The average carbon oxidation state of thermally modified wood as a marker for its decay resistance against *Basidiomycetes*

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ABSTRACT

It has recently been reported that the oxygen to carbon-ratio (O/C) of thermally modified wood is a reliable indicator for the resistance against attack by *Basidiomycete* fungi. The present theoretical study is an attempt to clarify causality between the O/C-ratio of thermally modified wood and its fungal resistance, as measured by standardized laboratory test procedures. It is shown that different wood species, with varying degree of thermal modification, reveal a remarkable correlation in elemental composition when plotted in a van Krevelen state diagram, suggesting a common modification chemistry shared by these species. The overall chemical reaction types responsible for the composition changes appear to be mainly dehydration, with some decarboxylation. The latter reaction decreases the mean overall oxidation state of carbon atoms present in thermally modified wood, leading to an inherently improved resistance against oxidation of the material. A known general correlation, between the average oxidation state of organic matter and the Gibbs free energy of the oxidation half-reaction, was found quantitatively consistent with the observed trend in the fungal resistance of thermally modified wood with the O/C-ratio.

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1. Introduction

It is a challenge for the wood and forest society to find techniques to upgrade abundant renewable lower-grade forest products into valuable raw materials and products, advancing a more sustainable world. Wood modification has been recognized as one of such key technologies. Thermal wood treatment is the most commercialized as well as the most investigated method for modifying wood composition. Depending on the wood cell wall polymer composition and the moisture content during the heat treatment, temperatures in the range of 160–240 °C are required to change the chemical composition of the polymers. A non-limitative listing of typical effects of thermal modification on wood properties is: a browned colour, lower affinity to moisture, lower extent of moisture swelling, increased brittleness, and − most interestingly − an increased resistance against fungal decay. Reviews on the different heating technologies used and the diverse physical and chemical effects of thermal modification on wood have been published [5,7].

Recently, CHN(O)-elemental analysis has been investigated for its use as a marker for the absolute degree of thermal modification of heat treated wood [2]. This technique revealed, unexpectedly, a relative wood species independence of calibration curves with fungal resistance performance, which is an indication of causality between these observables and the fungal resistance performance.

In this paper, we theoretically investigate a postulated causality between the elemental composition and the fungal resistance performance of thermally modified wood. The composition data are analysed in a van Krevelen diagram, showing that the average oxidation state of carbon in thermally modified wood is progressively decreased with increasing treatment intensity. Using a recently described thermodynamic correlation of the average carbon oxidation state and the oxidation resistance of organic substance [11], relative aerobic wood degradation rates are modelled and shown to be quantitatively consistent with the observed ones.

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2. Theory

2.1. The van Krevelen diagram for wood

In this work, the empirical carbon-normalized chemical formula CH_yO_x is used to represent oven-dried, nitrogen-free and ash-free wood ($y/x \approx 2$ and $x > 0.4$). Parameters x and y, corresponding to the molar O/C and H/C ratio respectively, are used as the co-ordinates in the van Krevelen diagram (Fig. 1). The diagonal line $y = 2x$ plays a central role in the present work as a reference representing carbohydrates $C(H_2O)_x$. All points above this line (i.e. $y > 2x$) are H-rich (reduced), whereas all points below are O-rich (oxidized), with respect to carbohydrates.

In case of a changing elemental composition, as occurs during thermal modification, corresponding trajectories can be visualized in the van Krevelen diagram. Wood is a composite material, mainly consisting of polysaccharides (cellulose and hemi-celluloses) and lignin which have a significantly different composition (Fig. 1). The composite wood is represented by a single point, reflecting the weighted composition average of its components (cellulose 45 mol%, hemicelluloses 25 mol% and lignin 30 mol% approximately). Hence, a change in the quantity of a wood component (without simultaneous chemical change) does not change its own position in the van Krevelen diagram, but can lead to a significant position shift of the composite wood. Since lignin and crystalline cellulose can be considered as rather stable components during thermal modification [7], the studied trajectories in the van Krevelen diagram will mainly relate to amorphous polysaccharide chemistry.

