

Agro-industrial wastes pyrolysis: comparison of the kinetic parameters obtained applying different models

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Abstract

Pyrolysis of regional agro-industrial wastes was studied using thermogravimetric analysis. Experimental data were analyzed using different kinetic methods: Kissinger, FWO, linear multiple regression and DAEM methods. The results showed that kinetic parameters values are in acceptable agreement applying different methods and can be used to understand the degradation mechanism during active pyrolysis. The E values calculated by the DAEM, FWO and Kissinger methods were higher than those obtained by the linear multiple regression method. The values of activation energy obtained from the Kissinger method are consistent with the range of values obtained by the FWO and DAEM methods and are very near to their average values (between 130.29 and 261.10 kJ/mol for all studied agro-industrial wastes). DAEM and FWO methods provides E and A distributions but linear multiple regression method provide the knowledge of kinetic triplets for each studied heating rate, presenting a slower good fit than the other methods. However, Kissinger method provides only one E and A values for all heating rates. Considering the application of FWO and DAEM methods, different kinds of reaction mechanisms are produced about a conversion values greater than 0.6-0.7 indicating the beginning of passive pyrolysis. A fluctuation of E was observed, also. All obtained results applying different methods reveal the process complexity and physical transformation the temperature-dependent or contributions of parallel reaction steps can affect this process. Experimental results showed that values of kinetic parameters are in acceptable agreement applying different methods and it could be an auspicious and justifiable feedstock for alternative methods.

Keywords: Regional agro-industrial wastes; Pyrolysis; Modeling; Thermogravimetric analysis; Kinetics

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1. Introduction

Efforts to reduce the use of the petroleum as an energy source and, due to an increase of interest in renewable energy resource, were proposed different alternatives. The use of lignocellulosic wastes is one of them. Also, the emission of harmful greenhouse gases to the environment is reduced. The thermochemical conversion processes are widely used to harness the energy content of biomass. Pyrolysis is one of these processes. This phenomenon is also an important step in combustion and gasification. Thereby, a thorough understanding of pyrolysis kinetics is vital to the assessment of these processes including the feasibility, design, and scaling of industrial biomass conversion applications [1, 2].

Generally, studying thermal behavior of biomass can be carried out in various systems but the most used and simplest system is a thermogravimetric analyzer [3]. Today, the researches of kinetics are one of the most important applications of thermal analysis.

Galwey et al. [4], Vyazovkin et al. [5], Brown et al. [6] and other authors recognize that solid state reaction are usually very complex to describe them by a pair of Arrhenius parameters (energy activation and pre-exponential factor) and the traditional set of kinetics model. A lot of kinetic methods have been proposed so as to obtain the parameters that characterize the thermal degradation process [7, 8].

Non-isothermal kinetics can be classified into model-free, also called the isoconversional method, and model-fitting categories. The essential assumption of the first method is that the reaction rate for a constant extent of conversion (α) depends only on the temperature (T) [9]. Isoconversional models are Kissinger [10], Flynn-Wall-Ozawa and distributed activation energies model (DAEM) methods [11, 12].

A model-fitting is the method used by Karaosmanoglu et al. (linear regression multiple) [13]. In this case, the Arrhenius equation is linearized to determine the kinetic parameters.

The objective of this work is to investigate the pyrolysis behavior and kinetics of six regional agro-industrial wastes. The data were analysed using different methods to simulate the biomass pyrolysis at different heating rates: Kissinger, Flynn-Wall-Ozawa, the linear regression multiple, and the distributed activation energies models (DAEM).

2. Methods and materials

This study focused on six wastes: 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.

The 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 [14,15]. Elemental analysis was performed using EuroEA3000 elemental analyzer. The results of elemental and ultimate analysis are shown in Table 1. To calculate the high heating value, the correlation proposed by Channiwala et al., [16] was used (Table 1):

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

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

Table 1. Results of proximate and ultimate analysis (dry basis, weight percentage) (HHV: Higher heating values)

	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 (%)*	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

*

By difference

2. 1. Thermogravimetric analysis

Thermogravimetric (TG) and derivative thermogravimetric (DTG) experiments were carried out using a TGA-50 Shimadzu microbalance, under nitrogen atmosphere, heated from room temperature to 1173 K. The experiments were performed at three different heating rates of 5, 10 and 15 K/min for each sample. The nitrogen gas with a flow rate of 100 mL/min was used. The reproducibility of the experiments was acceptable.

3. Kinetics analysis

The kinetic of biomass decomposition is based on a single reaction and can be expressed by Eq. 2:

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

where t , α , da/dt , $f(\alpha)$ and K are time, conversion degree or extent of reaction, the process rate, conversion function and rate constant, respectively. α can be defined as the mass fraction of 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 remaining after the reaction, respectively.

K is the temperature function. The k temperature dependence for the process is described by the Arrhenius Equation (Eq. 4):

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

where A , T , R and E are pre-exponential factor, absolute temperature, universal gas constant and is the apparent activation energy, respectively.

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

3. 1. Linear multiple regression method

Parameters of the reaction kinetics can be determined using the procedure applied by Karaosmanoglu et al. [13]. Global kinetics of the reaction can be written as:

$$\frac{-1}{w_0 - w_f} \frac{dw}{dt} = \left(\frac{w - w_f}{w_0 - w_f} \right)^n \quad (5)$$

where w_0 , w_f , w , dw/dt and n are the initial mass at the step start, the final mass at the step, the mass at any time, the change ratio of mass with time, the order of the reaction, respectively. Applying the Arrhenius Eq. (3), and combining this Eq. with Eq. (5), a linear form is obtained:

$$\ln \left[\frac{-1}{w_0 - w_f} \frac{dw}{dt} \right] = \ln(A) - \left(\frac{E}{RT} \right) + n \ln \left(\frac{w - w_f}{w_0 - w_f} \right) \quad (6)$$

where A is the pre-exponential factor and R , the universal gas constant (gas value). Eq. (6) may be written under the linear form:

$$y = B + Cx + Dz \quad (7)$$

$$y = \ln \left[\frac{-1}{w_0 - w_f} \frac{dw}{dt} \right] \quad (8)$$

$$x = \frac{1}{T} \quad (9)$$

$$z = \ln \left(\frac{w - w_f}{w_0 - w_f} \right) \quad (10)$$

The constants can be estimated by multi-linear regression for each stage using Microsoft Excel.

3. 2. Kissinger method

Kissinger's method assumes that the reaction rate has maximum value at the peak temperature (T_m) [10]. This assumption implies a constant extent of α at T_m . The Kissinger's Eq. is:

$$B = \ln(A); C = -\frac{E}{R}; D = n \tag{11}$$

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E}{RT_m} + \ln\left(\frac{AR}{E}\right) \tag{12}$$

This method can be used independently of α , so not need to know the reaction mechanism. By a plot of $\ln\left(\frac{\beta}{T_m^2}\right)$ versus $1/T$ gives E from the slope.

