Carbohydrate Polymers 80 (2010) 78–83

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Thermogravimetric analysis of fungus-degraded lime wood

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ARTICLE INFO

Article history:
Received 6 October 2009
Received in revised form 27 October 2009
Accepted 28 October 2009
Available online 30 October 2009

Keywords:
Lime wood
Biodegradation
Chaetomium globosum
Thermogravimetry

ABSTRACT

Lime wood samples decayed under the attack of the soft rot fungus *Chaetomium globosum*, for different durations, have been obtained. The degree of decay was determined by mass loss, which was of 50.4% after 133 days. The samples were analyzed by thermogravimetry.

The degradative modification of the wood due to presence of the fungus was evidenced by structural changes, also affecting thermal properties both with respect to wood hydrophilicity (evidenced mainly in the desorption process) and decomposition behavior.

The increased characteristic temperatures for water desorption and decreased temperatures for decomposition processes, as well as the lower thermal stability, could be explained by the formation of reactive species due to oxidation reactions induced by enzymes and the demethoxylation of lignin structure.

1. Introduction

Wood deterioration is an essential process in the environment, which recycles complex organic matter and is an integral component of life.

Wood consists of three types of polymers – cellulose, hemicelluloses, and lignin – that are strongly enmeshed and chemically bonded by non-covalent forces and by covalent cross-linkages. A great variety of fungi and bacteria can fragment these macromolecules by using a complex of hydrolytic or oxidative enzymes (Perez, Munoz-Dorado, de la Rubia, & Martinez, 2002). The main components of woody cell walls are degraded by various groups of organisms to different extents. Both the so-called brown rot and soft rot fungi, belonging to the Basidiomycetes and Ascomycetes respectively, decompose principally the polysaccharides. A third group, also Basidiomycetes, known as white rot fungi, attack the lignin and the polysaccharides either simultaneously or successively.

Although there are similarities in the chemical changes associated with brown rot and soft rot, the effects of these two types of decay on the cell wall morphology are quite different (Keilich, Bailey, & Liese, 1970).

Soft rot occurs preferably in hardwoods; the distinguishing feature of soft rot is the formation of cavities within the S2 layer of the secondary wall (Type 1). Soft rot cavities are initiated by fine penetration hyphae formed from hyphae in the lumina of wood cell walls. The penetration hypha grows through the innermost S3 layer of the cell wall to the cellulose-rich S2, where it either branches or grows axially within the cell wall following the orientation of the cellulose microfibrils. Fine hyphae exhibiting branching continue to extend for a short time, but then cease apical growth. At this stage, a cavity is formed within the secondary wall around the fine hypha, which increases in diameter as the cavity develops. This is then followed by a further phase of apical growth at the hyphal tip, producing a needle-like proboscis hypha. The process is repeated several times, leading to the formation of a spiral chain of cavities within the wood cell wall, all oriented to the angle of the cellulose microfibrils and each showing different stages of cavity expansion. The repetitive start and stop pattern of apical hyphal growth results in the gradual break-down of the wood cell wall layer of the secondary wall (Type 1 degradation) and is the characteristic mechanism of cell wall degradation. Discrete notches of cell-wall erosion by the hyphae growing within the lumina, in addition to the cavities formed by hyphae within the cell wall, are also frequently found in wood degraded by soft rot fungi. These erosion troughs, which are indistinguishable from those caused by the white rot fungi, have been attributed to a category of soft rot known as producing a Type 2 attack (Schwarze, 2007).

In soft rots, decay results from the activities of enzymes, secreted by the fungal hyphae, acting on specific cell wall components. The degradation is caused almost exclusively by polysaccharide splitting enzymes, i.e. hydrolases, such as cellulases, manases, xylanases, and by oligosaccharide splitting enzymes, i.e. glycosidases.

