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Effect of relative humidity on thermal degradation of Norway spruce (*Picea abies*) wood

Abstract The rate of thermal degradation of wood as a function of the extent of heat-bath treatment was investigated. At both 150°C and 170°C, the rate of degradation increased along with increasing relative humidity in the heating atmosphere. However, up to intermediate relative humidity (in the vicinity of 50%), the higher the temperature, the less was the effect of increasing relative humidity on the degradation rate. Furthermore, the greater the relative humidity, the less was the effect of increasing temperature on the degradation rate. On the other hand, between intermediate relative humidity and water-saturated conditions, the effect of increasing relative humidity on the degradation rate was the same regardless of the temperature, and the effect of increasing temperature on the degradation rate was the same regardless of the relative humidity. In moist conditions, significant thermal degradation occurred at temperatures as low as 150°C.

Key words Activation energy · Heat treatment · Relative humidity · Temperature · Thermal degradation

Introduction

Wood drying at temperatures above 100°C is known as high-temperature drying. As compared with conventional drying, it considerably shortens drying times, and thus production costs may be reduced. However, the exposure of wood to elevated temperatures can cause thermal degradation of its structure; that is, changes in composition, often accompanied by loss of mass. The cost in wood quality due to thermal degradation may then offset the lower produc-

tion costs. Otherwise, thermal degradation is utilized commercially, in heat treatment processes, to produce wood products with improved dimensional stability and reduced hygroscopicity.[1–5]

At temperatures between 100°C and 200°C, heating of wood produces water vapor, carbon dioxide, and traces of organic compounds.[6,7] Above 200°C, significant thermal degradation takes place, with major mass loss occurring beyond 250°C.[8–11] Lignin is recognized as the most thermally stable polymer of the three main wood components, and thus is more difficult to degrade than carbohydrates. Among the carbohydrates, hemicelluloses degrade more easily than cellulose, presumably due to a lower degree of polymerization, a nonlinear configuration, and a lack of crystallinity. As indicated by thermogravimetric analyses under an inert atmosphere, hemicelluloses, cellulose, and lignin degrade extensively in the temperature ranges of 250°–350°C, 300°–400°C, and 250°–450°C, respectively.[8]

The extent of thermal degradation depends on the temperature and on the duration of the exposure.[9,11,12] In addition, the presence of air (oxygen), acids, and water accelerates thermal degradation. The presence of air accelerates degradation because of oxidation reactions.[13] Carboxylic acids, mainly acetic acid, released during the heating of wood catalyze the degradation of polysaccharides by means of acidic hydrolysis.[14–17] In a closed system, thermal degradation is higher because of the increasing concentration of such acids.[13]

The presence of water not only catalyzes the hydrolysis of hemicelluloses,[18,19] but also appears to decrease the temperature levels at which thermal degradation is significant.[13,20] Sensitivity of wood to elevated temperatures increases as its moisture content increases. Therefore, a deeper knowledge of this phenomenon may be of importance for developing high-temperature drying processes. The objective of this study was to investigate the effect of relative humidity on thermal degradation. Spruce wood was subjected to atmospheres with different temperatures and relative humidity, and the losses of mass were measured. The combined effect of relative humidity and temperature on the thermal degradation is reported.

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Experimental

The wood material used in this study was Norway spruce *(Picea abies)* felled in Joensuu, Finland. Wood specimens with dimensions of 24 × 24 mm in cross section and 320 mm in length were prepared. All specimens were clear of visible flaws. Twenty-four groups containing 12 specimens each were formed, and each group was subjected to a particular heat-bath treatment. Heat-bath treatments were conducted in a stainless steel pressure vessel of 20 l in volume, equipped with a temperature gauge and a pressure gauge. To block direct radiation from the steel onto the specimens, a sheet of aluminum was positioned at the bottom and around the walls of the vessel.

