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 alternative for the production of energy. In this work, thermogravimetric analysis of poplar biomass was carried out and both the kinetic parameters (activation energy and frequency factor) and characteristic indexes were determined. Four poplar clones (UNAL, I-214, AF-2 and AF-8) under no fertilization (CONTROL) or under fertilization with either dehydrated composted sewage sludge (BIOSOLIDS) or sludge from dairy wastewater treatment (MUD) were used in this work. Five weight loss stages were identified in the DTG pyrolysis curves: moisture loss, active pyrolysis (two phases), passive pyrolysis and a high-rank pyrolysis phase. Among them, the second pyrolysis active phase was the most representative one. For this stage, BIOSOLIDS-UNAL poplars biomass was the one that achieved the highest weight loss values. The characteristic parameters and indexes (especially P and P_i indexes) also pointed to UNAL poplars under BIOSOLIDS fertilization as the most favourable for pyrolytic thermal conversion.

Keywords: bioenergy; biomass; kinetics; pyrolysis; thermal conversion.

1.- Introduction.

Current demand in the use of fossil fuels is causing a decrease in the reserves of these energy resources. Recent estimations about the duration of such reserves are not encouraging [1-3]. Therefore, it is necessary to search for new energy forms to mitigate this fossil fuels dependence. Nowadays, biomass obtained from energy crops is a good alternative to non-renewable energy sources [4]. This biomass energy is encompassed within the alternative energy sources. These alternative energies are those that derive from inexhaustible natural resources that can be drawn permanently [5]. An increase in fossil fuel prices and technological progress have allowed for the development of energy systems based on biomass. This energy is more efficient, reliable and respectful of the environment [6]. Recent studies show that the potential of available globally biomass is increasing and can supply, in a sustainable way, between a quarter and a third of the energy needs predicted for 2050 [7].

Among biomass energy sources, it should be highlighted the lignocellulosic crops. These ones are crops established for energy production. One of most common species employed in these crops is the poplar (*Populus* sp). Its use becomes even more noticeable in Europe [8-11]. In fact, several European countries are considering the use of this species within energy crops [12-14]. Its utilization is justified by the involved social and environmental benefits [15] such as the easy way to propagate through vegetative cuttings and their facility to grow under a wide variety of site and climatic conditions [10,16,17,9].

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 [18]. However, organic fertilization poses economic benefits that can make their use attractive. Today, certain studies [19] have tried to make a comparison between biomass yields depending on the type of fertilizer used. Utilization of organic stabilized residues as fertilizers, apart from economic benefits, can contribute to the closure of certain cycles (nutrients and pollutants). Organic amendments, in addition to providing increased rates of soil microbial biomass [20], are known for improving soil structure. These amendments increase the moisture retention capacity and the plant availability of nutrients [21]. Related to poplars, it has been proved that the application of a waste organic amendment significantly increased the trees growth without important changes in the soil solution nitrates or phosphates concentrations [22]. However, as it happens for inorganic fertilizers, it is essential to determine the right amount of fertilizer to be applied considering working conditions (as described in 2.1 section). An accurate fertilizer amount will probably reduce the risks of nutrients losses to surface or subsurface waters bodies.

Biomass from energy crops is mainly composed of cellulose, hemicellulose and lignin [23]. Lignocellulosic biomass has experimented an increase in its use with the aim to generate products like bio-based chemicals and polymers [24], ethanol [25,26] or bioethanol [27], among others. Pyrolysis involves heating of poplar biomass at temperatures between 673 and 923 K under a completely inert atmosphere (without O_2). The overall process is able to produce gases (syngas), liquids (bio-oil) and/or a solid residue (char). The elements produced are related to the conversion mechanism. This data, as well as an extensive information concerned this pyrolytic process is included in

a series of paper which aims are to take into account a review of the this process [28-30].

Taking into account the different types of biomass pyrolysis, fast pyrolysis is being one of the most studied. This is so due to the high bio-oil content that is achieved in this particular pyrolysis type. It is important not misunderstanding this bio-oil with bio-fuels, since both have different composition such as denoted in [31]. The bio-oil can be used in engines and turbines and its use as a feedstock for refineries is also being considered. Problems with the conversion process and subsequent use of the oil, such as its poor thermal stability and its corrosiveness, still need to be overcome [32]. The current literature is focusing on improving the fast pyrolysis process to achieve a bio-oil as optimized as possible [33]. Current trend is to look for new numerical models that help to understand the conversion process and implant it in the pyrolysis reactor design and optimization [34]. For this task, computational fluid dynamics (CFD) simulations, can play an important role [35].

Many researchers [36-39] have studied the biomass thermal decomposition under pyrolysis employing thermogravimetric analysis (TGA). In this work, which is based on a poplar energy crop during a four years' time period, the aim was to study the effect of organic amendments on the pyrolytic behavior (analyzing the thermal capacity and kinetic parameters) and on the biomass generation of four different poplar clones. Thermal behavior analyzed to identify a better biomass performance. This better performance will be evaluate according to the energy that a certain process needs to start (activation energy) as well as we also consider the speed at which the reactions take place (frequency factor). Parameters, the above ones, which are deeply described in 2.5 section.

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 labeled 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 (no fertilization) were considered in this work for comparison purposes. The first organic treatment, names as BIOSOLIDS, was a dehydrated sludge from the León (Spain) sewage treatment plant (STP). The second treatment, name 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).

The characteristics of the organic amendments used in this work can be seen in Table 1. The amendments were applied once a year throughout the four years duration of this study (from September 2009 to September 2013). The first fertilization was applied in September 2009 and then annually until the end of the project. Trees were established in April 2010 after the sanitation of the plot. Taking into account the treatments characteristics (Table 1), 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. Agronomic requirements of the crop were estimated according [40] and were of 29417 mg N/kg wet soil, having an availability of annual nitrogen of 15021 mg N/kg wet soil. The BIOSOLIDS treatment was employed as a basal dressing and the MUD treatment as a top dressing.

2.2.- Biomass Sampling

Biomass sampling was done following the guidelines established by [41]. Besides, this sampling was yearly carried out in September as described in [42]. 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, taking samples at different orientations. The sampled biomass amount was 150 grams of wood for each subplot. The samples were deposited in perforated plastic bags, which had been previously labeled.