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0144-8617/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2009.10.058

Thermal investigation methods are suitable for studying the physical properties of wood, providing information on the interaction between cellulose, lignin and low molecular weight substances, such as hemicelluloses, extractives, water, etc. The presence of water leads to the breaking of hydrogen bonds between hydroxyl groups. Studies on the thermal stability of wood components present great technical interest as woods are subjected to thermal treatments in many processes, such as drying, dimensional stabilization, thermo-mechanical pulping, and steam explosion, production of boards or panels and sterilization (Franceschi, Cascone, & Nole, 2008; Hou, Wang, & Wu, 2008; Silva et al., 2008; Sinha, Rout, & Barhai, 2008).

Thermogravimetry has proved to be a useful tool in elucidating the decomposition of various biomass materials. The slow heating rates of thermogravimetric analysis (TGA), the specific properties of cellulose and the different measurement systems (Grønli, Antal, & Varhegyi, 1999), among other factors, have been shown to exert a significant influence on the kinetic parameters. The situation is worse for wood because of the lower number of studies, the presence of several components, and the catalytic role played by inorganic matter in the reaction paths. On an indicative basis, for a slow rate of heating in thermogravimetry studies, primary wood degradation starts at about 500 K (Grønli, 1996), however, at fast rates, degradation is attained at about 573 K, the process being practically over at 700 K (Pyle & Zaror, 1984). At higher temperatures, secondary reactions of primary tar vapors also become active (Garcia, Font, & Marcilla, 1995). Reaction products are usually lumped into three main classes (liquids, char, and gas) (Di Blasi, 1993) whose relative amounts and composition are specifically dependent on the conversion unit (for instance, fixed-bed or fluid-bed reactors), but the heating rate and reaction temperature are certainly the most important process variables. Wood mass loss curves, obtained at slow heating rates, show several reaction zones, associated with component decomposition, which attains maximum rates at different temperatures (Antal & Varhegyi, 1995).

In the present study, thermogravimetry/derivative thermogravimetry (TG/DTG) is employed for a systematic investigation of the devolatilization behaviors of biodegraded lime wood samples. The main objectives are to quantify the differences between reference and decayed wood.

2. Experimental

2.1. Materials

Lime wood blocks ($50 \times 50 \times 3$ mm) were oven-dried at 103 ± 2 °C, until constant mass was reached. The samples were sterilized and exposed to *Chaetomium globosum* in Petri dishes containing 2% malt extract, 2% dextrose, 2% agar, in distilled water. The samples were pre-inoculated with the fungus 1 week prior to the test and then incubated at 28 °C for 133 days.

Fig. 1 shows images of reference lime wood, and *C. globosum* decayed lime wood samples. It may be easily observed that the fungus starts developing on the wood surface. By visual observation, it has been established that the growing period of fungus on the wood sample surface was of about 28 days; then the fungus reached maturity and formed spores, its attack becoming much aggressive. The visual aspect of the fungus colony on the wood surface is the same for the samples, exposed from 70 to 133 days.

2.2. Characterization method

Powdered wood sampled mainly from the surface was sieved and the fraction with an average diameter less than 0.2 mm was retained for analysis.

