Effect of applying organic amendments on the pyrolytic behavior of a poplar energy crop.

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Abstract

Thermal conversion of biomass derived from energy crops is one of the most booming alternatives when producing energy. In this work it was carried out the thermogravimetric analysis and the study of the kinetic parameters (activation energy and frequency factor) of poplar wood samples from four different clones (UNAL, I-214, AF-2 and AF-8). Poplars annually fertilized throughout four years with dehydrated composted sewage sludge (BIOSOLIDS) and sludge from dairy wastewater treatment (MUD) were compared with those from a CONTROL plot. Five stages of weight loss were identified within DTG profiles: moisture loss, active pyrolysis (two phases), passive pyrolysis and a high-rank pyrolysis phase. The application of BIOSOLIDS treatment showed a better pyrolytic thermal capacity (especially for UNAL clone) during the active and passive pyrolysis phase compared with the other treatments. When comparing the first with the last treatment year crops, results showed that the application of MUD significantly increased the volume of generated biomass (especially for AF-2 clone).

Keywords: energy crop; kinetics; poplar; pyrolysis; thermal conversion.

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1.- Introduction

Current demand in the use of fossil fuels is causing more than apparent decrease in the reserves of these energy resources and recent estimations about the duration of such reserves are not encouraging [1-3]. Therefore, it is necessary to search for new forms of energy that can alleviate (or at least decrease) this dependence on fossil fuels. Within these new forms of energy, renewables are considered essential. Also known by alternative energy sources, this type of energies derive from inexhaustible natural resources that can be drawn permanently [4]. Among them, it is biomass, which potential has been increasing during the last years. In 2006 only 5% of the world's primary energy consumption came from biomass, which is projected to increase to 10% by 2030 [5].

Within biomass energy sources it should be highlighted the case of lignocellulosic energy crops, which are crops for the production of solid biomass that will later be used with thermal purposes. The environmental benefits of these plantations are well documented and can be outlined acting as carbon sinks, thereby contributing to the reduction of greenhouse gas [6]. Within the species most commonly used as energy crops, the poplar (*Populus* sp) is one of the most studied ones for the production of energy in Europe [7-10]. In fact, several countries are considering the use of this species within energy crops [11-13]. Its utilizations is justified by the involved social and environmental benefits [14] related to poplars easy way to propagate through vegetative cuttings and their facility to grow under a wide variety of site and climatic conditions [8, 9, 15, 16].

Fertilization is another important aspect to consider in order to successfully establishing an energy crop. Traditionally, it has been opted for mineral fertilizers due to their high performance compared to the natural and/or organic ones. However, organic fertilization poses economic benefits that may impact their usability. Today, studies such as [17], have tried to make a comparison between biomass yields depending on the type of fertilizer used.

Utilization of organic stabilized organic residues as fertilizers, apart from economic benefits, would contribute both to the closure of certain cycles (nutrients and pollutants) and to giving an use to a waste that previously had none. Organic amendments, in addition to providing increased rates of soil microbial biomass [18], are known for improving soil structure, for helping to increase moisture retention capacity and for increasing the availability of nutrients for plants [19]. Regarding poplars, it has been proved that the application of a waste organic amendment significantly increased the trees growth but did not cause significant changes in the nitrates or in the phosphates concentrations in soil solution [20].

Biomass from energy crops is mainly composed of cellulose, hemicellulose and lignin [21]. In the last years has occurred an impressive increase in the supply of lignocellulosic biomass throughout the world. Therefore, research on its transformation into bio-based fuels, chemicals and, above all, energy has simultaneously progressed [22]. It is well known that, due to its resistance to enzyme and acid hydrolysis, lignocellulosic material cannot be effectively converted into energy through biochemical methods [23]. This problem can be overcome using thermochemical conversion processes. Specifically, a thermochemical process that has been applied successfully and is being studied by many authors is pyrolysis [24-26]. Pyrolysis is the thermochemical conversion of poplar biomass at temperatures between 673 and 923 K that takes place under a complete inert atmosphere (without O_2) [22] . The overall process is able to produce gases (syngas), liquids (bio-oil) and/or a solid residue (char), according to the conversion mechanism involved [23]. Optimization in the production of these products and characterization of them is now widely studied [27-32].

For a better understanding of the process, many researchers [33-36] have studied thermal decomposition of biomass under pyrolysis by thermogravimetric analysis (TGA). This is one of the most common techniques used for kinetic analysis of devolatilization process. Biomass devolatilization is referred to in terms of its three main components (lignin, cellulose and hemicelluloses).

An interesting study of the pyrolysis of wood and main wood compounds was carried out by [37], which revealed three stages during the thermal decomposition (TGA profiles) of wood: water evaporation, active and passive pyrolysis. Composition and concentration of the main components of the biomass has a high influence in the decomposition process of wood. The decomposition of hemicelluloses and cellulose takes place in active pyrolysis in the temperature range from 473 to 653 K and 523 to 653 K, respectively. Whereas lignin is decomposed in both stages: active and passive pyrolysis in the range from 453 to 1173 K [38].

The aim of this work, which is based on a poplar energy crop during a four years' time period (2010 to 2013), is studying the behavior of the application of different organic amendments on the pyrolytic behavior of the samples (analyzing the thermal capacity and kinetic parameters) and on the biomass generation of different poplar clones.

2.- Materials and methods

2.1.- Plots, poplar clones and fertilization

This study was carried out in a plot of 720 m^2 (45m x 16m) at the North-West of Spain (42 27.183 N, 05 53.650 W). Four different clones of genus *Populus* were used. Two of these clones were Spanish: *Populus x interamaricana* UNAL and *Populus x euramericana* I-214, which in this work were designated as UNAL and I-214, respectively. Also, two Italian clones specifically imported for biomass production were used: *Populus x euramericana* AF-2 and *Populus x euramericana* AF-8, which were designated as AF-2 and AF-8.

