PYROLYSIS CHARACTERIZATION OF EUCALYPTUS GLOBULUS SAMPLES TROUGHT SIMULTANEUS THERMAL ANALYSIS

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Abstract

Thermogravimetry and differential scanning calorimetry (Simultaneus Thermal Analysis -- STA) tests of Eucalyptus Globulus samples, collected in Cantabria last November, were analyzed. The study includes an analysis of "a priori" two kinds of sawdust and leaves and two random combinations of leaves and sawdust. The analysis was performed at different heating rates which led the nature of the process (exothermic or endothermic). The characteristics processes of wood (hemicelluloses, cellulose and lignin) were obtained as well the qualitative energies involved in each process. Two differential isoconversional methods (Ozawa derived and Kissinger) were used to obtain the apparent activation energy to deal with a comparative analysis between the two types of sawdust from eucalyptus branches with different diameter.

Introduction

The study of these fuel oils is essential to rate the risk of forest disaster, as it appears in the reference document of the Global Earth Observation System of Systems (GEOSS) [1] that concludes it becomes critical to prevent these kinds of fires.

More than half of the area in Cantabria is forest land. This community has a great bioclimatic capacity which makes its forest area a rich and diverse place with a high ecological and productive potential. However, this potential contrasts with the low rate of utilization of forest resources which has tried to level off by the public establishment of forestry law 43/2003. The regulation of forestry wood allows the industrial use of forest areas to make paper but it forces to paper mills for cleaning the terrain. The paper mill only uses the wood that has a branch diameter larger than 8 mm so it may clean the rest of products by making bundles of wood waste which are stored. The disposal of the waste products is expensive because of the climate change regulations so an economic valorization of the disposal process becomes important to ensure a sustainable equilibrium between regulations and industrial uses.

Biomass pyrolysis

The dominant chemical species of biomass can be categorized as cellulose, hemicellulose and lignin. Several minor components, including lignans, volatile oils, tannins, resins, proteins, etc. complete the organic fraction of the fuel. The inorganic fractions include biologically active materials, such as potassium and chlorine, particulate materials biologically incorporated into the plant, such as silica, and adventitious material included in the form of soil, process-related compounds such as clay in paper, and often impurities unrelated to biomass itself ranging from wastes (nails, paint, bottles, pipes, refrigerators, etc.) to process or shipping components (bale wires, mill blades, etc.).

Currently, the exact pyrolysis mechanisms of biomass are not clear, although substantial literature sources on biomass devolatilization kinetics and mechanisms are available.

Cellulose thermal decomposition models, together with phase changes and tar production, provide a framework from which a lot of investigators have developed mathematical descriptions of biomass devolatilization.

Some simple models of cellulose devolatilization appear in the literature. Broido and Nelson suggested a competitive reaction model for large cellulose samples [2], followed by a multi-step model [3] reported by Broido; and a third multi-step model by Bradbury, Sakai, and Shafizadeh [4]. All of these models were usually used to describe low temperature and low heating rates in the pyrolysis process. They are not applicable for simulating biomass conversion because they assume a constant ratio of the char to volatiles yield and cannot be extended to systems different from the one on which they were based.

Two-stage models (Di Blasi, [5]) can be profitably applied to simulate thermal conversion since they include the description of the primary degradation of solid and the secondary degradation of primary pyrolysis products.

Samples and Methods

The sample was obtained in November of a bundle of Eucalyptus SP waste on an eucalyptus plantation close to Santander in Cantabria. Once extracted and before any test, the remaining dust was cleaned.

Then, the samples were ground to transform them into a material ready to STA analysis. To collect the different types of samples, what we did was take the sawdust obtained from the twigs and we crushed leaves in a mortar. Finally, we randomly mixed leaves and branches.

The woody debris was classified in 5 samples:

- Sample A: Branches with a diameter higher than 15 mm.
- Sample B: Branches with a diameter higher than 15 mm and leaves
- Sample C: Branches with a diameter lower than 15 mm
- Sample D: Branches with a diameter lower than 15 mm and leaves
- Sample F: Leaves

Simultaneous Thermal Analysis

A Netzsch STA 449 F3 was used to study both the kinetic parameters and the enthalpies of sample decomposition. The mass of the samples were in the range of 4–9 × 10^{-6} kg. To obtain the weight a precision mass balance Sartorius was used, which has accuracy mass up to 5 micrograms.