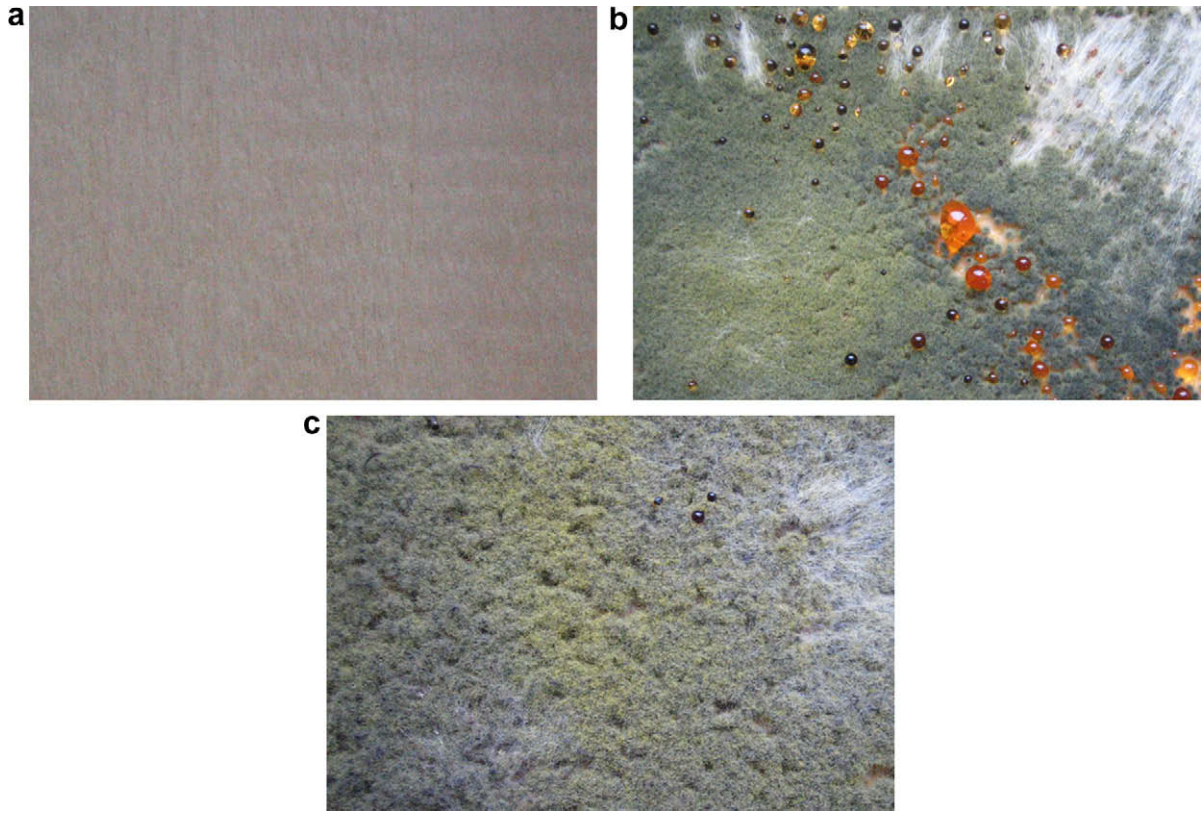

Fig. 1. Pictures with different stages of decay with *C. globosum* on wood: reference (a), after 49 days of exposure (b), after 91 days of exposure (c).

Thermogravimetry. Thermogravimetric analysis (TGA) was carried out under constant nitrogen flow (20 ml/min) at a heating rate of 15 °C/min, using a Mettler Toledo TGA/SDTA 851 balance. The heating scans were performed on 3–5 mg of sample, in the temperature range 25–600 °C. The kinetic parameters have been evaluated by integral methods using the VERSATILE commercial program, which gives kinetic parameters by various methods (see below). The deconvolution of the DTG curves was done by means of Grams/32 program (Galactic Industry Corporation) with Log-Normal functions.

3. Results and discussion

3.1. Mass loss data

During a 133-day period, at each 7-day interval, three lime wood samples were taken up from the exposure medium, mycelia were removed from their surfaces by repeated washing with twice-distilled water and then the samples were oven-dried to constant mass. The mass losses of individual samples were calculated, and used to determine mean mass percentage losses.

The fungus action manifested by the continuous decrease of the sample mass with an average mass loss rate of 0.49 wt.%/day in the first 70 days, and slower – of 0.29 wt.%/day – in the following period of 63 days. The average mass loss of the lime wood blocks after 133 days of exposure to *C. globosum* was of 50.4%.

3.2. TG/DTG results

Wood as a whole material undergoes a complex degradation scheme, which is greatly affected by its physical nature. During the thermal decomposition process of wood, small molecules are eliminated, and eventually a charred mass is left. Noncombustible products, such as carbon dioxide, traces of inorganic compounds and water vapors, are produced between 100 and 150 °C. At about 175 °C, some components begin to break-down chemically; low temperature degradation occurs at a low rate in lignin and hemicelluloses.