3. 3. Distributed activation energy model method

DAEM, developed by Vand [17], has been used for analyzing the complex reactions occurring during the pyrolysis of fossil and biomass fuels [18-21]. It assumes that number of parallel irreversible first order reactions that have different kinetic parameters occur simultaneously. E and A can be calculated by following Eq. [22]:

$$\ln\frac{\beta}{T^2} = \ln\frac{RA}{E} + 0.6075 - \frac{E}{RT} \tag{13}$$

3. 4. Flynn-Wall-Ozawa method

This method uses the Doyle’s approximation for determine the activation energy without knowing the reaction order. Finally, the Eq. represents this model:

$$\ln\beta = \ln\frac{AE}{Rg(\alpha)} - 5.331 - 1.052\frac{E}{RT} \tag{14}$$

For a constant conversion, a plot of $\ln\beta$ versus $1/T$, from the data at the different heating rates, leads to a straight line whose slope provides E calculation.

4. Results and discussion

4. 1. Characterization of the raw material

Ultimate and proximate analyses of the six wastes are shown in Table 1. Considering the first analysis, the peachpits have the highest C (53.01%) and H (5.90%) contents. Furthermore, the stalk has the highest N content (6.37%). among the six materials.

The high water content increases the energy requirements to carry out the thermal treatment, rises the residence time for drying and reduces the temperature. These aspects decrease the process efficiency. On the other hand, the low ash percentages minimize the production of fly and the bottom ash and affect positively the high heating value (HHV) [16]. These solids contain significant amounts of un- reacted carbon and sulfur [23], but the studied wastes contain very small amounts of this element in their compositions. The high organic matter content makes these wastes very suitable for thermal treatment [24].

4. 2. Thermal behavior

A typical decomposition of lignocellulosic wastes is shown in Figs.1-3. It can be seen that the pyrolysis could be divided into three stages. The first, dehydration (chemical release of water vapor) begins at temperatures of 373 K and then increases rapidly around 423 K. The second, called active pyrolysis corresponding to the maximum weight loss about 35 - 40%, is produced between 433 and 823 K. The little differences in this range, for all biomasses, is attributed to variations of hemicellulose, lignin and cellulose contents [25]. The temperature corresponding to the maximum weight loss rate of all wastes is similar for all cases, about 603K. A large amount of gas species such as CO₂, CO, CH₄ and H₂O are released in this stage [26]. The last step, called passive pyrolysis, is produced at high temperature, the weight loss is very smaller, possibly produced as a result of the decomposition of carbonaceous materials retained in char residues. It can be seen from Figs. 4-6.

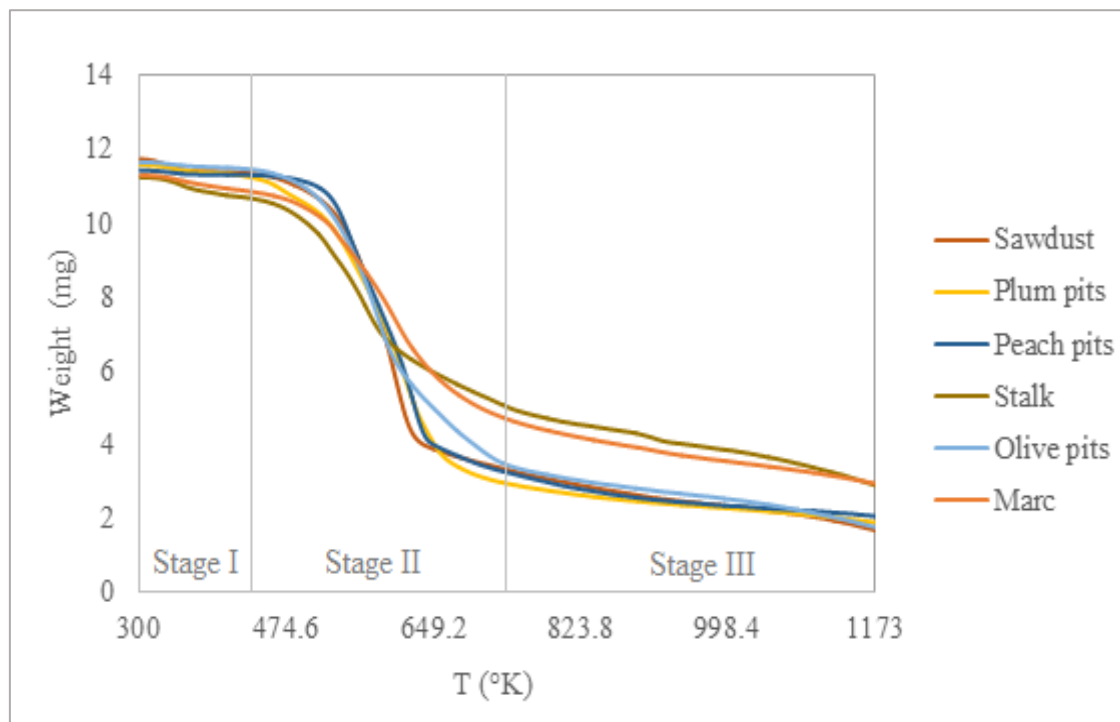


Fig. 1. TG curves for the studied biomass samples at 5 K/min.