2.3.- Biomass fuel analysis

The fuel properties of biomass were done in order to determine the elemental analysis and proximate analyses as well as the calorific value. Biomass from tree branches was analysed to determine the main thermal properties. 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). Regarding the elemental analysis, carbon (C) was determined according to

UNE-EN ISO 16948:2015. Sulphur (S) and Chlorine (Cl) content was established according to UNE-EN ISO 16994:2015; whereas the UNE-EN ISO 16948:2015 was followed for the determination of Hydrogen (H) and Nitrogen (N).

2.4. - Biomass volume estimation

Trees volume was calculated employing the mathematical expression proposed by [43], which is described in Eq. (1):

$$V_U = 0.3D^2H \qquad \qquad \text{(Eq. 1)}$$

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),

Height (H) and diameter (D) trees were measured once a year (September) during the four years of the project. A "Powefix" caliper was used to determine the basal diameter at a height of 5 cm from the seedling. Height was measured employing a "Haglöf Vertex v3 201 DME" high precision laser. For this study, authors defined the height as the distance between the base of the seedling and the apical sprout.

2.5 - Biomass thermogravimetric analysis and modeling of results

A protocol was followed with biomass samples before performing thermogravimetric analysis. Samples were dried by air-drying for a minimum of 72 hours. Then, samples were milled on a "Fritsch P-19" mill to a 1 millimeter particle size. Afterwards, using a "Retch MM200" ball mill, particle sizes around about 0.2 mm were obtained. After

these pre-treatments, samples were (for a period of time no longer than 2 days) in airtight containers at 291 K ± 5.

Non-isothermal pyrolysis runs were carried out in a TGA equipment, model SDT2960, which was calibrated (baseline, weight, temperature and heat flow) prior utilization. For each clone and treatment, composite milled samples were submitted to dynamic runs at 10 K·min^{-1} up to 1273 K. Three repetitive derivative thermogravimetric (DTG) curves were obtained for each composite sample in order to guarantee reproducibility of the results. All dynamic runs were carried out on a pan containing 7 ± 1 mg of the corresponding sample, which was verified to be an appropriate sample size to ensure representativeness and to avoid heat or mass transfer limitations. Inert atmosphere inside the furnace during temperature-programmed pyrolysis was obtained by means of a continuous nitrogen flow of 100 mL/min at a gauge pressure of 1 atm.

The different pyrolysis steps may be seen in the derivative thermogravimetric profiles (DTG). Using these profiles, both the mass lost and the temperature associated with each step can be determined. In order to study the kinetic characteristics and to determine the activation energy (E_a) and the frequency factor (A) values, the approximate integral method (AIM) was employed with DTG profiles as described by Calvo et al. [44] and Paniagua et al. [45]. The activation energy is associated with the energy required to start a chemical reaction. Peaks derived from thermogravimetric analysis started at different temperature values depending on the species and the treatment employed. The adjustment of these peaks is, therefore, essential to know the respective thermal properties. The frequency factor (A) is defined as the number of collisions between molecules involved in a reaction. A larger number of collisions involve a higher reaction rate; consequently, the time associated with the chemical

reaction will be lower. Therefore, this parameter is related to the speed at which chemical reactions occur. The numerical values of this parameter, as in the case of activation energy values, have been determined by the AIM.

2.6 –Characteristic indexes.

Certain indexes could be employed to complement the results obtained for TGA and kinetic parameters (A and E_a). The main advantage of these, apart from their calculation speed, is the immediate possibility that they offer to identify the thermal properties of a biomass source.

We will determine the indexes for each of the stages identified in the DTG profiles (active, passive and high-rank pyrolysis).

For all the values, a statistical analysis was done with the IBM SPSS v.23 software to identify significant differences. This analysis was based in a one-way ANOVA test with a 5% significance level (p).

2.6.1. - Determination of pyrolysis-peak temperature (T_P) and pyrolysis index (P_i).

Before calculating this parameter, it is need to define a series of variables that are part of it. The first one is that which has been named as pyrolysis-peak temperature (T_p). Theoretically, we can say that this variable is related to the minimum temperature at which the substance experiment the behaviour associated with the particular phase without the presence of an external agent. This variable, which is so similar to the ignition temperate (at combustion processes), can be determined with the DTG profiles and the protocol defined by [46,47].

The pyrolysis index (P_i) represents the pyrolysis capacity for each particular stage

(peak). The higher P_i, the easier the fuel pyrolysis occurs. This index was determined by the following equation [48]:

$$P_i = \frac{(\frac{dw}{dt})max}{t_p \cdot t_e}$$
Eq. (2)

where $(dw/dt)_{max}$ is the maximum pyrolysis rate (%/min), t_p is the time (min) at which the largest peak (at a temperature above 293 K) occurs and t_e is the time (min) associated with the T_p.

P_i index allows us to know the pyrolysis capacity of a system, the higher its value, the easier the pyrolysis of the biomass.

2.6.2. - Determination of pyrolysis burnout index (B_i).

The burnout index (B_i) denotes the pyrolysis capacity of a fuel and was here determined to evaluate the biomass burnout performance. This index values were estimated according to Eq.3 [48]:

$$B_i = \frac{(\frac{dw}{dt})max}{\Delta t_{1/2} \cdot t_p \cdot t_f}$$
Eq. (3)

$\Delta t_{1/2}$ is the time (min), in the first half of the DTG for the particular stage, since the half of the maximum DTG value is reached until achieve this DTGmax value (min), t_f is the time at which the end of the peak takes place (starting counting time zero to 293 Kelvin degrees and considering the final moment as that in which it reaches the 2% of DTG_{max}).

This index is very similar to the P_i with the difference that D_f gives greater importance to the end of the peak and does not consider the *pyrolysis-peak temperature.*

2.6.3. – Pyrolysis characteristic index (P).

This index can be used for a preliminary assessment of the pyrolysis performance and represents the energy required to pyrolize a fuel. This index would be the equivalent of the combustion characteristic factor (CCF), an idex employed during combustions [49].

This way, P index can be calculated in a very similar way to CCF:

$$P = \frac{(\frac{dw}{dt})_{max} \cdot (\frac{dw}{dt})_{mean}}{T_p^2 \cdot T_f} \qquad \text{Eq. (4)}$$

where $(dw/dt)_{mean}$ is the average pyrolysis rate considering the 1% of the DTG_{max} as the start and the end of the process (%/min), T_p is the pyrolysis-peak temperature (K) and T_f is the temperature value at which the end of the peak is achieved (1% of the DTG_{max}).