Table 1. Mass of samples analyzed.

	Mass A (g)	Mass B (g)	Mass C (g)	Mass D (g)	Mass F (g)
β=0.17 K s^{-1}	4.56x10^{-3}	7.29 x10^{-3}	5.21 x10^{-3}	7.78 x10^{-3}	4.87 x10^{-3}
β=0.33 K s^{-1}	6.96x10^{-3}	-	8.47 x10^{-3}	-	-
β=0.68 K s^{-1}	7.04 x10^{-3}	-	6.73 x10^{-3}	-	-

The tests were conducted in a nitrogen atmosphere. The sample holder within the platinum oven was purged with 10^{-6} $m^3 \cdot s^{-1}$ of nitrogen. Alumina crucibles were used.

All of these samples have the same pretreatment. First the sample was put in an oven with 333 K and a 25% of moisture during 48 hours to begin a process of drying. Then an isothermal process of 380 K during an hour was performed. After that the sample was heated up from 380 K to 1073 K at rates (β) of 0.17 $K \cdot s^{-1}$, 0.33 $K \cdot s^{-1}$ and 0.68 $K \cdot s^{-1}$.

Results and discussion

Below are the thermographs obtained in the STA (TGA, DTG and DSC) of the analyzed samples (Figures 1-5). Different processes related to decomposition of cellulose, hemicelluloses and lignin can be observed. In the following tables (Tables 2-11) a summary of the results is shown.

Sample A:

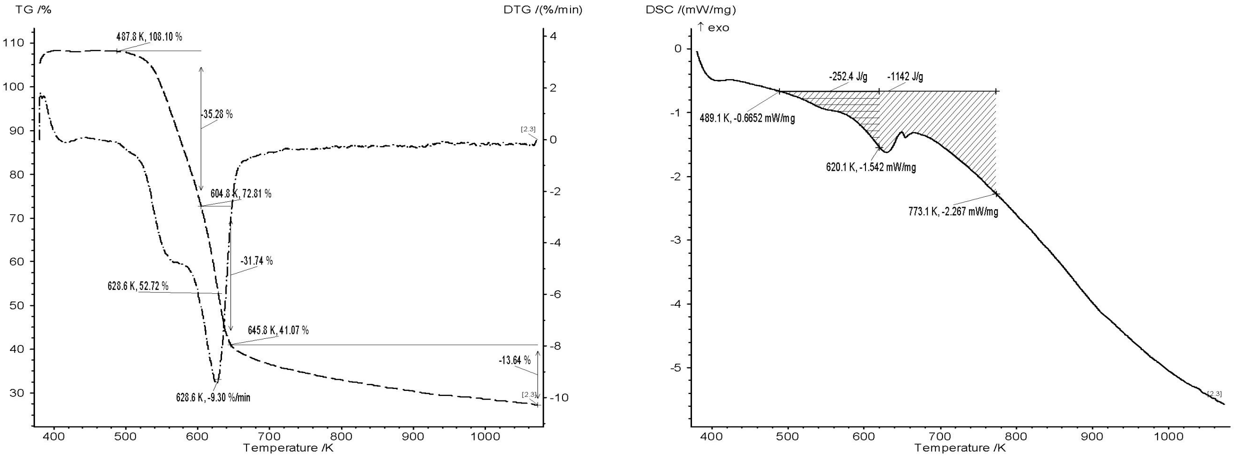


Figure 1. TG/DTG (left) and DSC (right) of sample A.

Table 2. Summarized values of the TG/DTG curves (Sample A) at 0.17 K s^{-1}.

Initial temperature (K)	Final temperature (K)	% mass	T$_{dtg\_peak}$(K)	% mass at DTG peak
487.6	604.6	-35.28	628.5	52.72
604.6	645.6	-31.74		
645.6	1073	-13.64		

Table 3. Summarized values of the DSC curves (Sample A) at 0.17 K s^{-1}.

