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A thermogravimetric study of structural changes of lime wood (*Tilia cordata* Mill.) induced by exposure to simulated accelerated UV/Vis-light

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ABSTRACT

A series of experiments were carried out to investigate photodegradation of lime wood (*Tilia cordata* Mill.) during artificial UV/Vis light irradiation for 600 h. Photodegradation of the wood samples was evaluated by thermogravimetry throughout the irradiation period at an interval of 100 h.

The alteration of wood was observed by means of the peak temperatures of DTG variation and by the mass losses observed during heating, evaluated on the basis of the measured thermal data. The results obtained indicate a shifting of the DTG maxima to lower temperatures which may be related to the decreasing in the stability components during photodegradation. The values of the overall activation energies corresponding of the decomposition process progressively decreases.

The decreased temperatures decomposition processes, weight losses and integral area of the peaks assigned to lignin, the increased integral area of the peaks assigned to hemicelluloses could be explained by new formed structures, mainly due to formation of reactive species.

1. Introduction

Interest in the photodegradation of wood is focused on understanding how it deteriorates and how wood surfaces can be protected during weathering. When wood is exposed outdoors above ground, a complex contribution of chemical and physical factors contributes to what is described as weathering. The weathering process is initiated by sunlight and its rate is enhanced by moisture (humidity), temperature, air and other pollutants, which are abundantly present in the outdoor environment. Apart from number of environmental parameters that contribute significantly to the degradation of wood, the rate of degradation may also be affected by the wood properties, e.g., presence of extractives [1] and kind of wood (i.e., softwood or hardwood). The chemical composition of constituent polymers of wood and basic anatomical properties of hardwood and softwood are different. For example, the chemical structure of softwood and hardwood lignin varies. Hardwood lignin, termed guaiacyl-syringyl lignin, consists of coniferyl alcohol and sinapyl alcohol derived units in varying ratios, whereas in softwood lignin, usually referred to as guaiacyl lignin [2,3].

The interaction of photon energy with polymeric compounds distributed at the wood surfaces involves complex physical and chemical reactions. The degradation is triggered by the formation of free radicals by UV irradiation. All the chemical constituents of wood are susceptible to degradation by sunlight. The quantum energies associated with light at UV region are sufficient to break many of the chemical bonds established between wood constituents. The effect of weathering on the physical and chemical structure of different wood species has been investigated extensively [1,4–8]. Chemical analysis of weathered wood surfaces indicated degradation of lignin and hemicelluloses and de-polymerization of cellulose upon exposure [1,9]. The consequences of photochemical reactions on wood surface chemistry are the loss of methoxyl group content of lignin, photo-dissociation of carbon–carbon bonds and formation of carbonyl based chromophoric groups.

Among the wood constituent polymers, lignin is the most sensitive to light. Photochemical reactions are initiated by the absorption of UV–vis light mainly by lignin, which leads to the formation of aromatic and other free radicals. These free radicals may then cause degradation of lignin and photo-oxidation of cellulose and hemicelluloses. This results in formation of colored unsaturated carbonyl compounds resulting in color changes, and yellowing of wood surfaces [4,5,10,11]. Photodegradation occurs through various pathways where chromophores in the wood surface absorb ultraviolet and visible radiations to create excited molecules. Such molecules participate in different pathways yielding various types of phenoxy radicals, which lead to chain cleavage or colored quinonoid molecules [12].

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In the present work, the structural changes undergone by the different components of the lime wood (*Tillia cordata* Mill.) were studied upon exposure to an accelerated environmental degradation process. The thermogravimetry was used for a systematic investigation of the lime wood photodegradation. The main objectives are to quantify the differences between untreated and treated wood, following the different thermogravimetric characteristics and to ascertain whether the mechanism, consists of a few parallel devolatilization reactions, and one set of kinetic data can be used with sufficient accuracy to establish the limits of such an approach.

