explaining the variation of E_a with the heating rate and according the phenomena described by Tahmasebi et al. [29].

In order to establish a picture of the energy application of these regional agro-industrial solid wastes (sawdust, marcs, stalks, peach plum and olive pits), TGA and DTG pyrolysis profiles were determined under inert atmosphere at different heating rate. To describe the pyrolysis behavior, the Coats Redfern and Sharp isoconversional methods were used [17,30]. The experimental data were fitted with several model and each one was evaluated with different statistical parameters. Using the model with the best fit, the activation energy and pre-exponential factor were calculated and their variation with the heating rate was evaluated. This study would be helpful in effective design and operation of thermochemical conversion units fed by different biomass.

2. Experimental

2.1. Materials

This study focused on the pyrolytic behavior of six kinds of lignocellulosic biomasses: peach, plum and olive pits from canneries and jam -industries, marc and stalk from wineries, and sawdust from the timber industry. All these industries are located in the San Juan province, Argentine.

Before the thermogravimetric analysis, the lignocellulosic biomass wastes were milled and sieved and the resulting 0.1–0.21 mm size fraction was used for the thermogravimetric tests.

The weight loss at 105 °C, ash and organic matter content were determined according to ASTM standards (ASTM D3173-87, ASTM D3172-89 (02)) [31,32]. Elemental analysis of the samples was performed using EuroEA3000 elemental analyzer. The results of elemental and ultimate analysis are shown in Table 1. In order to calculate the high heating value, the correlation proposed by Chaniwala and Parikh [33] was used (Table 1):

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

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

2.2. Thermogravimetric analysis

Thermogravimetric (TG) and derivative thermogravimetric (DTG) experiments of the powdered samples wastes were carried out using a TGA-50 Shimadzu microbalance, under nitrogen atmo-

Table 1
Results of proximate and elemental analysis (dry basis, weight percentage). Predicted values of high heating values (HHV).

	Peach pits	Stalk	Marc	Plum pits	Olive pits	Sawdust
C (%)	53.01	46.14	52.91	48.95	52.79	44.71
H (%)	5.90	5.74	5.93	1.38	2.57	1.48
N (%)	2.32	6.37	5.41	0.99	1.39	4.20
S (%)	1.88	4.21	5.34	0.27	0.50	0.28
O (%) ^a	36.89	37.54	30.41	48.41	42.75	49.33
Ash (% dry basis)	1.30	10.16	8.81	0.73	2.33	1.19
Volatile matter (% total weight)	79.10	55.84	68.60	77.86	77.25	80.90
Fixed carbon (% dry basis)	13.90	23.07	21.98	15.55	15.87	11.06
Weight loss at 105 °C (% total weight)	5.70	7.70	8.38	5.86	4.55	6.85
HHV (MJ/kg)	21.39	12.03	13.31	13.71	17.02	12.19

^a By difference.

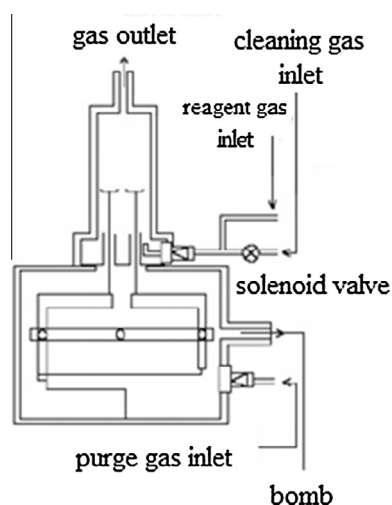


Fig. 1. Scheme of thermogravimetric analyzer.

Table 2
Characteristics of the used equipment in the thermogravimetric analyzer.

Speciation	
Maximum temperature	1373 K
Balance type	TOP PLAN differential parallel guide
Heating rate	±0.1 a 99.9 K/min
Minimum reading	0.001 mg
Measuring accuracy	±1%
Measurable range (TG)	±500 mg
Measurable range (DTA)	±1000 μv
Mass sample	1 g Max.

sphere. Fig. 1 and Table 2 show a scheme of the used equipment and its characteristics, respectively. The temperature increases from ambient temperature (298 K approximately) to 1173 K. This last temperature guarantees the highest decomposition. The experiments were performed at three different heating rates of 5, 10 and 15 °C/min for each sample. To mitigate the difference of heat and mass transfer, all samples weight were kept at 12 mg approximately. The inert gas used for pyrolysis was nitrogen with a flow rate of 100 mL/min. For each agro-industrial waste and heating rate, three replications were performed. The correction for the TG data was done using a blank experiment. The reproducibility of the experiments was acceptable.

3. Kinetics analysis

For the kinetic analysis, the experimental conversion, α , and experimental conversion rate ($d\alpha/dt$) were determined through Eqs. (2) and (3), respectively.

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad (2)$$

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

where m is the mass of the sample at a given time t ; m_0 and m_f refer to values at the initial and final mass of samples, A is the pre-exponential factor, E is the activation energy, R is the universal gas constant, T is a temperature in Kelvin and $f(\alpha)$ represents function commonly used for description of biomass thermal decomposition.