An interesting property of the van Krevelen diagram is that reactions involving the exchange of water molecules or carbohydrates (and -isomers) can only cause shifts parallel to the carbohydrate reference line in the van Krevelen diagram. These include a) water elimination reactions (dehydration), b) water addition reactions (hydration and hydrolysis), as well as c) some non-sugar (acetic acid and formaldehyde) elimination reactions, removing oxygen and hydrogen in 1:2 ratio. Hence, the reactions that are generally accepted as the main thermal modification reactions [7] (deacetylation, depolymerization, dehydration and condensation) belong to this class and cannot be individually resolved in the van Krevelen diagram. The overall effect of all these reactions is similar to dehydration, responsible for the hydrophobic character of thermally modified wood [16].

Model reactions can be visualized by vectors in the van Krevelen diagram (Fig. 1), which can be calculated from the conservation laws for species and mass, for a given mass change of the untreated wood reference.

2.2. Average carbon oxidation state of wood

The average carbon oxidation state of wood is determined by the relative abundance of its constituting elements carbon, hydrogen and oxygen, the electron affinity trend of these elements (122, 73, resp. 141 kJ/mol) and the number of valence states (4, 1, resp. 2). Hence, hydrogen has one electron donating valence state and oxygen has two electron accepting valence states, whereas carbon has four donating as well as four accepting valence states. Assigning formal charges to hydrogen ($+1$) and oxygen (-2), the formal average charge of carbon (Z) then follows from molecular charge neutrality: $Z.C + 1.H - 2.O = 0$, hence,

$$Z = 2(O/C) - (H/C) \tag{1}$$

The derivation of the expression (Eqn. (1)) closely follows the classical derivation of the oxidation state of an individual organic carbon atom [12]. Hence, Z is the arithmetic mean over all individual carbon oxidation states in a macromolecule. This quantity has recently received attention in geochemical carbon cycle studies to describe the carbon oxidation state of degraded organic matter [9]. The average oxidation state of carbon necessarily increases on oxidation, between the extreme values of -4 for fully reduced carbon (in CH_4) and $+4$ for fully oxidized carbon (in CO_2).

The expression for Z (Eqn. (1)) uses van Krevelen coordinates O/C and H/C and it follows that the carbohydrate reference line (Fig. 1) satisfies $Z = 0$. The class of wood chemical reactions exchanging water molecules or a carbohydrate (see Section 2.1) do not change the value of Z and have trajectories that run parallel to the reference line $Z = 0$. The average carbon oxidation state at any point in the van Krevelen diagram can be directly read as the vertical distance to the reference line (with $Z < 0$ for states above the reference line).

2.3. Stability of organic substance in aerobic environment

For all organic compounds, the Gibbs free energy change $\Delta G_{reaction}$ of the overall oxidation reaction with O_2 is negative (i.e. thermodynamically favoured) as a result of the large energy release, $\Delta G_{C\ red}$, in the reduction half-reaction of O_2 to H_2O. The oxidation half-reaction of organic matter $\Delta G_{C\ ox}$ [11], on the other hand, involves positive Gibbs free energy changes (i.e. must be activated), Fig. 2b. Moreover, $\Delta G_{C\ ox}$ was found to be strongly, linearly, correlated to Z (Fig. 2a), the average carbon oxidation state, effectively increasing stability with decreasing Z [11]:

$$\Delta G_{C\ ox} = 60.3 - 28.5Z \tag{2}$$

The apparent activation energy E_a of oxidation is equal to $\Delta G_{C\ ox}$ up to some unspecified constant, which accounts for non-standard thermodynamic reference conditions.