Two different organic amendments together with a CONTROL, in the absence of any fertilization, were considered in this work for comparison purposes. The first organic treatment, which was here designated as BIOSOLIDS, was a dehydrated sludge from the León (Spain) sewage treatment plant (STP). The second treatment, which was designated as MUD, was a liquid organic sludge from the wastewater treatment plant of a dairy industry. According to the number of poplar clones and organic amendments considered in this work, the experimental plot was subdivided into 12 subplots, each of which corresponding to a different poplar clone and a different organic treatment or control (Fig. 1).

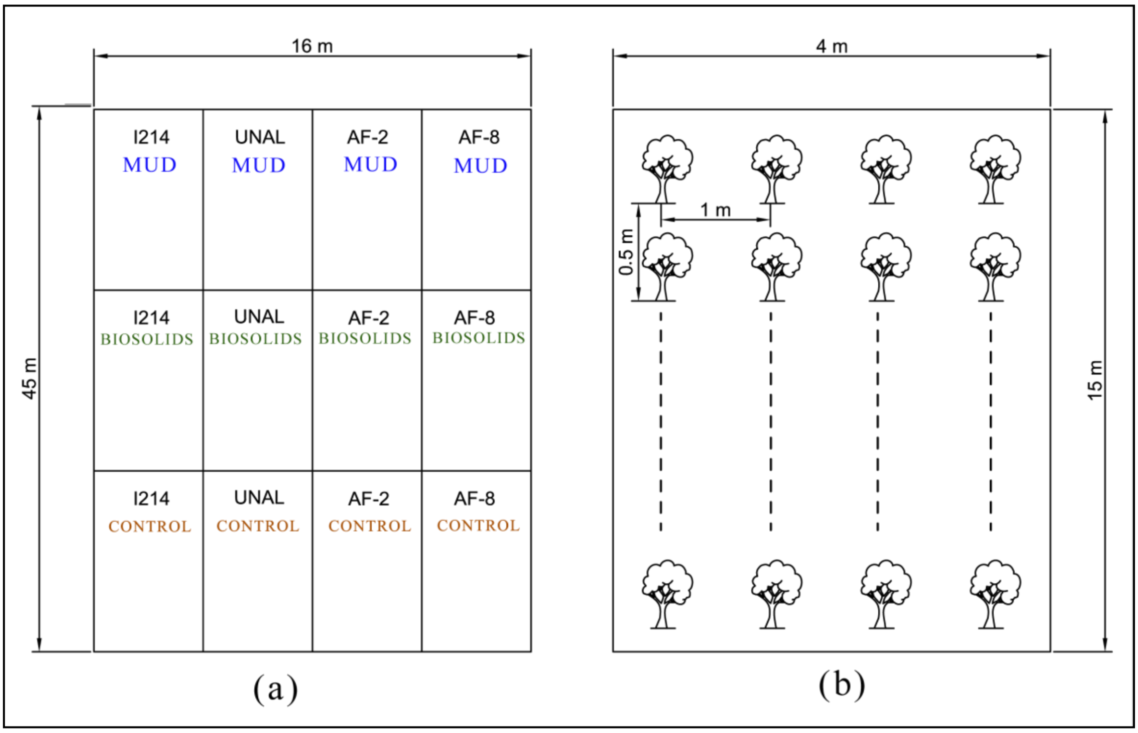

Fig. 1

The characteristics of the organic amendments used in this work can be seen in Table I. The above organic amendments were applied once a year throughout the four years' duration of this study. The first fertilization was applied in April 2010 after the sanitation of the plot. Taking into account the treatments characteristics (Table I), as well as the agronomic requirements of the crop, each year, a total amount of 143.8 kg of BIOSOLIDS and 1200 liters of MUD were applied to the corresponding subplots. The BIOSOLIDS treatment was employed as a basal dressing and the MUD treatment as a top dressing

Table I - Physicochemical characteristics of the organic amendments used. -

ELEMENTS	**BIOSOLIDS**	**MUD**
Dry matter (%)	92.0	1.4
pH	7.5	7.7
Conductivity (mS cm^{-1})	1.72	0.47
Organic matter (%)	37.5	60.0
Total nitrogen (%)	3.2	6.9
C/N ratio	7.0	5.0
Ammonia nitrogen (%)	0.08	0.21
Total phosphorus (mg kg^{-1})	31.1	16.0
Calcium (mg kg^{-1})	45.8	16.0
Magnesium (mg kg^{-1})	6.1	3.8
Potassium (mg kg^{-1})	3.2	5.3
Sodium (mg kg^{-1})	8.52	13.12

2.2.- Biomass Sampling

At each subplot, biomass sampling was yearly carried out in September as described elsewhere [39] and following the guidelines by [40]. Analogously to soil sampling, for the collection of biomass, subplots were considered as sampling units. Within each subplot, biomass sampling was carried out so to ensure that two consecutive trees were never sampled. The sampled branches were taken at approximately half the height of the tree, carrying out sampling at different orientations. The sampled mass was 150 grams of wood for each subplot. The samples were deposited in perforated plastic bags, which had been previously labelled.

2.3.- Biomass fuel analysis

The fuel properties of biomass were approached by elemental analysis and proximate analyses and by the determination of the calorific value. Biomass from the tree branches was analysed to determine these main properties affecting to thermal conversion. Moisture content was determined gravimetrically by the oven drying method. Higher heating value (HHV) at a constant volume was measured by means of an adiabatic oxygen bomb calorimeter. Proximate determinations were made according to modified procedures from ASTM D3172 to D3175 (Standard Practice for Proximate Analysis of Coal and Coke), E 870 (Standard Methods for Analysis of Wood Fuels), D 1102 (ash in wood) and E 872 (volatile matter). Elemental analysis of the biomass samples was carried out by a commercial laboratory, where standard analytical methods were used.