P index evaluates the characteristics of the pyrolysis; this is, if P increases, the pyrolysis peak temperature decreases and pyrolysis begins earlier.

3.- Results and discussion

3.1.- Elemental and proximate analyses

The elemental and proximate analyses as well as the calorific results can be observed in Table 2.

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. Carbon and hydrogen content showed in the samples are so close to other biomass sources like sawdust [50], pine [51], eucalyptus [52] oak [53] or wheat straw [54]. Also, related to the sulfur content, large sulfur content within the typical samples cause the formation of pollutants (mainly COS and H_2S) [55], which does not provide energy and its reaction generates sulphur 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. In the case of the HHV and ash content there is also a homogeneity in the samples (standard deviations between 0.13 -

0.44). In spite of this homogeneity, the low ash content (2.49%) present in the UNAL-BIOSOLIDS constitutes a fact to consider favorably this combination. It must be highlighted that ash contents negatively affects the heating value of biomass [56]. A 2-4 % variation in the ash may cause around 8% variations in process yields, which, ultimately, would result in economic consequences.

Other key parameter to characterize a bio-fuel is the heating value (energy produced when a fuel is completely oxidized). This parameter can be estimated, in addition to traditional analytics, through the use of empirical equations [57]. We have employed the advice equation propose by the above authors to verify the veracity data of our analytical HHV results. Knowing this fact, HHV values for this manuscript paper (Table 2) are very close for all clones and treatments, although the I-214 was the clone showing the lowest HHV under the three treatments. Calorific values obtained for poplar biomass were higher when comparing the results with rice straw [58] and so similar that oat varieties straws values [59]. Furthermore, HHV obtained for the poplar plot are in the line with the obtained values for other authors that have worked with wood as biomass source [60]. However, poplar biomass has a lower HHV than conventional fossil fuel like petrol or coal [61].

3.2. - Biomass volume.

Biomass volume results (Table 3) showed that volume was higher for the subplots that had been fertilized than for the CONTROL subplot (except for I-214 clone under BIOSOLIDS treatment). This may be associated with a higher poplar growth (both in diameter and height) once the amendment was applied. Furthermore, considering each treatment, MUD was the most favorable amendment. Under this treatment, virtually all

the clones (except I-214) provided an important increase in the volume quantity at the last year of 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.

Poplar biomass volume values are substantially lower than the volumes obtained by other authors [62] working with different clones of poplar. This fact may be due to the difference in conditions (weather, watering, pruning, etc.), as well as to the duration of the study. In this study, the effect was studied for 4 years and many studies have a longer duration.

3.3- Thermogravimetric analysis.

Biomass devolatilization is referred to in terms of its three main components (lignin, cellulose and hemicelluloses). As published in [63], three stages during the pyrolysis thermal decomposition (TGA profiles) of wood were identified: water evaporation, active and passive pyrolysis. 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) from 453 to 1173 K [64].

Differential mass loss curves (DTG (%/min)) corresponding to the thermal decomposition of poplar wood pyrolysis at a heating range of 10 K/min under nitrogen atmosphere for each treatment are shown in Fig. 2, 3 and 4. In these curves, five main different regions can be identified, their respective parameters has been summarized in Table 4. The first four regions are related to: water evaporation, active pyrolysis (which includes two peaks or regions) and passive pyrolysis. The fifth region (named by the authors as *high-rank pyrolysis*) appeared at 900 K. Although this peak has not been identified in the poplar biomass pyrolysis [64-67], other authors have attributed this

phase to the decomposition of carbonaceous materials retained in char residues from the pyrolysis [52].

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). The second region is the most representative one (active pyrolysis). It occurs in a range from 430 K to 720 K. In this region we can analyse two peaks (the first peak achieves the DTG_{max} at 500 K and the second one at approximately 620 K). It is thought that these two peaks are related to the hemicelluloses and cellulose decomposition. Like it was said, lignin is decomposed both in active and passive pyrolysis [63,68]. There is no any characteristic peak related to the lignin decomposition. In the passive pyrolysis phase (DTG_{max} at 760 K) there is a smaller mass loss compared with that occurring in the active pyrolysis.

From the point of view of the energy optimization within the pyrolysis process, it is desirable to have feedstocks with low ash contents. Besides, it would be better that these weight losses processes take place at low initial and final temperatures. Taking into account the above statement, for the CONTROL treatment (Fig. 2), is the AF2 clone which shows a best performance during the active pyrolysis process (it has higher DTG_{max} values). Otherwise, considering the passive pyrolysis stage, as well as the high-rank phase, UNAL clone is the one which higher DTG_{max} values. Regarding the temperature of the DTG_{max} for these last phases, values are quite similar, around 755 K for passive phase and 915 K in the case of high-rank. Under fertilization with BIOSOLIDS (Fig. 3) the UNAL clone shows higher DTG_{max} for active pyrolysis phase; although this maximum weight loss is delayed about 10 K respective the other clones (610 K – 620 K). In contrast, for passive and high-rank phases, I-214 is the one that has a better behaviour (reflected by the higher values of DTG_{max} and the temperature values at passive (755K) and high-rank (920K) phases. Finally, under fertilization with MUD

(Fig. 4), UNAL is the clone that denotes a higher DTG_{max} value for the three stages, having similar characteristic temperatures to the other clones (615K, 755K and 915K for active, passive and high-rank respectively).

If the two organic fertilizations are compared (Table 4), we realize that the DTG_{max} value is reached at a very similar temperature for both the active (620 K) and the passive (760 K) phases. Considering the visual expression of the DTG- profiles (Fig.2 to 4) at active pyrolysis phase, different DTG_{max} values have been determined for the different clones under either CONTROL or BIOSOLIDS treatments. On the contrary, under MUD, the DTG_{max} corresponding to the different clones are mostly homogeneous at this phase. Regarding the passive and high-rank phases, a number of trends can be obtained collectively. UNAL poplar clones were those that showed higher DTG_{max} values for MUD treatment and CONTROL subplots. Under BIOSOLIDS treatment this trend is not maintained.

Therefore, analyzing the previous trends, it can be said that the term analysis recommends the use of the UNAL poplar clone

3.4- Kinetic analysis.

Results of the kinetic parameters are shown in Table 5. Average activation energy values (without taking into account high-rank phase values) are between 280.64 and 361.18 kJ/mol). These values are all lower during the active pyrolysis phase than during the passive phase. This implies that, when samples are exposed to a pyrolytic process, a greater amount of energy is need to start the reactions during the passive phase is comparison with the active phase (independently of the treatment and clone). 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, is the UNAL clone which has the lowest E_a vales. Under the MUD fertilization, there is great homogeneity (especially in the active phase) on the E_a values, although the UNAL clone is the one showing the lowest E_a value for the passive pyrolysis.

