J Therm Anal Calorim (2011) 104:61–67
DOI 10.1007/s10973-010-1177-y

Energetic characterization of forest biomass by calorimetry and thermal analysis

María Villanueva · Jorge Proupín · José A. Rodríguez-Añón · L. Fraga-Grueiro · Josefa Salgado · Nieves Barros

ISBCXVI Special Issue

Abstract The rational and sustainable exploitation of natural resources is one the priority objectives of our consumer society as an unavoidable strategy for survival. In previous articles, research group TERBIPROMAT has established the bases for the elaboration of energy maps of forest biomass. With those data, it is possible to classify the species in terms of their energy content and of their possible application as biofuels following European Norm CEN/TS 14961/2005 on solid biofuels. Main forest species used in this study were Populus and Paulownia. These species have a fast growth and produce big amounts of energetic biomass. To complete this study a comparison with autochthonous forest species, Eucalyptus and Pinus, was made. In this study, a thermogravimetric analysis is employed to qualitative study the resistance to thermal degradation of different forest species. These studies complete those made through static bomb calorimetry, elemental analysis, and different mechanical tests trying to get relationships between thermal behaviour and some physical properties.

Keywords Bomb calorimetry · Thermogravimetry · Biofuels · Sustainability · Biomass

M. Villanueva (✉) · J. Proupín · J. A. Rodríguez-Añón · L. Fraga-Grueiro
Campus of Santiago de Compostela,
Faculty of Physics, University of Santiago de Compostela,
Santiago de Compostela, Spain
e-mail: maria.villanueva@usc.es

J. Salgado · N. Barros
Escola Politécnica Superior, Campus of Lugo,
University of Santiago de Compostela,
Santiago de Compostela, Spain

Introduction

The continuous energy and social crises experienced by the humankind in last 50 years not only slowed down the economic development of even rich industrialized countries, but sentenced to a deep and long social crises to the developing ones. As main causes of this world energetic problem we can mention the continuous increases in price of fossil fuels, specially crude oil, and the fact that the fuel reserves are limited. Nowadays, the solution more appropriate that governments and scientific suggest is the search of new alternative fuels satisfying the conditions of rationality and sustainability as base of the energy policy of industrialized countries, and a global response to this continuous energy crisis.

At the same time, the excessive use of traditional fossil fuels may cause ecological damages influencing the climatic change. For this reason, last 20 years the European policy on energy has focused on the search for alternative and renewable sources of energy where forest biomass, xyloenergy, should play a significant role.

At present, these are the principal reasons why alternative energies, and more specifically the energy obtained from biomass, are occupying a leading place in the research and development sector, making of this search a world wide top priority objective. Within these alternative energy sources, the biomass, that is the group of materials of biological origin capable of being used as xyloenergy sources, is becoming an important one.

This article focuses on four forest species: Eucalyptus, Pinus, Populus and Paulownia. Eucalyptus and Pinus were chosen because these forest formations have both high economical and ecological interest in Galicia (NW Spain), and Populus and Paulownia were selected and studied more in detail because these forest species are being introduced as base for futures extensive energy plantations. In Spain, the consortium made up of CIEMAT (Public Research Agency for excellence in energy and environment)-INIA (National Institute for Agriculture and Food Research and Technology) have a strategic plan to plant more than 30.000 ha with Paulownia and Populus in 10 years. Nowadays, Galician government is implementing an energy policy based on alternative energies, biomass and wind power specially. The main reasons for developing sustainable energy cultures are:

1. Galicia has 600000 ha of unproductive surface occupied with bush species without any ecological interest [1]. This important area could be used to design energy plantations and generate important ecological, economic and social benefits.
2. Nowadays, this excess of 'fuel' is generating important problems related with the forest fires. Particularly in Galicia, with a forest surface representing 11% of the whole Spanish one, in last 5 years forest fires devastated around 150000 ha [2].
3. Climatic conditions are appropriated for the vegetal productivity. This special feature could help to produce important quantities of biomass.