2.4. - Biomass volume estimation

In order to know the lignocellulosic growth, volume of the trees was calculated employing the mathematical expression proposed by [41] which is described in Eq. (1):

$$V_U = 0.3D^2H \tag{1}$$

where V_U the biomass volume (cm^3), D is tree diameter at basal height over bark (cm) and H is the tree height (cm),

During the four years of the project, height (H) and diameter (D) of the trees were measured once a year, in September. A caliper 'Powerfix' was used to determine the basal diameter at a height of 5 cm from the seedling. Then, the height was measured by a high precision laser (Haglöf Vertex v3 201 DME), as the distance between the base of the seedling and the apical sprout. Then, H and D were used for calculating approximate volumes of wood biomass, according Eq. (1).

2.5 - Biomass thermogravimetric analysis and modeling of results

Before thermogravimetric analysis, biomass samples were dried by air-drying for a minimum of 72 hours. Then, samples were milled on a Fritsch mill Model P-19 to a 1 millimeter particle size. Afterwards, by using a Retch ball mill model MM200, particle sizes around about 0.2 mm were obtained. After these pretreatments, samples were stored before thermogravimetric analysis (for a period of time no longer than 2 days) in airtight containers at 291.15 K ± 5.

Thermogravimetric analysis was carried out using a TGA Instrument SDT2960, which is able to supply a continuous measurement of sample weight as a function of time or temperature. Milled samples weighing 6–8 mg were placed in a pottery crucible and heated at 273.15 K·min^{-1} from ambient to 1273.15 K. This heating was carried out under a flow of 100 mL/min of nitrogen (at a gauge pressure of 1 atmosphere) to carry out the pyrolysis process

Thermogravimetric (TG) profiles of the samples were so obtained. Then, through the derivation of these TG profiles, the derivative (DTG) curves; in which may be seen the different pyrolysis steps, were determined. At these DTG curves, the temperature at which occurred each stage was noted, this parameter pointing to the operating temperature of the boiler. Also, the mass lost at each stage was determined. From DTG and TG curves, both the temperature and mass lost at each stage was determined for each clone and treatment.

In order to study the kinetic characteristics and to determine the activation energy (E_a) and the frequency factor (k_0) values, the approximate integral method (AIM) was employed [42], as it is next described.

The velocity of a chemical reaction increases with temperature. If a particular reaction is studied at different temperatures remaining constant the concentrations of the substances involved in such reaction, it is shown that the reaction speed (Eq. (2)) increases with temperature.

$$\frac{\mathrm{dx}}{\mathrm{dt}} = \mathrm{k}(\mathrm{a} - \mathrm{x})^{\mathrm{n}} \tag{2}$$

where dx/dt is the speed at which the chemical reaction occurs, k is the specific rate constant, a is the original amount, x refers the amount of substance transformed y n is the order of the reaction.

Since n is independent of temperature, an increase in the value of dx/dt necessarily implies that it is the parameter k which increases with temperature. The relationship between this constant k and reaction temperature T (measured in Kelvin degrees, K) is given by the relationship established by Van't Hoff and Arrhenius (1889), as shown in Eq. (3):

$$\ln \mathrm{k} = \ln \mathrm{A} - \frac{\mathrm{B}}{\mathrm{T}} \tag{3}$$

where k is the specific rate constant, A is the exponential factor or frequency factor (value of k at infinite temperature), B is a parameter that Arrhenius associated with the activation energy (E_a) and T refers to the temperature (K). Then, if $ln\ (k)$ are represented versus $1/T$, experimental results will give a straight line with intercept equal to $ln(A)$ and slope equal to $(-B)$.

Proposed Arrhenius and Van't Hoff expression (Eq. (3)) can be expressed exponentially by Eq. (4):

$$\mathrm{k} = \mathrm{A} \cdot\ \mathrm{e}^{-\mathrm{B}/\mathrm{T}} \tag{4}$$

In 1869 Arrhenius found that B constant was closely related to the activation energy (E_a), so that Eq. (4) become Eq. (5) or Arrhenius equation

$$\mathrm{k} = \mathrm{A} \cdot\ \mathrm{e}^{-\mathrm{E_a}/\mathrm{R}\cdot\mathrm{T}} \tag{5}$$

where k is the specific rate constant, A or k_0 refers to the frequency factor (proportional to the frequency of collision of the molecules), E_a is the activation energy of the reaction (J/mol) T is the absolute temperature (K) and R corresponds to the universal gas constant (8.314 J/mol·K).

Applying logarithms in the above expression, Eq. (5), it is obtained Eq. (6):

$$\ln \mathrm{k} = \ln \mathrm{A} - \frac{\mathrm{E_a}}{\mathrm{R}} \cdot \frac{1}{\mathrm{T}} \tag{6}$$

If we proceed to the calculation of differentials with respect to the absolute temperature, Eq. (7) results:

$$\frac{\mathrm{d}\,(\ln \mathrm{k})}{\mathrm{dT}} = \frac{\mathrm{E_a}}{\mathrm{R{\cdot}T^2}} \tag{7}$$

Grouping terms we obtain Eq. (8):

$$\mathrm{d}(\ln \mathrm{k}) = \frac{\mathrm{E_a}}{\mathrm{R}} \cdot \frac{\mathrm{dt}}{\mathrm{T^2}} \tag{8}$$