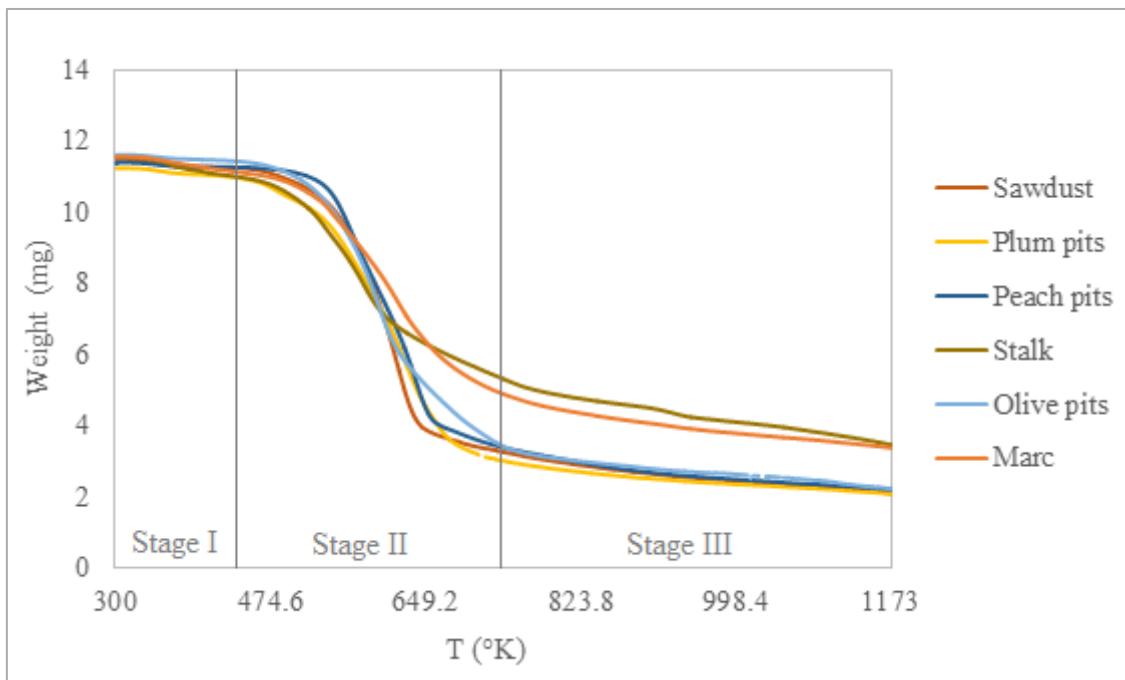


Fig. 2. TG curves for the studied biomass samples at 10 K/min.

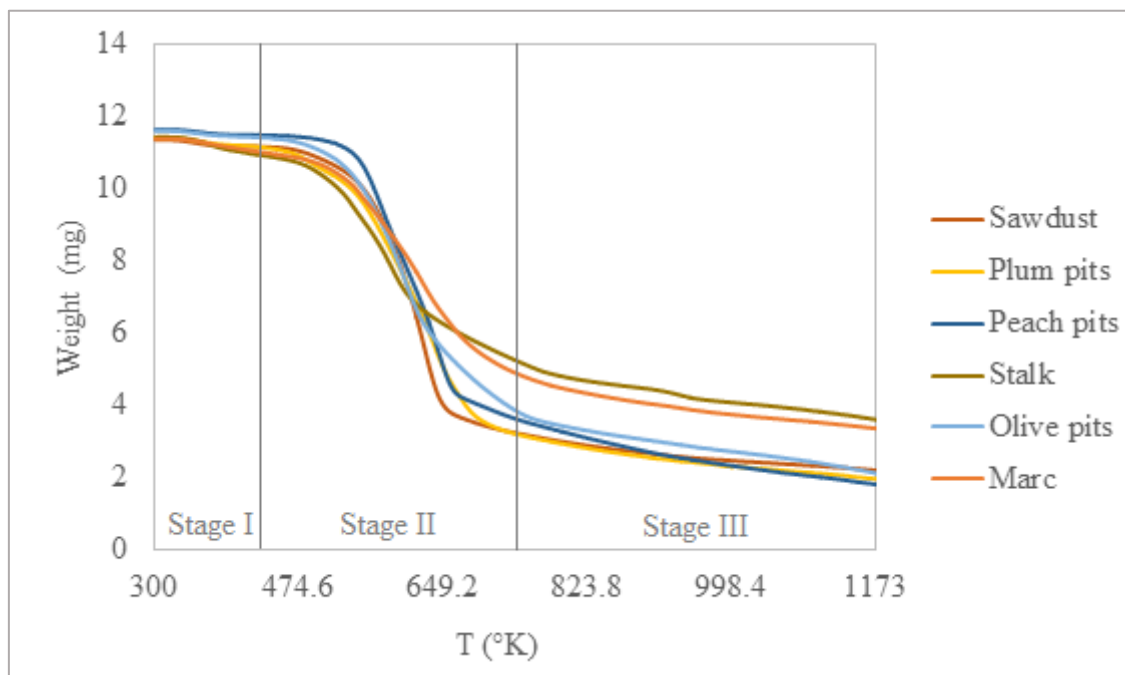


Fig. 3. TG curves for the studied biomass samples at 15 K/min.

Regard to the DTG curves (Figs. 4-6), during the active pyrolysis, the peach pits and stalk wastes presents a first peak on their decomposition curve and that corresponds to the time when the maximum decomposition rate of hemicellulose is reached [27]. The peak, resulting from the cellulose degradation, is accompanied by a shoulder at low temperature, which is related to hemicellulose degradation. The DTG curves obtained for the other wastes do not exhibit it, because the hemicellulose and cellulose are decomposed together forming bigger peak [28]. The main peak on the DTG decomposition curve corresponds to the time when the maximum decomposition rate of cellulose is reached. Thermal decomposition of lignin does not have such a significant behavior as the other two compounds; moreover, the maximum decomposition rate overlaps with that of cellulose, meaning that the global minimum on the DTG curve is also enhanced by the decomposition of lignin [29-31].

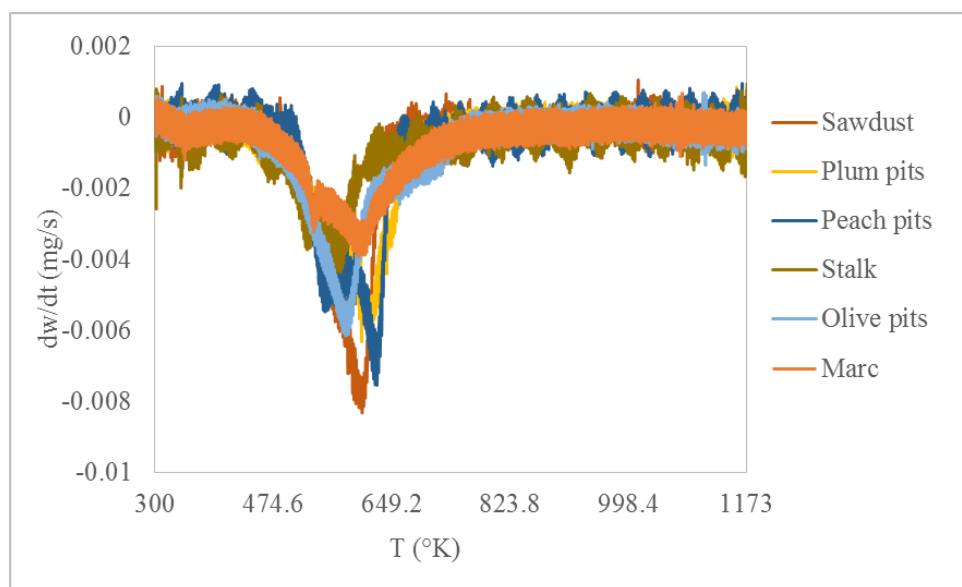


Fig. 4. DTG curves for the studied biomass samples at 5 K/min.