1st process (K)	2nd process (K)	3rd process (K)	1st Energy (J/kg)x10^3	2nd Energy (J/kg)x10^3	Total (J/kg)x10^3
489	620	773	252.4	1142	6750

Sample B

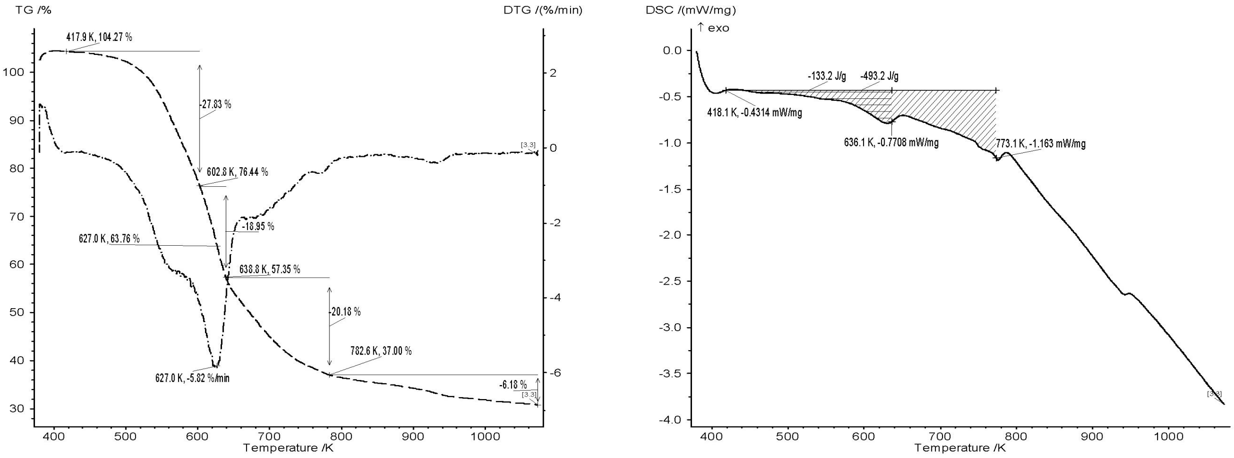


Figure 2. TG/DTG (left) and DSC (right) of sample B.

Table 4. Summarized values of the TG/DTG curves (Sample B) at 0.17 K s^{-1}.

Initial temperature (K)	Final temperature (K)	% mass	T_{dtg_peak}(K)	% mass at DTG peak
417.8	602.6	-27.83	626.9	63.76
602.6	638.6	-19.08		
638.6	782.5	-20.36		
782.5	1073	-6.19		

Table 5. Summarized values of the DSC curves (Sample B) at 0.17 K s^{-1}.

1st process (K)	2nd process (K)	3rd process (K)	1st Energy (J/kg)x10^3	2nd Energy (J/kg)x10^3	Total (J/kg)x10^3
418	636	773	133.2	493.2	3656

It is important t do a correct interpretation of the thermographs, taking into account that the main criteria was the mass loss and each different tendency in TG related with a change in DTG has been considered as a process. The TG/DTG shows clearly differentiated hemicellulose and cellulose devolatilization process (first peak of DTG and second peak of DTG Figures 1-3). The process of pyrolysis of samples was endothermic at 0.17 K.s^{-1}.

The sample B had a process more than the sample A due to the presence (light) of leaves in the sawdust analyzed. The results showed (Tables 2 and 4) that the leaves led a more difficult process of devolatilization (% mass at DTG peak A 52.72 against 63.76).

The energetic analysis was only comparative (Tables 3 and 5) but shows a more endothermic behavior in the sample without leaves, probably due to the fact that the mass releases by the sample was lower in the sample B.

Sample C:

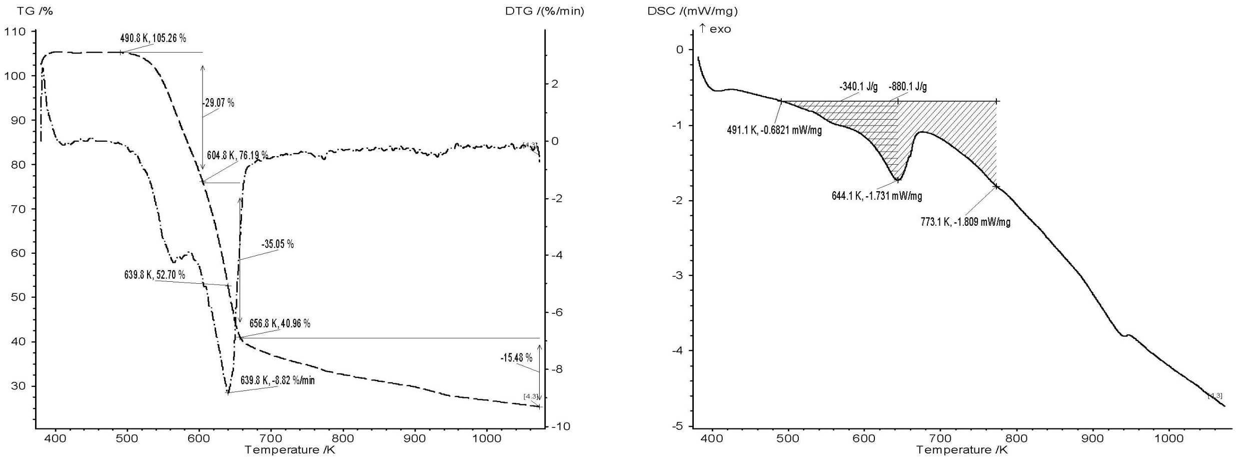


Figure 3. TG/DTG (left) and DSC (right) of sample C.

Table 6. Summarized values of the TG/DTG curves (Sample C) at 0.17 K s^{-1}.

Initial temperature (K)	Final temperature (K)	% mass	T_{dtg_peak}(K)	% mass at DTG peak
490.6	604.6	-29.07	639.6	52.70
604.6	656.7	-35.23		
656.7	1073	-15.58		

Table 7. Summary values of the DSC curves (Sample C*)* at 0.17 K s^{-1}.

1st process (K)	2nd process (K)	3rd process (K)	1st Energy (J/kg)x10^3	2nd Energy (J/kg)x10^3	Total (J/kg)x10^3
491	644	773	340.1	880.1	5278

Sample D:

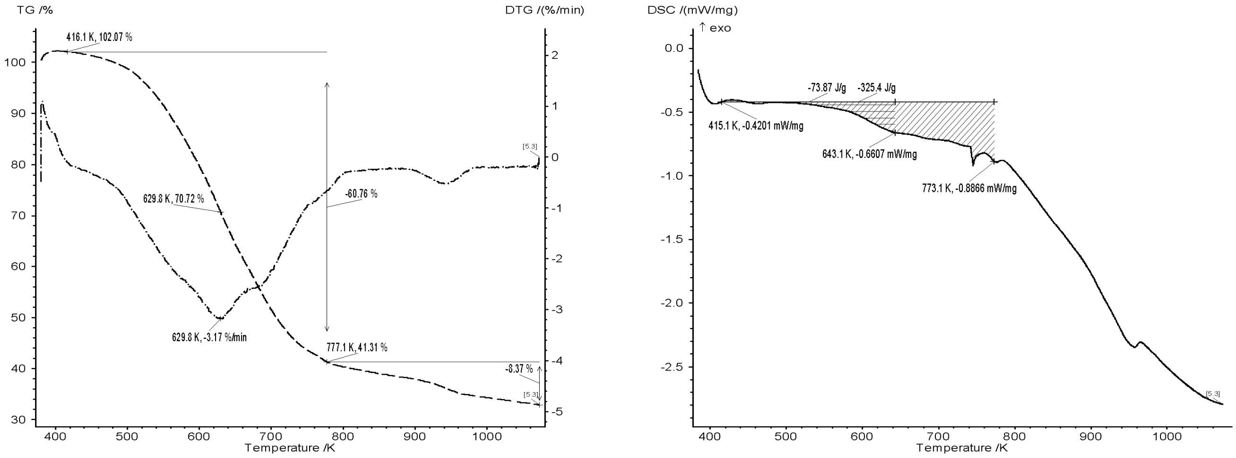


Figure 4. TG/DTG (left) and DSC (right) of sample D.

Table 8. Summarized values of the TG/DTG curves (Sample D) at 0.17 K s^{-1}.

Initial temperature (K)	Final temperature (K)	% mass	T_{dtg_peak}(K)	% mass at DTG peak
416	777	-60.76	629.6	70.72
777	1073	-8.37		

Table 9. Summary values of the DSC curves (Sample D*)* at 0.17 K s^{-1}.

1st process (K)	2nd process (K)	3rd process (K)	1st Energy (J/kg)x10^3	2nd Energy (J/kg)x10^3	Total (J/kg)x10^3
415	643	773	73.87	325.4	2733

The results showed (Tables 6 and 8) that the leaves led a more difficult process of devolatilization (% mass at DTG peak A 52.70 against 70.72), and also note that DTG thermograph of sample D does not show the processes of cellulose and hemicellulose clearly.