For non-isothermal conditions, when the temperature varies with time with a constant heating rate defined by:

$$\beta = \frac{dT}{dt} \quad (4)$$

Considering the expression of heating rate, Eq. (3) can be rewritten as follows:

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

Integrating Eq. (5), the following expression can be obtained:

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

Eq. (6) can be integrated when the right had side is expanded into an asymptotic series and higher order terms are ignored:

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

The term $2RT/Ea$ can be neglected since it is much less than unity for the thermal decomposition of lignocellulosic materials. Plotting the left hand side of Eq. (7), which includes $\ln \frac{g(\alpha)}{T^2}$ versus $1/T$, gives E and A from the slope and intercept respectively.

Coast Redfern, and Sharp methods are applied [17,30]. Table 3 lists several reaction models ($f(\alpha)$ and $g(\alpha)$) used in this work to describe biomass thermal decomposition.

3.1. Model validation

In order to predict the active pyrolysis behavior, the second peak of DTG curves was considered in all cases. The fitting of the experimental data of $g(\alpha)$ and $f(\alpha)$ versus temperature for to the proposed models (Table 3) was performed by means of the Marquardt-Levenberg [34] algorithm, using Data Fit 9.1 software. To estimate the E and A parameters, least squares nonlinear regression was used.

The reaction model determination is a fundamental step in kinetic studies, since it is a theoretical function that helps to describe and improve the understanding of the reaction. For that, with the purpose of evaluate each models, an estimation of the

Table 3
Expressions for the most common reaction mechanisms in solid state reactions.

Reaction model	Symbol	f(α)	g(α)
Reaction order			
Zero order	R1	$(1 - \alpha)^n$	α
First order	R2	$(1 - \alpha)^n$	$-\ln(1 - \alpha)$
nth order	R3	$(1 - \alpha)^n$	$(n - 1)^{-1} (1 - \alpha)^{1-n}$
Diffusional			
One dimensional diffusion	D1	$1/(2\alpha)$	α^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		$n\alpha^{(1 - 1/n)}$; $n = 2/3, 1, 2, 3, 4$	α^n ; $n = 3/2, 1, 1/2, 1/3, 1/4$
Exponential law		$\ln(\alpha)$	α
Avrami - Erofeev	AE	$n(1 - \alpha)[- \ln(1 - \alpha)]^{(1 - 1/n)}$; $n = 1, 2, 3, 4$	$[- \ln(1 - \alpha)]^{(1/n)}$; $n = 1, 2, 3, 4$
Contracting geometry		$1/2 \alpha$	
Contracting area		$(1 - \alpha)^{(1 - 1/n)}$; $n = 2$	$1 - (1 - \alpha)^{(1/n)}$; $n = 2$
Contracting volume		$(1 - \alpha)^{(1 - 1/n)}$; $n = 3$	$1 - (1 - \alpha)^{(1/n)}$; $n = 3$

parameter values is needed. The statistical parameter determined apart from the determination coefficient, R^2 , were the reduced chi-square, χ^2 , defined by:

$$\chi^2 = \frac{\sum_1^N (X_{\text{exp},i} - X_{\text{pre},i})^2}{N - z} \quad (8)$$

where $X_{\text{exp},i}$ is the experimental value, $X_{\text{pre},i}$ is the predicted value, N is the number of experimental data points, and z is the number of parameters in the model.

4. Results and discussion

4.1. Characterization of the raw material

Ultimate and proximate analysis of the six agro-industrial wastes from San Juan province are shown in Table 1. Considering the first analysis, the olive pits has the highest carbon (52.79%) and hydrogen (2.56%) contents. Furthermore, the sawdust has the highest nitrogen content (4.19%) among the six materials. The results shown in Table 1 are in agreement with those of other investigators: 52.30% C, 5.20% H, 0.50% N, 0% S and 42% O in wood reported by Prasad et al. [35]; 49.87% C, 5.11% H, 1.38% N, 0.12% S and 42.07% O, in stalk reported by Valente et al. [36]; 46.88% C, 4.83% H, 0.93% N, 0.36% S, and 41% O in cotton husk reported by Bhavanam and Sastry [37].

Taking into account the immediate analysis results, the weight loss at 105 °C of all analyzed biomass wastes varies between 4.55 and 8.38%. It is necessary to consider that a high water content increases the energy requirements to carry out the thermal treatment, rises the residence time for drying and reduces the temperature, resulting in incomplete conversion of the hydrocarbons. These aspects decrease the process efficiency.

Regarding the ash content of the agro-industrial wastes, it presents a great variation, between 0.73%, for plum pits, and 10.16% for stalk (dry basis). A low percentage of it ash content will minimize the production of fly and the bottom ash and affect positively the high heating value (HHV) [33]. Dermibas and Arin [38] determined the HHV for 16 different biomass fuel and reported similar values, Quirino et al. [39] reported similar values for wood, too.

Concerning to the volatile contents, the obtained values (55.84–80.90 wt%) are comparative to the results reported by Jeguirim and Trouvé [40] (68.4 wt%), Daouk et al. [41] (83.3 wt%, approximately) and Crnkovic et al. [42] (79.7–98.6 wt%).

About fixed carbon, it was observed that the results of Jeguirim and Trouvé (18.4 wt%) and Daouk et al. (15.4 wt%, approximately) are similar to the obtained values in this work (between 11.06 and 23.07%, dry basis).

In general, these solids contain significant amounts of unreacted carbon and sulfur [43], but the studied agro-industrial wastes contain very small amounts of this last element in their compositions. The high content of organic matter makes these wastes very suitable for thermal treatment [44].