   In order to achieve this study we use different techniques such as:

   – calorimetric measurements using a bomb calorimeter IKA C5000 to obtain the calorific values of the different forest species.
   – thermogravimetric analysis to study the behaviour of the different forest species to be degraded using a TGA7 Perkin Elmer.
   – other physico-chemical characteristics such as density, moisture, volatile compounds at 950 °C, or ashes in bomb at 1200 °C.

Experimental

The first step of the experimental procedure was obtaining of the sample. Sampling is one of the most important stages in this kind of study because the usefulness of the experimental results depends greatly on the samples being representative. Sample procedure was designed by Research Group TERBIPROMAT [3]. Next it is necessary the preparation of the samples of Populus and Paulownia to make the different physico-chemical tests [4].

1. *Moisture determination is a key parameter for LHV calculation* It was determined as the mass loss after drying of the sample in a Selecta 200210 natural desiccating oven, at 105 °C, to constant mass [5–7]. In parallel way a study of mass loss under environmental conditions (22 °C) and at 50 °C was made during 9 days. These temperatures were chosen because they are the current ones in storing and drying places in biomass plants. Moisture is also crucial in cost studies for transportation and storage of biomass, fuel performance and also during the autoignition processes in boilers.
2. *Preparation of the sample* The dry sample was ground using two mills of different power, a Retsch SM-1 blade mill and a IKA A11 Basic grinder, to homogenize the sample as much as possible (less than 1 mm), thus making easier the preparation of the sample pellets to be used in the different test [4].
3. *Determination of actual and bulk density* [8–10] Both were determined using an analytical balance Mettler XS104 with a special kit for densities. It complements thermodegradation studies supplying data for a better understanding of the process, as woods with high densities exhibit different behaviour as those with low densities regarding both to flammability and calorific values. Actual and bulk densities have a great influence on transportation and storage costs, and also in combustion properties such as specific thermal conductivity.
4. *Elementary analysis* This study was made for three kinds of samples: original sample, ashes obtained in Muffle furnace at 600 °C and ashes obtained in bomb calorimeter at 1200 °C. These data are very important to assess both quantity and quality of ashes produced during the combustion of Paulownia and Populus in boilers. Wood chemical composition, mainly in the case of mineralized compounds, could have an influence on delaying combustion as it affects directly on flammability. Elemental chemical composition was determined at the University of Santiago de Compostela General Services to Support Research. The main equipments used were a Fisons EA-1108 Element Analyzer for C, H, N and S, and a Carlo Erba EA1108 Elemental Analyzer for O. Obtained results are decisive in the valuation of the emission of gas contaminants produced during combustion (dioxins, furans, NO_x, SO_x, or HCN), corrosion problems in heaters, and bad operation in boilers.
5. *Calorific value using a bomb calorimeter IKA C5000 following DIN 51900, ISO 1928, ASTM D240, ASTM D4809, ASTM D5865, ASTM D1989, ASTM D5468, and ASTM E711 rules* Calorific value is the energy contained in a mass unit of forest biomass. Two calorific values must be pointed out, the higher heating value (HHV), that is determined experimentally in the laboratory [11], and the lower heating value (LHV) that can be calculated, from HHV. Both calorific values are related through the equation:

$$\mathrm{LHV} = \mathrm{HHV}(1-W)-24.42(W+9\mathrm{H_d}), \quad (1)$$

where LHV corresponds to the lower heating value of the dry sample, HHV is the higher heating value, W is the moisture percentage content and H_d is the hydrogen percentage of the dry sample. The heat of vaporization of water is taken as 2441.8 kJ kg^{-1}, and the water formed during combustion is 9 times the hydrogen content (%). The knowledge of LHV for the different tree species making up the forest vegetation becomes a realistic indicator of the energetic state of the forest biomass. HHV is determined by combustion of the forest sample in a static bomb calorimeter under an oxygen atmosphere (30 atm). This parameter is crucial for the design and/or selection of the boiler and in the energy production [12].

