Influence of thermo-vacuum treatment on thermal degradation of various wood species

Luigi Todaro[1] · Angelo Rita[1] · Rachele Pucciariello[2] · Marisabel Mecca[2] · Salim Hiziroglu[3]

Received: 27 July 2016 /

Abstract Solid wood has a certain amount of resistance to fire exposure. Recently, there is also great interest in characterization of the thermal behaviour of treated wood due to increasing demand of such products within the perspective of sustainability of environment. The objective of this study was to evaluate and predict the thermal decomposition process of samples from different wood species, Norway spruce (*Picea abies* Karst.), common ash (*Fraxinus excelsior* L.) and Turkey oak (*Quercus cerris* L.), so that such data can be used for enhanced design of wood products for more effective and better utilization in different applications. Spruce and ash samples were treated at a temperature of 190 °C for 2 h while Turkey oak specimens were steamed at a temperature of 110 °C for 24 h before they were thermally treated at a temperature of 160 °C for 3 h. A thermo-gravimetric analysis of the samples highlighted intraspecific differences in mass loss and the stage of thermal degradation between treated and untreated specimens. The degradation of the wood was characterized by twofold reaction stages, with an exception of Norway spruce samples, which exhibited a one-stage reaction. In addition, thermal treatments affected chemical composition of wood. The obtained results will be helpful in determining the applicability of these materials according to their thermal degradation properties.

✉ Angelo Rita
angelo.rita@unibas.it

[1] Scuola di Scienze Agrarie, Forestali, Alimentari e Ambientali, Università della Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza, Italy

[2] Dipartimento di Scienze, Università della Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza, Italy

[3] Department of Natural Resource Ecology and Management, Oklahoma State University, Stillwater, OK 74078, USA

1 Introduction

Heat treatment of wood is getting more and more popular in the last several decades and it is one of the environmentally friendly methods to protect and to extend the service life of wood. It is a well-known fact that thermal modification enhances overall dimensional stability and biological durability of wood along with changing its colour without using chemicals (Esteves and Pereira 2008). However, heat treatment adversely influences mechanical properties of wood including bending strength, compression strength and hardness due to modification of chemical structure of its main components, namely hemicelluloses, cellulose, lignin, and extractives.

Although many studies have been carried out on the improvement of overall properties of wood, there is a recent increasing interest in the characterization of the thermal degradation of treated wood products (e.g., Cademartori et al. 2013; Jones 2015; Martinka et al. 2014; Todaro et al. 2015a), which could be related to both increased demand for heat-treated wood as well as newly developed environmental management policies (e.g., Life Cycle Analysis studies according to ISO 14040: 2006 and ISO 14044: 2006). The thermal decomposition process of wood and wood products is based on a series of complex reactions that are influenced by many factors, such as the heating rate, temperature, pressure, exposure time, moisture, composition of biomass material and the size of particles. Modern methods of thermal analysis are especially useful for determining the characteristics of the kinetic regime of decomposition of wood, particularly thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), which allows for a quantitative evaluation of effective kinetic parameters and reaction heat during substance decomposition in different phases, while minimizing the impact of factors of mass and heat transfer. In the literature, numerous works

describe TGA and the behaviour of various types of biomass (Gasparovic et al. 2010; Poletto et al. 2010) during thermal degradation. Due to the complexity of the thermal decomposition reactions of wood, extensive studies have assessed the individual behaviour of the cellulose, hemicellulose and lignin (Qu et al. 2011; Sebio-Puñal et al. 2012). Typical woody biomass contains 40–50% cellulose, 25–35% hemicellulose and 10–40% lignin (Mohan et al. 2006). By comparing the thermogravimetric curves of several hardwood and softwood species, Grønli et al. (2002) revealed a devolatilization mechanism in these samples consisting of three parallel reactions resulting from the degradation of the three main components of wood. Gasparovic et al. (2010) examined the pyrolysis of wood through thermogravimetry and revealed that thermal decomposition of wood via TGA proceeds in three stages, namely water evaporation, active and passive pyrolysis so that decomposition process of wood depends on the ratio and concentrations of such components.

Recently, differences between treated and untreated samples from Norway spruce (*Picea abies* Karst.), common ash (*Fraxinus excelsior* L.) and Turkey oak (*Quercus cerris* L.) were found regarding their pH, calorific values, ash contents and wettability characteristics (Todaro et al. 2015a, b). The increased demand for wood as interior and exterior building material encouraged to conduct a further and more detailed analysis in this area. There is very little information on thermogravimetric analyses of treated and untreated samples from Norway spruce, common ash and Turkey oak wood samples. Therefore, the objective of this work was to evaluate thermal decomposition of such species so that such data can be used for more efficient and effective use of these species in different applications.