2. Experimental

2.1. Materials

Lime wood blocks (50 × 50 × 3 mm) were oven-dried at 105 °C, until constant weight was reached (TAPPI T 264 cm-97). The samples were exposed to artificial light from a mercury lamp ($200 < \lambda < 700$ nm, incident light intensity 39 mW/cm^2) at a temperature of 40 °C and 60% relative humidity in a commercial chamber (CH 250 Angelantoni Ind. Italy). The samples were removed from chamber at regular intervals ranging from 0 to 600 h.

2.2. Characterization method

The powder samples were obtained by removing the top layer of the irradiated surface of the specimens using a sharp razor blade and were thermally analyzed and compared with non-irradiated (reference) sample.

Thermogravimetric analysis (TGA) was carried out under constant nitrogen flow (200 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 Versatile commercial program which gives kinetic parameters by various methods. The deconvolution of the derivative thermogravimetric curves (DTG) was done by means of Grams/32 program (Galactic Industry Corporation) with Log-Normal functions.

3. Results and discussions

The photodegradation of wood is undoubtedly more complicated than that of synthetic homopolymers because it consists of some high molecular weight polymers (lignin, cellulose, and hemicelluloses) and low molecular weight extractives that differ in their susceptibility to light radiation. Furthermore, it is clear that the precise mechanisms and reaction pathways involved in the photodegradation of each of these components have not been fully elucidated. However, the key step involved in the photodegradation of wood appears to be photolysis and fragmentation of lignin, resulting in the formation of aromatic radicals [2]. These free radicals may then induce further degradation of lignin and photo-oxidation of cellulose and hemicelluloses. Free radical reactions may be terminated by reaction of radicals with photodegraded lignin fragments, forming colored unsaturated carbonyl compounds, which explains why wood initially yellows when exposed to light.

The TG/DTG curves performed on reference and photodegraded lime wood samples are shown in Fig. 1. In Fig. 1(a) are given the percentage of mass loss as a function of the temperature (TG), while in Fig. 1(b) are given the derivative thermogravimetric curves (DTG).

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 vapor are produced up to 130 °C. At about 150 °C, some components begin to break down chemically; low temperature degradation at low rate occurs in lignin and hemicelluloses. The mass loss between 300 and 500 °C corresponds to the degradation of cellulose and has also been associated to the pyrolitic degradation of lignin involving fragmentation of inter-unit linkages decomposition, and condensation of the aromatic rings [13].