The mass loss occurring between 300 and 500 °C corresponds to the degradation of cellulose and has been also associated with the pyrolytic degradation of lignins, involving the fragmentation of inter-unit linkages, and the condensation of the aromatic rings (Beall, 1986).

Above 450 °C, all volatile materials are driven off and in the presence of the air, the residual char undergoes oxidative reactions (Wegner, 1989). The lignin component contributes to char formation, and the charred layer helps to insulate the material from further thermal degradation. In such a complex material as wood, the thermogravimetric processes of all components overlap, the predominant being that of cellulose degradation, cellulose presenting a high rate of mass loss in its decomposition interval.

Fig. 2 shows the results of thermogravimetric tests performed on the reference and decayed lime wood. Fig. 2a gives the percentage of mass loss as a function of temperature (TG), while Fig. 2b presents the derivative thermogravimetric curves (DTG). Water loss is observed below 130 °C, and the further thermal degradation takes place as a two-step process. In particular, it is seen that the water desorption percent in decayed wood is higher than in reference wood.

Several parameters were evaluated from the thermograms presented in Fig. 2, for each step: the "onset" of each thermogravimetric step (T_i), the temperature corresponding to the maximum rate of mass loss (T_m), and the temperature corresponding to the end of the stage (T_f) for each step, (the errors of temperature determination are of ±2 °C), the amount of desorbed water (as percentage of mass loss below 140 °C), and the mass loss of the two processes of thermal degradation (as percentage from the initial mass) (the errors of mass loss determination are <1%).

The range of temperatures within which degradation occurs was estimated from the DTG curves and the mass loss percentage was read from the TG plots.

For the first step, the temperature corresponding to the maximum mass loss rate increases from 74 °C for reference to 80 °C for decayed lime wood. The temperature of the end of the stage increases with increasing the time of exposure to the microorganisms from 119 °C for reference lime wood to 135 °C for lime wood exposed for 133 days. Also the mass loss for this process increases with increasing exposure time. This may be explained by the formation, after biodegradation, of oxidized structures that interact stronger with water molecules.

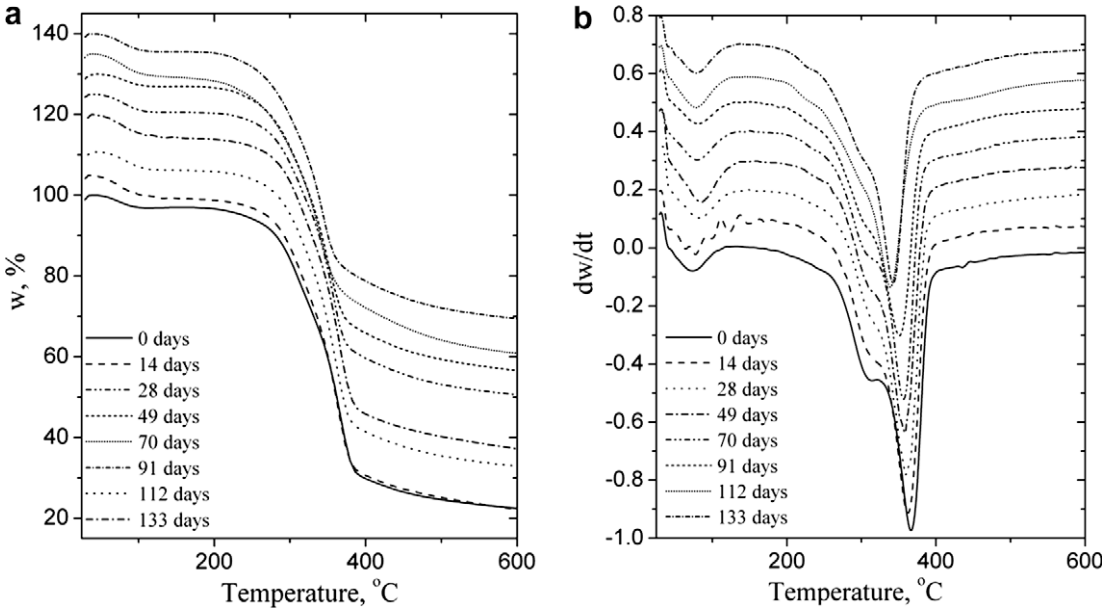

Fig. 2. TG (a) and DTG (b) curves for reference (solid line) and decayed (dashed lines) lime wood samples at different exposure intervals.