In this study, it was hypothesized that thermal treatment might differentially affect the thermal decomposition of selected wood species. To support this hypothesis, the results of thermogravimetric analyses performed on Norway spruce, common ash and Turkey oak wood samples were reported. The main goal of this study was to compare the intraspecific effect of treatment (control vs. treated) through examination of the influence of thermo-treatment on thermal decomposition.

Therefore, it is of practical significance to understand and predict the thermal decomposition process of wood so that this knowledge can aid in designing a better composite generation process and estimation of the influence of wood thermal decomposition (Yao et al. 2008).

2 Materials and methods

2.1 Sample preparation and heat treatment

A total of six sawn boards of Norway spruce and six of common ash with dimensions of 32 mm × 150 mm × 1000 mm, having a moisture content of 20%, were used for the experiments. The thermo-vacuum plant facility used for the test, following the description of Ferrari et al. (2013a), was a semi-industrial prototype with an internal diameter of 1.7 m, modified to perform thermo-vacuum treatments at high temperature (up to 250 °C). The cylinder walls were heated by diathermic oil circulating between double layers of steel.

Norway spruce and common ash specimens were dried to a moisture content of 0% in the same cylinder prior to the thermo-vacuum treatments. The drying process of the samples for spruce and ash having an initial moisture content of 20% was carried out at 100 °C and a pressure not exceeding 25,000 Pa, corresponding to a water boiling temperature of 65 °C (Ferrari et al. 2013a).

In the next step, samples of the abovementioned species were exposed to the thermo-vacuum treatment. Each thermo-vacuum treatment consisted of a heating phase that started at a temperature of 100 °C and reached a maximum of air temperature of 190 °C followed by a thermal treatment phase with a constant air temperature of 190 °C for 2 h. Three-hour cooling phase decreased the temperature of the samples to 100 °C. The heating rate of the air was 12 °C/h. The temperature variation of the diathermic oil, air, and wood samples was measured using thermocouples.

Turkey oak logs were, instead, initially steamed at a temperature of 110 °C and a pressure of 140,000 Pa, for 24 h and then cut into 32-mm-thick boards. The reason for the different treatment is that each type of wood is associated with one specific type of treatment, because of the different nature of hardwood and softwood. In fact, in the case of Turkey oak the wood is very prone to crack during treatment with high level of internal tension. After sawing all the boards were seasoned for 5 months until reaching a moisture content of 20–25%. The steamed boards were subjected to an artificial drying under low-pressure conditions (20,000–23,000 Pa) and at low temperature (starting from 55 °C up to 90 °C in 8 days), in a thermo-vacuum cylinder (WDE-Maspell s.r.l., Italy). Turkey oak wood was dried until its moisture content was 0% and then thermally treated at 160 °C for 3 h (Ferrari et al. 2013b).

2.2 Chemical composition and thermogravimetric analysis of the samples

The chemicals were extracted from 1.0 g (m_0) powdered samples of three types of species with 300 mL of an ethanol/toluene (1/2, v/v) solution in a Soxhlet apparatus for 7 h and evaporated under vacuum (m_1). The extractive content was expressed as a percentage of the initial mass (m_0) of the samples. The resulting insoluble residue was mixed with 15 mL of an H_2SO_4 solution (72%) and stirred frequently for 2 h at room temperature according to TAPPI UM 250 (1991). The mixture was then diluted to 3% (w/w)

with 560 mL of distilled water, heated under reflux for 4 h, filtered and washed with 500 mL of water. The residue was dried at a temperature of 105 °C to a constant mass (m_2), and the lignin residue of each sample was finally determined. The complement percentage of the samples represented the holocellulose content.

Thermogravimetric analysis (TGA) is a widely used technique for measuring the weight change of a material as a function of temperature (Prime et al. 2009). At a controlled heating rate, the weight loss of approximately 10 mg sample can be recorded as a function of temperature. The powdered wood samples having particle size less than 0.3 mm were used for the test.