The comparative analysis between the values of % mass loss related with the hemicelluloses and cellulose decompositions from the samples without leaves (samples A and B) showed that the % of hemicelluloses in the sample A was bigger than this one in the sample C (Tables 2 and 6). The % of cellulose seems to be bigger for the sample C.

The energetic analysis (Tables 7 and 9) also shows a more endothermic behavior in the sample without leaves. In order to compare the results obtained for samples A and C, the values of reaction energy of sample A were bigger for two of the three phases of the process analyzed but not the release of volatiles (around 52 % in both samples). The ratio between energy of sample A and energy of sample B for each phase is the same (around 1.3) in the phases 2 and 3 but not for the first phase.

Sample F:

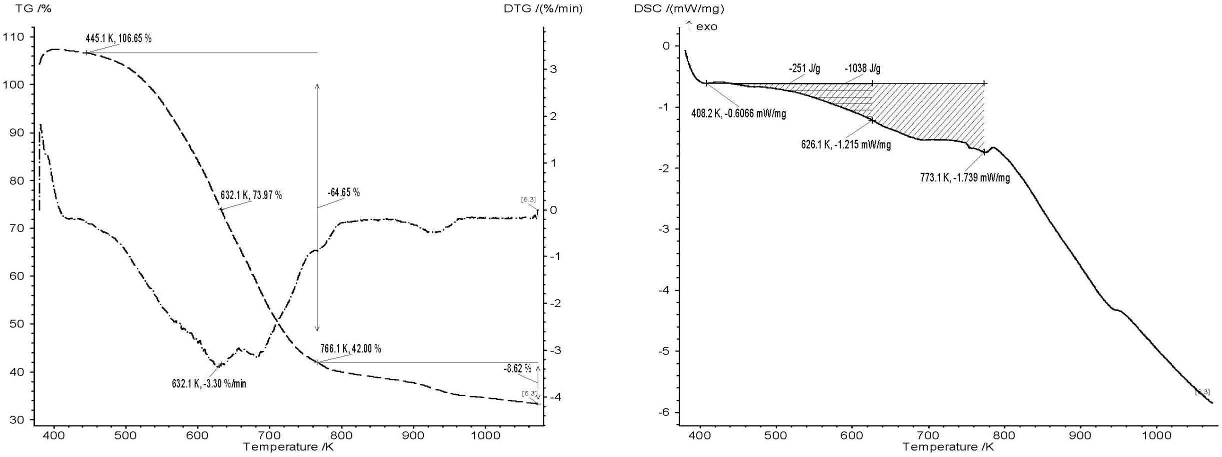


Figure 5. TG/DTG (left) and DSC (right) of sample F.

The thermograph TG/DTG of the leaves was similar than the sample D what wont to say that the sample D had a big quantity of leaves.

Table 10. Summarized values of the TG/DTG curves (Sample F) at 0.17 K s^{-1}.

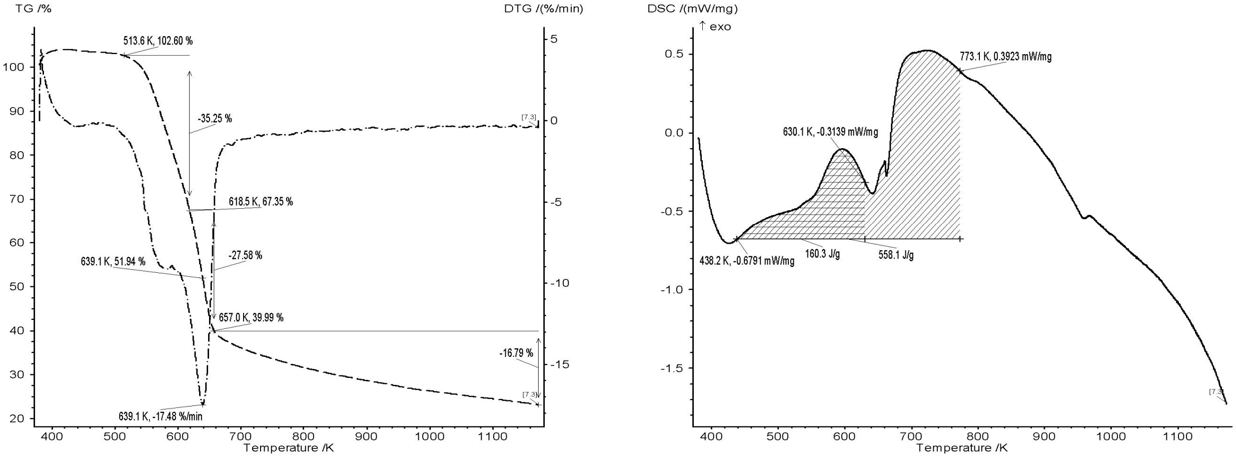
Initial temperature (K)	Final temperature (K)	% mass	T_{dtg_peak}(K)	% mass at DTG peak
445	766	-64.65	632.1	73.97
766	1073	-8.62		