2.4. Fungal resistance prediction for thermally modified wood

Heating of wood to a sufficiently high temperature is known to lead to an improved resistance of wood to degradation by fungi, caused by the chemical modification of the cell wall polymers. In an accelerated wood fungal resistance test, the optimal environmental conditions for growth of aggressive Basidiomycetes species are
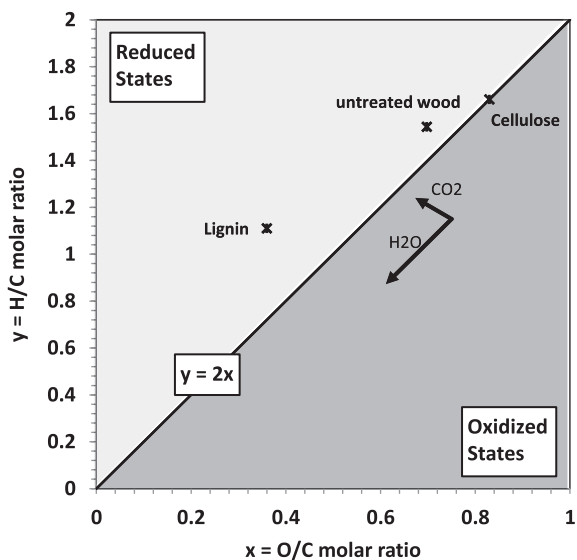

Fig. 1. van Krevelen diagram, with the carbohydrate reference line $y = 2x$ and the positions of lignin, cellulose and composite wood. Vectors indicate the composition effect of 10% mass loss by dehydration ("H_2O") and decarboxylation ("CO_2") reactions.
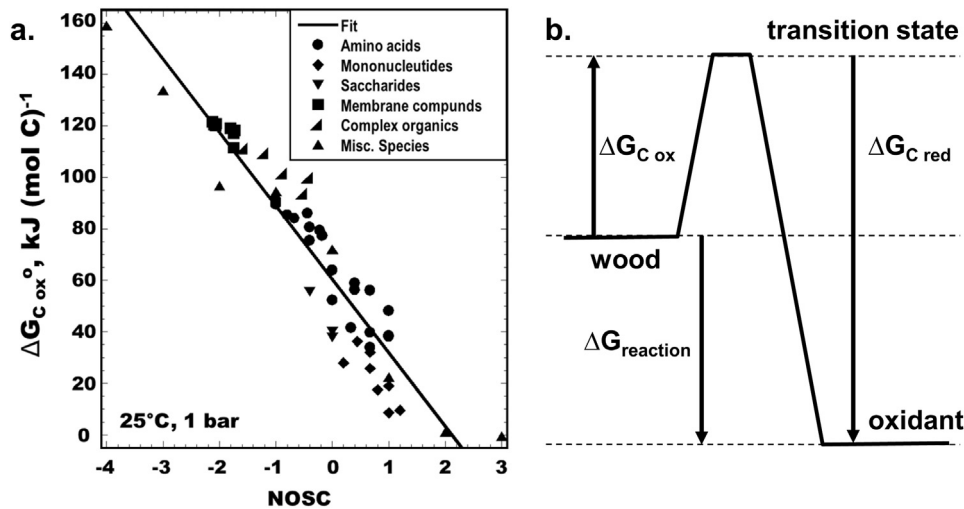
Fig. 2. a. Correlation between the Gibbs free energy of oxidation half reaction ($\Delta G_{C\ ox}$) with NOSC (Nominal Oxidation State of Carbon = Z), reprinted from Ref. [11] with permission from Elsevier. b. Energy level diagram. Oxidation proceeds as an electron pair transfer from wood via a transition state to the oxidant.

ensured, to measure the decay of a test specimen in comparison with a non-durable reference, quantified by the so-called X-value = WL (weight loss by fungus) of test specimen/WL of reference. By linear approximation, the ratio of weights losses may also be expressed as the ratio of weight loss rates (k):

$$X = WL_{test}/WL_{ref} \approx k_{test}/k_{ref} \qquad (3)$$

Recalling the linear Z-dependence of the Gibbs free energy of organic oxidation half-reactions (Eqn. (2)), the apparent activation energy E_a for oxidation will show the same Z-dependence of 28.5 kJ/mol per unit ΔZ (Fig. 2a). Consequently, the weight loss rate by oxidation will have an Arrhenius form

$$k_{test(ref)} = k_0 \exp\left(\left(E_{a0} + 28.5\ Z_{test(ref)}\right)/RT\right) \qquad (4)$$