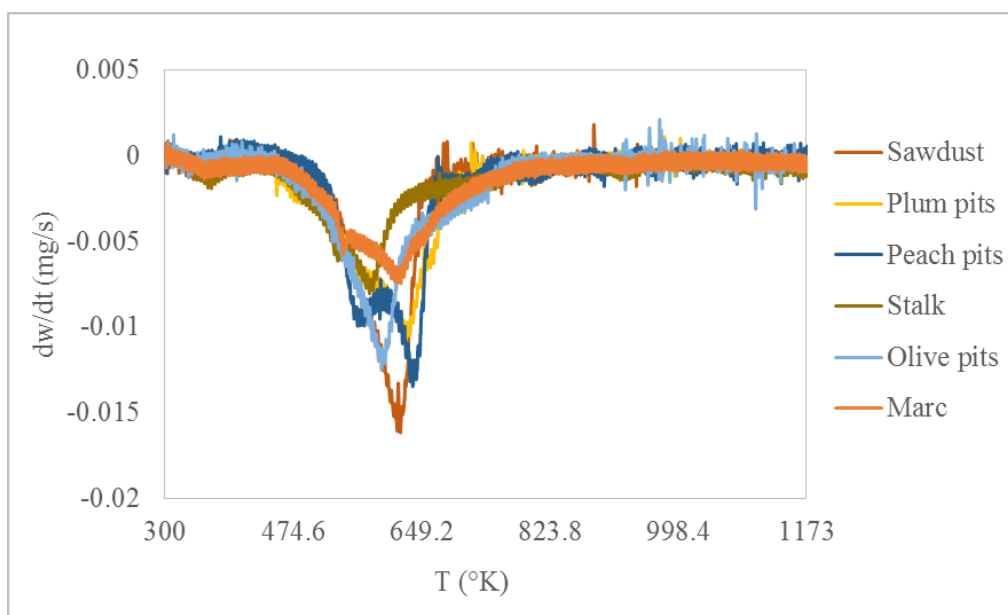


Fig. 5. DTG curves for the studied biomass samples at 10 K/min.

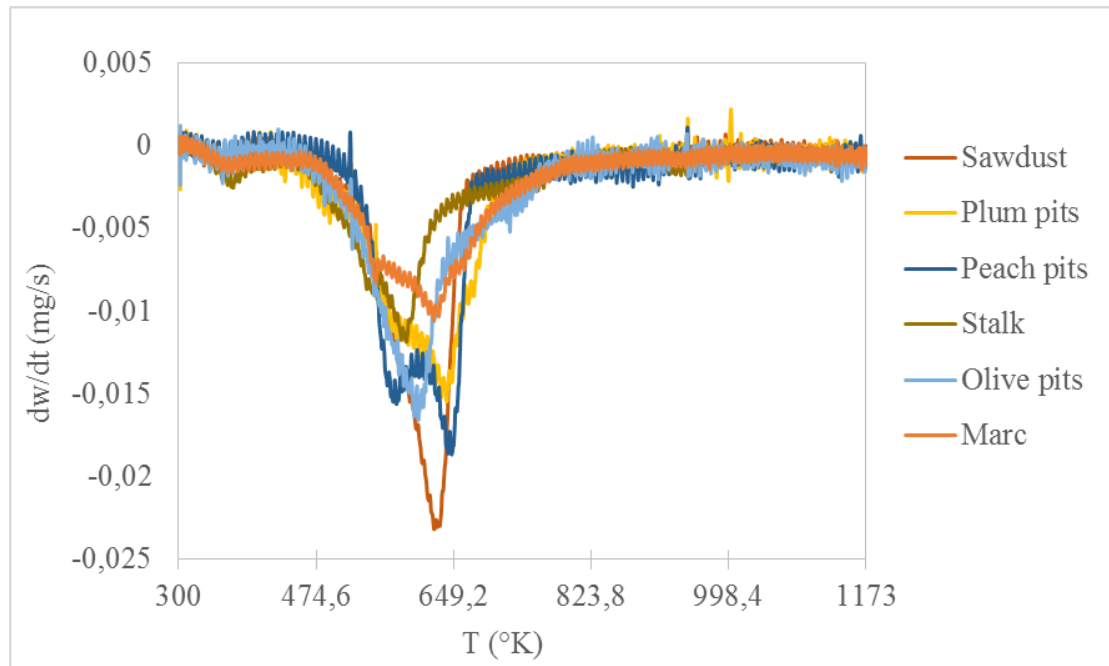


Fig. 6. DTG curves for the studied biomass samples at 15 K/min.

The effect of the heating rate is shown in Fig. 7 for the sawdust. The same behavior is applied at all biomasses. With increasing heating rate, the curves are shifted to the right and the peak height of the DTG curves increases, affecting the maximum weight loss rate (Fig. 7). This is related to the heat and mass transfers [32], which are higher when the burning time is lower due to stronger thermal shock being acquired in a short time and the greater temperature gradient between the inside and outside, which does not favor the volatile matter release [33, 34].

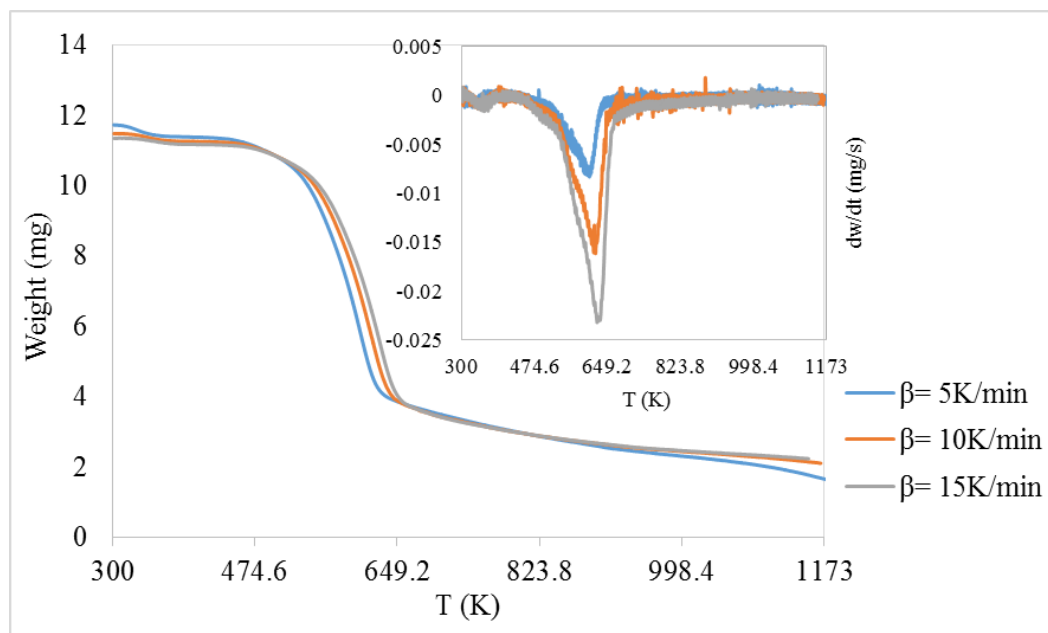


Fig. 7. Comparison of the weight loss rates for sawdust.