TGA was carried out with a Mettler TC-10 Thermobalance (Novate Milanese, Italy). The samples were heated from 25 to 500 °C at a 10 °C/min heating rate under air flow. The variation in the mass of the samples was recorded as TG (i.e., variation of the mass as a function of temperature) and TGD (i.e., first derivative of the thermogravimetric curve): the combination of the two thermograms provides a clear indication of the number of stages of thermal degradation.

3 Results and discussion

Table 1 displays the holocellulose content of treated samples decreased by 11.1, 3.6 and 11.8% in spruce, ash and Turkey oak, respectively, compared to those of untreated wood. In contrast, the lignin content of the samples was relatively higher in treated samples compared with those of untreated specimens by 26.6, 10.2 and 20.3%, respectively.

The change in lignin content is recognized to be strongly dependent on the temperature and time of treatment, and on the wood species characteristics (Hill 2007). It is generally accepted that the increase of lignin content in thermo-treated wood is due to the loss of polysaccharide material occurring during heating. However, as suggested by Esteves and Pereira (2008), the increase in lignin content of the thermo-treated wood could not be considered pure lignin since polycondensation reactions occur in the cell wall of other wood components, with consequent polymerization, thus increasing the apparent lignin content.

A large increment in the percentage of extractives (242.9%) was observed in the case of treated Turkey oak sample compared with that of untreated wood. A moderate increase in extractive contents due to thermal treatment was recorded as 7.4 and 5.6% for spruce and ash, respectively.

The different stages of the degradation of the three wood species are presented in Table 2.

The phases of degradation of the wood materials were observed between temperature levels ranging from 200 to 500 °C. The main decomposition process, which is active pyrolysis, occurred in a range from approximately 200 to 400 °C as illustrated in Fig. 1.

Figure 1 also shows both the residual mass (%) and dm/dT curves for the different samples tested at a heating rate of 10 °C/min. The TGA and DTG graphics provide information about when pyrolysis reactions are taking place and the rates of fractional conversion. Within the DTG graphics, there are three notable aspects, namely, the location of the peaks, the relative height of the peaks, and the broadness of the DTG graphics on the temperature scale. From room temperature up to 100 °C, the TG thermograms showed a loss of mass due to the changes of free water corresponding to a maximum generally located at approximately 60 °C in the DTG curves as shown in Fig. 1. Differences in changes

Table 1 Percent holocellulose, lignin contents and extractives in Norway spruce, common ash and Turkey oak samples

Sample	Holocellulose (%)	Lignin (%)	Extractives (%)
Norway spruce			
CTRL	69.1	28.2	2.7
Treated	61.4	35.7	2.9
Common ash			
CTRL	72.8	23.6	3.6
Treated	70.2	26.0	3.8
Turkey oak			
CTRL	73.0	25.6	1.4
Treated	64.4	30.8	4.8

Table 2 Stages of degradation in the active zone of the samples

Sample	Degradation	Temperature range (°C)	Maximum peak (°C)	Loss of mass (%)
Norway spruce				
CTRL	1st stage	200–373	336	62
	2st stage	–	–	–
Treated	1st stage	200–373	337	62
	2st stage	–	–	–
Common ash				
CTRL	1st stage	200–300	299	21
	2st stage	300–400	327	45
Treated	1st stage	200–300	299	22
	2st stage	300–400	326	44
Turkey oak				
CTRL	1st stage	200–309	291	25
	2st stage	309–373	333	34
Treated	1st stage	200–369	316	57
	2st stage	–	–	–