Table 11. Summary values of the DSC curves (Sample F*)* at 0.17 K s^{-1}.

1st process (K)	2nd process (K)	3rd process (K)	1st Energy (J/kg)x10^3	2nd Energy (J/kg)x10^3	Total (J/kg)x10^3
408	626	773	251	1038	6162

The results obtained in the sample F (leaves) were self consistent about the % mass loss in the first steps of the process (73.97% at peak) as can be shown in Table 10. Regarding the energies (Table 11) there are not a reference to compare these ones.

In order to obtain an idea of the kinetics of the process, the apparent energy of activation, E, was obtained through a derived Ozawa method summarized in [6] and also by Kissinger method [7]. For this analysis at least three heating rates were needed.



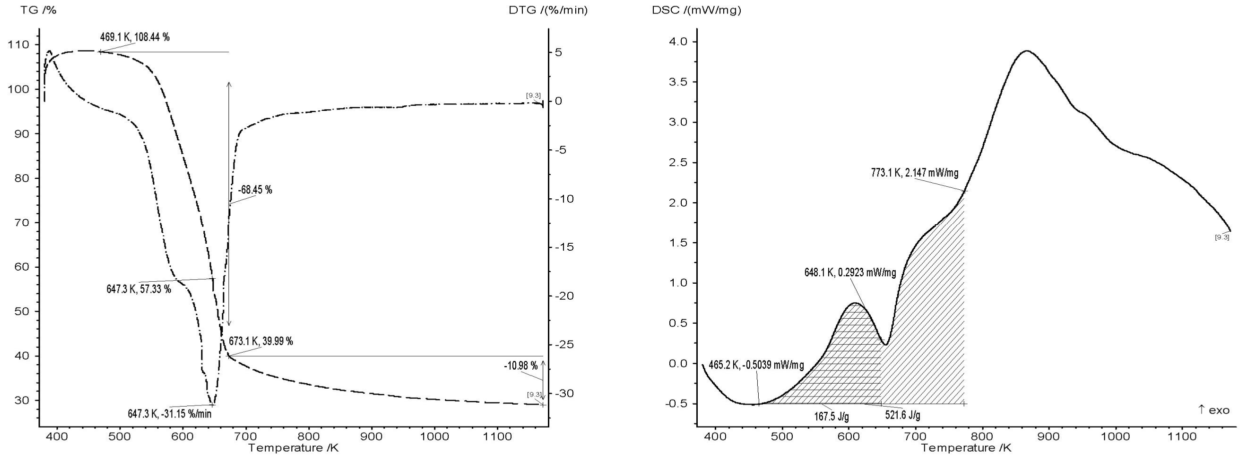


Figure 6. TG/DTG (left) and DSC (right) of sample A at 0.33 K·s^{-1} (top) and 0.68 K·s^{-1} (bot.)

Table 12. Summary of the tests of sample A

Heating Rate	Temperature DTG peak (K)	% mass at DTG peak
0.17 K·s^{-1}	628.5	52.72
0.33 K·s^{-1}	639.1	51.94
0.68 K·s^{-1}	647.1	33.32

Table 13. Summary enthalpies of the DSC curves (Sample A*)*

Sample A	1st Energy (J/kg)x10^3	2nd Energy (J/kg)x10^3	Total (J/kg)x10^3
0.17 K·s^{-1}	252.4	1142	6750
0.33 K·s^{-1}	-160.3	-558.1	-950.4
0.68 K·s^{-1}	-167.5	-521.9	-2036

ATSM E698:
From the data we draw the following:

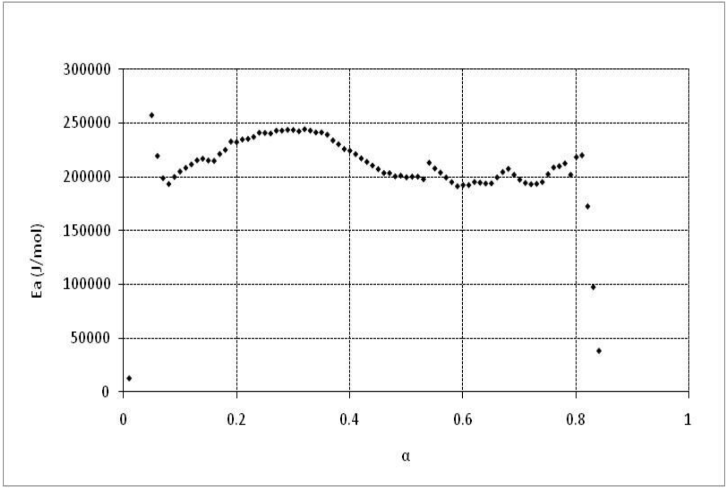


Figure 7. Summary of ATSM E698 method (Sample A)

By Kissinger method and supposing a one step process during the main process of mass loss the apparent energy of activation was 236612.785 J/mol.