4. 3. Kinetic analysis

The greatest weight loss is produced during the active pyrolysis, for that the second peak is considered in all cases in order to carry out the kinetic study.

4. 3. 1. Linear multiple regression method

Fig. 8 shows the comparison between the experimental data and the model results. The founded activation energies and pre-exponential factors and reaction orders (Table 2) of the active pyrolysis step were very close in agreement with literature data for other biomasses [35]. For all cases, the reaction order n is smaller to 1. R^2 values obtained are shown in Table 2 and they vary between 0.83 and 0.94. Jeguirim et al. obtained similar values during the cellulose and hemicellulose decomposition step of arundodonax [36].

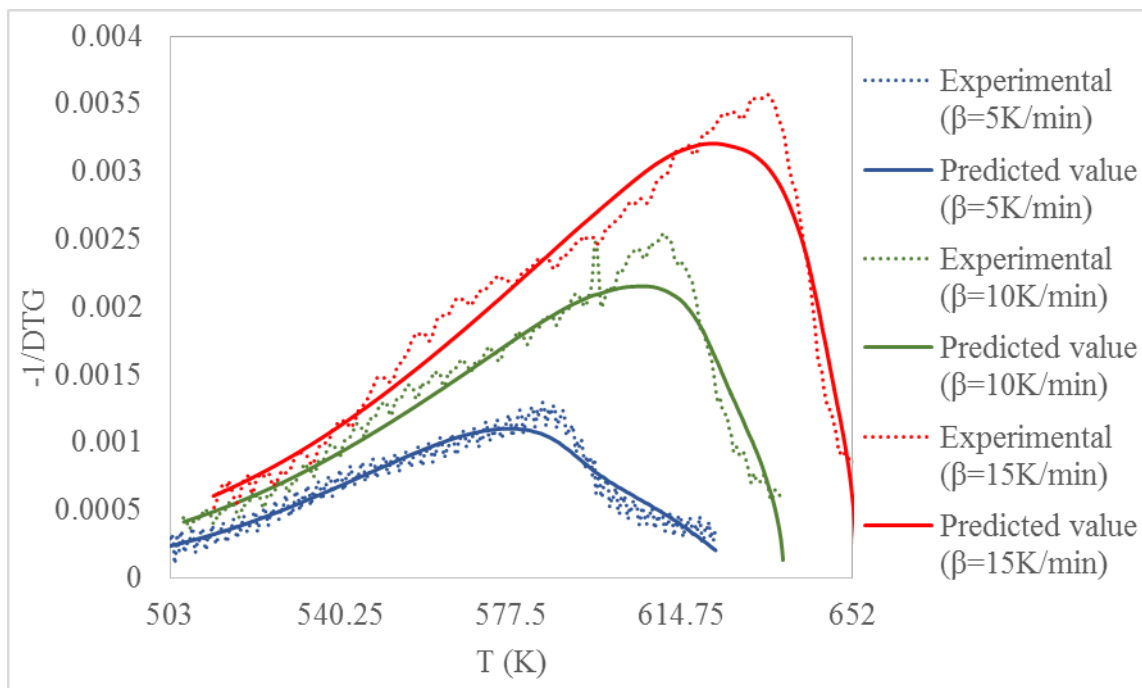


Fig. 8. Comparison of experimental and predicted value for plum pits at different heating rate by linear regression method.

4. 3. 2. Kissinger method

Using these methods, the activation energy was obtained at the temperature of maximum reaction rate (Fig. 9). This temperature, for all cases, has been determined from the first derivative of the curves at different heating rate.

Table 2. Pre-exponential factor and activation energy obtained using linear multiple regression method

Agro-industrial wastes	Heating rate (°C/min)	E (KJ/mol)	A (s ⁻¹)	n	R ²
Sawdust	5	91.37	5.81*10 ⁵	0.72	0.92
	10	92.14	8.41*10 ⁵	0.60	0.92
	15	89.72	5.33*10 ⁵	0.65	0.92
Plum pits	5	77.28	2.51*10 ⁴	0.60	0.91
	10	58.21	4.24*10 ²	0.54	0.92
	15	55.12	2.52*10 ²	0.51	0.94
Peach pits	5	87.23	2.30*10 ⁵	0.76	0.83
	10	87.47	2.83*10 ⁵	0.81	0.86
	15	82.52	1.03*10 ⁵	0.77	0.87
Stalk	5	60.57	9.97*10 ²	0.86	0.88
	10	60.48	1.66*10 ³	0.68	0.91
	15	61.07	2.38*10 ³	0.76	0.91
Olive pits	5	64.73	2.06*10 ³	0.79	0.88
	10	64.90	3.30*10 ³	0.55	0.88
	15	69.10	1.00*10 ⁴	0.78	0.92
Marc	5	64.35	1.42*10 ³	0.93	0.83
	10	60.77	9.62*10 ²	0.70	0.85
	15	55.36	3.33*10 ²	0.57	0.91

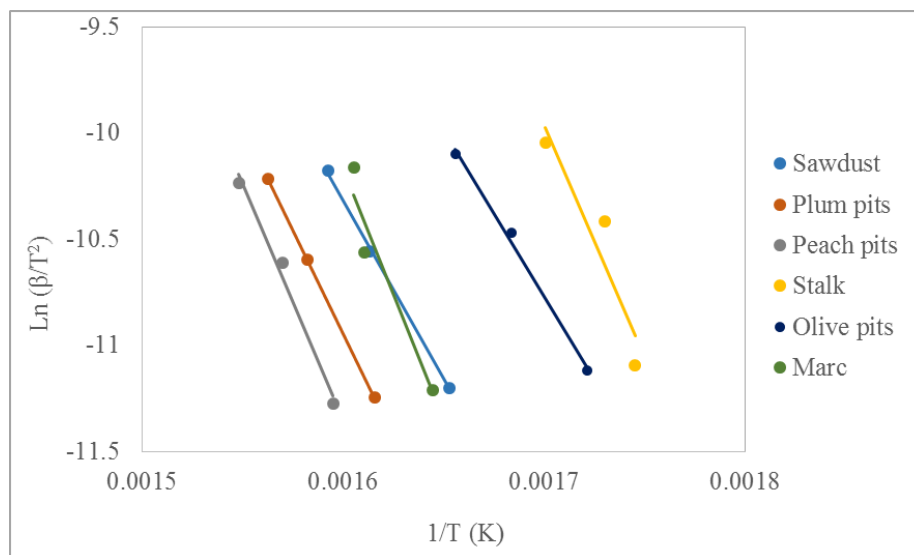


Fig. 9. Kissinger method applied to all biomass at different heating rates.