If the above expression (Eq. 8) is integrated between T_1 (which has an associated value of $k = k_1$) and T_2 ($k = k_2$), we obtain:

$$\int_{\mathrm{k_1}}^{\mathrm{k_2}} \mathrm{d}\,(\ln \mathrm{k}) = \frac{\mathrm{E_a}}{\mathrm{R}} \cdot \int_{\mathrm{T_1}}^{\mathrm{T_2}} \frac{\mathrm{dt}}{\mathrm{T^2}} \tag{9}$$

$$[\ln \mathrm{k}\,]_{\mathrm{k_1}}^{\mathrm{k_2}} = \frac{\mathrm{E_a}}{\mathrm{R}} \cdot \left[\frac{-1}{\mathrm{T}}\right]_{\mathrm{T_1}}^{\mathrm{T_2}} \tag{10}$$

$$\ln \mathrm{k_2} - \ln \mathrm{k_1} = \frac{\mathrm{E_a}}{\mathrm{R}}\left[- \frac{1}{\mathrm{T_2}} - \left[\frac{1}{\mathrm{T_1}}\right]\right] = \frac{\mathrm{E_a}}{\mathrm{R}}\left[\frac{1}{\mathrm{T_1}} - \frac{1}{\mathrm{T_2}}\right] \tag{11}$$

$$\ln\left[\frac{\mathrm{k_2}}{\mathrm{k_1}}\right] = \frac{\mathrm{E_a}}{\mathrm{R}}\left[\frac{1}{\mathrm{T_1}} - \frac{1}{\mathrm{T_2}}\right] = \frac{\mathrm{E_a}}{\mathrm{R}} \cdot \frac{\mathrm{T_2 - T_1}}{\mathrm{T_1 - T_2}} \tag{12}$$

The activation energy (E_a) of a certain reaction might be obtained through the Eq. (12) from the values k_1 determined to T_1 and k_2 determined to T_2. Generally the calculation of this parameter does not usually run in this way to avoid the error associated with the use of only two experimental points.

To mitigate this disadvantage, can be carried out a number of transformations on the above equations in order to estimate the kinetic parameters of activation energy (E_a) or the frequency factor (k_0 or A). The processing carried out in this paper is based on expressing the mass loss rate (Eq. (12)) related to Arrhenius expression for the kinetics of a chemical reaction.

$$\frac{\mathrm{dx}}{\mathrm{dt}} = \mathrm{k_0} \exp\left(-\frac{\mathrm{E}}{\mathrm{R \cdot T}}\right) \mathrm{f(x)} \tag{13}$$

Where x is the mass conversion factor, Eq. (14):

$$\mathrm{x} = \frac{\mathrm{m_0 - m}}{\mathrm{m_0 - m_f}} \tag{14}$$

Being m_0 the initial sample mass (g), m the initial sample mass at time t (s) and m_f is the final mass sample (g)

$k_O$or A is the frecuency factor ($1/s$ in a first order kinetics), E o $E_a$is the activation energy and $f(x)$ is the sample transformation function.

Eq. (13) can be transformed to different expressions depending on the method employed to obtain the kinetic parameters k_O and E_a. In this study, it was used the approximate integral method (AIM).

Using this method, Eq. (13) is transformed to obtain the derivative of x with respect to the absolute temperature (T). For the case of a constant heating rate, this equation can be written in the manner reflected in Eq. (15).

$$\frac{dx}{dt} = \frac{k_O}{q} \exp\left(-\frac{E}{R \cdot T}\right) f(x) \tag{15}$$

where $q$is the constant heating rate (Eq. (16)):

$$q = \frac{dT}{dt} \tag{16}$$

In this paper an only constant heating rate was employed (273.15 K/min).

Eq. (15) can be solved only when the kinetic parameters of the reaction are assumed or known, which is obtained using the values of the TGA. As it has been defined in Eq. (14), in the conversion factor x is verified that $f\ (x)\ =\ (1 - x)$. Substituting this value into Eq. (15) it is obtained Eq. (17):

$$\frac{dx}{dt} = \frac{k_O}{q} \exp\left(-\frac{E}{R \cdot T}\right) (1 - x) \tag{17}$$

The integrated form of Eq. (16) is given by Eq. (17):

$$\int_0^{x} \frac{dx}{1-x} = \frac{k_0}{q} \int_{T_0}^{T} \exp\left(-\frac{E}{R \cdot T}\right) dT \tag{18}$$

Given that the second member of Eq. (17) is not directly integrable, it must be solved numerically or by approximate solutions. There are several solutions proposed for this term [43-45] . Among them, the [45] solution proposes to $T_0 = 0$, the approximate solution shown in Eq.(19).

$$\int_0^{x} \frac{dx}{1-x} \cong \frac{R \cdot T^2}{E} \left[\frac{1-2\frac{R \cdot T}{E}}{1-5\left\{\frac{R \cdot T}{E}\right\}^2} \right] \exp\left(-\frac{E}{R \cdot T}\right) \tag{19}$$

Substituting this expression into Eq. (18) and rearranging the equation obtained, we get:

$$\ln\left(\frac{-\ln(1-x)}{T^2}\right) = \ln\left[\frac{k_0}{q} \cdot \frac{R}{E} \cdot \frac{1-2\frac{R \cdot T}{E}}{1-5\left\{\frac{R \cdot T}{E}\right\}^2}\right] - \frac{E}{R} \cdot \frac{1}{T} \tag{20}$$

The first term of the second member of Eq. (20) tends to be relatively constant in the temperature range employed; such that when it is represented the first member against 1/T a straight line (whose slope is E_a/R (negative slope)) is obtained. This way activation energy E_a value can be determined and, once known its value, we may infer the frequency factor values.

$$E_a = -R \cdot \text{slope} \tag{21}$$

To know the values of the above kinetic parameters, activation energy (E_a), and frequency factor (k_0), are vital to complement the information provided by the thermogravimetric analysis. The activation energy is associated with the energy required to start a chemical reaction. Thus, the peaks derived from thermogravimetric analysis start at different temperature values depending on the species and the treatment. The adjustment of the peaks is considered, therefore, essential to know these thermal properties.

The frequency factor (k_0) is identified as the number of collisions between molecules involved in a reaction. A larger number of collisions involves a higher reaction rate; consequently, the time associated with the chemical reaction will be lower. This parameter (k_0) is a key tool to clarify results when temporary differences are apparent in DTG profiles. The numerical values of this parameter will be calculated by the AIM, in the same way that the activation energy (E_a).