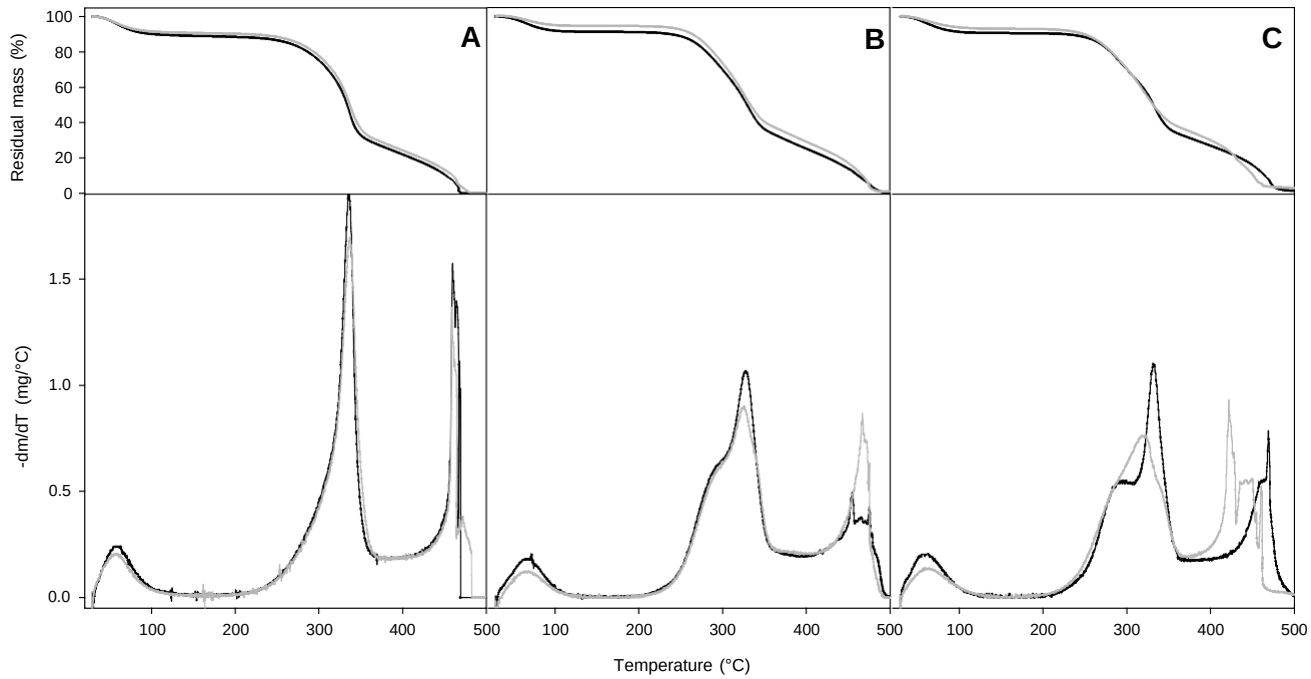

Fig. 1 TGA (*upper panels*) and DTG (*lower panels*) thermograms of untreated (*black line*) and treated (*grey line*) wood: Norway spruce (**a**), common ash (**b**) and Turkey oak (**c**)

of free water (%) between treated and untreated samples can be clearly observed for all species as displayed in Table 3.

Further thermal degradation of the samples took place as a two-step process. These two steps can be more or less evident depending on the type of wood and the applied thermal treatment. In fact, hemicellulose started decomposing at lower temperatures than that of cellulose, but due to the superposition of the degradation intervals of these compounds, hemicellulose decomposition appears as evident shoulder, rather than a well-defined peak. The second step is associated with reaching the maximum due to cellulose decomposition, followed by a rapid decay and a long tail. The wide range of temperatures over which lignin decomposes hinders the appearance of a peak attributable to this component as also found by Grønli et al. (2002).

For all tested wood samples, whether treated or untreated, decomposition began at 200 °C and ended at 400 °C (Fig. 1). In the case of untreated and treated Norway spruce samples, only one peak was evident, corresponding to cellulose decomposition, centred at 336 or 337 °C (Table 3), while a long tail occurred towards lower temperatures, likely corresponding to hemicellulose degradation. The percentages of mass loss (%) at 400 °C were 78 and 76 for untreated and treated spruce, respectively. In contrast, for untreated and treated common ash, the hemicellulose shoulder was clearly evident and was located at a temperature of 299 °C, while the cellulose peak occurred at 327 and 326 °C; the percentages of weight loss (%) at a temperature of 400 °C were 75 and 71 for untreated and treated common ash, respectively.

For untreated Turkey oak specimens, a clearly separated shoulder for hemicellulose was present at a temperature of 299 °C, and the cellulose peak occurred at 333 °C. On the other hand, treated Turkey oak showed a peak at a temperature of 316 °C with a less sloping baseline than untreated wood, hindering the identification of the hemicellulose shoulder. The percentages of mass loss (%) at 400 °C were found as 74 and 70 for untreated and treated Turkey oak, respectively.

In general, degradation temperature up to 200 °C of wood is expected to be related to the heat stability of individual chemical components, and differences in thermal stability

Table 3 Percentage of free water and residual char for untreated (CTRL) and treated woods

% of mass loss	Temperature (°C)	Norway spruce		Common ash		Turkey oak	
		CTRL	Treated	CTRL	Treated	CTRL	Treated
Free water	100	9.8	8.3	8.1	4.9	8.8	6.2
Residual char	400	21.7	24.0	24.6	28.9	26.6	29.7

of the species can be attributed to the variation in their chemical composition (Poletto et al. 2010). Both Qu et al. (2011) and Raveendran et al. (1996) showed that the three wood polymers decompose independently without interfering with each other. However, the fundamental composition differences among species may affect their thermal stability (Popescu et al. 2011).