The obtained values for this parameter vary between 130.29 and 197.50 kJ/mol for all studied agro-industrial wastes. The activation energy was highest to winery wastes and smallest to olive pits. They are also very close with the value reported by Slopiecka et al. [37]. The smallest R² value was obtained for the marc (Table 3). Pre-exponential factor was calculated from Eq. (8) derived from the intercept of plotting regression line. The results obtained vary between $1.22 \cdot 10^{11}$ and $2.92 \cdot 10^{16} \text{ s}^{-1}$.

Table 3. Pre-exponential factor and activation energy obtained using Kissinger method

Parameters	Agro-industrial wastes					
	Sawdust	Plum pits	Peach pits	Olive pits	Stalk	Marc
E (kJ/mol)	139.72	161.97	184.99	130.29	183.10	197.50
A (s ⁻¹)	2.63*10 ¹¹	1.18*10 ¹³	7.55*10 ¹⁴	1.22 *10 ¹¹	1.89*10 ¹⁶	2.92*10 ¹⁶
R ²	0.99	1	0.98	0.99	0.88	0.93

4. 3. 3. Flynn-Wall-Ozawamethod

For the investigated process, activation energy was evaluated from the straight line slope of the Eq. (9). Fig.10 shows the linear fitting at seven values of α for peach pits; and Fig. 11 presents the variation of E with α . Pronounced different behavior is observed for winery wastes: The E value increases with α . For the other solid wastes do not show a high variation. Due to the activation energy is dependent on conversion for all cases; the reaction mechanism is not the same in the whole decomposition process indicating the existence of a complex multi-step mechanism that occurs in the solid state, particularly in the marcs and stalks cases [5]. Table 4 shows the kinetic parameters values. These are comparable with values obtained by Ounas et al. [38].

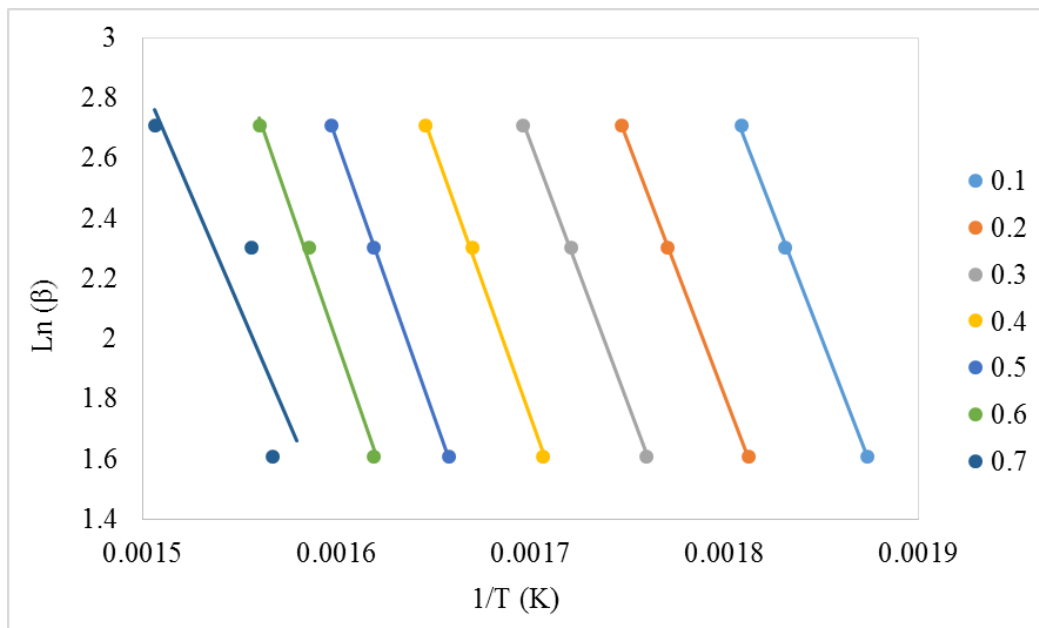


Fig. 10. Regression lines to conversion of 10–70% based on the FWO method for peach pits.

4. 3. 4. Distributed activation energy model method

The Eq. (10) was used to calculate the values of activation energy at each selected level of conversion rate α from the Arrhenius plot of $\ln(\beta/T^2)$ versus $1/T$. These plots are drawn at conversions from 0.1 to 0.7, they are linear as can be seen in Fig.12. The Arrhenius plots are linear and parallel up to a conversion of 0.7, and above these conversions the plots are nonlinear and follow different behavior due to the different chemical reactions occurring [22]. The coefficient of correlation (R^2) for all the lines drawn at various conversions (0.1–0.7) is greater than 0.90, which indicates the best fit, whereas the coefficient of correlation for the conversions greater than 0.8 is very low. This behavior suggests that the materials have

different kinds of reaction mechanisms at the end of the decomposition process (passive pyrolysis). However, the stalk presents different behavior for conversions equal to 0.6 and 0.7, giving inconsistent results. The olive pits present the same behavior just for the conversion equal to 0.7. The activation energy values are reported in Table 4. The E dependence with the α shows that the decomposition is not a single reaction stage, but includes the contributions of parallel reaction steps on the global reaction rate (Fig. 13). The results are in good agreement with those obtained for another investigator in fungal pretreated corn stover [39].

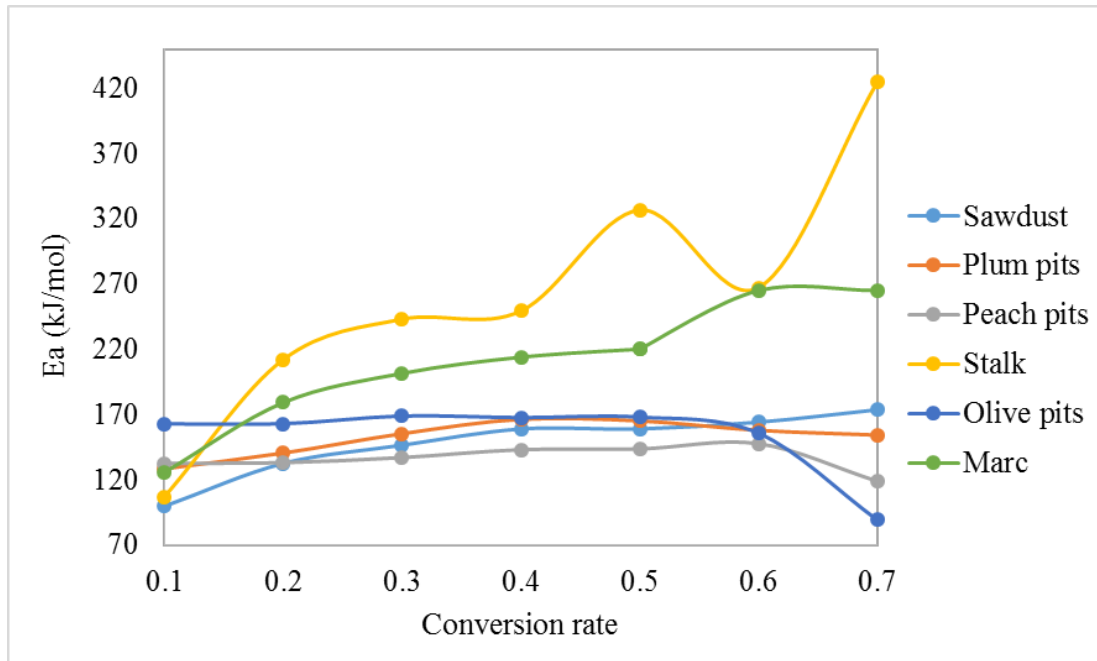


Fig. 11. Dependence of activation energy on the extent of conversion evaluated from the FWO method.