3.- Results and discussion

3.1.- Elemental and proximate analyses

The results concerning the elemental analysis and proximate analyses as well as the calorific values of the samples can be observed in Table II

Table II – Elemental, proximate analyses and calorific value of biomass sampled for each subplot -

		Elemental analysis				Proximate analysis			Calorific value
		C[a]	H[a]	N[a]	S[a]	Volatiles[a]	Ash[a]	Moisture[a]	HHV[b]
CONTROL	UNAL	49.5	5.80	0.56	0.11	79.9	3.28	7.9	19.78
	I-214	48.9	5.66	0.68	0.10	80.3	3.62	8.6	19.48
	AF-2	49.7	5.81	0.66	0.11	79.3	2.93	8.5	19.80
	AF-8	49.1	5.7	0.53	0.12	78.5	3.82	8.2	19.60
BIOSOLIDS	UNAL	49.6	5.86	0.55	0.11	81.3	2.49	8.9	19.73
	I-214	49.0	5.74	0.74	0.10	79.0	3.43	8.5	19.46
	AF-2	49.6	5.80	0.69	0.12	81.1	3.12	6.0	19.75
	AF-8	49.5	5.82	0.60	0.09	79.0	3.23	6.3	19.77
MUD	UNAL	49.6	5.95	0.40	0.08	81.2	2.65	8.2	19.70
	I-214	49.1	5.87	0.56	0.16	80.1	2.57	10.4	19.55
	AF-2	49.4	5.91	0.67	0.09	79.7	2.90	6.6	19.78
	AF-8	49.7	5.78	0.64	0.09	78.8	3.61	8.8	19.83

[a] In percentage. All values are in dry basis except moisture

[b] HHV: high heating value (MJ/kg)

In order to select a raw material as a biofuel, it should be taken into account that a high content of carbon and hydrogen are desirable, since both elements are the basis of many molecules resulting from the pyrolytic process. Also, related to the sulfur content, large sulfur content within the typical samples cause the formation of pollutants (mainly COS and H_2S) [46], which does not provide energy and its reaction generates sulfur oxides, which are potent air pollutants. All the samples show very uniform values for the elemental analysis, so it does not enable the selection of a particular clone. Something similar occurs when we review the proximate analysis. It is not possible to select the clone with the highest volatile content and lowest ash content, since these values are similar for all the clones and treatments considered. Concerning the heating value (energy produced when a fuel is completely oxidized), it is one of the key parameters to characterize a biofuel but, afresh, HHV values in Table II are very close for all clones and treatments, although the I-214 was the clone showing the lowest HHV under the three treatments.

3.2. - Biomass volume.

Biomass volume data (Table III) show that the volume at the last year is larger than at the first year. Likewise, data volumes were higher for the subplots that had been fertilized than for the control subplot (without I-214 clone under BIOSOLIDS treatment). Taking into account the average increase in the volume of the trees, it can be said that under the treatment MUD results are higher. Under this treatment, except for I-214, the rest of clones here considered provided biomass volumes of the same order of magnitude at the last year of the study. On the other hand, it must be highlighted that AF-2 was the clone showing the largest increase of biomass volume under organic fertilization, either with BIOSOLIDS or with MUD.

Table III – Poplar biomass volume (cm^3) calculated as Eq. (1) for each treatment and clone -

	TREATMENTS					
	CONTROL		**BIOSOLIDS**		**MUD**	
	First year[1]	Last year[2]	First year[1]	Last year[2]	First year[1]	Last year[2]
CLONE	Mean	Mean	Mean	Mean	Mean	Mean
UNAL	57	845	51	880	110	1530
I-214	19	652	26	538	41	748
AF-2	54	942	57	1174	144	1679
AF-8	27	716	46	861	69	1271
Treatment mean (cm^3)	**39**	**789**	**45**	**863**	**91**	**1402**
Treatment SD	19	130	13	61	45	441

SD.: Standard deviation

[1] First year: the year when it was first applied the corresponding treatment (2010)

[1] Last year: the year when it was last applied the corresponding treatment (2013)

3.3- Thermogravimetric analysis.

Differential mass loss (DTG (% · min $^{-1}$)) thermograms of thermal decomposition of poplar wood pyrolysis at a heating range of 10 K· min^{-1} under nitrogen atmosphere for each treatment are shown in Fig. 2, 3 and Fig. 4. Mainly, in these thermograms, five different regions can be identified. The first four regions are related to: water evaporation, active pyrolysis (which includes two peaks or regions) and passive pyrolysis. The weight loss stage which takes places at high temperatures (high-rank pyrolysis) has an uncertain origin, appeared at 900K and not appears in the thermal profiles of certain references that have worked with pyrolysis [22, 23, 38, 48].

The first region, which takes place from 325 K to 375 K is related to the loss of water (moisture loss or adsorbed water loss) in biomass samples. This first phase is not mentioned in the results because it is considered not representative when obtaining energy from it. At this heating rate (10 K · min^{-1}), the most representative pyrolysis (active pyrolysis) occurs in a range from approximately 430 K to 720 K. In this region we can analyse two peaks (the first peaks achieves his temperature DTG$_{max}$ value to 500 K and the other at approximately 620 K). It is thought that these two peaks are related to the hemicelluloses and cellulose decomposition, while lignin is decomposed in both regions of active and passive pyrolysis without characteristics peaks [37, 47]. Passive pyrolysis (temperature DTG$_{max}$ value to 760 K) there is a less mass loss compared with that which occurred in the active pyrolysis.