6. *Determination of volatile compounds in muffle furnace at 950 °C* [13–15] The presence of volatile compounds can change the fuel behaviour in boilers generating, performance variations and serious problems in the operation.
7. *Bomb and muffle furnace ashes at 1200 and 600 °C, respectively* [16–18] These data are a reference to know the remains (ashes and slags) that Populus and Paulownia could generate if they were used as a solid fuel. Ashes values obtained, both at 600 and 1200 °C, have a great influence in the emission of particulate matter to the atmosphere and also in cost derived from the collection and processing of these wastes.
8. *Fixed carbon* [16–18] It is the residual fraction (in percentage) from pyrolized fuel deducting the ashes. The greater the percentage in fixed carbon in a solid fuel, the greater calorific value, and therefore better fuel.
9. *Thermodegradation* For thermogravimetric analysis, powder samples about 10 mg in mass were used. Thermogravimetric analysis was performed using a thermogravimetric analyzer (TGA7) from Perkin Elmer controlled by a PC. The system was operated in the dynamic mode in the temperature range 50–700 °C, at heating rate 10 °C min^{-1}. All the experiments were carried out under a dry nitrogen atmosphere (balance purge gas 25 mL min^{-1} and sample purge gas 35 mL min^{-1}). The behaviour of a forest species before thermodegradation [19–21] supplies information about three very important and different items that help to evaluate the response of a forest fuel to be used in a heating. In the first place, the 'resistance' of a forest species to be degraded. In the second place, the maximum temperature that can tolerate (this is related to the energy that the different kinds of forest biomass can generate [22, 23]). In the third place, the thermal stability supplies information about the homogeneity of the response of a forest fuel.
10. *Analysis of ashes obtained at 600 and 950 °C* [16–18] Obtained values are used to decide the procedure of processing and disposal of the obtained ashes.

Every test was made in triplicate and during this procedure four different balances were used: a SARTORIUS BA 210 D (maximum capacity: 199.99999 g and readability: 0.01/0.1 mg), a double scaled Salter EP-22KA (maximum capacity: 20 kg and readability: 0.1/1 g), a Kern ALT 220-5DAM connected to the calorimeter (maximum capacity: 219.99999 g and readability: 0.01/0.1 mg) and a Mettler Excellence XS104 (maximum capacity: 120 g and readability: 0.01/0.1 mg).

The objective of the knowledge of each studied property is to certify the obtained solid fuel from biomass according to European standards for solid biofuels CEN/TS 14961/2005.

Results and discussion

In Table 1, it must be emphasized the high value of the moisture in the Paulownia. Paulownia is a fast growing forest species and for this reason the logging period for biomass obtention is as short as 5–7 years. Other species such as Pinus or Eucalyptus have periods of 15–20 years between consecutive cuttings. Populus have an intermediate behaviour between Paulownia and Pinus: it is recommended about 10 years of wait between consecutive cuttings and reasonable values of moisture (about 50%) are obtained. Because of the high values of moisture in Paulownia, installations dedicated to the use of biomass for the elaboration of solid fuels must be near the production zone (less than 15 km) and they must have natural drying places to avoid excessive cost in the transportation and drying. The main problem is that this drying process increases the solid fuel price.

Figure 1a shows that Paulownia and Populus have a similar behaviour when exposing to a controlled environment (22 °C) for 9 days. Both forest species lose the same water quantity (18% in Paulownia and 16% in Populus). Changing environmental conditions, 50 °C during 9 days (see Fig. 1b), Paulownia has a higher and faster loss of weight; Paulownia loses about 56% of its weight and