It is widely accepted that the thermal process can be described in two main phases corresponding to the major peaks observed in the DTG as reported by Raveendran et al. (1996). In particular, the first phase, referred to as the active zone, mainly corresponds to the degradation of hemicellulose and cellulose polymers, ranging temperature levels from 200 to 350 °C, while the second one is referred to as the passive zone. Carbon oxide is released in the active zone, whereas volatile organic compounds (VOC) are mainly formed in the passive zone during this process.

There is a number of interesting considerations that can be drawn from this analysis. In particular, drying at temperatures below 100 °C takes place with a corresponding peak in the DTG curve, representing the release of water vapour, as reported by Helsen et al. (1999). Humidity rate corresponding to water linked with the hydrophilic constituents' hemicellulose and cellulose remains constant. Notably, the apparently greater moisture is released from untreated species, which can be related to the difference in water adsorption after thermal treatment (Esteves and Pereira 2008). According to Kim et al. (2010), the depolymerisation of hemicellulose starts before cellulose degradation takes place at an approximate temperature of 200 °C after that, the main degradation of cellulose occurs.

It is a fact that the differences in the thermal decomposition of hemicellulose and cellulose are not well known. The higher activity of hemicellulose during thermal decomposition might be attributed to its chemical structure. Hemicellulose has a random amorphous structure and is easily hydrolysed (John and Thomas 2008; Yang et al. 2006). In contrast, the cellulose molecule is a long polymer of glucose units, and its crystalline regions improve the thermal stability of wood (Yang et al. 2006). Since the temperature intervals of hemicellulose and cellulose decomposition partially overlap each other, hemicellulose decomposition at the first region usually appears as a more or less pronounced 'shoulder', instead of a well-defined peak.

The peaks for cellulose and hemicellulose were also pronounced for the common ash and untreated oak specimens, whereas no hemicellulose peak was visible for the spruce and treated oak samples. These differences could be explained based on the cellulose-to-hemicellulose ratios calculated from the chemical composition data, as it is evident that a low cellulose-to-hemicellulose ratio produces a clear separation of the hemicellulose peak, which is why common ash and untreated oak showed more visible separation of the hemicellulose peak than those of spruce and treated oak. A partial explanation for the missing hemicellulose peak in oak might be the effect of the steaming treatment, causing loss of a portion of the present hemicellulose compounds (Esteves and Pereira 2008; Todaro et al. 2013; Yin et al. 2010).

Another visible difference in the analysis was the height of the recorded peaks, which can be related to the rate of decomposition. Although the treatment was the same for only the spruce and ash, but not for Turkey oak, some interesting findings can be highlighted. In the peaks obtained for both treated and untreated samples, spruce showed higher decomposition rates than common ash and oak. According to Stamm (1956), this behaviour could be caused by the amount of holocellulose (i.e., the combination of hemicelluloses and cellulose), lignin and extractives as displayed in Table 1.

The different configuration of the curve peaks as observed in Fig. 1 (narrow for the softwood and broad for the hardwoods) suggested complex and non-equivalent degradation processes between species (Grønli et al. 2002; Sebio-Puñal et al. 2012), even when the same heat treatment was applied as in the case of spruce and ash samples. In the last stage of the analysis, weight loss of the samples takes place due to decomposition of lignin, without displaying characteristic peaks (Gasparovic et al. 2010; Strezov et al. 2003). The broadness of the DTG curve is associated with decomposition of lignin and extractive which both decompose over a broad range of temperature levels. The thermal stability of lignin is therefore quite high and it is difficult to decompose (Yang et al. 2006). In fact, lignin has different structure with three types of benzene-propane units, which are heavily cross-linked and exhibit higher molecular weight than those of hemicellulose and cellulose (John and Thomas 2008; Yang et al. 2006). Multiple lines of evidences clearly reported that extractives derived from different species decompose at temperature levels up to 550 °C (e.g., Raveendran et al. 1996; Mészáros et al. 2007), whereas lignin decomposes between 180 and 900 °C (Gasparovic et al. 2010) without characteristic peaks. Accordingly, Sebio-Puñal et al. (2012) highlighted the importance of extractives in char formation and stated that displacement of the thermogravimetric curve towards higher temperatures could be observed.