With respect to the high-rank pyrolysis phase, the CONTROL treatment is the one showing a better behaviour about the E_a values. Under this treatment, the lowest E_a values were determined for the UNAL clones for virtually the three treatments.

Again and considering the activation energy values, we have verified that the UNAL clone was the one that better results global denoted

Concerning frequency factor, the values were higher during the passive pyrolysis than during the active pyrolysis. The passive pyrolysis phase occurs faster than the active pyrolysis phase. This can be seen in the thermograms (Fig. 2, 3, and 4) through peaks which occur in a narrow temperature ranges (750 – 770 K). For the MUD treatment, A values were higher than for the other treatments, being the AF-2 clone the one having higher values for both active and passive pyrolysis phases. Another aspect derived from the results of the frequency factor is the behaviour of AF-8 clone for CONTROL treatment. Under these conditions, this clone (AF-8) is the one which had a higher A value (5.5 E+62 1/s) than the rest of clones for the same treatment during the passive pyrolysis phase. The second active pyrolysis and the passive phases are the temperatures ranges at which reactions occur faster (higher A values).

Comparing E_a values with other biomass sources [44], it can be stated that poplar

pyrolysis denoted higher activation energy values. Although it is true that there are few studies with the aim to analyze the kinetic parameters during the pyrolysis (and much less that work independently with each phase), we are able to compare the kinetic parameters showed by the pyrolysis of poplar clones with certain biomass sources, like rice husk [69], rice straw, cellulose or corncob [70]. Both the activation energy and the frequency factor values are higher for poplar pyrolysis; something that could be related to the specific biomass composition and the heating rate used during this work.

3.5- Characteristic indexes results.

Having carried out the estimation of the mentioned thermal indexes (Table 6) and its corresponding statistical analysis, the main discussion that can be stated for each particular index is summarize in the following paragraphs. Information, the following, which must take into account that the statistical analysis (appendix I of the supplementary material files) denoted that no significant differences were identified for any of the cases studied

3.5.1.- Pyrolysis-peak temperature (T_P) and pyrolysis index (P_i).

Lower T_p values are advisable, since, in this way, each phase (peak) will start with lower energy expenditure. Considering each phase, T_p values are very similar to each other, with virtually no differences between clones and treatments. As could be expected, when we advance in the DTG profile, the associated T_p values are greater.

Pi values are higher during the active phase. Making a global analysis of all treatments and clones combinations for this index, it can be said that UNAL clone is the one that generally reflects a better behavior. Behavior that, in average values for the three phases, was better appreciated after applying BIOSOLIDS treatment.

3.5.2.- Pyrolysis burnout index (B_i).

This parameter is very similar to the previous one. B_i index gives greater importance to the final part of each stage, without considering the pyrolysis-peak temperature.

In this index, although it is still maintained that the values for active phase are higher than the values for the rest of the phases, a clear trend cannot be identified in the results, as it happened in the previous case.

3.5.3.- Pyrolysis characteristic index (P).

This index may be the most useful of all that have been calculated. The previous statement is made on the basis that, although it is true that null references have estimated this index for the specific case of pyrolysis, there are certain references that have obtained the equivalent index for the specific case of combustion, CCF (Combustion characteristic factor), and, therefore, a comparison with them can me make.

Again, the values of the active phase are higher than other stages. The values related to this active pyrolysis phase will be those used to establish a comparison with other references. Authors have selected this phase since it is the most representative phase during the DTG profiles as well as the P values associated with this peak are so close to other references CCF data.

For the nine cases studied (three phases and three treatments), in five of them the UNAL clone showed higher values; being remarkable the particular case of the combination UNAL – BIOSOLIDS for the active pyrolysis phase. Under this treatment the UNAL clone experiences an increase in the value of the index ($2.5 \cdot 10^{-7} \frac{\%}{min^2 \cdot K^3}$) that is not experienced with MUD treatment. Fact, the above, that advises us to use this clone and treatment.

Comparing P values obtained for our pyrolysis samples with CCF (also called S or S_N) of certain biomass sources, it can be said that the values obtained are lower during pyrolysis. While for the case of the P index during the active pyrolysis phase, values between 1.6 and 2.6 have been obtained, for the S_N, other authors have achieved higher values: 3.9 for wheat straw and even values close to 5 for blends with coal [71]. As the proportion of fossil fuels in a mixture increases, the value of both indexes decrease. This is because if we compare their values separately, we can see how fossil fuels have lower P or CCF values than most biomass sources. Moreover, for our case study, the values obtained are near of greater to $2 \cdot 10^{-7}$, so that, for this active phase, poplar samples have a good thermal performance [72].

4.- Conclusions.

According to biomass fuel properties, differences between the poplar clones or treatments studied in this work were not appreciable. However, under the MUD treatment, it was verified a remarkable increase of the biomass volume over the first year of treatment. DTG curves determined for poplar biomass samples showed five weight loss stages, namely, moisture loss, first active pyrolysis, second active pyrolysis, passive pyrolysis and a high-rank pyrolysis phase. Among them, the second active pyrolysis was the most representative of the whole pyrolysis process and it was the combination BIOSOLIDS-UNAL the one that achieved higher lost weight values at this stage. Besides, the application of BIOSOLIDS treatment led to lower energy expenditure within the active and passive phases of the poplars pyrolysis as inferred by the lower activation energy values. Regarding the reactions speed (estimated by the frequency factor parameter), there were no appreciable differences between the different

poplar clones or treatments. On the whole, the UNAL clone under BIOSOLIDS fertilization showed the most favorable pyrolytic behavior.

5.- Acknowledgements

6.- List of acronyms

Treatments

CONTROL: Name of the treatment in which no fertilizer was applied to soil.

BIOSOLIDS: Name of the treatment in which dehydrated composted sewage sludge was applied to soil.

MUD: Name of the treatment in which sludge derived from a dairy wastewater was applied to soil.