4.2. Thermogravimetric analysis

Considering the TGA results, the agro-industrial wastes pyrolysis could be divided into three stages according to the weight loss rate. The initial decrease in weight is due to water release, principally. This phenomenon is produced below 473 K, and it occurs in all studied lignocellulosic biomass. The second stage, called active pyrolysis, corresponding to the maximum weight loss about 35–40%, is produced between 473 and 823 K. The temperature corresponding to the maximum weight loss rate of all studied biomass wastes is similar for all cases, about 603 K. A large amount of gas species such as CO_2 , CO , CH_4 and H_2O are released in this stage, indicating that they mainly come from this stage [45].

The last stage, called passive pyrolysis, is produced at high temperature, the weight loss is very smaller. Still, there remained little residue at 1223 K, i.e., about 20% of original weight. It can also be seen from Figs. 2–4 that the pyrolysis process has similar charac-

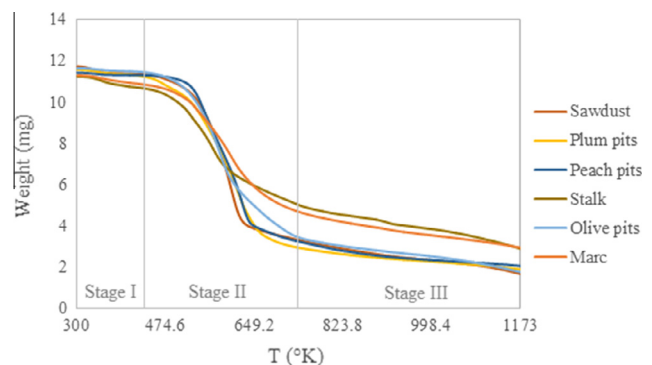


Fig. 2. TG curves for the studied biomass samples at 5 °C/min.

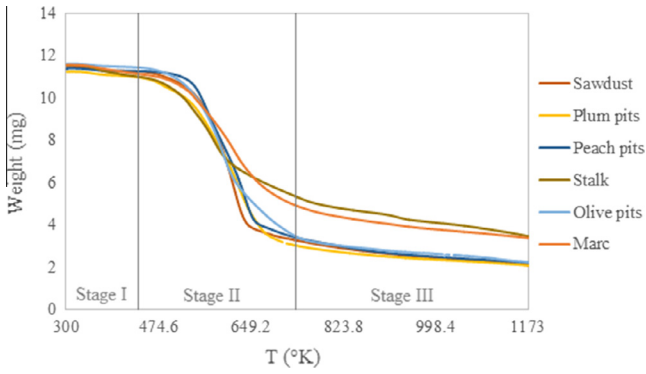


Fig. 3. TG curves for the studied biomass samples at 10 °C/min.

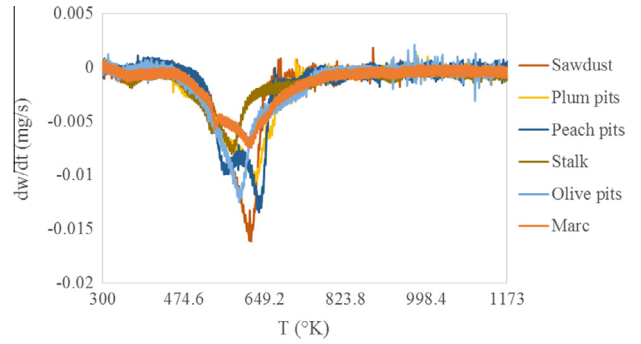


Fig. 6. DTG curves for the studied biomass samples at 10 °C/min.

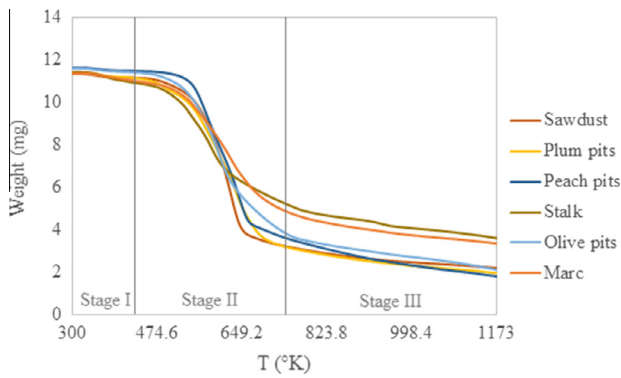


Fig. 4. TG curves for the studied biomass samples at 15 °C/min.

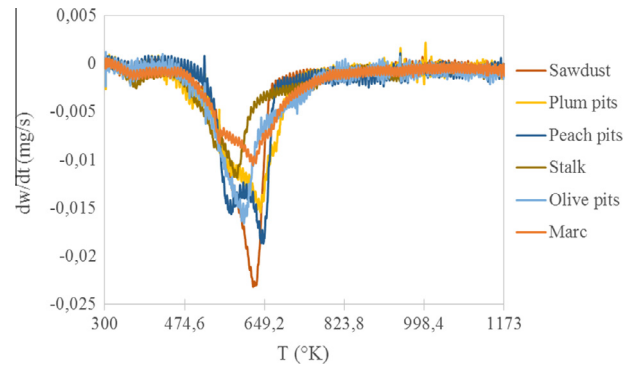


Fig. 7. DTG curves for the studied biomass samples at 15 °C/min.

teristics: the temperature ranges at three pyrolysis stages, the temperature of start and finish pyrolysis, and maximum pyrolysis rate.