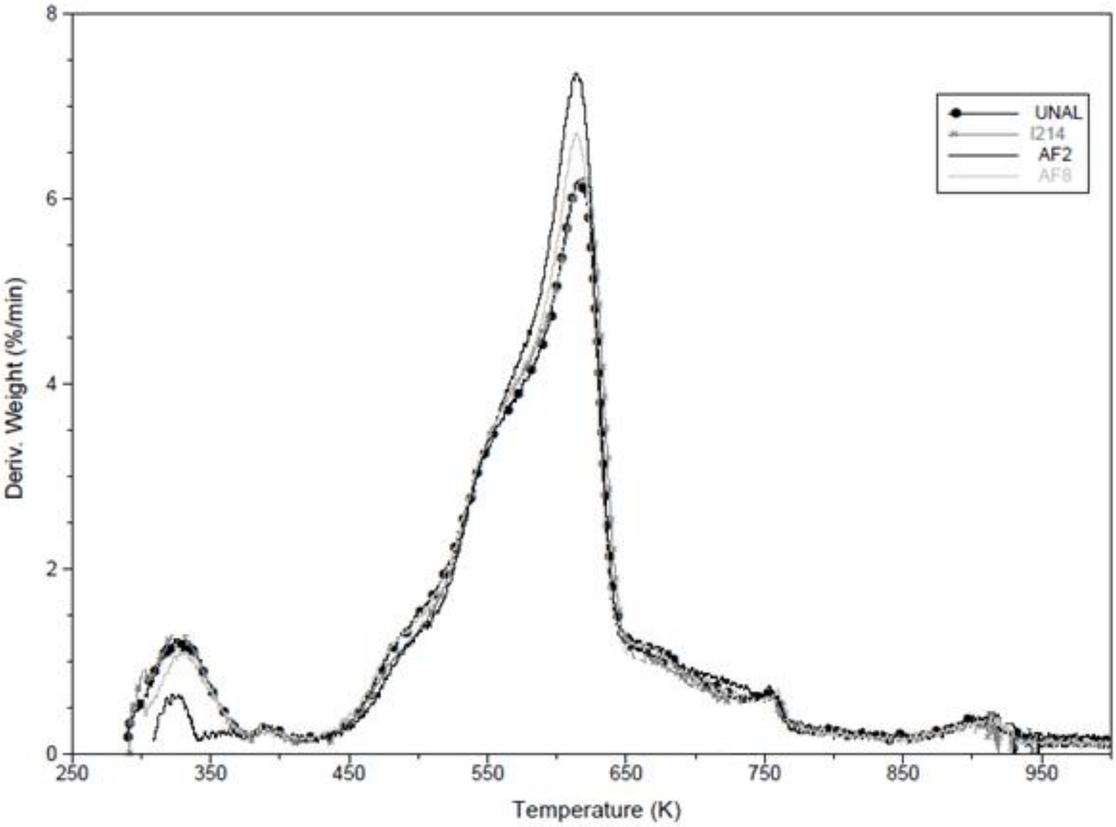

Fig. 2 - DTG of poplar samples during CONTROL treatment for pyrolysis process

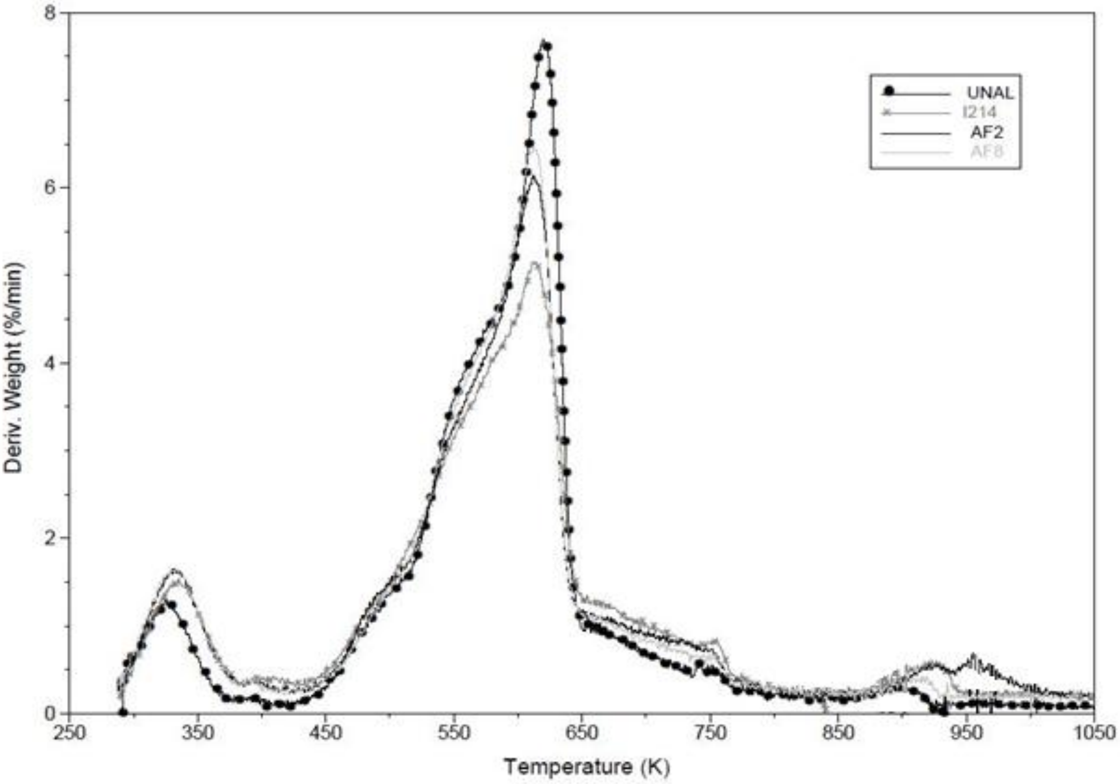

Fig. 3 - DTG of poplar samples during BIOSOLIDS treatment for pyrolysis process -