Clones

UNAL: clone with the same name (UNAL) of the Populus x interamericana species employed in this study

I-214: clone with the same name (I-214) of the Populus x interamericana species employed in this study

AF-2: clone with the same name (AF-2) of the Populus x euramericana species employed in this study

AF-8: clone with the same name (AF-8) of the Populus x euramericana species employed in this study

7. - References

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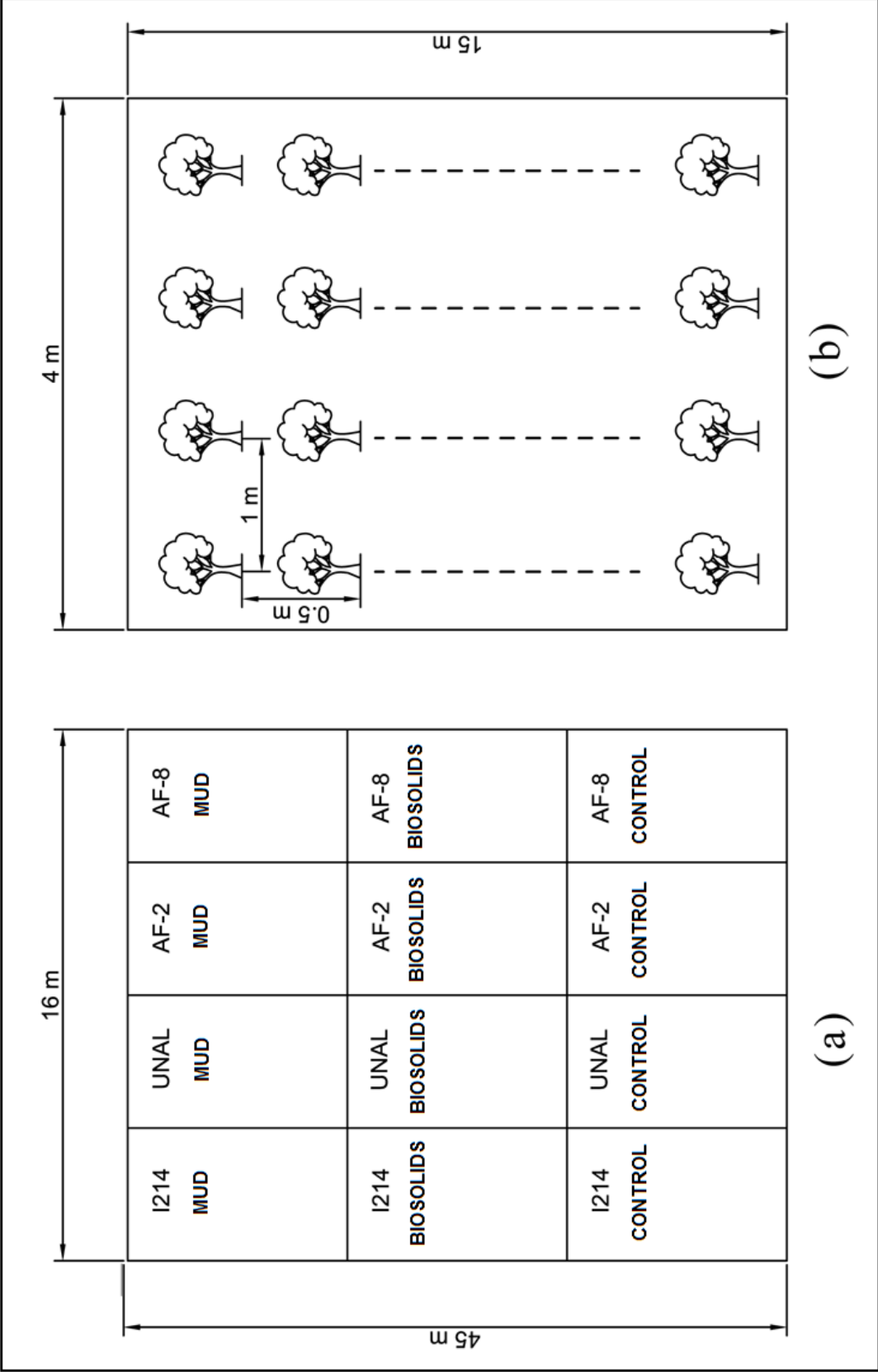
Fig. 1

Main plot (a) and one of the subplots (b). - I214, UNAL, AF-2 and AF-8 are the poplar clones. MUD and BIOSOLIDS are the amendments compared with the subplots without treatment (CONTROL).
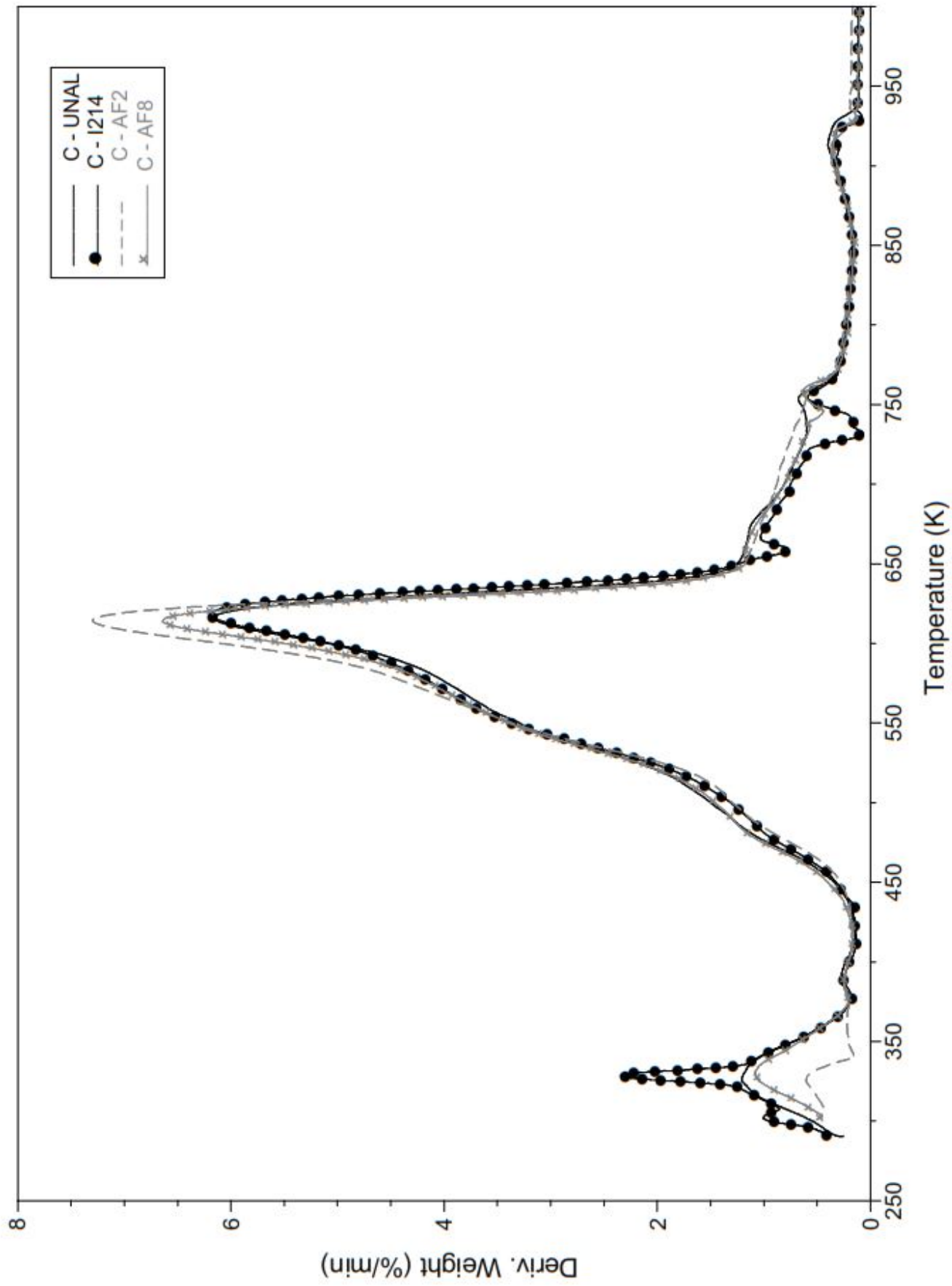
Fig. 2