Table 1
Thermogravimetric data for reference and decayed lime wood samples for the second process.

Parameters	Time (days)							
	0	14	28	49	70	91	112	133
T_i	154.2	156.4	158.3	160.5	162.7	166.9	171.2	173.3
T_m	366.5	362.4	359.8	358.6	356.1	350.8	338.7	342.6
T_f	544.2	540.7	539.9	538.4	538.4	521.6	518.8	514.1
$\Delta w\%$	75.3	75.8	71.4	69.2	68.7	68.3	66.4	63.8

Most of the mass is lost during the second step, mainly corresponding to the thermal degradation of wood components. It takes place from 150 to 550 °C, the mass loss ranging from 77% to 64%. The decomposition of wood is a very complex process consisting in several overlapping reactions and/or in successive processes of decomposition – Fig. 2b. In the case of the reference wood sample, the degradation occurs at higher temperatures than that of the decayed samples – Table 1.

As may be observed from Table 1, the temperatures corresponding to the maximum decomposition rate (T_m) and to the end of stage (T_f) decrease linearly and the mass loss occurring during the decomposition process shows an exponential decrease with increasing the time of exposure (see Table 1 and Fig. 3). This indicates a higher extent of sample degradation.

Because the temperature intervals of hemicelluloses, cellulose and lignin decomposition partially overlap each other; the hemicelluloses and/or amorphous cellulose decomposition step usually appears as a more or less pronounced shoulder instead of a well-defined peak. As biodegradation advances, this shoulder, in the DTG curves, becomes weaker.

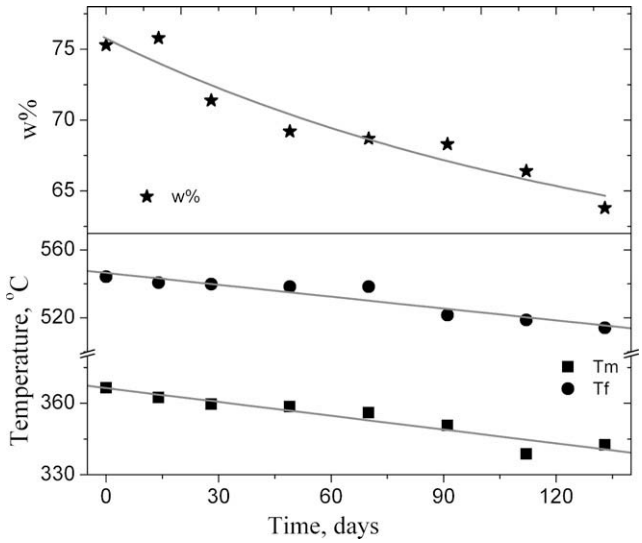

Fig. 3. Dependence of thermal characteristics vs. exposure time for the second process.

Usually, three main zones have been identified, associated with the devolatilization of the main components of the wood (Orfao, Antunes, & Figueiredo, 1999; Teng & Wei, 1998). These zones have been evidenced by the deconvolution of the DTG curves (Fig. 4).