The greatest weight loss is produced during the active pyrolysis, for that the second peaks are considered in all cases in order to carry out the kinetic study. At this stage, the biomass is completely dried, and its main components (hemicellulose, cellulose and lignin) are decomposed with the temperature increasing. During this stage, gaseous compounds are released, a fraction of them are condensable and they form the liquid fraction produced during this phenomenon [46]. These peaks are produced between 423 and 823 K (Fig. 5–7).

When the heating rate increased, weight loss rates also increased (Fig. 8) because this phenomenon is mainly affected by mass transfer. So, it would take a longer time of the heat conduction from the particle external to the interior as the heating rate increased. So that, at the same temperature, the pyrolysis in higher heating rate was less efficient, especially for the biomass contain-

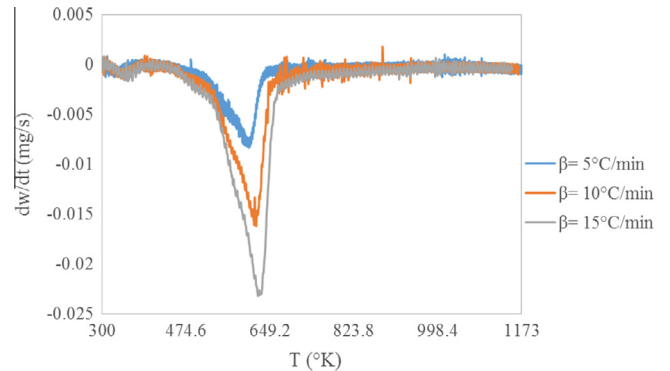


Fig. 8. Comparison of the weight loss rates for sawdust.

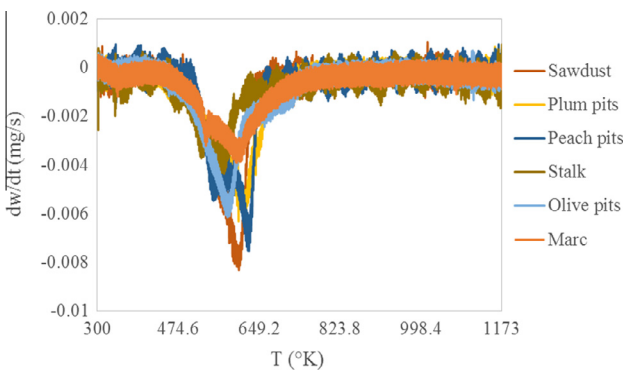


Fig. 5. DTG curves for the studied biomass samples at 5 °C/min.

ing high volatile component. This conclusion was agreed well with Lah [47]. When the heating rate increased, the peaks of maximum decomposition have no displacement with respect to temperature. This was because the reaction time is the same in all the cases, indicating that no more energy is required to achieve the same conversion.

For the active pyrolysis of stalk and peach pits wastes, two distinct peaks following a long tail were observed in the DTG curves. According to the literatures, the hemicellulose decomposition mainly occur in the temperature range from 493 K to 588 K with the maximum decomposition rate at about 533 K [48–50]. Therefore, the first peak is mainly linked to its decomposition. The temperature range and the peak temperature of the second DTG peak are very close to cellulose pyrolysis [50–57]. This indicates that the second DTG peak is mainly linked to the cellulose decomposition. The lignin reacts between 473 K and 873 K, which means that when hemicellulose and cellulose react, the lignin also is

decomposing, but not governing the overall reaction [58]. According to the literature [59], the temperature characteristics of lignin pyrolysis and char formation is similar to that of the DTG tail (passive pyrolysis). Senneca et al. [60] and Cao et al. [61,62] pointed out that in the temperature range of the DTG tail there would be also the aromatization of the residual char.

4.3. The results of the kinetic models

The kinetic modeling through isoconversional equations was performed in order to estimate the activation energy (E), pre-exponential factor (A), and reaction order (n), using non-isothermal thermogravimetry experiments data. The highest R^2 values and the smallest χ^2 values are presented for the contraction geometry's model, contracting volume, for all agro-industrial wastes using differential and integral isoconversional methods. This model describes the pyrolysis characteristics of biomass wastes obtained by nonisothermal TGA and it assumes that nucleation occurs rapidly on the surface of the particle. The rate of degradation is controlled by the resulting reaction interface progress toward the center of the solid [63]. The Coats Redfern isoconversional method showed better results.

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.

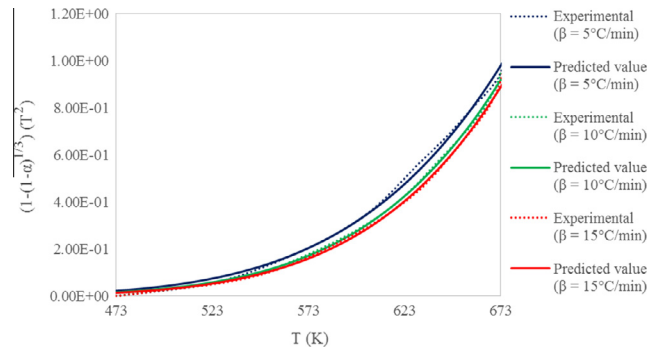


Fig. 9. Comparison of experimental and predicted values of $g(\alpha)$ for plum pits under inert atmosphere at different heating rates.

