



## Effect of water vapor in air on thermal degradation of paper at high temperature



Emilia Vänskä\*, Minna Luukka, Iina Solala, Tapani Vuorinen

Department of Forest Products Technology, School of Chemical Technology, Aalto University, P.O. Box 16300, FI-00076 Aalto, Finland

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### ABSTRACT

Thermal degradation of lignocellulosic materials has been studied widely because of its importance in several applications. While a variety of thermal treatment setups has been proposed, this paper introduces a thermal treatment method where high temperature is combined with presence of water vapor in an atmospheric oven chamber. The performance of the device was evaluated at temperature and volume fraction of water vapor ranges of 175–300 °C and 1–98%, respectively. The impact of the treatment was assessed by observing the changes in paper sheets, specifically brightness, light absorption coefficient, burst strength, ultraviolet resonance Raman spectra and the degree of polymerization of cellulose. The results demonstrated that the adapted thermal treatment device functions within the tested ranges of temperature and volume fraction of water vapor. In this study water vapor was found to accelerate hydrolytic thermal degradation of fully bleached paper sheets in terms of thermal yellowing and strength deterioration. In contrast, the empirical findings with lignin-containing paper provided new information on how the residual lignin increases its resistance towards water vapor introduced thermal degradation. This was demonstrated by the results of ultraviolet resonance Raman spectra and light absorption coefficient, which suggested that the thermal degradation of lignin is substantially enhanced in the presence of oxygen.

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### 1. Introduction

High density papers, e.g., baking papers are widely used for many food processing applications at high temperatures. High density papers are often produced from chemical pulps using intensive mechanical refining which leads to a fiber net resistant to grease, water and air. However, for some applications, a better thermal stability in terms of sheet strength and color is desirable.

In the past decades, the practical significance of the thermal stability of cellulosic materials has stimulated a considerable amount of literature. So far, most of the studies have focused on fire-retardant building materials and textiles, pyrolysis of biofuels, thermal stability of cellulose composites, and aging of cellulosic papers [1–8]. Although numerous studies have attempted to explain the thermal degradation of paper, the influence of different components in fibers and impact of thermal treatment conditions still remain partially unclear [9–12].

Three generally accepted reactions in thermal degradation of carbohydrates occur simultaneously: hydrolysis of glycosidic

bonds, oxidation of hydroxyl groups and dehydration of cellulose backbone. Chemical cross-linking is known to follow these reactions [6]. Interactions between hydrolysis and oxidation mechanisms are important, since the formation of carboxylic groups from hydroxyl groups catalyzes the hydrolysis. This further introduces new reducing end group for oxidation. Water forms as a by-product of oxidation of hydroxyl and carboxyl groups and it also accelerates hydrolysis of glycosidic bonds [5,10,13]. The studies agreed that simultaneously with water evolution, cellulose degradation starts to proceed via oxygen-driven reactions [11,14]. The first phase of thermal degradation consists of evaporation of adsorbed water at 100 °C, whereas 200 °C is considered as the minimum temperature for dissipation of chemically bound water [15,16].

Thermal treatments have been formerly performed using water bath for temperature control [17]. A major limitation of this method is that it does not allow studying thermal treatments above the boiling point of water. Consequently, thermal treatment studies at temperatures above 100 °C have typically been conducted with a non-pressurized heating chamber in the presence of air [4]. A serious weakness associated with this method, however, is that it is not able to provide information on thermal degradation in the presence of humidity. In the absence of a climate chamber, the desired relative humidity has been attained by adding water to the

\* Corresponding author. Tel.: +358 503841635.

E-mail address: [emilia.vanska@aalto.fi](mailto:emilia.vanska@aalto.fi) (E. Vänskä).

sample or the heating chamber [4,18,19]. The key problems with these methods are both repeatability and reliability of the experiments. Thus, a pressurized autoclave is crucial when combining water vapor with temperatures over 100 °C [20]. When analyzing thermal degradation mechanisms, previous studies have adapted gas chromatography combined with mass spectrometry (GC-MS), nuclear magnetic resonance (NMR) spectroscopy, high-performance liquid chromatography (HPLC), differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TGA), and Fourier transform infrared spectroscopy (FTIR) [15–17,20–23]. Such analyses have revealed detailed information about the degradation products and the accrued chromophores but have failed to provide sufficient amount of thermally treated samples for paper analyses. In addition DSC, DTA and TGA require oxygen-deficient circumstances while revealing inadequate information on thermal degradation under atmospheric conditions. Studying the thermal degradation of paper, optical and physical properties have been found to be important [2,24], however considerable sample amounts are required for analysis. Moreover, the presence of oxygen and water enhances the thermal degradation of lignocellulosic materials by lowering the activation energy and the onset of thermal degradation [4,9,15,25].