In the ratio of weight losses k_{test}/k_{ref}, E_{a0} and k_0 are divided out and the result only depends on the difference $\Delta Z = Z_{test} - Z_{ref}$.

$$X \approx \exp(28.5\Delta Z/RT) \qquad (5)$$

This simple equation (Eqn. (5)) without adjustable parameters is validated in the next chapter using literature data on the fungal resistance of thermally modified wood species, analysed by elemental composition analysis.

3. Results

The data set used for validation of the theoretical model contains data on fungal mass losses obtained from literature data on a series of thermally modified wood species with known elemental composition ([3], Figs. 3 and 4). The reported results were obtained from different test *Basidiomycete* species *Poria placenta*, *Gloeophyllum trabeum* and *Coniophora puteana*, three aggressive brown rot fungi, all showing similar trends. Five European wood species, Poplar, Beech, Ash, Pine and Fir, were analysed at 4 different thermal treatment levels, characterized by their relative thermal mass loss (0, 5, 10, and 15%) of oven-dried weight compared to untreated dry weight. The thermal modifications were performed at different temperatures ranging from 200 to 230 °C, for several heating rates and heating durations, under atmospheric conditions with nitrogen as a shielding gas. The typical total duration time was between 10 and 24 h for all runs [3].

By plotting the elemental ratio data for samples from Chaouch [3], a remarkable correlation appears (Fig. 3). Data from other sources [4,10,13] fit well to this correlation. It is noted that the correlation holds for wood species form the softwood group (Pine, Douglas, Fir) and hardwood group (Beech, Ash, Poplar) and is independent on the density (compare measured values in Ref. [3]: Poplar 437 kg/m^3 versus Beech/Ash 653/675 kg/m^3). Untreated wood appears to have a quite universal value for O/C ≈ 0.7.

The slope of the correlation line deviates significantly from a dehydration trajectory (solid line, Fig. 3) and consequently the average oxidation state Z is changing,

$$\Delta Z = 0.84\Delta O/C, \qquad (6)$$

bearing the same (negative) sign as the change in O/C. Eqn. (5) relates the change in average oxidation state ΔZ to the predicted mass loss ratio X, which may be transformed back to WL using Eqn. (3), and with Eqn. (6), WL$_{ref}$ ≈ 30%, O/C$_{ref}$ = 0.7 and RT = 2.45 kJ/mol (T = 294 K):

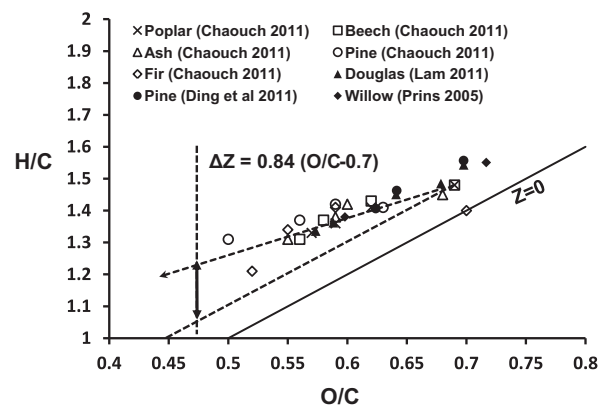$$WL_{test} = WL_{ref}X \approx 30\%\exp\{9.77(O/C - 0.7)\} \qquad (7)$$