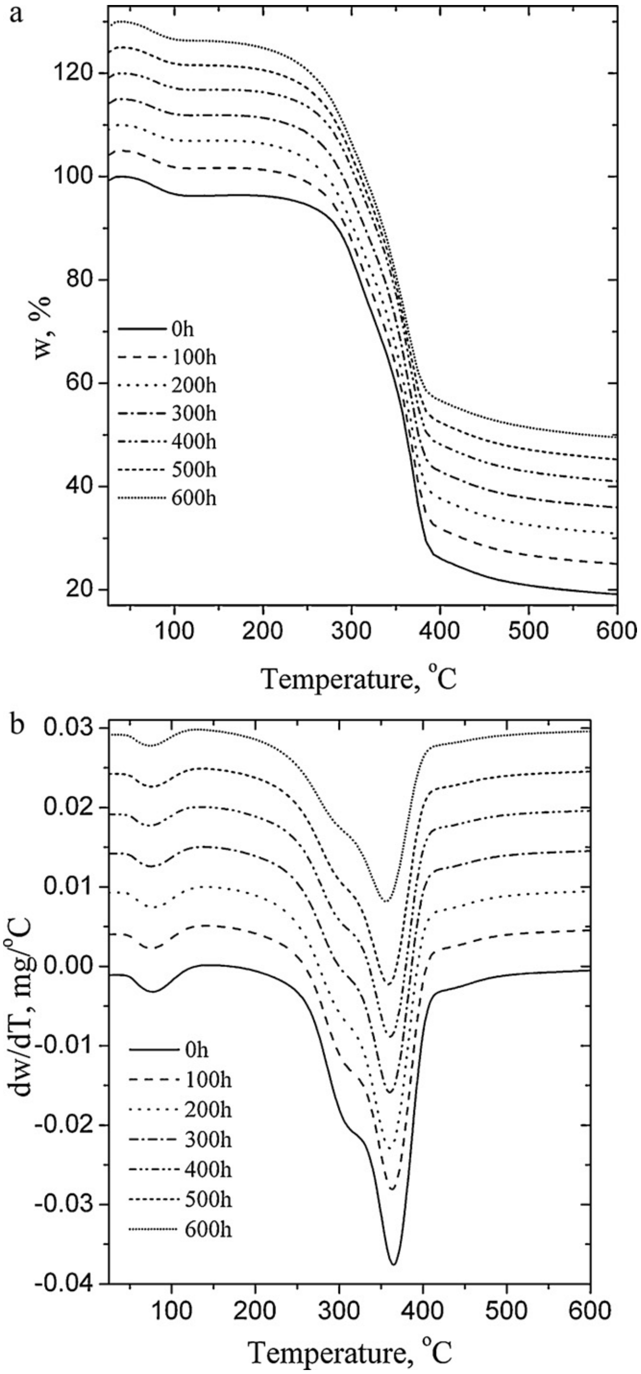

Fig. 1. TG/DTG curves of photodegraded and reference lime wood samples.

From the thermograms of Fig. 1(a) several parameters were evaluated for each step of mass loss: the "onset" temperature (T_i), the temperature corresponding to the maximum rate of mass loss (T_m), and the temperature corresponding to the end of stage (T_f).

Table 1
Thermogravimetric data for reference and photodegraded lime wood samples.

Parameters	Time (h)						
	0	100	200	300	400	500	600
First process							
T_i (°C)	47.1	47.8	48.2	48.5	48.6	49.0	49.3
T_m (°C)	77.3	76.1	78.9	77.3	74.1	76.1	74.5
T_f (°C)	126.6	126.2	126.2	124.5	125.1	123.7	120.1
w (%)	3.6	3.6	3.5	3.2	3.2	3.3	3.2
Second process							
T_i (°C)	177.7	178.2	180.6	181.1	180.6	181.6	182.7
T inf (°C)	317.1	315.1	311.7	311.7	310.6	310.2	307.2
T_m (°C)	369.7	366.8	366.1	365.8	364.4	362.3	360.5
T_f (°C)	509.9	508.9	508.9	506.9	506.9	506.9	506.9
w (%)	75.7	75.3	74.9	74.3	74.3	74.4	74.2

The amount of desorbed water (as percentage of mass loss below 127 °C), and the mass loss of the process of thermal degradation (as a percentage from the initial mass) were determined. The range of temperatures in which degradation occurs was estimated from DTG curves and the weight loss percentage was read from the TG plots.

For the first step, the temperature corresponding to the maximum mass loss rate is between 77 °C for reference and 74 °C for 600 h photodegraded lime wood. The temperature of the end of the stage decreases with increasing the time of exposure, from 127 °C for reference lime wood to 120 °C for lime wood exposed 600 h. It is seen that the water desorption percent in photodegraded wood is lower than in reference one (see Table 1).

Most of the mass is lost during the second step, corresponding to the thermal degradation for wood components. This one takes place from 178 to 510 °C, the mass loss ranges from 76 to 74 wt%. The decomposition of wood is a very complex process consisting in several overlapping reactions and/or in successive processes of decomposition – Fig. 1(b). In the case of reference wood sample, the degradation occurs at higher temperatures than in the case of photodegraded samples – Table 1.

From Fig. 2 is observed that the temperatures corresponding to the maximum decomposition rate (T_m) and those corresponding to the end of stage (T_f) decreases following exponential curve. In the same time, the weight losses for the decomposition process show an exponential decrease with the increasing exposure time. This indicates a higher extent of degradation of the samples.