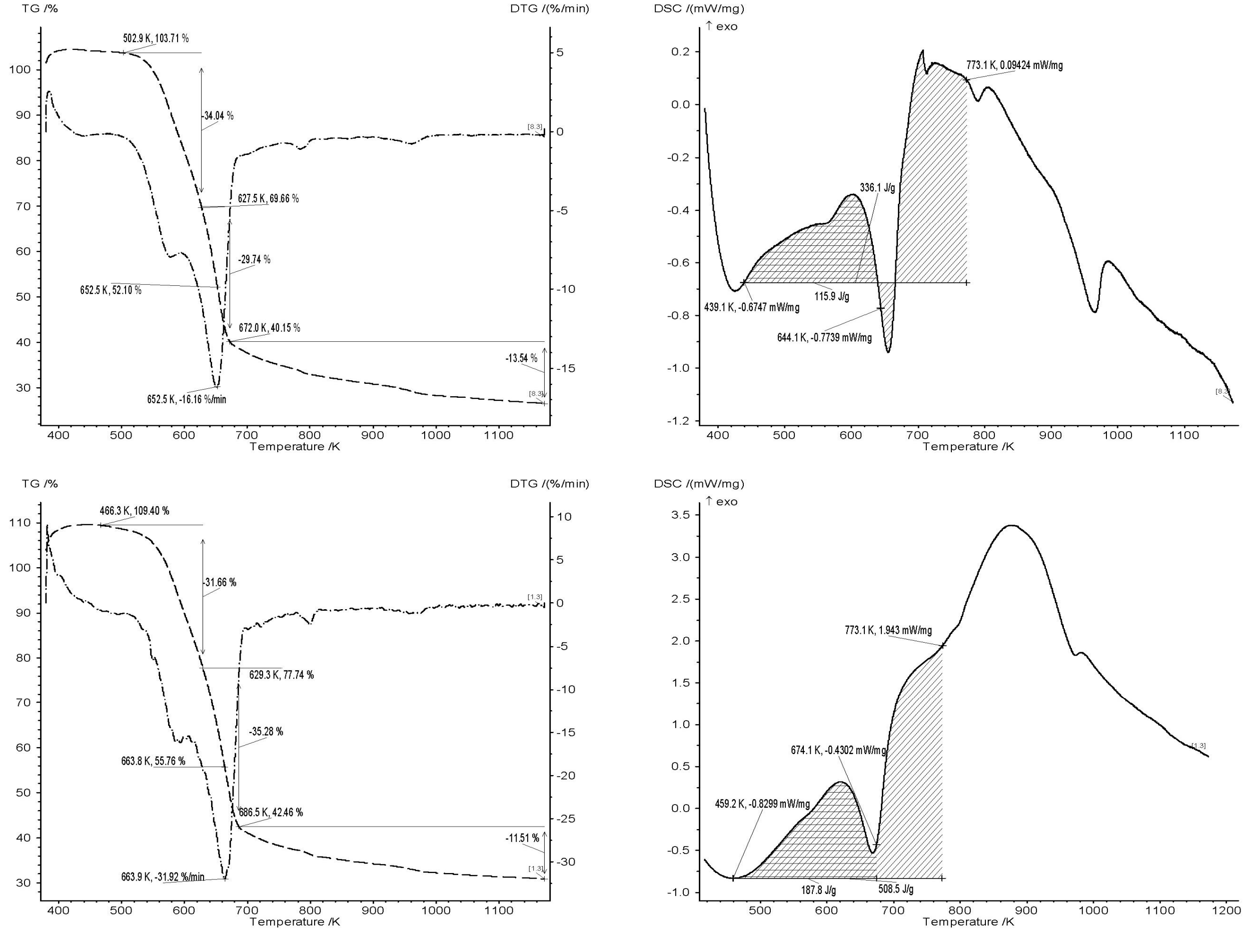


Figure 8. TG/DTG (left) and DSC (right) of sample A at 0.33 K·s^{-1} (top) and 0.68 K·s^{-1} (bot.)

Table 14. Summary of the process in sample C

Heating Rate	Temperature DTG peak (K)	% mass at DTG peak
0.17 K·s^{-1}	639.6	52.7
0.33 K·s^{-1}	652.3	52.1
0.68 K·s^{-1}	663.7	55.76

Table 15. Summary enthalpies of the DSC curves (Sample C)

Sample A	1st Energy (J/kg)x10^{3}	2nd Energy (J/kg)x10^{3}	Total (J/kg)x10^{3}
0.17 K·s^{-1}	340.1	880.1	5278
0.33 K·s^{-1}	-115.9	-336.1	-597.5
0.68 K·s^{-1}	-187.8	-508.5	-1876

ATSM E698:

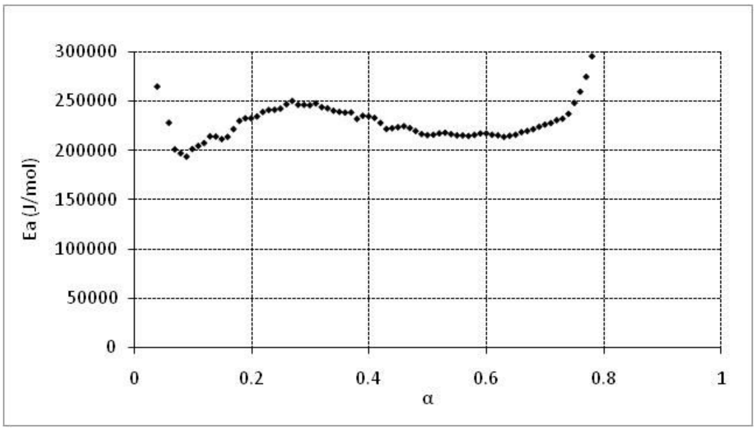


Figure 9. Summary of ATSM E698 method (Sample C)

By Kissinger method and also supposing a one step reaction the apparent energy of activation was 193235.482 J/mol.

No differences were found between the two kinds of eucalyptus samples (branches diameter bigger and lower than 0.015 m) by comparison of ASTM E 698 method. Both samples showed an initial stage of lower activation energy (more or less 200000 J/mol) and a second stage with an increase in this value (around 250000 J/mol) and a third stage where the method had no significant results (coal formation). Using Kissinger method, however, both samples were different. The sample A had bigger activation energy than sample C that should be due to the matured wood in Sample A. Indeed, the hypothesis of one step process seems to be a source of error for the results.

The DSC results showed that the samples were clearly different since the process at 0.17 $K\cdot s^{-1}$ was more endothermic than the same in sample C and processes at 0.33 $K\cdot s^{-1}$ and 0.68 $K\cdot s^{-1}$ were more exothermic in the sample A.

Conclusions

The bundles of waste eucalyptus had a mixture of branches, leaves and other inorganic substances that had strong importance in the process of energetic valorization. Cause of that the pretreatment of waste from the bundles was needed. This pretreatment is not only a preheating process but also a filtering of leaves and other residuals previous to the valorization process (gasification, fast pyrolysis).

The character endothermic or exothermic of the process is strongly related to heating rate so the industrial pyrolysis processes bases in higher heating rates such as fast pyrolysis can be considered as an important source of energy.

The differences showed between sample A and C were important if we consider a global one step process or few processes (hemicelluloses, cellulose and lignin) were conducted. The simplified schemes of pyrolysis based on coupled TGA and DSC can show accurate results that allow a valorization computational [8] of the expected energies produced.

References

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