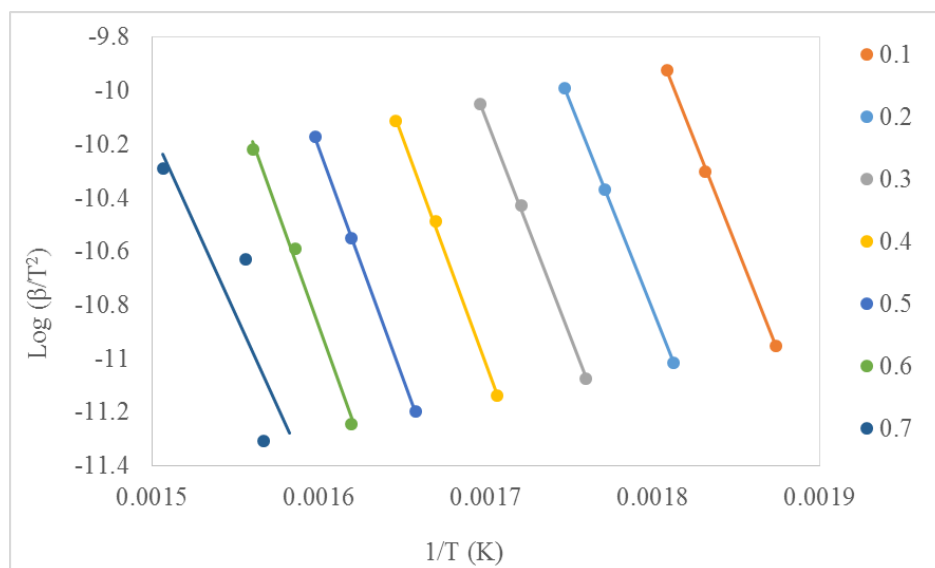


Fig. 12. Regression lines to conversion of 10-70% based on the DAEM method for peach pits.

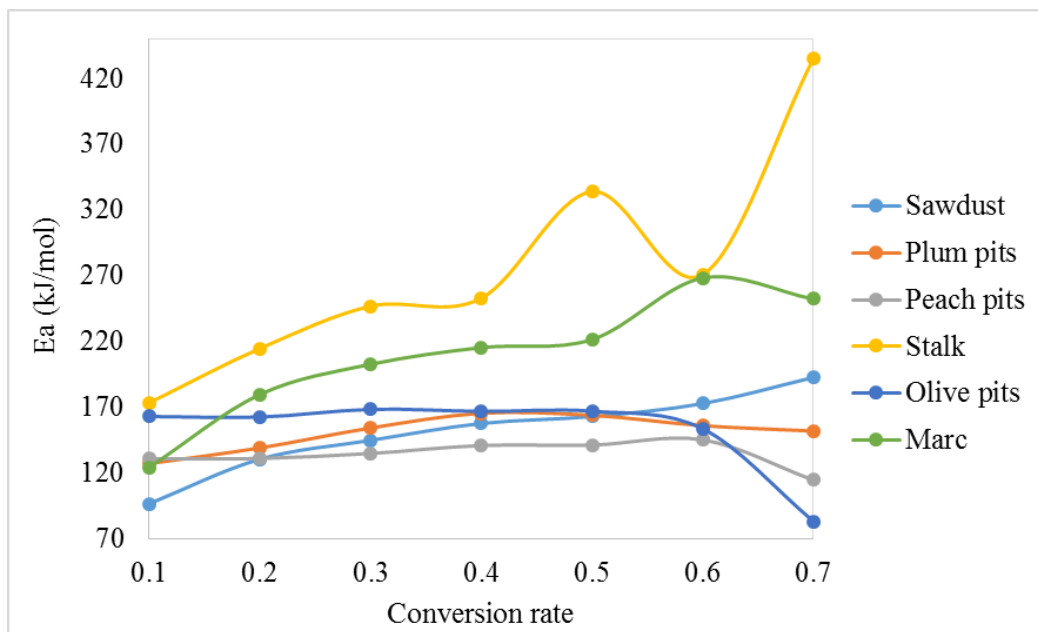


Fig. 13. Dependence of activation energy on the extent of conversion evaluated from the DAEM method.

4. 3. 5. Comparison between analyzed kinetics parameters

Solid fuels are not homogeneous and the results are sensitive to experimental conditions. Although, thermogravimetry provides general information on the overall reaction kinetics and it can be used as a tool for providing comparisons of the kinetic data with the variation of different operating variables. It is recommended that multiple heating rate programs should be used for the kinetic computations [6]; however, single heating rate methods can be performed to evaluate activation energies. Both techniques were used in this study.

The results from the single heating rate kinetic methods (linear multiple regression) and multiple heating rate kinetic methods (Kissinger, Flynn-Wall-Ozawa and DAEM) are very different.

The FWO and DAEM methods can estimate activation energy as a function of conversion without supposing the reaction model and allow detecting multi-step kinetics as a dependence of activation energy on conversion in contradistinction to Kissinger method which generated a single value of the E for the whole process [40].

The values of activation energy obtained from the Kissinger method (Table 3) are consistent with the range of values obtained by the FWO and DAEM methods and are very near to their average values. Considering the other researchers work, Çepeliogüller et al. [41] studied the kinetic behavior of refuse derived fuel (RDF) during the pyrolysis at different heating rate and they obtained similar results. They calculated the kinetic parameters using different methods including FWO and KAS models (isoconversional models). These researcher observed that E are similar trend for α equal 0.1, 0.2-0.7 and the average E values are obtained applying FWO and KAS models are very closer. Ma et al. [42] analyzed the palm kernel shell pyrolysis. They determined the kinetic parameters using FWO and KAS methods at different heating rates. These researchers observed a fluctuation of E due to the interactive reactions related to cellulose, hemicellulose and lignin degradation.