Each group of specimens was oven-dried at 85°C for 48 h before the heat-bath treatment, and the mass of any specimen was measured. Dry masses were determined by further drying an additional group of reference specimens at 85°C for 48 h and subsequently at 103°C for 24 h. The specimens were then placed in the vessel along with a predetermined amount of liquid water. The temperature in the vessel was raised from an initial temperature of about 35°C up to the setup temperature. Water vapor pressure and consequent relative humidity were determined by subtracting air pressure from the total pressure. Once the setup temperature was reached, the specimens were subjected to isothermal treatment, at the end of which the vessel was allowed to cool to room temperature (Fig. 1). Heat-treated specimens were oven-dried at 85°C for 48 h and subsequently at 103°C for 24 h. Mass loss of any specimen was determined on a dry mass basis after drying at 103°C for 24 h. The experimental parameters and the mass loss for each heat-bath treatment are shown in Table 1.

Data analysis

The rate of temperature increment during heating was determined by the relative humidity in the atmosphere (Fig. 2), the heating efficiency being limited by the heat transfer efficiency of the system. Thus, the extent of any
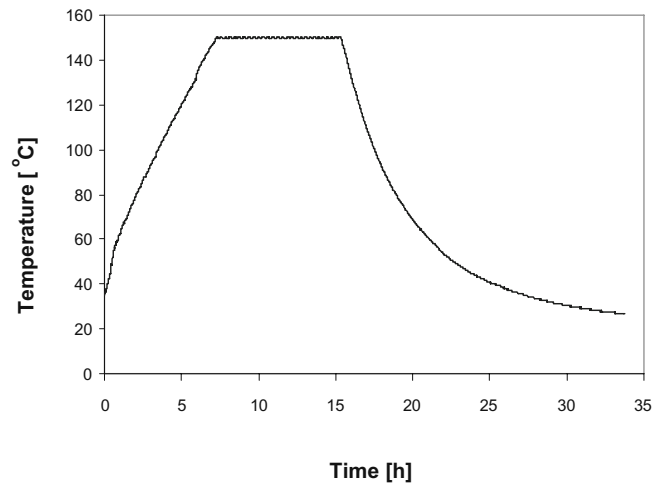

Fig. 1. Example of temperature change in the vessel for the entire heat-bath treatment. The example corresponds to a heat-bath of 8 h at 150°C in water-saturated conditions

Table 1. Process parameters and loss of mass for each heat-bath treatment

Setup temperature (°C)	Liquid water added into vessel[a] (g)	Relative humidity[b] (%)	Isothermal treatment (h)	Loss of mass (%)
120	–	15	0	–
	–	9	2	–
	–	5	8	–
	1000	100	0	–
	1000	100	2	–
	1000	100	8	–
150	–	8	0	–
	–	8	2	0.2 (0.3)
	–	8	8	0.4 (0.3)
	75	60	0	0.6 (0.2)
	75	51	2	1.0 (0.2)
	75	57	8	2.1 (0.3)
	1000	100	0	1.8 (0.5)
	1000	100	2	3.0 (0.7)
	1000	100	8	6.9 (1.3)
170	–	10	0	1.5 (0.5)
	–	15	2	2.1 (0.7)
	–	15	8	2.8 (0.9)
	65	55	0	2.4 (0.4)
	65	50	2	3.2 (0.5)
	65	61	8	7.2 (0.5)
	1000	100	0	6.2 (0.9)
	1000	100	2	10.9 (1.0)
	1000	100	6	15.3 (0.8)