In order to calculate the activation energy and pre-exponential factor, the contraction geometry model and the Coats Redfern isoconversional method were used. Table 4 shows the obtained kinetics parameters and the statistical parameters values for different studied agro-industrial wastes. For this model, the R^2 and χ^2 values were between 0.97–0.99 and 3.87×10^{-5} and 1.00×10^{-4} , respectively. The higher values of R^2 , and the lower values of χ^2 , the better is the goodness of fit. Fig. 9 shows the comparison of experimental data and the predicted values for plum pits at different heating rates.

Table 4
Pre-exponential factor and activation energy obtained and the statistical parameters values.

Agro-industrial wastes	Heating rate β ($^{\circ}\text{C}/\text{min}$)	Temp range active pyrolysis ($^{\circ}\text{C}$)	Peak temp ($^{\circ}\text{C}$)	Mass loss rate maximum (mg/s)	Kinetics parameters		Statistical parameters	
					E (kJ/mol)	A (s^{-1})	R^2	χ^2
Sawdust	5	218	332	0.008	52.82	3.87×10^8	0.97	2.30×10^{-3}
		379						
		200	347	0.016	63.68	6.41×10^9	0.99	9.00×10^{-4}
Plum pits	10	383						
		169	355	0.023	68.93	2.51×10^{10}	0.99	3.59×10^{-4}
		429						
Plum pits	15	179	346	0.005	58.04	9.31×10^8	0.99	3.87×10^{-5}
		398						
		190	359	0.011	61.73	3.53×10^9	0.99	1.74×10^{-4}
Plum pits	15	432						
		179	367	0.015	62.60	5.96×10^9	0.99	1.77×10^{-4}
		465						
Peach pits	5	228	354	0.008	58.79	1.20×10^9	0.99	6.11×10^{-4}
		381						
		232	364	0.013	66.46	9.75×10^9	0.99	1.99×10^{-4}
Peach pits	10	398						
		223	373	0.019	68.99	2.28×10^{10}	0.99	3.42×10^{-4}
		400						
Stalk	5	186	300	0.004	38.96	2.01×10^7	0.99	1.08×10^{-3}
		365						
		193	305	0.008	42.60	8.54×10^7	0.99	8.97×10^{-4}
Stalk	10	382						
		182	315	0.012	44.94	2.04×10^8	0.99	6.76×10^{-4}
		384						
Olive pits	15	186	308	0.006	46.75	9.56×10^7	0.99	7.80×10^{-4}
		471						
		185	321	0.012	53.20	6.09×10^8	0.99	8.46×10^{-4}
Olive pits	10	485						
		194	331	0.017	56.40	1.95×10^9	0.99	3.37×10^{-4}
		498						
Marc	5	196	335	0.009	52.03	2.67×10^8	0.99	1.43×10^{-4}
		481						
		209	348	0.007	57.16	1.44×10^9	0.99	1.41×10^{-4}
Marc	10	495						
		206	350	0.011	56.62	3.39×10^9	0.99	2.15×10^{-4}
		514						

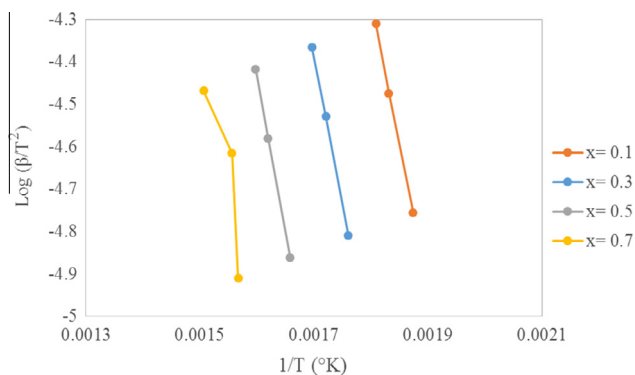


Fig. 10. The typical Coats Redfern plot of peach pits.

The obtained values of activation energy vary between 38.96 and 68.99 kJ/mol for all studied agro-industrial wastes. The calculated values of E_a vary slightly with the heating rate for each biomass. The increasing of heating rate leads to a simultaneous increase of the heat effect [64,65]. Increasing the heating rate signifies that higher temperature is required to set off the pyrolysis process. The highest value of the energy activation was predicted for peach pits at heating rate equal to 15 °C/min and the smallest value of this parameter was calculated for stalk at 5 °C/min. It is necessary to note that activation energy represent the minimum energy requirement for a reaction started, in other words, higher value of activation energy means slower reaction rate and more difficulty of starting a reaction. The found activation energy values are similar to obtained values by Jaroenkhasemmesuk and Tip-payawong [66]. The calculated values of pre-exponential factor were about 2.01×10^7 and $2.51 \times 10^{10} \text{ s}^{-1}$. This parameter also augments with the heating rate increase. In this point, it is important to consider that the frequency factor obtained from standard iso-conversional techniques is tainted by association with the reaction model that must be assumed to permit its calculation [23]. According to Tahmasebi et al. [29], the kinetic rate is controlled by the occurrence of the temperature-dependent physical transformation.