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 photodegradation advances this shoulder, in the DTG curves, becomes better defined. The second region is associated with the attainment of the maximum, mainly because of cellulose decomposition, followed by a rapid decay and a long tail. The wide range of temperatures, where lignin decomposes, hinders the appearance of a peak attributable to this component.

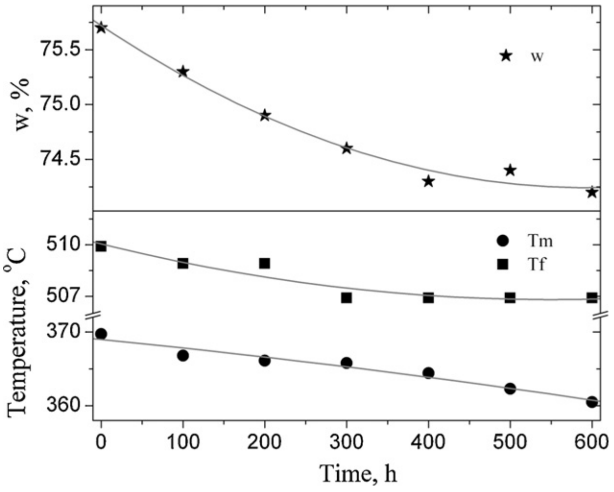

Fig. 2. Dependence of thermal characteristics vs. exposure time for the second thermogravimetric step.

Usually, three main zones have been identified, associated with the decomposition of the main components of the wood [14,15]. These zones have been evidenced by deconvolution of the DTG curves (Fig. 3).

The shoulder temperature (308 °C for reference wood) for peak assigned to decomposition of hemicelluloses and amorphous cellulose, the temperature (319 °C for reference wood) of the peak assigned mainly to lignin decomposition and the temperature (370 °C for reference wood) of the peak assigned to cellulose decomposition decreases.

Shifting of the temperature of the shoulder assigned to decomposition of hemicelluloses and amorphous cellulose to lower values should be explained by appearing of carbon, alkoxy and formyl radical structures after photodegradation. The integral area of this peak increases constantly from 25.3 to 26.4% (Fig. 4).

The lignin decomposition shows a large interval of temperatures from 150 to 465 °C, the temperature for the maximum of this peak decreases from 319 to 308 °C showing the occurrence of the phenolic radicals, which in turn transforms into *o*- and p-quinonoid structures. The integral area of this peak increases from 25.5% (reference wood) to 26.7% (200 h photodegraded lime wood) in the first stages of photodegradation, while starts to decrease to 24.1% for 600 h photodegraded lime wood – see Fig. 4.

The third peak may be due to the loss of –OH groups of monomer units of cellulose and the break-down of the pyranosic rings; the temperature of this peak is shifted to lower values, from 370 to 360 °C. The integral area of this peak decreases from 49.2% to 47.5% at 200 h of the photodegradation process, while increases to 49.5% for 600 h (Fig. 4).

The overall kinetic parameters of the entire 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 and Redfern (CR) [16], Flynn–Wall (FW) [17], van Krevelen et al. (vK) [18] and Urbanovici–Segal (US) [19].

The values of the overall activation energies corresponding of the decomposition process lay in 120–107 kJ/mol intervals, with progressively decreasing values for photodegraded samples. The values of the overall activation energies calculated by van Krevelen method are higher (157–139 kJ/mol) (Table 2 and Fig. 5).