Standard deviations are indicated in parentheses
[a] An additional amount of about 8 g of water was contained within any group of specimens
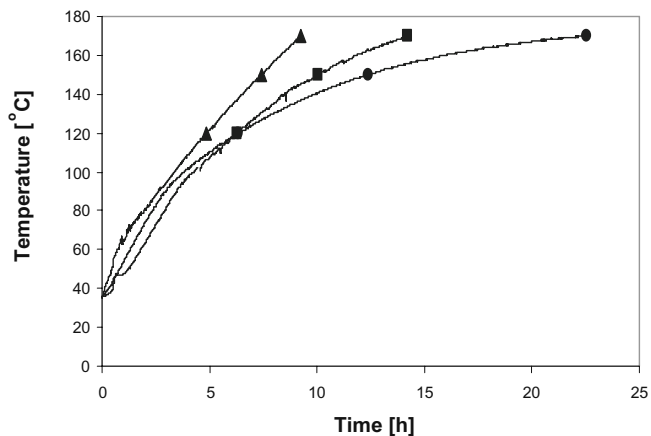[b] Relative humidity computed at the instant of reaching the setup temperature

Fig. 2. Rate of temperature increment during heating in different relative humidity conditions. *Circles*, relative humidity range 5%–15%; *squares*, relative humidity range 50%–61%; *triangles*, water-saturated conditions

Fig. 3. Plots of $\ln(m_f/m_0)$ versus extent of heat-bath treatment for **a** setup temperature 150°C and **b** setup temperature 170°C. *Symbols* are the same as in Fig. 2. *Bars* indicate 95% confidence intervals

heat-bath treatment, including heating, isothermal, and cooling stages, was computed as:

$$H = \int_0^{t_f} (T(t) - T_0)dt \tag{1}$$

for $T(t) - T_0 \geq 0$, where H [°C · h] is the extent of heat-bath treatment, $T(t)$ [°C] is the temperature in the vessel at time t, T_0 [°C] is a reference temperature, and t_f [h] is the duration of the process. The reference temperature was defined as the highest temperature at which mass loss does not occur, regardless of relative humidity conditions. A reference temperature of 120°C was chosen based on the data in Table 1.

The rate of mass loss as a function of the extent of heat-bath treatment was approached as a first-order reaction:

$$\frac{-dm}{dH} = Km \tag{2}$$

where m [g] is the mass of wood, and K [°C · h]$^{-1}$ is the reaction rate constant. By integrating Eq. 2, we obtain:

$$\ln m = -KH + C \tag{3}$$

where C is the integration constant; for $H = 0$, $C = \ln m_0$, where m_0 is the initial mass of wood. Substituting and rearranging, Eq. 3 can be rewritten as:

$$\ln \frac{m_f}{m_0} = -KH \tag{4}$$

where m_f is the final mass of wood after the treatment.

The plots of $\ln(m_f/m_0)$ versus the extent of heat-bath treatment for setup temperatures of 150°C and 170°C are shown in Fig. 3. Data are grouped according to relative humidity. Linearity indicates that the reaction rate within any relative humidity interval is accurately determined by Eq. 4. Furthermore, it indicates that the reaction rate is independent of reaction time. Therefore, degradation kinetics appears to be characterized by the setup temperature and the relative humidity in the heating atmosphere. It is,
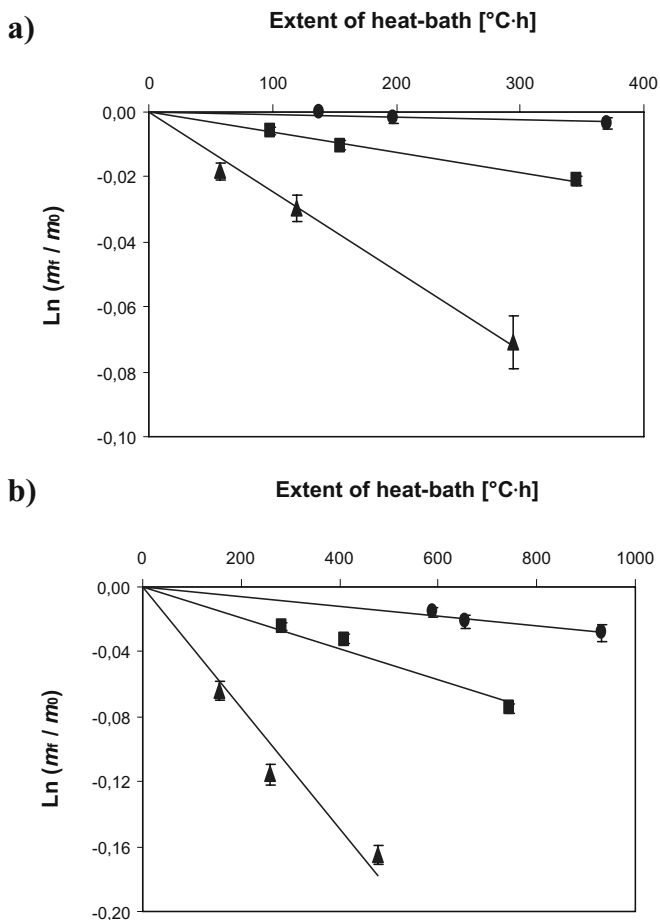
however, worth noting that the apparent linearity of the logarithm of residual mass as a function of the extent of heat-bath treatment depends on the choice of the reference temperature T_0.