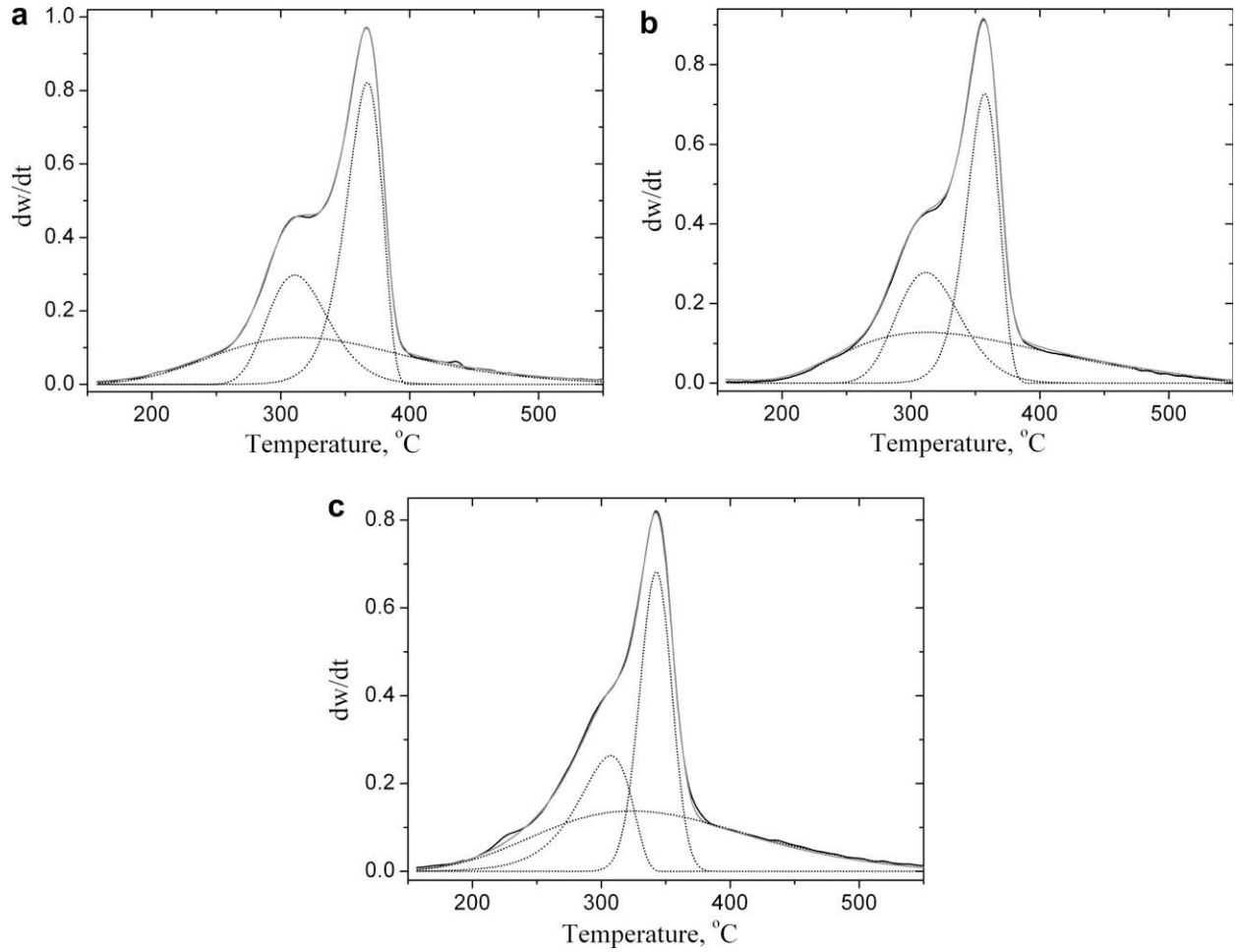

Fig. 4. Devolatilization rates of the reference wood (a), 70 days-decayed wood (b) and 133 days-decayed wood (c) measured (black line) and simulated (gray line).