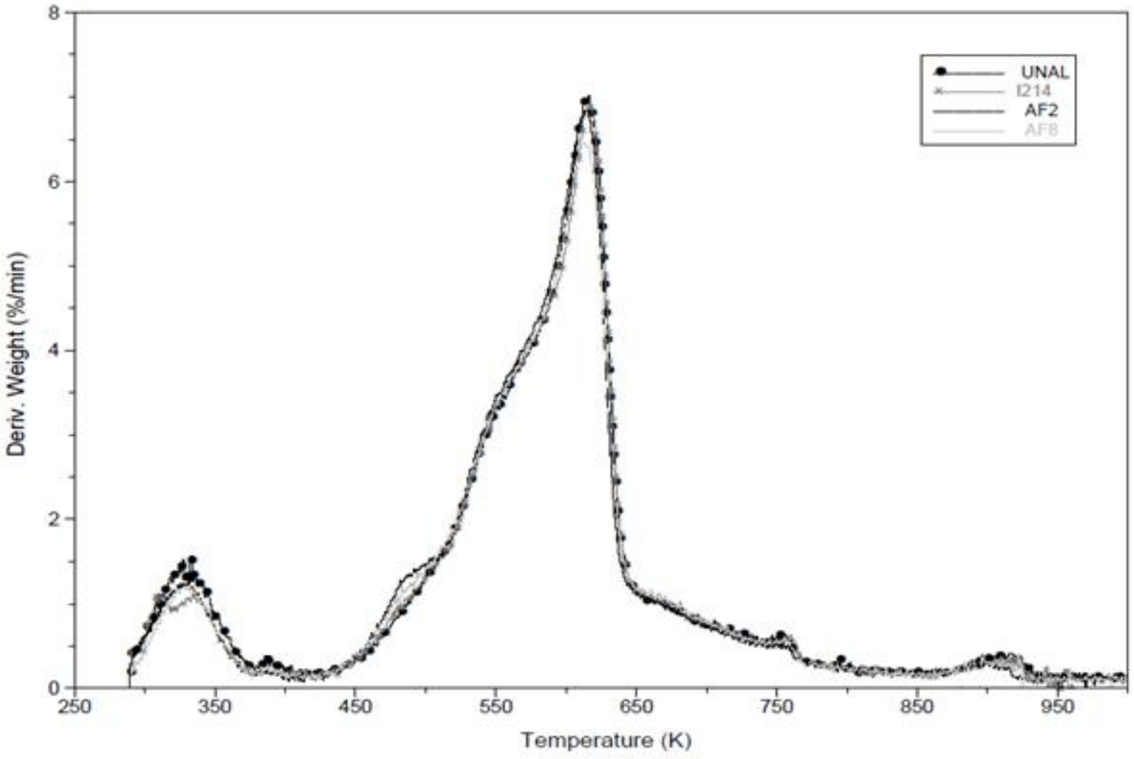

Fig. 4 - DTG of poplar samples during MUD treatment for pyrolysis process

From the point of view of the energy optimization within the pyrolysis process, large weight losses are desirable with low initial and final temperatures. Taking into account the above statement, for the CONTROL treatment (Fig. 2), is the AF2 clone which denotes a best performance during the active pyrolysis process (it showed higher DTG_{max} values). Otherwise, considering the passive pyrolysis stage, all the clones have virtually a very similar behavior for this treatment. Under fertilization with BIOSOLIDS (Fig. 3) are the UNAL and I-214 the clones showing higher DTG_{max} values than the other clones for active and passive pyrolysis stages respectively. Furthermore, during active pyrolysis, the clone UNAL, apart from showing notable loss weight values, is delayed about 10 K with respect to the other clones. Finally, under fertilization with MUD (Fig. 4), there is a very similar behavior among clones UNAL, I214 and AF-2 during the active pyrolysis stage. All of them show very similar DTG_{max}

values that are reached at similar temperatures. The clone AF8 showed slightly lower values of this parameter. This tendency of similarity in the behavior of the clones remains during passive pyrolysis, in which we are not able to select a clone according of its better behaviour.

If the three treatments are compared (Fig. 3 and Fig. 4), we realize that the DTG_{max} value is reached at a very similar temperature for both active pyrolysis (620 K) and passive pyrolysis (760 K). For the particular case of the active pyrolysis phase, during CONTROL and BIOSOLIDS treatments there are differences between the values of DTG_{max}, something that is not kept during the treatment MUD (where there is homogeneity in these values). Regarding the passive pyrolysis phase, the behavior of the four clones is very similar for all three treatments (visual differences are not appreciated). This is a fact that is also true in what we call as the fifth stage of weight loss within thermograms (with DTG_{max} to 920 K). During CONTROL and MUD and CONTROL treatments there are not differences between the behavior of the clones. For BIOSOLIDS treatment there is a more visible differentiation. The I214 and AF2 clones are those with the highest values DTG_{max} associated. Values which are obtained at higher temperatures compared with the other two clones (for that reason we can say that the peaks associated with these clones are delayed certain Kelvin degrees)

3.4- Kinetic analysis.

Approximate integral method (AIM) was employed to the determination of the activation energy (E_a) and the frequency factor (k_0) associated with each DTG stage as described in the *2.4. “Biomass thermogravimetric analysis and modeling of results”* section.

Results of the kinetic parameters are shown in Table IV. Activation energy values are all lower during the active pyrolysis phase than during the passive phase. This denotes that a greater amount of energy is needed to start the reactions during the passive phase is comparison with the active phase (regardless of treatment and clone employee) when we carried out the pyrolysis of the biomass samples. Furthermore, under BIOSOLIDS treatment, activation energy average values are lower in comparison with the other treatments for the active and passive pyrolysis phases. Among samples from poplars fertilized with BIOSOLIDS, the I-214 clone is the one showing the lowest E_a values. For the CONTROL treatment, it cannot be said that a particular clone present a better behavior about the activation energy during the different phases refers. Although during the second active prylosysis phase and during passive phase the UNAL and I-214 clones have lower E_a values, this is something that is not kept to the early phase of the active pyrolysis. Under the MUD fertilization, there is great homogeneity (especially in the active phase) about what to the results of E_a refers. The UNAL clone is the one showing the lowest E_a value for the passive pyrolysis.