Results and discussion

The rate of thermal degradation of wood as a function of relative humidity for setup temperatures of 150°C and 170°C is plotted in Fig. 4. The reaction rate was computed independently for every heat-bath treatment. At both setup temperatures, the rate of degradation increased, seemingly exponentially, with increasing relative humidity in the heating atmosphere. It is known that between 100°C and 200°C, heating of wood produces water vapor and noncombustible products such as carbon dioxide and carboxylic acids, mainly acetic acid.[6,7] These degradation products may increase the pressure in a closed vessel, which was indeed observed during the isothermal phases of the experiments (Fig. 5). The formation of acetic acid, which results from the thermolysis of the acetyl groups linked to the xylose
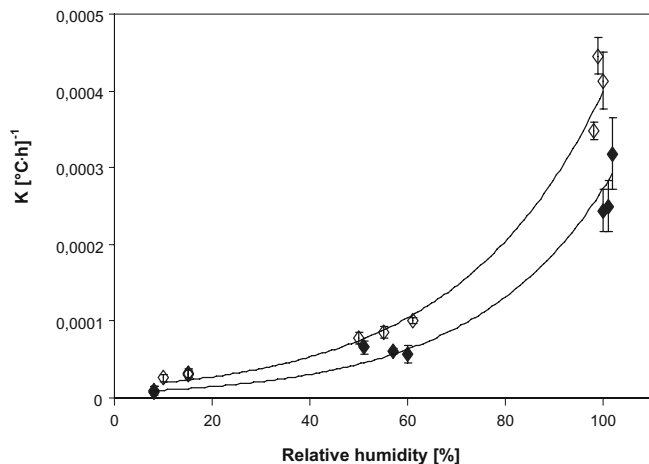
Fig. 4. Rate of degradation as a function of relative humidity. *Filled symbols*, setup temperature 150°C; *open symbols*, setup temperature 170°C. *Bars* indicate 95% confidence intervals. Data regarding water-saturated conditions have been slightly shifted along the *x*-axis for visual clarification
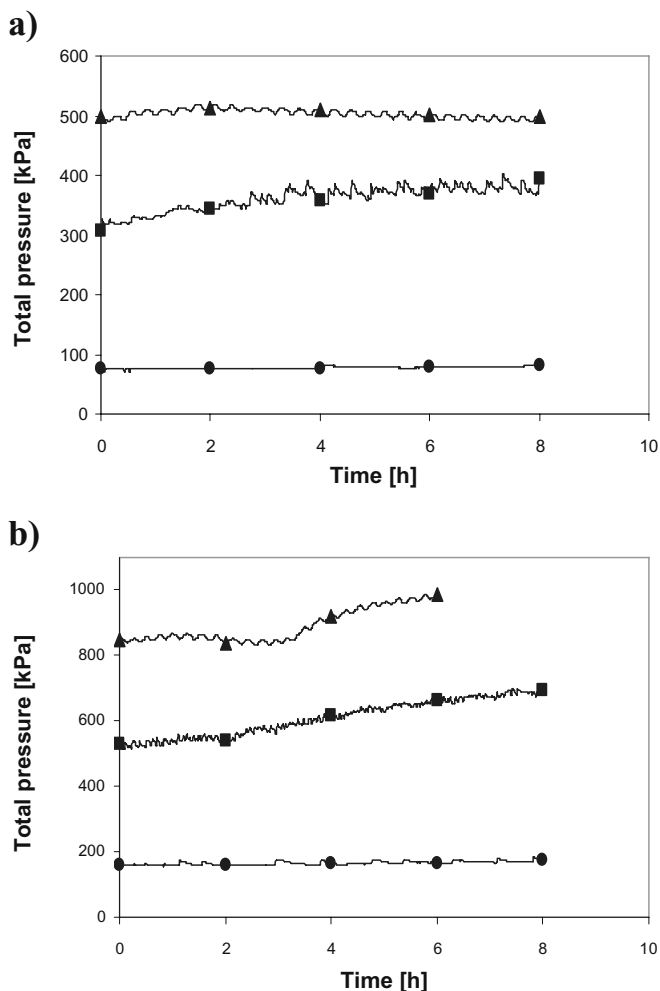
a)