Table 1 Own moisture results

Own moisture/%	
Paulownia	70.74
Populus	47.76
Eucalyptus	54.54
Pine	55.55

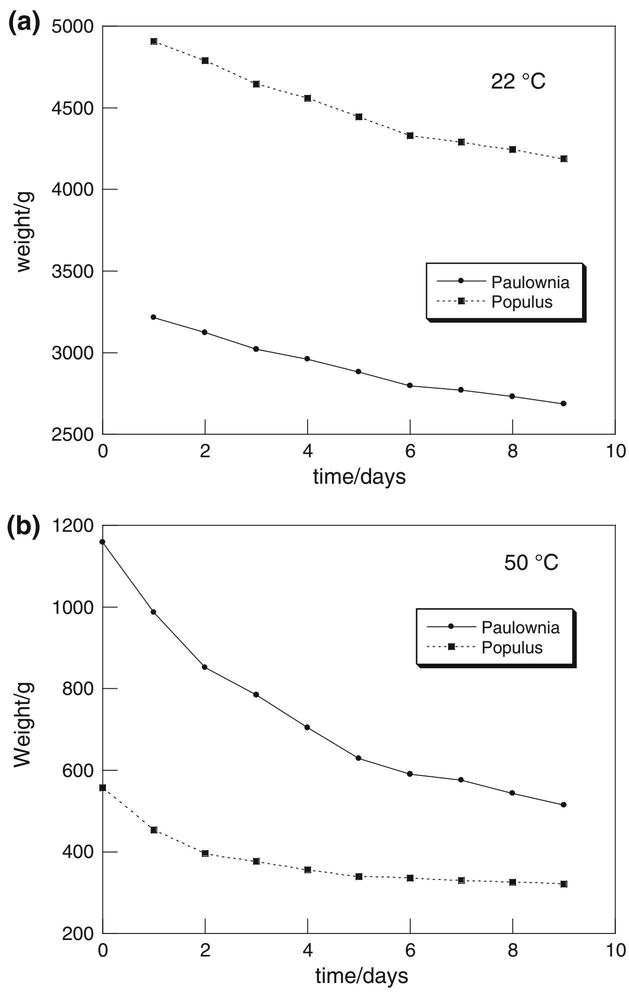

Fig. 1 Lost moisture at 22 °C (**a**) and at 50 °C (**b**) for Paulownia and Populus

Populus about 42%. The main reason of this behaviour can be on the actual density values, that is much greater in Populus than in Paulownia. Because of its actual density, populous has a less porous structure and it can keep its own moisture more stable in any situation, even in the case of changes on the environment humidity.

Obtained actual density for Populus is as expected, but that for Paulownia is lower than expected. Fast growing species have generally lower densities than those for long-lived species. Values for Pinus and Eucalyptus are higher, as it can be seen in Table 2. Low actual density values must be taken into account when designing transportation and logistics for this kind of biomass to not increase costs.

In case of bulk densities (see Table 3), Paulownia and Populus show high values, that can be due to their high moisture contents.

Elemental composition analysis results are presented in Table 4. As it can be observed, obtained values for the four studied species are in concordance with those considered as reference values for all species. These analyses were made to prevent possible emissions of contaminant gases when using Paulownia and Populus as fuel biomass. It must be pointed out that *S* and *N* values are much lower than those obtained for Eucalyptus and Pinus.

Calorific values of Paulownia and Populus are lower than those determined for Eucalyptus or Pinus. Younger trees have lower calorific values because they have lower lignin content (lignin percentage content increases with age). The HHV of lignin is 25900 kJ kg^{-1} whilst HHV of cellulose is 18200 kJ kg^{-1} [19, 24]. Furthermore, species with high moisture content, such Paulownia, must be dried before the preparation of fuel biomass to avoid performance fluctuations when using in industrial and domestic heaters (Table 5).

Both Populus and Paulownia show reasonable volatile compound values (Table 6).

Bomb and muffle furnace ashes results are very low (Table 7). The lower content in ashes makes easier waste

Table 2 Actual density results

Actual density/kg m^{-3}	
Paulownia	417.86
Populus	661.53
Eucalyptus	1034.83
Pinus	932.18

Table 3 Bulk density results

Bulk density/kg m^{-3}	
Paulownia	854.23
Populus	880.10

Table 4 Elemental composition analysis results

Elemental composition/%	C	H	N	S	O
Paulownia	46.22	6.61	0.16	0.07	41.85
Populus	47.86	6.50	0.32	0.07	41.25
Eucalyptus	45.73	5.82	1.23	0.13	47.09
Pinus	52.63	6.21	1.53	0.25	39.38

Table 5 HHV and LHV results

	HHV/kJ kg^{-1}	LHV/kJ kg^{-1}
Paulownia	18325.50	3209.50
Populus	18840.50	7929.69
Eucalyptus	20225.14	7228.41
Pinus	20503.70	7436.36