DTG of poplar samples during CONTROL (C) treatment for pyrolysis process.
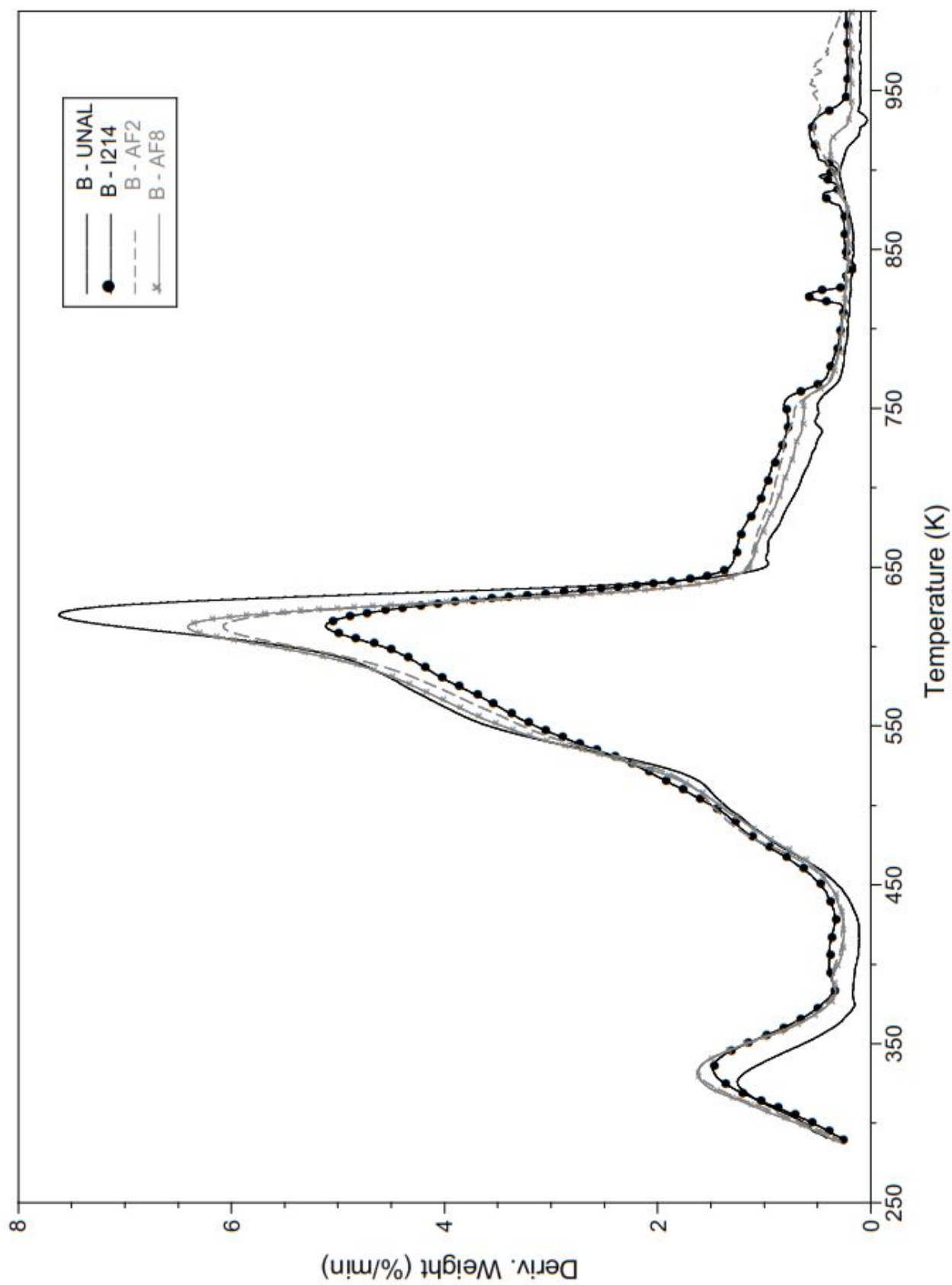
Fig. 3