Fig. 10 showed the typical Coats Redfern plots, where the $\text{Log}(\beta/T^2)$ versus $1/T$ is plotted. It can be seen that the fitted lines are almost parallel with a conversion rate increase from 10 to 70%, indicating that the energy activation values may be a few different. This also implied the possibility of a simultaneous reactions mechanism (Table 4) [67].

5. Conclusions

The Cuyo Region, particularly San Juan Province, Argentine, contains readily available biomass waste materials that can be used as feedstock to produce fuels and chemicals, thus improving the economy of the area and contributing to the technological development of renewable energy sources. The study of thermal degradation and kinetics in a thermobalance provided useful information to assess the feasibility of the valorization of six lignocellulosic wastes (sawdust, marcs, stalks, peach, plum and olive pits) by pyrolysis.

The thermogravimetric curves indicate that although the materials are highly heterogeneous due to their content of wood, bark and leaves, their pyrolytic behavior is similar. The analysis of the TG curves of these wastes showed that their pyrolysis decomposition is divided into three stages according to the weight loss rate: the first stage is due to water release, the second stage, called active pyrolysis and the last stage, called passive pyrolysis. It was also possible to observe a heat transfer limitation when the heating

rates increased, making the influence of the heating rate in the TG curves evident.

In order to describe the kinetic behavior during the active pyrolysis, different models were selected. The contraction geometry's model showed the best fitting for all experiments, assuming that the contracting volume is the controlling step of the pyrolysis rate. The kinetic parameters were calculated using this model.

The E_a variation with the heating rate can be due to the kinetic rate of active pyrolysis is controlled by the occurrence of physical transformation the temperature-dependent which is not mass dependent.

The kinetic parameters indicate that the pyrolysis pathways of the six agro-industrial wastes similar to other lignocellulosic materials, proving the feasibility of their valorization by pyrolysis.

Even though, a variation of kinetic parameters values with heating rate exists, the isoconversional methods application to biomass pyrolysis suitably describe the degradation of these wastes, confirming that this simple model is adequate for studying different kinds of lignocellulosic materials.

In order to use these agro-industrial solid wastes for the energy production, the thermal decomposition under different atmosphere must be studied. These researcher works are important to evaluate other thermal process like the combustion and the gasification of these wastes.

References

- [1] N. Mosier, C. Wyman, B. Dale, R. Elander, Y.Y. Lee, M. Holtzapple, Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresour. Technol.* 96 (2005) 673–686.
- [2] Sims, Taylor, From first to second generation biofuel technologies, *Int. Energy Agency* (2008) 1–124.
- [3] K. Raveendran, A. Ganesh, K.C. Khilar, Pyrolysis characteristics of biomass and biomass components, *Fuel* 75 (1996) 987–998.
- [4] S. Ensoz, M. Can, Pyrolysis of pine (*Pinus Brutia* Ten.) chips: 1. Effect of pyrolysis temperatures and heating rate on the product yields, *Energy Sourc. Part A: Recov. Utiliz. Environ. Effects* 24 (2002) 347–355.
- [5] R. Mythili, P. Venkatchalam, P. Subramaniam, D. Uma, Characterization of bio-residues for bio-oil production through pyrolysis, *Bioresour. Technol.* 138 (2013) 71–78.
- [6] C. Selim, T. Yıldırım, Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis, *Bioresour. Technol.* 156 (2014) 182–188.
- [7] M.V. Kök, R. Pamir, Pyrolysis kinetics of oil shales determined by DSC and TG/DTG, *Oil shale* 20 (2003) 57–68.
- [8] M.V. Kök, Coal pyrolysis: thermogravimetric study and kinetic analysis, *Energy Sourc.* 25 (2003) 1007–1014.
- [9] M.V. Kök, O. Karacan, Pyrolysis analysis and kinetics of crude oils, *J. Therm. Anal. Calorim.* 52 (1998) 781–788.
- [10] D. Borah, M. Barua, M.K. Baruah, Dependence of pyrite concentration on kinetics and thermodynamics of coal pyrolysis in non-isothermal systems, *Fuel Process. Technol.* 86 (2005) 977–993.
- [11] A. Aouad, L. Bilali, M. Benchanã, A. Mokhlisse, Kinetic aspect of thermal decomposition of natural phosphate and its kerogen. Influence of heating rate and mineral matter, *J. Therm. Anal. Calorim.* 67 (2002) 733–743.
- [12] M.V. Kök, Temperature-controlled combustion and kinetics of different rank coal samples, *J. Therm. Anal. Calorim.* 79 (1998) 175–180.
- [13] K. Ross, D. Godfrey, Effect of extractives on the thermal decomposition of wheat, triticale, and flax crop residues: a kinetic study, *Int. J. Biomass Renew.* 1 (2012) 19–31.
- [14] J. Flynn, L. Wall, General treatment of the thermogravimetry of polymers, *J. Res. Natl. Bur. Stand.* 70 (1966) 487–523.
- [15] S. Vyazovkin, C. Wight, Kinetics in solids, *Annu. Rev. Phys. Chem.* 48 (1997) 125–149.
- [16] M. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H. Anderson, A. Kemmler, R. Keuleers, J. Janssens, J. Desseyne, C. Li, T. Tang, B. Roduit, J. Malek, T. Mitsuhashi, Computational aspects of kinetic analysis. Part A: the ICTAC kinetics project—data, methods, and results, *Thermochim. Acta* 355 (2000) 125–143.
- [17] A. Coats, J. Redfern, Kinetic parameters from thermogravimetric data, *Nature* 201 (1964) 68–69.
- [18] H. Friedman, Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic, *J. Polym. Sci. Part C: Polym. Symposia* 6 (1964) 183–195.
- [19] L. Aranzazu Rios, P. Cárdenas Muñoz, J. Cárdenas Giraldo, A. Rojas González, J. Carrero Mantilla, Kinetic models of polymer thermal decomposition: a review, *Rev. Ing. Univ. Medellín* 12 (23) (2013) 113–130.
- [20] J. Cai, R. Liu, C. Sun, Logistic regression model for isoconversional kinetic analysis of cellulose pyrolysis, *Energy Fuels* 22 (2008) 867–870.

