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# 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.

## 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 coordinates 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 hemicelluloses) 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].

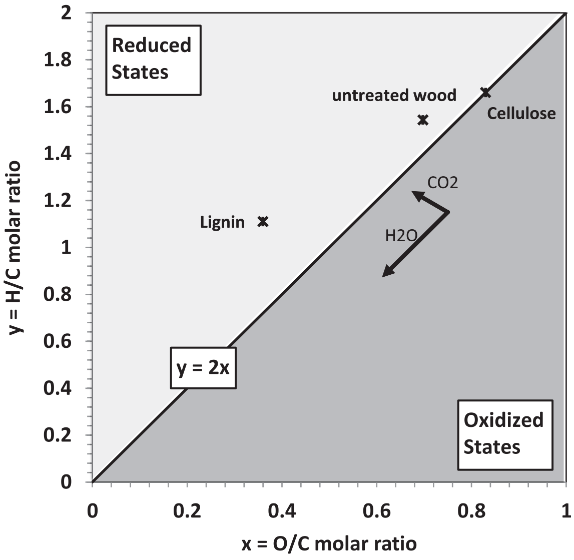

**Fig. 1.** van Krevelen diagram, with the carbohydrate reference line $y = 2x$ and the positions of lignin, cellulose and composite wood. Vectors indicate the composition effect of 10% mass loss by dehydration ("$H_2O$") and decarboxylation ("$CO_2$") reactions.

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

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

The apparent activation energy $E_a$ of oxidation is equal to $\Delta G_{\text{C ox}}$ 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