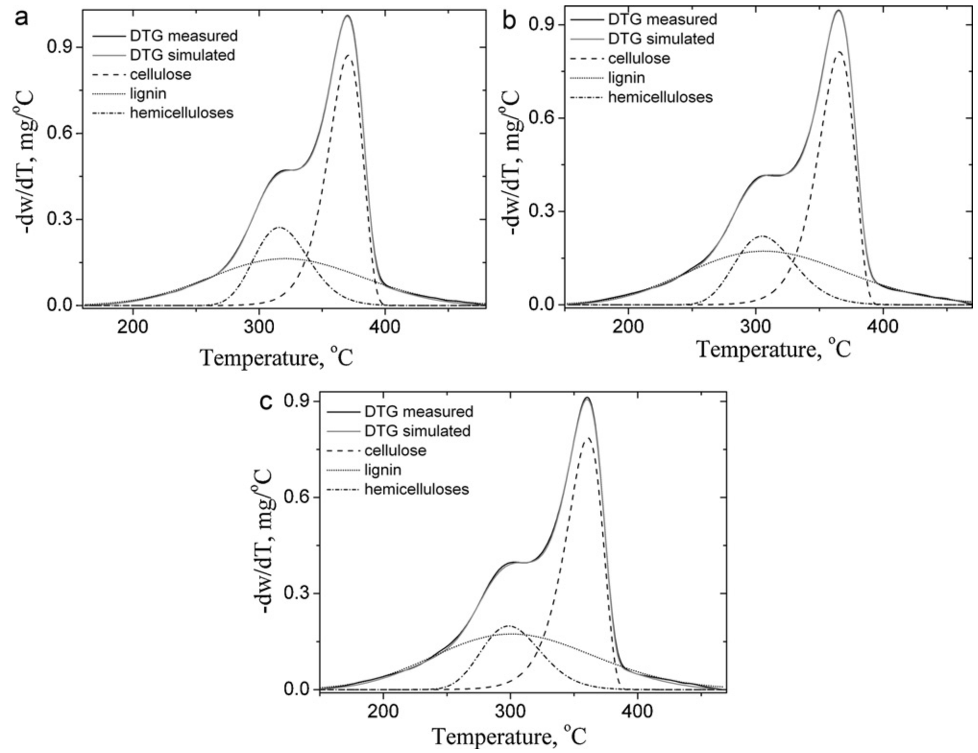

Fig. 3. Devolatilization rates of the reference wood (a), 300 h photodegraded wood (b) and 600 h photodegraded wood (c) measured (black line) and simulated (gray line).

The reaction order was 1.1 and 1.2, for reference and photodegraded wood, respectively, indicating that the reaction mechanism for wood decomposition is controlled by a reaction order law.

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

The changes in structure and composition occurred as consequences of the photodegradation process were observed also by FT-IR spectroscopy. In this case a considerable decreases in the intensities of the characteristic aromatic lignin band at 1505 cm^{-1} and other associated bands was obtained.

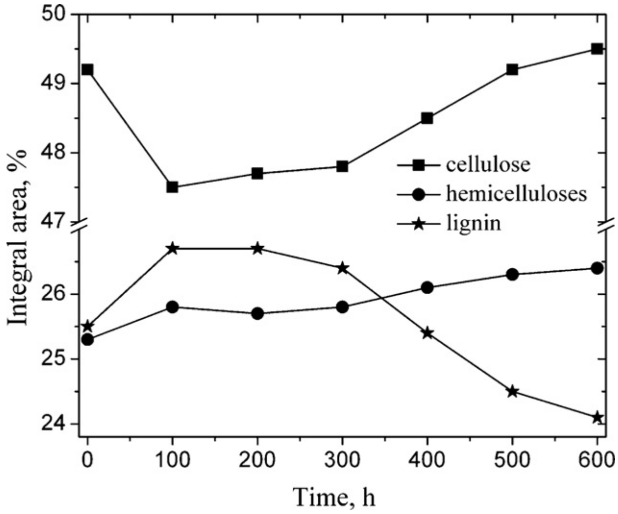

Fig. 4. Dependence of integral area vs. exposure time for the deconvoluted peaks assigned to decomposition of the components of the wood according to literature data.

The carbonyl formation corresponded well with lignin degradation, indicating a close relationship between them. Comparing the rate of carbonyl formation and lignin decay clearly showed that the former is remarkably higher than the latter, indicating the formation of carbonyl bands at 1738 cm^{-1} probably resulted from not only lignin oxidation but also from reactions occurring in other components of the wood.