- [21] J.H. Flynn, A general differential technique for the determination of parameters: energy of activation, preexponential factor and order of reaction (when applicable), *J. Therm. Anal.* 37 (1991) 293–305.
- [22] S. Vyazovkin, A. Lesnikovich, Estimation of the pre-exponential factor in the isoconversional calculation of effective kinetic parameters, *Thermochim. Acta* 128 (1998) 297–300.
- [23] S. Vyazovkin, C. Wight, Isothermal and non-isothermal kinetics of thermally stimulated reactions of solids, *Int. Rev. Phys. Chem.* 17 (1998) 407–433.
- [24] C. Li, T. Tang, Isoconversion method for kinetic analysis of solid-state reactions from dynamic thermoanalytical data, *J. Mater. Sci.* 34 (1999) 3467–3470.
- [25] S. Vyazovkin, Modification of the integral isoconversional method to account for variation in the activation energy, *J. Comput. Chem.* 22 (2001) 178–183.
- [26] P. Budrugeac, E. Segal, Where is the confusion?, *ICTAC News* 36 (2003) 63–64.
- [27] A. Burnham, L. Dinh, A comparison of isoconversional and model-fitting approaches to kinetic parameter estimation and application predictions, *J. Therm. Anal. Calorim.* 89 (2007) 479–490.
- [28] P. Garn, Kinetics of thermal decomposition of the solid state: II. Delimiting the homogeneous-reaction model, *Thermochim. Acta* 160 (1990) 135–145.
- [29] A. Tahmasebi, J. Yu, Y. Han, X. Li, A study of chemical structure changes of Chinese lignite during fluidized-bed drying in nitrogen and air, *Fuel Process. Technol.* 101 (2012) 85–93.
- [30] J.H. Sharp, B.N.N. Achar, in: *Proceeding of the International Clay Conference, 1966*, pp. 1–67.
- [31] ASTM D3173–87, Standard Test Method for Moisture in the Analysis Sample of Coal and Coke. (1996).
- [32] ASTM D3172–89, Standard Practice for Proximate Analysis of Coal and Coke (2002).
- [33] S.A. Channiwal, P.P. Parikh, Unified correlation for estimating HHV of solid, liquid and gaseous fuels, *Fuel* 81 (8) (2002) 1051–1063.
- [34] DataFit 9.1, Trial Version. Retrieved from <http://www.oakdaleengr.com/download.htm> on May 20, by Siyu Chen, 2008.
- [35] L. Prasad, J. Subbarao, J.P. Subrahmanyam, Pyrolysis and gasification characteristics of Pongamia residue (de-oiled cake) using thermogravimetry and downdraft gasifier, *Appl. Therm. Eng.* 63 (2014) 379–386.
- [36] M. Valente, A. Brillard, C. Schönneck, J. Brillhac, Investigation of grape marc combustion using thermogravimetric analysis. Kinetic modeling using an extended independent parallel reaction (EIPR), *Fuel Process. Technol.* 131 (2015) 297–303.
- [37] A. Bhavanam, R.C. Sastry, Kinetic study of solid waste pyrolysis using distributed activation energy model, *Bioresour. Technol.* 178 (2014) 126–131.
- [38] A. Demirbas, G. Arin, An overview of biomass pyrolysis, *Energy Sourc.* 24 (5) (2002) 471–482.
- [39] W. Quirino, A. Vale, A. Andrade, V. Abreu, A. Azevedo, Poder calorífico da madeira e de materiais lignocelulósicos, *Rev. Madeira* 89 (2005) 100–106.
- [40] M. Jeguirim, G. Trouvé, Pyrolysis characteristics and kinetics of Arundo donax using thermogravimetric analysis, *Bioresour. Technol.* 100 (2009) 4026–4031.
- [41] E. Daouk, L. Van de Steene, F. Paviet, S. Salvador, Thick wood particle pyrolysis in an oxidative atmosphere, *Chem. Eng. Sci.* 126 (2015) 608–615.
- [42] P.M. Crnkovic, C. Koch, I. Ávila, D.A. Mortari, A.M. Cordoba, A. Moreira dos Santos, Determination of the activation energies of beef tallow and crude glycerin combustion using thermogravimetry, *Biomass Bioenergy* 44 (2012) 8–16.
- [43] F. Pinto, H. Lopes, R. Andre, I. Gulyurtlu, I. Cabrita, Effect of catalysts in the quality of syngas and by-products obtained by co-gasification of coal and wastes. 2: heavy metals, sulphur and halogen compounds abatement, *Fuel* 87 (7) (2008) 1050–1062.
- [44] A. Demirbas, Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues, *J. Anal. Appl. Pyrol.* 72 (2) (2004) 243–248.
- [45] A. Chouchene, M. Jeguirim, B. Khiari, F. Zagrouba, G. Trouvé, Thermal degradation of olive solid waste: influence of particle size and oxygen concentration, *Resour. Conserv. Recycl.* 54 (2010) 271–277.