Fig. 3. van Krevelen diagram, for different heat-treated wood species. Solid line: $Z = 0$ reference. Broken line: modification trajectory pointing towards increasing treatment intensity.
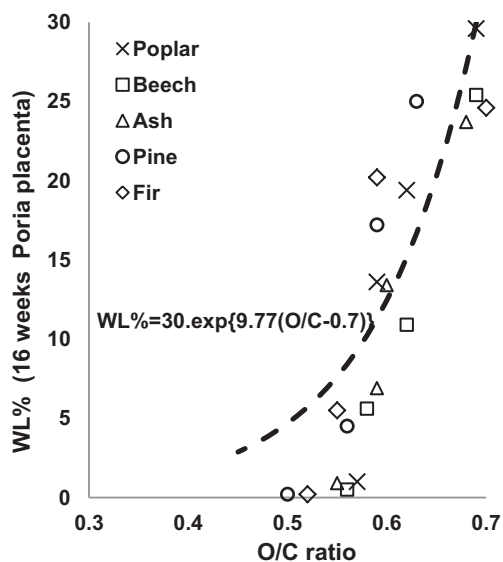
Fig. 4. Weight loss data on 5 wood species by 16 weeks *Poria placenta* exposure versus O/C-ratio [3]; broken line: our predicted WL% versus O/C relation, with expression.

which has been used to draw the broken curve in Fig. 4.

4. Discussion

4.1. Sugar reactions

Heat-treatment is a method to modify the chemical composition of wood, whereby nearly all measurable physical and chemical properties are modified, notably the fungal resistance, hygroscopicity, colour and strength. Hemicelluloses are being deacetylated and depolymerized to single sugars, which are subsequently dehydrated leading to volatile by-product or re-condensation by-products [7], leaving the redox-state Z unchanged. Proximate wood analysis data can be successfully correlated with the strength properties of wood and changes therein made by pyrolysis [14]. On the other hand, the correlation of fungal resistance with proximate analysis data of thermally modified wood is weak compared to correlations with elemental composition [2].
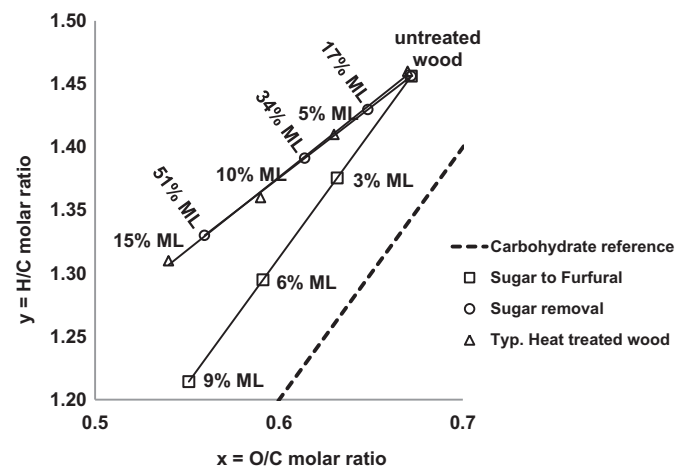

Fig. 5. Calculated composition effect of pentose sugar conversion to furfural (squares) sugar removal (circles), compared to typical thermal modification experiment (triangles). ML = overall mass loss of the conversion.

Moreover, the typically measured hemicelluloses mass losses in thermally modified wood are far too small to cause a noticeable composition change by a "hemicellulose loss" (see Fig. 5). Based on this mass loss inconsistency, it is ruled out that hydrolysed sugars are mineralized or volatilized to any significant degree, able to explain the more lignin-like residual elemental composition. Dehydration reactions on an extensive scale (involving appr. 30% of all wood sugars), on the other hand, can explain the magnitude of the change in O/C with a limited associated mass change (Fig. 5). The dehydration products (furans) may be partially trapped in [8] and partially chemically condensed to [18] the cell wall.