DTG of poplar samples during BIOSOLIDS (B) treatment for pyrolysis process.
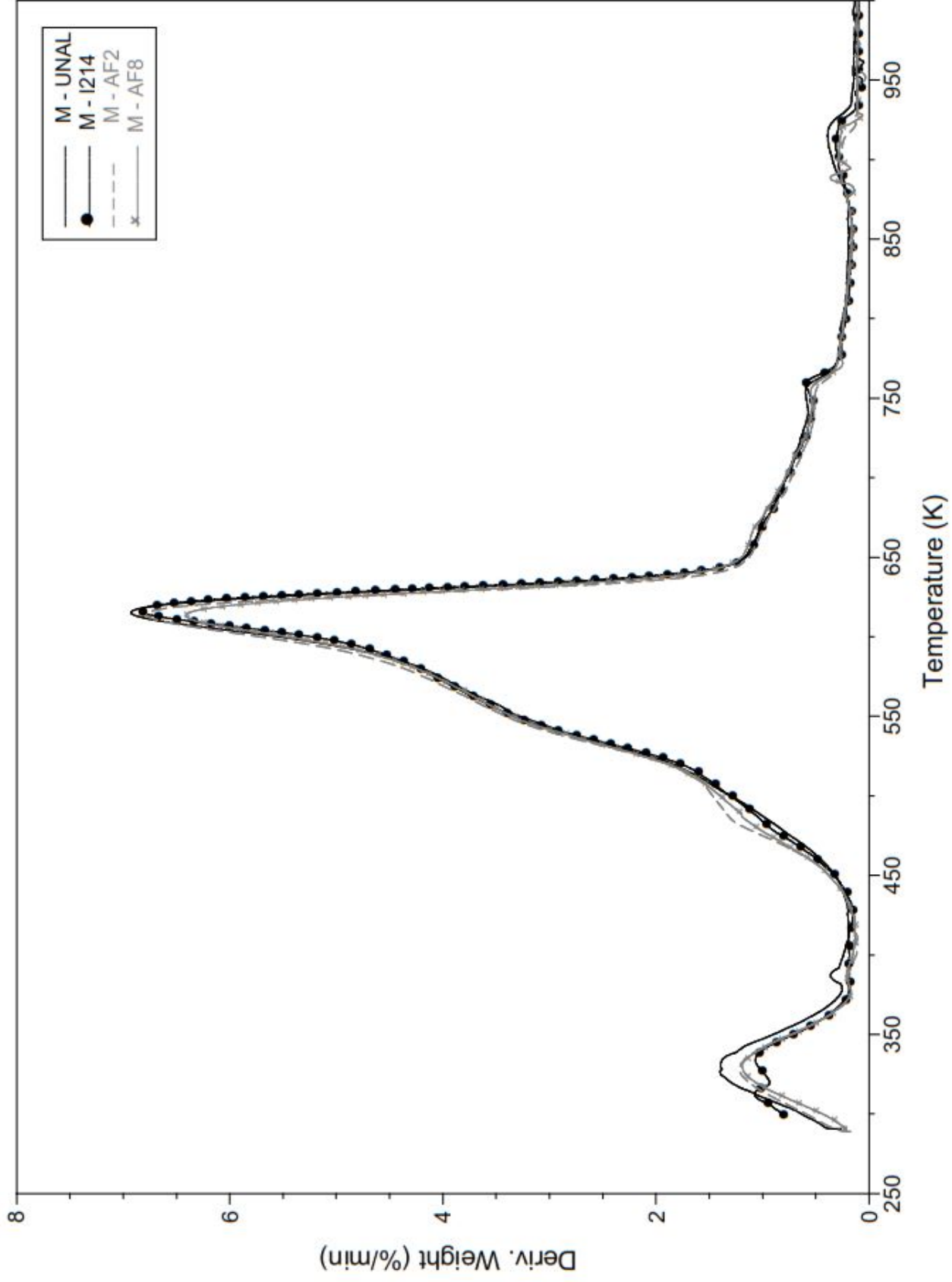
Fig. 4

DTG of poplar samples during MUD (M) treatment for pyrolysis process.

Appendix I – Thermal indexes statistical analysis (one-way ANOVA) -

Peak	Treatment						Clones					
	Active		Passive		High-rank		Active		Passive		High-rank	
	F	p	F	p	F	p	F	p	F	p	F	p
T_e	0.054	0.948	0.722	0.234	1.145	0.246	0.863	0.454	0.504	0.690	1.846	0.217
D_i	0.213	0.812	3.050	0.097	2.633	0.126	1.281	0.345	0.543	0.666	0.141	0.933
D_f	0.706	0.519	0.615	0.562	1.117	0.369	0.795	0.530	0.447	0.726	0.745	0.555
S	0.355	0.710	1.800	0.220	2.805	0.113	0.726	0.565	0.291	0.831	0.266	0.848
R_M	0.152	0.861	0.463	0.644	2.836	0.111	0.993	0.444	3.262	0.080	1.417	0.307

Table 1 Physicochemical characteristics of the organic amendments used. -

ELEMENTS	BIOSOLIDS	SD	MUD	SD
Dry matter (%)	92	4.3	1.4	0.2
pH	7.5	1.3	7.7	1.5
Conductivity (mS/cm)	1.72	0.23	0.47	0.09
Organic matter (%)	37.5	2.3	60	4.9
Total nitrogen (%)	3.2	0.7	6.9	1.6
C/N ratio	7	0.7	5	0.6
NH_4^+ - N (mg/kg)[a]	896.56	84.20	2282.61	245.23
NO_3^- - N (mg/kg)[a]	314.71	57.22	588.22	88.54
Phosphorus (mg /kg)[a]	31.1	8.8	16	1.4
Calcium (mg/kg)[a]	45.8	9.5	16	2.2
Magnesium (mg/kg)[a]	6.1	0.5	3.8	0.3
Potassium (mg/kg)[a]	3.2	0.6	5.3	0.7
Sodium (mg/kg)[a]	8.52	1.1	13.12	2.5

[a] On a dry basis
SD.: Standard deviation

Table 2 **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)

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

TREATMENTS

CLONE	CONTROL		BIOSOLIDS		MUD	
	First year[1] Mean	Last year[2] Mean	First year[1] Mean	Last year[2] Mean	First year[1] Mean	Last year[2] 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: values obtained for 2010
[2] Last year: values obtained for 2013

Table 4 Characteristic parameters obtained from the DTG pyrolysis curves obtained for the biomass from the different subplots.