Quinine formation is combined with the decay of aromatic structures (loss of the skeletal vibration at 1505 and 1600 cm^{-1}) and the formation of conjugated carbonyl groups (increase of the carbonyl absorption at the 1738 cm^{-1}) [20].

It is known that the rate of photodegradation for carbohydrates depends markedly on the intensity and energy distribution of the light. When cellulose is subjected to sunlight, the glycosidic linkages are cleaved, which causes a loss of strength and degree of polymerization [4].

When cellulose is exposed to light with wavelengths longer than 340 nm in the presence of oxygen, alkoxy and carbon radicals due to the cleavage of glycosidic bonds are noticed, while wavelengths longer than 280 nm, in addition to chain scission, dehydrogenation takes place, preferentially at the C-l and C-5 positions are registered.

Dehydroxymethylation due to the cleavage of the C-5/C-6 side chain of cellulose is observed when cellulose is exposed to light longer than 254 nm [4], with formation of carbon radicals, alkoxy radicals, formyl radicals, and hydrogen atoms in irradiated cellulose.

Generally, alkoxy radicals generated in cellulose are stable compared to carbon radicals. The carbon radicals readily undergo secondary termination reactions.

The possible chain scission of the cellulose by glicosidic linkage cleavage and possible dehydrogenation sites is shown in Fig. 6 marked by grey lines.

The reactive groups available in lignin consist of ethers of various types, primary and secondary hydroxyl groups, carbonyl

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

Parameters		Time (h)						
		0	100	200	300	400	500	600
Coats–Redfern	*E* (kJ/mol)	119	113.4	109.9	109.4	108.9	107.3	106.5
	n	1.1	1.1	1.1	1.2	1.2	1.2	1.2
Flynn–Wall	*E* (kJ/mol)	122.6	117.3	113.9	113.5	113	110.6	107.8
	n	1.1	1.1	1.1	1.1	1.2	1.2	1.2
van Krevelen	*E* (kJ/mol)	157	150.1	146.1	145.8	142.3	139.3	139
	n	1.2	1.2	1.2	1.3	1.3	1.3	1.3
Urbanovici–Segal	*E* (kJ/mol)	125	115.9	114.1	112.6	111.9	110.5	109.6
	n	1.2	1.2	1.2	1.2	1.2	1.2	1.2

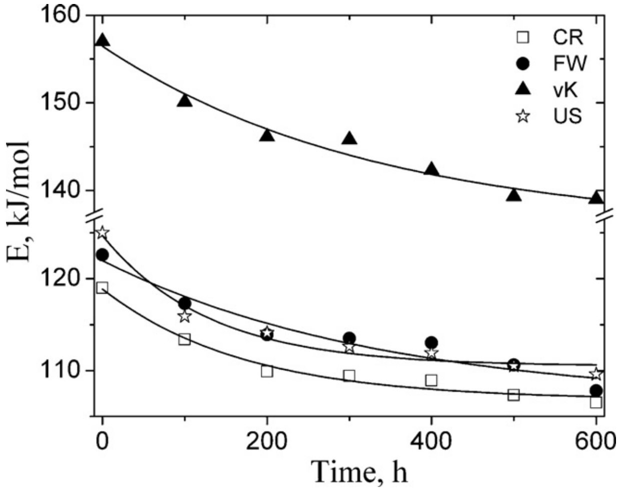

Fig. 5. Dependence of overall activation energy vs. exposure time for the second process.