The stage of thermo-oxidative decomposition of samples within the range of 400–550 °C includes the processes of carbonization which is an active char and oxidation of the carbonized product. The carbonized products of wood decomposition are completely oxidized at a temperature of 500 °C and lost their mass. Depending on the pyrolysis temperature, the char fraction contains an inorganic material which is ash to varying degrees as well as any unconverted organic solids and carbonaceous residues produced from the thermal decomposition of organic components (Mohan et al.

2006; Todaro et al. 2015a; Yaman 2004). The oxidation of the residual char of treated oak proceeded at a lower temperature peaked at 421 °C compared with the char of untreated oak (peaked at 470 °C) as illustrated in Fig. 1. On the other hand, for spruce and ash material, differences in the mass loss of residual material (Table 3) were observed between treated and untreated samples within the same temperature range (400–494 °C).

The mechanism and kinetics of secondary char formation have yet to be determined. According to Raveendran et al. (1996) and Várhegyi et al. (2004), the rate of char yield is directly related to the contents of lignin and extractives which exhibit aromatic nuclei and unsaturated groups in their structure, that contribute significantly to the carbonization process. The present results seem to confirm this; in fact, as the thermo-treatment increased the lignin and extractive content in wood material (Todaro et al. 2015a; Yildiz et al. 2006), the residual char of treated material was found to be higher compared with untreated wood. The question of the charring rate of timber-based products during a fire holds a central position in research on the fire resistance of timber buildings and structures. This is only logical because the fire resistance limit of constructions is determined by taking into account the total time from the beginning of fire exposure of a timber structural member to the onset of charring and the time from the onset of charring to reaching the limiting critical state.

4 Conclusion

In this study, thermogravimetric processes occurring in wood species subjected to thermo-vacuum treatment exhibited distinct patterns. In this regard, the findings suggested that the thermal degradation of the specimens was characterized by a two-stage reaction, with the exception of Norway spruce samples, which exhibited a one-stage reaction. It is argued that comparisons between treated and untreated samples should be carefully considered because during heat treatment, simultaneous degradation of compounds occurs in wood, involving the different substances present in cellulose, lignin and extractives, which behave differently for softwood and hardwood. The authors stress the need for investigations by differential scanning calorimetry (DSC) for a better understanding of the thermal degradation of the main wood compounds.

Acknowledgements This work was supported by the Italian Ministry of Education, University and Research MIUR-PRIN 2015 (Grant No. 2015YW8JWA) granted to LT. The research was also carried out in the framework of the project 'Smart Basilicata', which was approved by MIUR (Notice n.84/Ric 2012, PON 2007–2013 of 2 March 2012) and funded with the Cohesion Fund 2007–2013 of the Basilicata Regional authority. The authors' thanks are due to Prof. G. Gorrasi for the technical assistance.

References

Cademartori PHG, dos Santos PS, Serrano L, Labidi J, Gatto DA (2013) Effect of thermal treatment on physicochemical properties of Gympie messmate wood. Ind Crops Prod 45:360–366

Esteves B, Pereira H (2008) Wood modification by heat treatment: a review. Bioresources 4:370–404

Ferrari S, Cuccui I, Allegretti O (2013a) Thermo-vacuum modification of some European softwood and hardwood species treated at different conditions. Bioresources 8(1):1100–1109

Ferrari S, Allegretti O, Cuccui I, Moretti N, Marra M, Todaro L (2013b) A revaluation of turkey oak wood (*Quercus cerris* L.) through combined steaming and thermo-vacuum treatments. BioResources 8(4):5051–5066

Gasparovic L, Korenova Z, Jelemensky L (2010) Kinetic study of wood chips decomposition by TGA. Chem Pap 4:174–181

Grønli MG, Varhegyi G, Di Blasi C (2002) Thermogravimetric analysis and devolatilization kinetics of wood. Ind Eng Chem Res 41:4201–4208

Helsen L, Van den Bulck E, Mullens S, Mullens J (1999) Low-temperature pyrolysis of CCA-treated wood: thermogravimetric analysis. J Anal Appl Pyrol 52:65–86

Hill CA (2007) Wood modification: chemical, thermal and other processes (vol 5). Wiley, New York