Table 4. Activation energy for conversion range of 0.1–0.7 using FWO and DAEM methods

Agro-industrial wastes	α	DAEM model E (kJ/mol)	A (s ⁻¹)	FWO model E (kJ/mol)	A (s ⁻¹)	Difference (%)
Sawdust	0.1	96.41	9,17*10 ⁰⁸	99.88	2,01*10 ¹⁵	3.60
	0.2	130.33	3,99*10 ¹¹	132.7	9,82*10 ¹⁷	1.79
	0.3	144.62	3,25*10 ¹²	146.58	8,53*10 ¹⁸	1.34
	0.4	157.51	2,11*10 ¹³	159.07	5,80*10 ¹⁹	0.98
	0.5	162.74	2,97*10 ¹³	164.25	8,52*10 ¹⁹	0.92
	0.6	172.63	1,22*10 ¹⁴	173.81	36,*10 ²⁰	0.68
	0.7	192.54	3,14*10 ¹⁵	192.9	9,59*10 ²¹	0.19
	Average	150.97		152.74		
Plum pits	0.1	126.96	4,95*10 ¹²	128.59	9,75*10 ¹⁸	1.28
	0.2	138.86	4,97*10 ¹²	140.62	1,17*10 ¹⁹	1.25
	0.3	154.03	3,47*10 ¹³	155.43	8,85*10 ¹⁹	0.90
	0.4	165.28	1,07*10 ¹⁴	166.46	2,92*10 ²⁰	0.71
	0.5	163.7	2,58*10 ¹³	165.26	7,56*10 ¹⁹	0.94
	0.6	155.82	2,24*10 ¹²	158.03	6,95*10 ¹⁸	1.40
	0.7	151.71	4,51*10 ¹¹	154.38	1,48*10 ¹⁸	1.73
	Average	150.91		152.68		
Peach pits	0.1	130.62	9,08*10 ¹¹	132.75	2,12*10 ¹⁸	1.63
	0.2	130.84	3,20*10 ¹¹	133.25	8,57*10 ¹⁷	1.81
	0.3	134.66	3,29*10 ¹¹	137.17	8,72*10 ¹⁷	1.83
	0.4	140.73	4,75*10 ¹¹	143.2	1,34*10 ¹⁸	1.72
	0.5	141.04	2,08*10 ¹¹	143.78	6,20*10 ¹⁷	1.91
	0.6	145.01	2,35*10 ¹¹	147.78	7,36*10 ¹⁷	1.87
	0.7	114.37	2,69*10 ⁰⁸	119.01	9,23*10 ¹⁴	3.90
	Average	133.90		136.71		
Olive pits	0.1	162.81	7,25*10 ¹⁵	163.00	1,53*10 ²²	0.12
	0.2	162.38	7,01*10 ¹⁴	163.08	1,67*10 ²¹	0.43
	0.3	168.23	6,54*10 ¹⁴	168.97	1,67*10 ²¹	0.44
	0.4	166.69	1,72*10 ¹⁴	167.77	4,66*10 ²⁰	0.64
	0.5	166.82	7,31*10 ¹³	168.15	2,09*10 ²⁰	0.79
	0.6	153.47	1,47*10 ¹²	155.83	4,58*10 ¹⁸	1.51
	0.7	82.97	1,86*10 ⁷	89.38	2,10*10 ⁷	7.17
	Average	151.91		153.74		
Stalk	0.1	173.23	4,01*10 ¹⁸	107.18	1,64*10 ¹⁷	38.13
	0.2	214.58	1,15*10 ²¹	212.24	2,41*10 ²⁷	1.09
	0.3	246.72	1,41*10 ²³	243.19	3,25*10 ²⁹	1.43
	0.4	252.86	6,16*10 ²²	249.38	1,54*10 ²⁹	1.38
	0.5	334.01	2,10*10 ²⁹	326.82	5,56*10 ³⁵	2.15
	0.6	270.82	1,90*10 ²²	264.26	2,10*10 ²⁹	2.42
	0.7	435.35	8,09*10 ³²	424.65	2,10*10 ²⁹	2.46
	Average	275.37		261.10		
Marc	0.1	124.09	2,53*10 ¹²	125.89	5,04*10 ¹⁸	1.45
	0.2	179.57	5,84*10 ¹⁶	179.3	1,35*10 ²³	0.15
	0.3	202.56	1,09*10 ¹⁸	201.3	2,78*10 ²⁴	0.63
	0.4	215.27	2,38*10 ¹⁸	214.07	6,57*10 ²⁴	0.56
	0.5	221.39	1,76*10 ¹⁸	220.22	5,20*10 ²⁴	0.53
	0.6	268.21	2,70*10 ²¹	265.1	5,58*10 ²⁷	1.17
	0.7	252.21	1,17*10 ¹⁹	250.41	4,09*10 ²⁵	0.72
	Average	209.04		208.09		

On the other hand, regression linear method obtained very different energy activation values. Table 5 shows the average values comparison between all methods used.

The FWO and DAEM methods allow estimating activation energy and pre-exponential factor as a function of conversion. The other applied methods give a single value of E for the complete process and complexity may not be exposed [5]. On the other hand, the linear multiple regression method produces different E values for considered in this work, showing that the kinetic rate is controlled by the occurrence of different phenomena which is not mass dependent. These results are similar to those obtained from Coast Redfern method [43].

Table 5. Activation energy obtained by the methods used

Agro-industrial wastes	Activation energy (kJ/mol)			
	Kissinger	FWO	DAEM	Linear regression
Sawdust	139.72	152.74	150.97	64.83
Plum pits	161.97	152.68	150.91	39.50
Peach pits	184.99	136.71	133.90	66.61
Stalk	194.36	261.10	244.28	45.94
Olive pits	130.29	153.74	163.41	52.20
Marc	197.50	208.09	209.04	34.17

5. Conclusion

Different methods were applied to the obtained kinetics parameters of the regional agro-industrial wastes pyrolysis. These methods should lead to same value of activation energy, however, unfortunately, they produce different activation energy values. The activation energies of thermal decomposition calculated by the DAEM, FWO and Kissinger methods were higher than those obtained by the linear multiple regression method. This last method can be easily applied, and obtained the average E value, but the DAEM and FWO methods can reflect the E and A distribution of the whole pyrolysis process and is more descriptive of the pyrolysis reaction than the linear multiple regression method. It is important to consider that last mentioned method provide the knowledge of kinetic triplets (A , E , $f(\alpha)$). Nevertheless, they are unable to reveal the multistep nature of solid state reactions. Instead, Kissinger method gave results very similar to those obtained using the DAEM and FWO methods, obtaining in this case A values, too. So, the application of these last methods reveals that E are similar trend for α equal 0.1-0.6, 0.7 and a fluctuation of this parameter.

Experimental results showed that values of kinetic parameters are in acceptable agreement applying different methods and it could be an auspicious and justifiable feedstock for alternative methods. Considering all obtained results, it is significant to note that the all method applications reveal the process complexity, it should be affected by physical transformation the temperature-dependent or includes the contributions of parallel reaction steps, among others.

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