b)

Fig. 5. Examples of pressure change in the vessel during the 8-h isothermal phase of the experiments. **a** Setup temperature 150°C; **b** setup temperature 170°C. *Symbols* are the same as in Fig. 2

units of the hemicelluloses,[21,22] further catalyses the degradation of amorphous carbohydrates, reducing their degree of polymerization.[14–17] In the presence of water, the formation of acetic acid is accelerated because the hydronium ions generated by water autoionization catalyze the splitting of acetyl groups.[18,19] Obviously this is likely to increase the rate of degradation in wood, as observed in Fig. 4.

In dry conditions (relative humidity range 5%–15%), the mean value of the degradation rate was $8.75 \times 10^{-6}°C^{-1} \cdot h^{-1}$ at 150°C and $2.94 \times 10^{-5}°C^{-1} \cdot h^{-1}$ at 170°C. At intermediate relative humidity (50%–61%), the mean value of the degradation rate was $6.13 \times 10^{-5}°C^{-1} \cdot h^{-1}$ at 150°C and $8.80 \times 10^{-5}°C^{-1} \cdot h^{-1}$ at 170°C. These reaction rates indicate that thermal degradation at intermediate relative humidity, as compared with dry conditions, is three times faster at a setup temperature of 170°C, but seven times faster at 150°C. Thus, it appears that up to intermediate relative humidity, the lower the temperature, the more significant is the increase in the reaction rate as relative humidity increases. Chemical reaction rates in food products have been reported to increase along with increasing molecular mobility of the reactants.[23,24] High temperatures tend to soften the wood polymers, thus increasing their mobility. The softening point at which amorphous polymers change from a glassy state to a rubbery state is denoted as the glass transition temperature. In a dry climate, the softening of the hemicelluloses is reported to take place in the vicinity of 180°C, but along with increasing relative humidity, the glass transition temperature is reduced.[14,25] During a heat-bath treatment in dry conditions, hemicelluloses are expected to be rather stiff at 150°C, but somewhat more viscous at 170°C. Therefore, the effect of increasing relative humidity on the degradation rate is likely to be more significant at 150°C because hemicelluloses will be plasticized.