Talking about the final phase of weight loss (that is given at about 920 K), is the CONTROL treatment the one showing a better behavoir about the E_a values. In this treatment, the UNAL clones can be identified by the lowest E_a value. Something that is not kept for the BIOSOLIDS and MUD treatments, in which, these lower values are associated with the AF-2 and I-214 clones respectively.

Concerning k_0, the values were higher during the passive pyrolysis than during the active pyrolysis. Somewhat obvious if we think that the passive pyrolysis phase occurs faster than the active pyrolysis phase. This can be seen in the thermograms (Fig. 2, Fig. 3 and Fig. 4) through peaks which occur in a narrow temperature ranges (750 – 770 K).

During the application of MUD treatment, k_0 values were higher than for the other treatments, being the AF-2 clone that having higher values for both active and passive pyrolysis phases. Another aspect derived from the results of the frequency factor is the behavior of AF-8 clone for CONTROL treatment, which has a value far higher (5.5 E+62 1/s) than the rest of clones for the same treatment during the passive pyrolysis phase. In general, for high-rank pyrolysis, the reactions are faster (higher values of k) under the BIOSOLIDS treatment

On the whole, when applying a certain treatment, the activation energy associated with each particular clones decreases. Special interest is the application of BIOSOLIDS treatment on kinetic values. During the second active phase pyrolysis, the application of this treatment decreases the activation energy of all the clones (except UNAL), which is maintained during the passive phase.

Table IV – Kinetic parameters for the biomass sampled

The results of activation energy (E_a) and frequency factor (k_0) were obtained by AIM method. R^2 is the linear fitting associated to the regression straight derived from the representation of the parameters of the Eq. (21)

	CONTROL				**BIOSOLIDS**				**MUD**			
	UNAL	I-214	AF-2	AF-8	UNAL	I-214	AF-2	AF-8	UNAL	I-214	AF-2	AF-8
Active pyrolysis (500 K)												
E_a (kJ mol^{-1})	91.82	103.02	83.29	83	77.07	83.31	85.83	87.94	71.32	88.83	94.12	81.12
k_0 (1/s)	2.7E+07	5.4E+08	1.2E+06	2.2E+06	4.3E+05	3.6E+06	5.0E+06	6.7E+06	7.5E+04	1.2E+07	6.5E+07	1.6E+06
R^2	0.9925	0.9906	0.9914	0.9919	0.9903	0.9909	0.9891	0.9901	0.9910	0.9921	0.9911	0.9903
Active pyrolysis (620 K)												
E_a (kJ mol^{-1})	235.49	265.72	267.03	287.11	285.74	192.72	217.56	223.78	275.49	268.71	282.18	241.01
k_0 (1/s)	5.0E+17	1.3E+20	2.0E+20	1.6E+22	6.8E+21	1.2E+14	1.9E+16	6.7E+16	1.3E+21	2.9E+20	6.1E+21	1.9E+18
R^2	0.9900	0.9913	0.9939	0.9900	0.9910	0.9906	0.9900	0.9900	0.9911	0.9902	0.9926	0.9915
Pasive pyrolysis (750 K)												
E_a (kJ mol^{-1})	604.19	639.56	729.94	944.93	464.31	441.29	519.13	688.96	606.36	717.91	772.07	697.28
k_0 (1/s)	5.5E+39	1.1E+42	3.3E+48	5.5E+62	1.1E+30	2.0E+28	8.0E+33	3.2E+45	5.3E+39	1.1E+47	1.9E+51	1.3E+46
R^2	0.9920	0.9900	0.9919	0.9909	0.9902	0.9906	0.9928	0.9902	0.9910	0.9918	0.9900	0.9902
High-rank pyrolysis (920 K)												
E_a (kJ mol^{-1})	159.08	249.65	314.22	259.15	316.79	647.88	316.70	1040.66	330.59	249.82	408.12	573.39
k_0 (1/s)	3.0E+06	6.4E+11	4.3E+15	1.9E+12	1.1E+16	2.5E+34	1.1E+15	1.4E+57	4.1E+16	5.4E+11	2.2E+21	1.7E+31
R^2	0.9920	0.9914	0.9938	0.9921	0.9933	0.9906	0.9909	0.9903	0.9927	0.9937	0.9943	0.9919

4.- Conclusions.

Related to the biomass fuel properties, there were no appreciable differences between the clones and treatments as the elemental and proximate analysis denoted. BIOSOLIDS fertilization treatment caused that the UNAL clone achieved higher loss weight values than other treatments and clones during the second pyrolysis active phase At the passive phase, there is homogeneity in the results obtained, although it is true that when BIOSOLIDS are applied we can see a slight increase in the DTG profiles. The application of this treatment also allows (in general) lower energy expenditure within the active and passive (lower activation energy values can be observed). According to the reaction rate (described by k_0) there were no appreciable differences between the different treatments and clones. Biomass volume estimation showed that, under MUD treatment, a remarkable increase in volume over the first year of treatment was experienced. Being this increase more pronounced for AF-2 clone. Therefore, although, in accordance to the second active pyrolysis phase (the most representative of the DTG profiles), it is recommended to use the UNAL clone under the BIOSOLIDS treatment, notable differences were not been identified comparing the thermal behavior of the samples

By contrast, to mention the amount of biomass generated (volume), appreciated differences have been denoted, being able to recommend the use of AF-2 clone under MUD treatment.

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CAPTIONS TO FIGURES

Fig. 1 Main plot (a) and one of the subplots (b)

Fig. 2 DTG of poplar samples during CONTROL treatment for pyrolysis process

Fig. 3 DTG of poplar samples during BIOSOLIDS treatment for pyrolysis process

Fig. 4 DTG of poplar samples during MUD treatment for pyrolysis process