	CONTROL				BIOSOLIDS				MUD			
	UNAL	I214	AF-2	AF-8	UNAL	I214	AF-2	AF-8	UNAL	I214	AF-2	AF-8
Active pyrolysis - 620 K												
T_0 (K)	433.24	441.31	439.51	443.1	441.31	443.1	441.31	434.13	439.51	438.62	429.65	434.13
T_f (K)	653.82	654.72	652.92	647.54	651.13	652.03	651.13	648.44	645.72	648.44	650.23	654.72
DTG_{max} (%/min)	6.19	6.20	7.34	6.65	7.66	5.14	6.09	6.44	7.02	6.90	6.84	6.46
T_{DTGmax} (K)	615.26	619.75	615.26	616.19	620.64	613.47	610.78	611.68	616.16	616.16	614.37	612.57
Passive pyrolysis - 750 K												
T_0 (K)	724.66	744.39	729.14	742.59	722.87	728.25	721.97	724.66	726.45	730.04	722.87	721.07
T_f (K)	773.08	771.29	773.98	778.46	770.39	773.08	771.29	770.39	774.87	775.77	769.49	769.49
DTG_{max} (%/min)	0.70	0.60	0.60	0.67	0.48	0.81	0.68	0.65	0.63	0.62	0.48	0.56
T_{DTGmax} (K)	754.25	754.25	758.73	758.73	753.35	756.04	752.46	754.25	756.04	760.53	756.94	756.04
High-rank pyrolysis - 920K												
T_0 (K)	861.85	866.33	869.92	872.61	862.75	874.4	871.71	858.26	869.02	874.4	860.06	860.95
T_f (K)	937.17	947.93	929.1	933.59	925.52	945.24	996.35	933.59	938.97	933.59	924.62	930
DTG_{max} (%/min)	0.41	0.24	0.32	0.33	0.27	0.55	0.52	0.38	0.38	0.32	0.30	0.33
T_{DTGmax} (K)	915.65	921.93	909.37	913.86	901.3	924.62	946.14	912.96	914.75	912.96	901.3	896.82

T_0 : initial temperature of the process; T_f : final temperature of the process; DTG_{max} : largest value of DTG in the considered process; T_{DTGmax} :temperature associated to DTG_{max}.

Table 5 – Kinetic parameters for the biomass sampled

	CONTROL				BIOSOLIDS				MUD			
	UNAL	I214	AF-2	AF-8	UNAL	I214	AF-2	AF-8	UNAL	I214	AF-2	AF-8
Active pyrolysis I (500K)												
E_a (kJ/mol)	91.82	103.02	82.39	83.00	77.07	83.31	85.83	87.94	71.32	88.83	94.12	81.12
A (1/s)	2.7E+07	5.4E+08	1.3E+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	0.991	0.9921	0.9911	0.9903
Active pyrolysis II (620K)												
E_a (kJ/mol)	235.49	265.72	267.03	287.11	285.74	192.72	217.56	223.78	275.49	268.71	282.18	241.01
A (1/s)	5.0E+17	1.3E+20	2.0E+20	1.6E+22	6.8E+21	1.2E+14	1.9+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
Passive pyrolysis (750K)												
E_a (kJ/mol)	604.19	639.56	729.94	944.93	464.31	441.29	519.13	688.96	606.36	717.91	772.07	697.28
A (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 (920K)												
E_a (kJ/mol)	159.08	249.65	314.12	259.15	316.79	647.88	316.70	1040.66	330.59	249.82	408.12	573.39
A (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

The results of activation energy (E_a) and frequency factor (A) were obtained by AIM method. R^2 is the linear correlation coefficient.

Table 6 – Characteristic indexes results.

	CONTROL			BIOSOLIDS			MUD		
	T_p (K)			T_p (K)			T_p (K)		
	Active	*Passive*	*H-R*	*Active*	*Passive*	*H-R*	*Active*	*Passive*	*H-R*
UNAL	540	680	900	545	760	880	540	755	910
I-214	525	750	920	540	755	920	545	755	910
AF-2	520	750	910	530	740	910	530	755	900
AF-8	545	755	920	520	750	900	525	740	900
	P_i (%/min^3)			P_i (%/min^3)			P_i (%/min^3)		
	Active	*Passive*	*H-R*	*Active*	*Passive*	*H-R*	*Active*	*Passive*	*H-R*
UNAL	7.6E-03	4.0E-04	1.1E-04	9.1E-03	3.1E-04	8.1E-05	8.0E-03	2.8E-04	9.9E-05
I-214	8.1E-03	2.8E-04	8.3E-05	6.4E-03	3.8E-04	1.4E-04	8.2E-03	2.7E-04	7.9E-05
AF-2	9.8E-03	2.8E-04	9.5E-05	7.9E-03	3.5E-04	1.4E-04	8.8E-03	2.3E-04	7.0E-05
AF-8	8.1E-03	2.9E-04	8.6E-05	8.7E-03	2.9E-04	9.9E-05	8.5E-03	2.6E-04	7.7E-05
	B_i (%/min^4)			B_i (%/min^4)			B_i (%/min^4)		
	Active	*Passive*	*H-R*	*Active*	*Passive*	*H-R*	*Active*	*Passive*	*H-R*
UNAL	3.0E-03	4.0E-04	7.4E-05	4.2E-03	2.4E-04	3.9E-05	3.4E-03	6.8E-04	9.4E-05
I-214	2.7E-03	3.2E-04	1.2E-04	2.2E-03	5.2E-04	1.1E-04	3.6E-03	6.4E-04	5.8E-05
AF-2	4.4E-03	4.5E-04	7.1E-05	2.7E-03	2.9E-04	6.0E-05	3.6E-03	3.2E-04	6.7E-05
AF-8	3.6E-03	4.7E-04	1.0E-04	2.7E-03	4.6E-04	8.5E-05	3.2E-03	3.1E-04	3.8E-05
	P ((%/min)$^2 \cdot$ K^{-3})			P ((%/min)$^2 \cdot$ K^{-3})			P ((%/min)$^2 \cdot$ K^{-3})		
	Active	*Passive*	*H-R*	*Active*	*Passive*	*H-R*	*Active*	*Passive*	*H-R*
UNAL	1.7E-07	1.3E-09	2.0E-10	2.5E-07	7.1E-10	1.0E-10	1.9E-07	8.2E-10	1.7E-10
I-214	1.8E-07	7.1E-10	1.2E-10	1.2E-07	1.4E-09	3.8E-10	2.0E-07	7.2E-10	1.1E-10
AF-2	2.6E-07	7.7E-10	1.6E-10	1.6E-07	1.1E-09	3.3E-10	2.1E-07	5.4E-10	8.7E-11
AF-8	2.0E-07	8.5E-10	1.3E-10	1.9E-07	8.1E-10	1.8E-10	1.9E-07	6.5E-10	1.0E-10

(T_p) pyrolysis-peak temperature; (P_i) pyrolysis index; (B_i) burnout index; (P) pyrolysis characteristic index