Thermal yellowing of cellulose occurs when paper is exposed to heat. Heat-induced yellowing has been demonstrated to be connected to oxidation of furan compounds. The resulting conjugated  $\pi$  bonds are responsible for the dark color of the pulp. Aromatic structures, visible at UV–Vis absorbance 280 nm, have also been detected in thermally treated cellulosic materials [26]. In addition chromophores result from condensation of the dehydration products of phenolic compounds [22]. 4-deoxy-4-hexenuronic acid (HexA), formed during kraft pulping, acts as a chelating agent. When hydrolyzed during thermal aging, metal ions are liberated, which also introduces colored substances [19]. Manganese and iron together with dicarboxylic acids have been found to form these substances [17,19]. Also furoic acid degradation products of HexA function as intermediate substances for thermal yellowing [20,27]. Glucuronic acid of glucuronoxylan was found to form reductive acid, which is able to catalyze the autohydrolysis and introduce the dark color into pulp [22]. Furthermore, the thermal yellowing and chromophore formation depend on residual lignin [28], carbonyl [29] and carboxyl group content [20], the amount of radical species [26] and low molecular weight ( $M_w$ ) carbohydrate compounds [20,30], as well as metal hydroxides [18,30]. Further, transition metal ions ( $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mn}^{2+}$ ) deepen the thermal yellowing by acting as Lewis acids accelerating hydrolysis [20].

After heat treatment, paper not only changes color but also perishes and becomes brittle. Paper strength is determined by a combination of individual fiber strength and bonding between the fibers. Carboxyl groups together with carbonyl groups can promote cross-linking reactions and produce ether, ester, hemiacetal and hemiketal linkages [31]. Also, intermolecular water elimination occurs between hydroxyl groups, resulting in crosslinks by ether linkages between neighboring chains. These new linkages between cellulose chains increase the brittleness of the paper [10,15]. Paper strength increases at the initial stage of thermal treatment by increased bond strength introduced by crosslinking but deteriorates fast because of a decrease in individual fiber strength by degradation of glucosidic bonds [32]. The presence of alkali metal cations (e.g.  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) complexes with glycosidic oxygen (C–O bond) has been shown to accelerate the rate of chain scission [33,34]. In addition the autooxidation of cellulose is catalyzed by the transition metal cations, since formation of metal hydroxides in the presence of water introduces hydrogen ions, which further promote hydrolysis of linkages and cross-linking [18,30]. Among these

factors, the rate of oxidation depends on pH, temperature, and access to oxidizing agents [35].

This research aimed at implementing a method that would enable the study of the degradation of paper at high temperatures in the presence of water vapor. Systematic results from the isothermal treatments were obtained with different high density papers with and without residual lignin at 175–300 °C and 1–98% volume fraction of water vapor. The introduced thermal treatment procedure has allowed the examination of the effect of water vapor on the thermal degradation of cellulosic pulps at high temperatures, providing sufficient sample amounts for standard paper analyses [36]. In the presence of water vapor, the implemented device enables to reach thermal treatment temperatures that are higher than with conventional climate chambers. The present study introduces a novel method for studying the thermal degradation of paper sheets at high temperatures and in both dry and humid conditions.

## 2. Materials and methods

### 2.1. Materials

Metsä Tissue, Düren (Germany) provided fully bleached high density paper (FHD) from kraft pulp in a grammage of 45.6 g/m<sup>2</sup>. Siliconized unbleached high density paper (UHD) in a grammage of 45.0 g/m<sup>2</sup> was commercially available baking paper. These paper grades were selected to study the performance of the atmospheric oven chamber at different temperatures and volume fraction of water vapor ( $\phi_{\text{H}_2\text{O}}$ ). In addition, oxygen delignified (OD), and fully bleached (FB, bleaching sequence DE<sub>EP</sub>DP) softwood kraft pulps (80% pine, 20% spruce) were studied for evaluating the development of the strength properties during thermal treatments. OD and FB pulps were supplied by Metsä Fibre, Kemi (Finland). Industrially refined fully bleached (IR-FB) kraft pulp with Schopper-Riegler number ( $^{\circ}\text{SR}$ ) 84 was investigated as an industrially refined reference pulp, provided by Metsä Tissue, Mänttä (Finland). Development of the degree of polymerization (DP) during thermal treatments was evaluated with non-refined fully bleached (NR-FB, bleaching sequence DE<sub>EP</sub>DP) pine kraft pulp with  $^{\circ}\text{SR}$  14, supplied by Metsä Fibre, Rauma (Finland).

### 2.2. Hypochlorous acid modification

Carbonyl groups are known to enhance the thermal yellowing of cellulosic pulps [37]. Hypochlorous acid oxidation, based on the method described by Zhou et al. [29], was adopted to increase the amount of carbonyl groups in the fully bleached pulp. Wet disintegration (30,000 rounds) was performed for 200 g of oven dried pulp before heating the pulp with water in an aqueous solution at 100 °C. Sodium acetate buffer was prepared by adding 0.5 M sodium hydroxide into 1.0 M acetic acid solution until pH reached a value of 5.0. 60 mL of this solution was applied to buffer the pulp suspension at pH 5, after which the pulp was placed into a MC mixer and sodium hypochlorite (NaOCl) solution was added to generate 0.4% charge of active chlorine on the dry weight of the pulp. The final consistency of the pulp suspension was 10%. The oxidation reaction time was 1 h at 50 °C. After the treatment, the hypochlorous acid modified (FBH) pulp was washed with 8 L of deionized water to stop the reaction.

### 2.3. Refining

Intensive refining for OD, FB and FBH pulps was performed to imitate high density papers. Before laboratory refining, pulps were disintegrated according to the standard method ISO 5263. Refining

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