In water-saturated conditions, the mean value of the degradation rate is $2.70 \times 10^{-4}°C^{-1} \cdot h^{-1}$ at 150°C and $4.02 \times 10^{-4}°C^{-1} \cdot h^{-1}$ at 170°C. Accordingly, thermal degradation in water-saturated conditions is about 4.5 times faster than at intermediate relative humidity, irrespective of the setup temperature. This might be due to the fact that during a heat-bath treatment at intermediate relative humidity, hemicelluloses are in a viscous state at both 150°C and 170°C. Increasing relative humidity up to saturated conditions increases the rate of degradation, but the effect is expected to be the same at both temperatures because the hemicelluloses hardly change their state. Thus, from dry to water-saturated conditions, the increase in the degradation rate along with increasing relative humidity cannot be a simple exponential function.

On the other hand, temperature dependency of a reaction rate is often described in terms of activation energy, which can be computed by means of the Arrhenius equation. In the present case, however, the frequency factor of the equation must be replaced by a constant with dimension that is inverse to the dimension of the extent of heat-bath treatment H. The modified Arrhenius equation is:

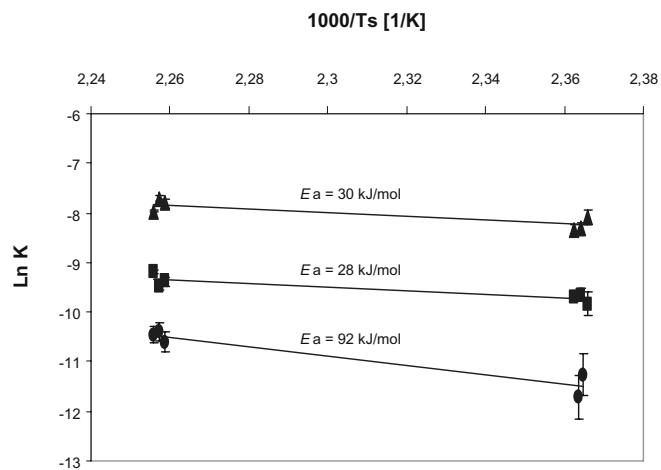$$K = A \exp^{\frac{-E_a}{RT_s}} \tag{5}$$

1000/Ts [1/K]

Fig. 6. Temperature dependency of the degradation rate in different relative humidity conditions. *Symbols* are the same as in Fig. 2. *Bars* indicate 95% confidence intervals. Data have been slightly shifted along the *x*-axis for visual clarification

carefully schedule drying temperatures according to moisture conditions.

where K $[°C \cdot h]^{-1}$ is the reaction rate, A $[°C \cdot h]^{-1}$ is a pre-exponential factor replacing the frequency factor, E_a [kJ/mol] is the apparent activation energy, R is the universal gas constant $(8.31\ J \cdot mol^{-1} \cdot K^{-1})$, and T_S [K] is the setup temperature. Equation 5 can then be rewritten as:

$$\ln K = \ln A - \frac{E_a}{R}\frac{1}{T_S} \tag{6}$$

and, as shown in Fig. 6, plotting ln K versus the reciprocal of the setup temperature for each relative humidity interval results in a straight line, with the slope E_a/R and the intercept ln A.

According to Fig. 6, the apparent activation energy in a dry climate is the highest, which means that the temperature dependency of the degradation rate in dry conditions is higher than in moist conditions. Similar results have been reported by Stamm.[13] Furthermore, heating of wood at intermediate relative humidity or in water-saturated conditions gives similar apparent activation energies (Fig. 6). In other words, up to intermediate relative humidity, the dryer the climate, the higher is the temperature dependency of the degradation rate. However, between intermediate relative humidity and water-saturated conditions, the temperature dependency appears to be the same. This is in agreement with the effect of increasing relative humidity on the degradation rate being the same regardless of the setup temperature.

Relative humidity plays an important role in thermal degradation of wood. Increasing relative humidity not only increases the rate of degradation of wood components, but also reduces the temperature level at which thermal degradation occurs. For instance, significant mass loss occurs when wood is exposed for several hours to atmospheres with high relative humidity and temperatures as low as 150°C. In dry conditions, however, mass loss at the same temperature is negligible. To avoid or minimize thermal degradation, high-temperature drying processes should

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