- [46] C. Di Blasi, Modeling chemical and physical process of wood and biomass pyrolysis, *Prog. Energy Combust. Sci.* 34 (2008) 47–90.
- [47] B. Lah, D. Klinar, B. Likozar, Pyrolysis of natural, butadiene, styrene-butadiene rubber and tyre components: modelling kinetics and transport phenomena at different heating rates and formulations, *Chem. Eng. Sci.* 87 (2013) 1–13.
- [48] H. Yang, R. Yan, H. Chen, C. Zheng, D.H. Lee, D.T. Liang, In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin, *Energy Fuels* 20 (2006) 388–393.
- [49] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, *Fuel* 86 (2007) 1781–1788.
- [50] J. Cai, W. Wu, R. Liu, G.W. Huber, A distributed activation energy model for the pyrolysis of lignocellulosic biomass, *Green Chem.* 15 (2013) 1331–1340.
- [51] M.J. Antal, G. Varhegyi, E. Jakab, Cellulose pyrolysis kinetics: revisited, *Ind. Eng. Chem. Res.* 37 (1998) 1267–1275.
- [52] A.G. Brabury, Y. Sakai, F. Shafizadeh, A kinetic model for pyrolysis of cellulose, *J. Appl. Polym. Sci.* 23 (1979) 3271–3280.
- [53] R. Capart, L. Khezami, A.K. Burnham, Assessment of various kinetic models for the pyrolysis of a microgranular cellulose, *Thermochim. Acta* 417 (2004) 79–89.
- [54] P. Rantuch, K. Balog, Thermogravimetric analysis of cellulose insulation and determination of activation energy of its thermo-oxidation using nonisothermal, model-free methods, *Polym. Adv. Technol.* 25 (2014) 1169–1174.
- [55] P.E. Sanchez-Jimenez, L.A. Perez-Maqueda, A. Perejon, J.M. Criado, Generalized master plots as a straightforward approach for determining the kinetic model: the case of cellulose pyrolysis, *Thermochim. Acta* 552 (2013) 54–59.
- [56] P.E. Sanchez-Jimenez, L.A. Perez-Maqueda, A. Perejon, J. Pascual-Cosp, M. Benitez-Guerrero, J.M. Criado, An improved model for the kinetic description of the thermal degradation of cellulose, *Cellulose* 18 (2011) 1487–1498.
- [57] V. Mamleev, S. Bourbigot, M. Le Bras, J. Yvon, J. Lefebvre, Model-free method for evaluation of activation energies in modulated thermogravimetry and analysis of cellulose decomposition, *Chem. Eng. Sci.* 61 (2006) 1276–1292.
- [58] Y.J. Rueda-Ordóñez, K. Tannous, Isoconversional kinetic study of the thermal decomposition of sugarcane straw for thermal conversion processes, *Bioresour. Technol.* 196 (2015) 136–144.
- [59] J. Cho, S. Chu, P.J. Dauenhauer, G.W. Huber, Kinetics and reaction chemistry for slow pyrolysis of enzymatic hydrolysis lignin and organosolv extracted lignin derived from maplewood, *Green Chem.* 14 (2012) 428–439.
- [60] O. Senneca, R. Chirone, P. Salatino, L. Nappi, Patterns and kinetics of pyrolysis of tobacco under inert and oxidative conditions, *J. Anal. Appl. Pyrol.* 79 (2007) 227–233.
- [61] X. Cao, K.S. Ro, M. Chappell, Y. Li, J. Mao, Chemical structures of swine-manure chars produced under different carbonization conditions investigated by advanced solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy, *Energy Fuels* 25 (2011) 388–397.
- [62] X. Cao, K.S. Ro, J.A. Libra, C.I. Kammann, I. Lima, N. Berge, et al., Effects of biomass types and carbonization conditions on the chemical characteristics of hydrochars, *J. Agric. Food Chem.* 61 (2013) 9401–9411.
- [63] P.W.M. Jacobs, F.C. Tompkins, Classification and theory of solid reactions, in: W.E. Garner (Ed.), *Chemistry of the Solid State*, Academic Press, New York, 1955 (Chapter 7).
- [64] M. Amutio, G. Lopez, R. Aguado, M. Artetxe, J. Bilbao, M. Olazar, Kinetic study of lignocellulosic biomass oxidative pyrolysis, *Fuel* 95 (2012) 305–311. 4.
- [65] L. Sanchez Silva, D. Lopez Gonzalez, A.M. Garcia Minguillan, J.L. Valverde, Pyrolysis, combustion and gasification characteristics of Nannochloropsis gaditana microalgae, *Bioresour. Technol.* 130 (2013) 321–331.
- [66] C. Jaroenphasemmesuk, N. Tippayawong, Thermal degradation kinetics of sawdust under intermediate heating rates, *Appl. Therm. Eng.* 103 (2016) 170–176.
- [67] L. Zhijia, J. Zhenhui, F. Benhua, L. Xing, Thermal decomposition characteristics of chinese fir, *Bioresources* 8 (4) (2013) 5014–5024.