The absence of significant sugar loss from heat treated wood is further supported by the calorific value trend in mild heat treatments. A 15% sugar loss would necessarily cause a similar loss of calorific value, but it does change by only a few percent [13]. Dehydration reactions leave the calorific value relatively invariant, and are indeed to be expected under the prevailing acid high-temperature treatment conditions [6,18]. Water is the main volatile reaction product in mild heat treatments [13,17].

4.2. Elemental composition changes during the thermal modification

It is observed that the modification trajectories in the van Krevelen diagram (Fig. 3) are not exactly running in the direction of a pure dehydration trajectory (slope -2), but significantly less inclined. For reasons explained above, in conjunction with Fig. 5, this cannot be ascribed to an increasing lignin content, but must be related to some hydrogenation or deoxygenation reaction, the latter being confirmed by the presence of a significant quantity of carbon dioxide in the volatile products of mild heat treatments [13,17]. Prins [13] measured a carbon dioxide yield of 2.9% of the initial dry mass from willow (12.8% total mass loss), which leads to a good agreement between the change in Z from the measured composition data (-0.067) and calculated (-0.069) by the subtraction of 2.9% of CO_2 from the initial wood composition. Carbon dioxide might be the reaction product of β-activated decarboxylation [12], promoted by the formation of new carbonyl-groups as a result of dehydration.

The combustion of wood substance with residual air oxygen in the heating equipment and the wood lumen can be ruled out as the origin of the large quantity of CO_2. Firstly, producing 2.9% CO_2 by combustion of wood of 500 kg/m^3, requires 37 m^3 (STP) of air per m^3 wood, which is not supposed to be present in a thermal modification reactor. Secondly, CO_2 emission from combustion is accompanied with O_2 addition, which gives no net chemical reducing effect, opposed to thermal decarboxylation.

Other volatile degradation products, than water and carbon dioxide, were considered as modifying eliminations, such as carbon monoxide, formic acid and methanol. However, none of these compounds was found to cause any significant composition effect in the quantity produced during mild thermal modification (volatile yield data [13]).

The exact reason for the universal modification trajectory in the van Krevelen diagram remains obscure, requiring further research.

4.3. Thermal mass loss versus O/C ratio as a marker for degree of modification

The strong linear correlation between O/C and H/C for various heat treated woods (Fig. 3) reduces the required number of parameters for specifying the composition change to just one, explaining the success of the O/C-marker for thermally modified wood [2]. This is illustrated by linear relations in the dry mass loss by heat treatment versus O/C (Fig. 6), reflecting that dehydration is
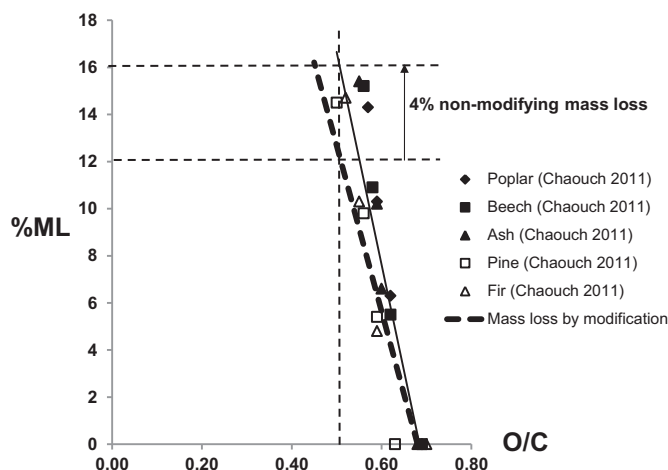
Fig. 6. O/C-mass loss correlation (solid line: average for the 5 wood species, broken line: molar mass loss calculated from the universal trajectory in Fig. 3).

the most significant thermal modification reaction. However, the calculated relative change in molar mass predicts much lower mass losses than actually measured (Fig. 6), since the molar mass loss accounts only for mass loss by components that are able to modify the elemental composition. The logical consequence of this notion is that if O/C is a true marker for the degree of thermal modification, the thermal mass loss is not, and vice versa.