The shoulder temperature (311 °C for reference wood) for the peak assigned to the devolatilization of hemicelluloses and amorphous cellulose decreases; also, the temperature (367 °C for reference wood) of the peak assigned to cellulose devolatilization and that (315 °C for reference wood) of the peak assigned to lignin devolatilization decrease. The shifting of the temperature of this shoulder to lower values (from 311 °C for reference to 306 °C for 133-day decayed wood) should be explain by the appearance of oxidized structures after the action of cellulases and hemicellulases. The integral area of this peak is almost constant for the 70-day decayed wood – of 25%, then it started to decrease to 21% for the 112-day decayed wood, increasing up to 29% for the 133-day decayed wood. The lignin decomposition shows a large interval of temperatures – from 150 to 550 °C. The integral area of this peak decreases at the beginning from 33% (reference wood) to 29.7% (14-day decayed lime wood) and that starts to increase to 45.3% for lime wood decayed for 133 days. The third peak may be due to the loss of –OH groups of the cellulose monomer units and to the break-down of the pyranozic rings; the temperature of this peak is also shifted to lower values, from 367 to 343 °C. The integral area of this peak decreases from 41.8% to 25.8% (Fig. 5).

The very large temperature region where the decomposition takes place indicates that the volatile decomposition products formed during heating evolve with a very slow rate, with many changes in the reaction mechanism. It is well known that the decomposition of wood is accompanied by a carbonization process, so that the deposition of a carbon layer even during this process could decrease the rate of the decomposition products, evolution. The quantity of the residues at 600 °C is of 22.9% for reference wood, and of 23–31.7% for decayed wood.

The overall kinetic parameters of the decomposition region, which involved overlapped processes (decomposition, crosslinking between carbohydrate polymers and/or between lignin and carbohydrate polymers or some of the thermal degradation products recombined during heating), were evaluated by the four integral methods proposed by: Coats–Redfern (CR) (Coats & Redfern, 1964), Flynn–Wall (FW) (Flynn & Wall, 1966), van Krevelen (vK) (van Krevelen, van Heerden, & Huntjens, 1951) and Urbanovici–Segal (US) (Urbanovici & Segal, 1984). These parameters are significant only in comparing similar samples recorded under the same conditions.

Each evaluation method gives different values for kinetic parameters, but the variation with the heating rate is similar. The values of the overall activation energies corresponding to the decomposition process lie within the 146–112 kJ/mol interval, progressively decreasing for decayed samples until reaching the values for the 112-day decayed wood, and then increasing to 120 kJ/mol for the 133-day decayed wood. The values of the overall activation energies calculated by van Krevelen method are higher (195.8–160 kJ/mol) (Table 2 and Fig. 6).

The reaction order was 2.0 for reference wood and increased to 2.1 or 2.2 for decayed wood, respectively, indicating that the reaction mechanism for wood decomposition is controlled by a reaction order law.

Thermogravimetric analysis of wood indicates that structure and composition changes have occurred as a consequence of the degradation process caused by the activity of enzymes, and thus, it could be used as a complementary characterization technique for these types of materials.

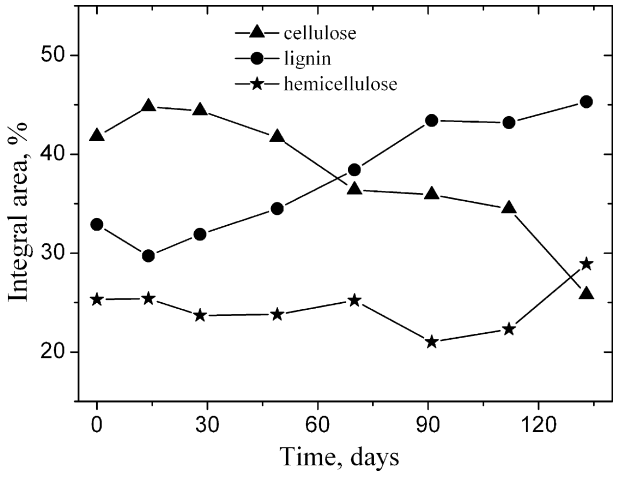

Fig. 5. Dependence of integral area vs. exposure time for the deconvoluted peaks assigned to components of the wood according to literature data.