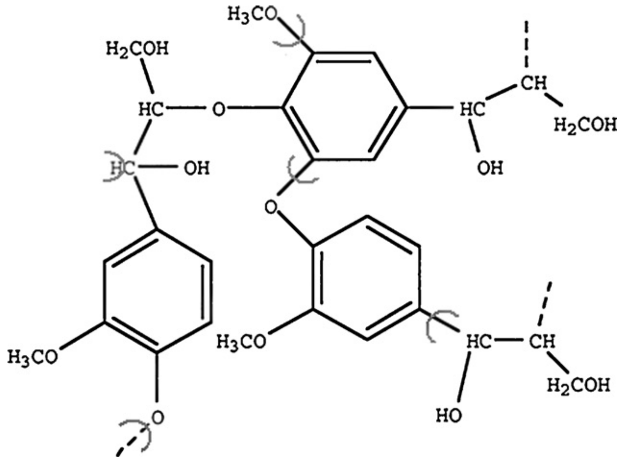

Fig. 7. Possible cleavage sites followed by chromophores formation under UV radiation for lignin.

groups, and carboxyl groups. There also exist a number of aromatic and phenolic sites and activated locations capable of interacting with light to initiate free-radical chain reactions. Lignin is sensitive to light with wavelengths shorter than 350 nm. The possible cleavage sites followed by chromophores formation under UV radiation for lignin are shown in Fig. 7.

The phenolic hydroxyl group is an important source that reacts with light rapidly to produce a phenolic radical, which in turn transforms into *o*- and p-quinonoid structures by demethylation or by cleavage of the side chain. Whitening of lignin can be observed when it is exposed to light with wavelengths longer than 400 nm. It seems that carbon–carbon bonds adjacent to α-carbonyl groups are photodissociated via the Norris type I reaction. However, the Norris type I reaction does not occur efficiently in those structures with ether bonds adjacent to the α-carbonyl group. In this case, the α-carbonyl group appears to absorb light effectively and transfer such energy to the p-aryl ether linkage that leads to the cleavage of the ether bond to generate phenolic and carbon radicals.

4. Conclusion

In this paper several correlations between the photodegradation processes and thermogravimetric characteristics of lime wood samples have been established.

The shape of DTG curves depends on the exposure time of wood to the UV light. The peak temperatures assigned to devolatilization of hemicelluloses and amorphous cellulose decreases.

Shifting of the shoulder temperature at 308 °C to lower values is due to formation of carbon radical, alkoxy radical, formyl radical structures after photodegradation, which make the hemicelluloses and amorphous cellulose less stable. DTG peaks deconvolution allows making some correlations with lime wood components decomposition.

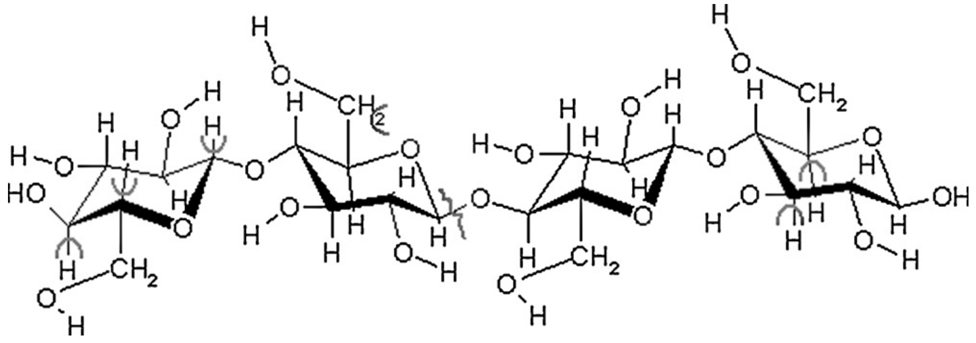

Fig. 6. Possible chain scission by glicosidic linkages cleavage and dehydrogenation sites under UV radiation for cellulose.

The lignin decomposition shows decreases of the temperature of exposed wood, meaning the formation of the phenolic radicals, which in turn transforms into *o*- and p-quinonoid structures. The third peak may be due to the loss of –OH groups of monomer units of cellulose and the break-down of the pyranosic rings; the temperature of this peak is shifted to lower values and the integral area of this peak decreases in the 0–200 h period of exposure and then increases.

The global kinetic parameters for the main peak decrease with increasing exposure time of the wood to the UV light evidencing one more the formation of different structures due to photodegradation process.

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