4.4. Influence of oxidation stability on fungal resistance

The calculated effect of the average carbon oxidation state Z along the universal thermal modification trajectory, parameterized by O/C, and its sequential effect on the activation energy of oxidation was given by a simple expression (Eqn. (5).) for the X-value, known from fungal resistance testing. The model prediction is calculated rather than fitted to the experimental data and found reasonably consistent with the observed correlation between fungal mass loss and O/C (Fig. 4). The model reflects the increased inherent chemical oxidation resistance for increasingly chemically reduced organic substance, found with increased degree of thermal modification.

Increasing antioxidant behaviour with heat treatment intensity has been independently reported for a number of wood species using ESR (Electron Spin Resonance spectroscopy) and a DPPH-assay [1] and has been successfully correlated with standardized fungal resistance test results using ESR and a TEMPOL-assay [15].

The steepness in the weight loss − O/C correlation (Fig. 4) is not fully explained by the model prediction. Moreover, fungal decay seems to be completely inhibited below O/C ≈ 0.55, which is also not predicted by the oxidation stability model, which may be attributed to another degradation rate-limiting factor, manifested at severe treatment conditions.

4.5. Artefacts of the fungal test procedure

Fungal resistance tests are biological tests, which have an inherent difficulty of reproducibility. The outcome may depend on the test fungus species and strain, the virulence and several experimental details. The fungal resistance model presented in this work is deemed to represent the weight loss − O/C correlation under the most optimal conditions for decay, with oxidation as the rate-limiting factor.

The outcome of fungal resistance experiments may also depend on the total exposure time to the test fungus. The X-value (Eqn. (5)) was derived using a linear approximation for X being the ratio of

weight loss rates. This approximation is reasonable as long as the fungal reference mass decay does not saturate too much and the fungal exposure time is much larger than the colonization time. Both conditions seem to be met in the used fungal resistance tests, for the fungus species used.

4.6. Other possible reasons for fungal resistance of heat treated wood

The present theory on the oxidation stability of thermally modified wood adds a new possible explanation to the debate on the cause(s) of fungal resistance. The simultaneous loss of food calorific value and moisture sorption capacity on removal of hemicelluloses is commonly taken as the obvious reason for increased fungal resistance. However, as argued in this work, hemicelluloses are not removed, but dehydrated to furans leading to subsequent formation of carbonaceous condensation products within the wood structure. These products may be toxic or indigestible for fungi, but their significant presence in heat treated wood of lower degree of thermal modification does not lead to a full improvement of decay resistance.

The decrease in equilibrium moisture content has also been considered as a reason for fungal resistance. The availability of water as a reactant, solvent and swelling agent is essential in wood decay, but is not a limitation under high humidity conditions. The reduced ability of thermally modified wood to swell, connected to the reduced saturation moisture content of the cell wall, may be a decay inhibiting mechanism, operated via diffusion hindrance of degrading agents.

5. Conclusions

The quantitative theory in this work related the average carbon oxidation state to an inherent stability against oxidation and subsequently to the fungal resistance thermally modified wood. This theory does not intend to explain the complex fungal degradation mechanisms, but rather poses an semi-empirical thermodynamic limit on the relative degradation rates by fast degrading *Poria placenta* brown rot on heat-treated wood in comparison to untreated wood. The parameter-free theory was verified and found in reasonable agreement with published experimental fungal resistance results on a series of heat treated woods with known elemental composition.

The elemental composition of several thermally modified wood species shows a universal correlation between the molar elemental ratios O/C and H/C. This correlation is partly understood on the basis of elimination reactions of small molecules, e.g. water and carbon dioxide. The elimination of volatiles, notably carbon dioxide, has a chemically reducing effect on wood, quantified by the average carbon oxidation state $Z = 2(O/C) - H/C$. Further research, assuring the relation between the composition of the volatile yield during heat-treatment of wood and its carbon oxidation state, is important for its potential to in-line process monitoring of the wood modification degree.

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