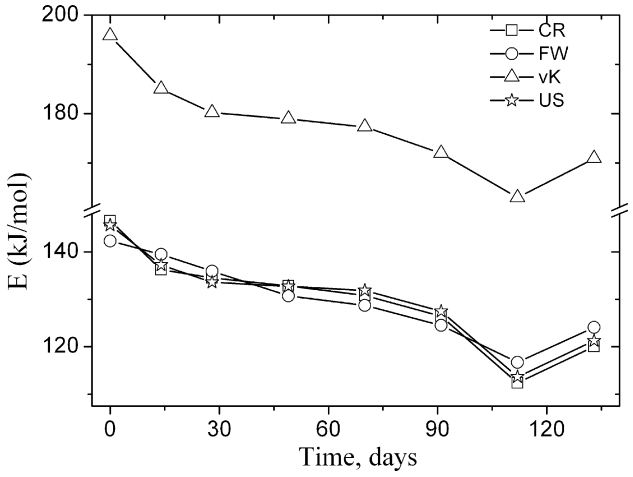

Fig. 6. Dependence of overall activation energy vs. exposure time for the second process.

Table 2
Overall kinetic parameters of the second thermogravimetric process for undecayed and decayed lime wood samples.

Parameters		Time (days)							
		0	14	28	49	70	91	112	133
Coats–Redfern	E (kJ/mol)	146.5	136.2	134.5	132.8	130.8	126.4	112.4	120.1
	n	2.0	2.0	2.0	2.1	2.1	2.1	2.1	2.1
Flynn–Wall	E (kJ/mol)	142.3	139.4	135.9	130.7	128.7	124.5	116.7	124.1
	n	1.9	2.0	2.0	2.0	2.0	2.0	2.1	2.1
van Krevelen	E (kJ/mol)	195.8	184.9	180.2	178.9	177.3	171.9	160.0	170.9
	n	2.2	2.2	2.2	2.3	2.3	2.3	2.4	2.4
Urbanovici–Segal	E (kJ/mol)	147.6	137.2	133.6	132.7	131.9	127.5	113.7	121.3
	n	2.0	2.0	2.0	2.1	2.1	2.1	2.1	2.1

The TG/DTG results show that at the beginning of the biodegradation process the demethoxylation of lignin takes place, followed by the formation of oxidized structures.

It is known that, generally, soft-rot decay is characterized by attacking wood under moist conditions and usually involving the softening of the woody tissue surfaces. Particularly, *C. globosum* is characterized by the specific action on carboxyl and acetyl groups in hemicelluloses. This fungus attacks actively cellulose and hemicelluloses. Also, *C. globosum* has been shown to cause the depletion of lignin in beech wood (Savory & Pinion, 1958). The lignin remaining in decayed wood was deficient in methoxyl and more acid-soluble than that in the reference wood. As to their capacity of decomposing lignin, soft rot fungi are classified as belonging inbetween white and brown rot fungi, their demethoxylase is, however, far more pronounced than that of the other rot fungi.

In our case, the same behavior was observed, as that suggested before. Demethoxylation was observed also by decreasing the bands which are assigned to different vibrations of methoxyl groups in lignin (Popescu, Popescu, & Vasile, submitted for publication).

4. Conclusion

The present study establishes several correlations between the enzymatic degradation processes and thermogravimetric characteristics of lime wood samples.

The shape of DTG curves depends on the time of exposure of wood to *C. globosum*. The peak temperatures assigned to the devolatilization of hemicelluloses and amorphous cellulose decrease. The shifting of the temperature of this shoulder to lower values is due to the formation of oxidized structures after the enzymatic degradation, which makes wood less thermally stable. The integral area of this peak is almost constant for the 70-day decayed wood, it decreases for the 112-day decayed wood, and then increases for the 133-day decayed wood. The second peak of degradation assigned to lignin decomposition shows a large interval of temperatures – from 150 to 550 °C. The integral area of this peak decreases at first, then starts to increase. The third peak may be due to the loss of –OH groups of the cellulose monomer units and to the break-down of the pyranozic rings; the temperature of this peak is also shifted to lower values and the integral area of this peak decreases.

The global kinetic parameters for the main peak decrease with increasing the time of exposure of the wood to the attack of microorganisms, evidencing once more the formation of a less thermally stable structure.

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