Table 6 Volatile compounds results at 950 °C

Volatile compounds at 950 °C/%	
Paulownia	0.94
Populus	1.05

Table 7 Bomb and muffle furnace ashes results

	Bomb ashes at 1200 °C/%	Muffle furnace ashes at 600 °C/%
Paulownia	0.32	0.97
Populus	0.36	1.21
Eucalyptus	0.84	Not calculated
Pinus	0.28	Not calculated

Table 8 Fixed carbon results

Fixed carbon/%	
Paulownia	28.98
Populus	49.28

processing generated in combustion (lower cost) and it generates lower problems in domestic heaters (particulate matter emissions or chimney blockage).

Table 8 shows fixed carbon results. These values are a bit higher to the collected ones in the references. In any case, these fixed carbon values are very appropriate from the energetic point of view.

Figures 2 and 3 show thermal degradation behaviour and thermodegradation rate of the four forest species, respectively. Table 9 shows onset and endset temperatures, residue values at 650 °C, and temperatures at points of higher thermodegradation rate.

- As it can be observed, Paulownia seems to be the species that worse resists the increase of temperature: Paulownia has the lowest onset and endset temperatures (see Table 7). Onset temperatures have been calculated as the intersection between the tangent to the maximum rising slope and the extrapolated baseline. Endset temperatures were calculated as the intersection between the tangent to the maximum rising slope and the extrapolated 'ending' baseline where no mass changes were detected any more.
- Paulownia has the lower residue (at 650 °C).
- Paulownia reaches its highest rate of mass change at the lowest temperature comparing to the other species studied. Data of the maximum rate of mass change and slope of TG curve are crucial characteristics when fuel biomass is designed because it is related to the time of consumption of fuel biomass (thermodegraded matter percentage in onset is the highest for the four species).

From same figures it can also be observed that Pinus is the species that better resists an increase of temperature. Moreover, this species has the longest range between onset and endset temperatures. Pinus reaches its maximum rate of mass change at 391.6 °C and the residue at 650 °C is the higher for the four species studied.

More information from Fig. 2 can be extracted:

- Pinus and Eucalyptus have a first peak at 80 °C approximately due to moisture and volatile compounds losses. This water was caught from the environment when preparing samples.
- Four species show a second peak. This main decomposition step corresponds to the thermal degradation of the majority part of the cellulose and hemicellulose and an important part of lignin [19]. Paulownia has also a previous peak at 228.59 °C probably caused by the