ISO 14040 (2006) Environmental management—Life cycle assessment - Principles and framework (ISO 14040:2006). International Standard. ISO, Geneva, p. 20

ISO 14044 (2006) Environmental management—Life cycle assessment - Requirements and guidelines (ISO 14044:2006), ISO, Geneva

John MJ, Thomas S (2008) Biofibres and biocomposites. Carbohyd Polym 71:343–364

Jones JC (2015) Letter: fire loads and the calorific value of wood. Fuel 159:975

Kim UJ, Eom SH, Wada M (2010) Thermal decomposition of native cellulose: influence on crystallite size. Polym Degrad Stabil 95:778–781

Martinka J, Hroncová E, Chrebet T, Balog K (2014) The influence of spruce wood heat treatment on its thermal stability and burning process. Eur J Wood Prod 72:477–486

Mészáros E, Jakab E, Várhegyi G (2007) TG/MS, Py-GC/MS and THM-GC/MS study of the composition and thermal behavior of extractive components of Robinia pseudoacacia. J Anal Appl Pyrolysis 79:61–70

Mohan D, Pittman CU, Steele PH (2006) Pyrolysis of wood/biomass for bio-oil: A critical review. Energ Fuel 20:848–889

Poletto M, Dettenborn J, Pistor V, Zeni M. Zattera A (2010) Materials produced from plant biomass. Part I: evaluation of thermal stability and pyrolysis of wood. Mater Res 13:375–379

Popescu MC, Popescu CM, Lisa G, Sakata Y (2011) Evaluation of morphological and chemical aspects of different wood species by spectroscopy and thermal methods. J Mol Struct 988:65–72

Prime RB, Bair HE, Vyazovkin S, Gallagher PK, Riga A (2009) Thermogravimetric Analysis (TGA). In: Menczel JD, Prime RB (eds) Thermal Analysis of Polymers: Fundamentals and Applications. Wiley, Hoboken

Qu T, Guo W, Shen L, Xiao J, Zhao K (2011) Experimental study of biomass pyrolysis based on three major components: Hemicellulose, cellulose, and lignin. Ind Eng Chem Res 50:10424–10433

Raveendran K, Ganesh A, Khilar KC (1996) Pyrolysis characteristics of biomass and biomass components. Fuel 75:987–998

Sebio-Puñal T, Naya S, López-Beceiro J, Tarrío-Saavedra J, Artiaga R (2012) Thermogravimetric analysis of wood, holocellulose, and lignin from five wood species. J Therm Anal Calorim 109:1163–1167

Stamm AJ (1956) Thermal degradation of wood and cellulose. Ind Eng Chem 48:413–417

Strezov V, Moghtaderi B, Lucas J (2003) Thermal study of decomposition of selected biomass samples. J Therm Anal Calorim 72:1041–1048

TAPPI UM 250 (1991) Acid-soluble lignin in wood and pulp, in: 1991 TAPPI Useful Methods, Tappi

Todaro L, Dichicco P, Moretti N, D'Auria M (2013) Effect of combined steam and heat treatments on extractives and lignin in sapwood and heartwood of Turkey oak (*Quercus cerris* L.) wood. Bioresources 8:1718–1730

Todaro L, Rita A, Cetera P, D'Auria M (2015a) Thermal treatment modifies the calorific value and ash content in some wood species. Fuel 140:1–3

Todaro L, Rita A, Moretti N, Cuccui I, Pellerano A (2015b) Assessment of thermo-treated bonded wood performance: comparisons among Norway spruce, common ash, and Turkey oak. Bioresources 10:772–781

Várhegyi G, Grønli MG, Di Blasi C (2004) Effects of sample origin, extraction, and hot-water washing on the devolatilization kinetics of chestnut wood. Ind Eng Chem Res 43:2356–2367

Yaman S (2004) Pyrolysis of biomass to produce fuels and chemical feedstocks. Energ Convers Manage 45:651–671

Yang H, Yan R, Chen H, Zheng C, Lee DH, Liang DT (2006) In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. Energ Fuel 20:388–393

Yao F, Wu Q, Lei Y, Guo W, Xu Y (2008) Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis. Polym Degrad Stabil 93:90–98

Yildiz S, Geze ED, Yildiz UC (2006) Mechanical and chemical behavior of spruce wood modified by heat. Build Environment 41:1762–1766

Yin Y, Berglund L, Salmén L (2010) Effect of steam treatment on the properties of wood cell walls. Biomacromolecules 12:194–202