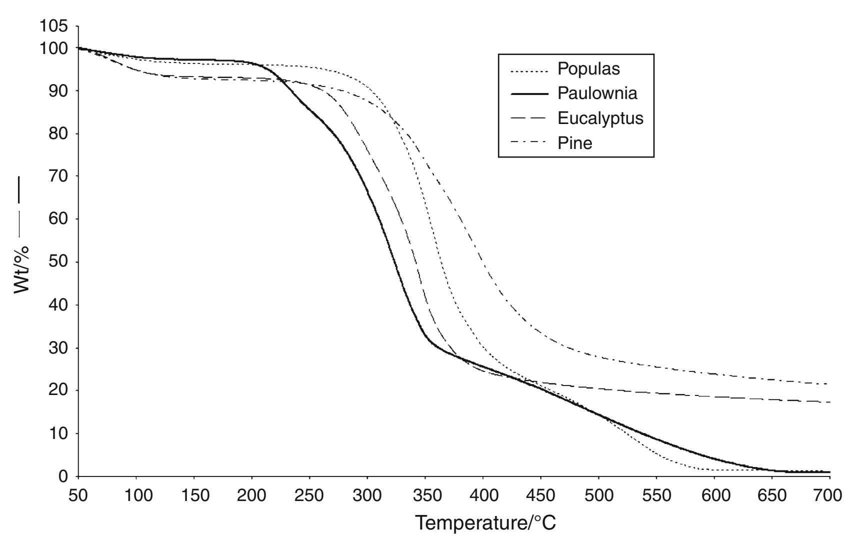

Fig. 2 TG curves for the four species studied

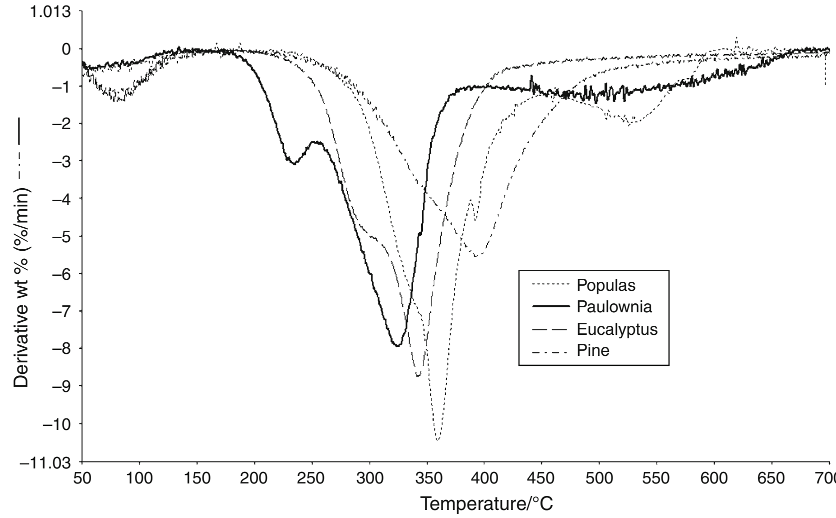

Fig. 3 DTG curves obtained from TG ones

Table 9 Decomposition characteristics obtained from TG and DTG curves

Samples		Eucalyptus	Pinus	Paulownia	Populus
DTG curve	PT/°C	341.5	391.6	325.4	359.3
	A/%	72.4	64.2	33.0	59.6
Onset	*T*/°C	289.5	316.1	288.5	315.9
				214.0	492.4
	W/%	81.0	85.0	73.0	86.0
				95.0	16.0
Endset	*T*/°C	370.5	441.0	350.7	384.5
				288.5	
	W/%	30.0	35.0	33.0	36.0
				73.0	
Residue at 650 °C	*R*/%	18.6	23.9	1.4	1.4
Secondary peaks	PT/°C	80.4	77.6	84.8	90.0
				228.6	393.2
				522.0	525.4
	A/%	4.8	7.4	1.0	1.3
				3.0	3.0
				10.0	9.9

PT Peak temperature in °C, *A* area in percentage, *T* temperature in °C, *R* residue in percentage, *W* weight in percentage

thermodegradation of cellulose and carbohydrate-rich young tissues.

– Paulownia and Populus have a third peak corresponding to the 'secondary' loss of the remaining lignin and other residual compounds. This peak does not appear in Eucalyptus and Pinus curves.

Conclusions

Forest fuels from fast growing species such as Eucalyptus and Pinus have a better thermal stability and higher calorific values than other 'in fashion' energetic species, such as Populus or Paulownia. Therefore, with less quantity of fuel material the same quantity of energy can be obtained.

Other important conclusion is the amount of ashes at 650 °C. Eucalyptus and Pinus have about 20% of residual mass whilst the other species have values about 1.5% of residual mass. The reason can be that barks and leaves of Eucalyptus and Pinus have a high content in mineral salts. For this reason should be interesting to remove the barks and leaves before using this material as a forest fuel. In future studies it would be interesting to perform isothermal experiments at temperatures similar to those reached during combustion in conventional heaters.

Paulownia is less advisable species from the energetic point of view because it has a high own moisture, low heating value (especially LHV) and less thermal stability. Even though, Populus has a high HHV and LVH, low own moisture, an insignificant ash percentage and a high thermal stability, similar to Pinus or Eucalyptus.

We can conclude that Pinus could be the most appropriate species to elaborate fuel because it has a very high heating value, a suitable own moisture and the highest thermal stability of the four studied species. The problem of its high residue value could be reduced substantially eliminating the bark.

References

1. Ministerio de Agricultura, Pesca y Alimentación, Tercer Inventario Forestal Nacional. 1997–2006, Madrid:Ed. Ministerio de Medio Ambiente 2000.
2. PLADIGA 2010. Consellería de Medio Rural. Dirección Xeral de Montes. Xunta de Galicia. 2010. http://mediorural.xunta.es/fileadmin/arquivos/forestal/pladiga/2010/

1_MEMORIA_WEB_PLADIGA_2010.pdf. Accessed 14 Sep 2010.
3. Núñez-Regueira L, Proupín-Castiñeiras J, Rodríguez-Añón JA. Energy evaluation of forest residues originated from *Eucalyptus globulus* Labill in Galicia. Bioresour Technol. 2002;82:5–13.
4. Forest products laboratory, Word Engineering Handbook, New Jersey: Prentice; 1990.
5. Ragland KW, Aerts DJ, Baker AJ. Properties of wood for combustion analysis. Bioresour Technol. 1991;37:161–8.
6. Kemp RB. Nonscanning calorimetry. In: Gallagher PK, editor. Handbook of thermal analysis and calorimetry. Amsterdam: Elsevier; 1999. p. 1032.
7. ASTM D3173-03 (2008) Standard test method for moisture in the analysis sample of coal and coke.
8. Blake GR, Hartge KH. Bulk density. In: Klute A, editor. Methods of soil analysis, part 1 physical and mineralogical methods. 2nd ed. Madison: American Society of Agronomy, Inc. and Soil Science Society of America, Inc; 1998. p. 363–75.
9. Blake GR, Hartge KH. Particle density. In: Klute A, editor. Methods of soil analysis, part 1 physical and mineralogical methods. 2nd ed. Madison: American Society of Agronomy, Inc. and Soil Science Society of America, Inc; 1998. p. 377–82.
10. Forest products laboratory. Wood handbook: Wood as an engineering material. Agric. Handbook t2 (rev) Washington, DC: US Department of Agriculture 1987.
11. Hubbard W, Scott D, Waddington G. Experimental thermochemistry, Rossini F., 1, Chap. 5. New York: Interscience Publishers Inc; 1956. p. 77–87.
12. Núñez-Regueira L, Rodríguez-Añón J, Proupín-Castiñeiras J, Labarta-Carreño C. Use of bomb calorimetry to assess recovery of waste industrial mineral oils through regeneration. J Therm Anal Calorim. 2002;70:93–101.
13. ASTM E872-82 (2006) Standard test method for volatile matter in the analysis of particulate wood fuels.
14. ASTM D3175-07 (2006) Standard test method for volatile matter in the analysis sample of coal and coke.
15. ISO 562:2010 Hard coal and coke-determination of volatile matter.
16. Standard test method for ash in Wood D 1102-84 Reapproved 2007.
17. ASTM D3174-04 (2003) Standard test method for ash in the analysis sample of coal and coke from coal.
18. ISO 1171:2010 Solid mineral fuels-determination of ash.
19. Liodakis S, Bakirtzis D, Lois E. TG and autoignition studies on forest fuels. J Therm Anal Calorim. 2002;69:519–28.
20. Kwok QSM, Jones DEG, Nunez GF, Charland JP, Dionne S. Characterization of bio-fuel and bio-fuel ash. J Therm Anal Calorim. 2004;78:173–84.
21. Strezov V, Moghtaderi B, Lucas JA. Study of decomposition of selected biomass samples. J Therm Anal Calorim. 2003;72:1041–8.
22. Leroy V, Cancellieri D, Leoni E. Relation between forest fuels composition and energy emitted during their thermal degradation. J Therm Anal Calorim. 2009;96(1):293–300.
23. Cuña Suárez A, Tancredi N, Pinheiro CPC, Yoshida MI. Thermal analysis of the combustion of charcoals from *Eucalyptus dunnii* obtained at different pyrolysis temperatures. J Therm Anal Calorim. 2010;100(3):1051–4.
24. Núñez-Regueira L, Rodríguez-Añón JA, Proupín J, Mouriño B, Artiaga-Diaz R. Energetic study of residual forest biomass using calorimetry and thermal analysis. J Therm Anal Calorim. 2005;80:457–64.