

THERMAL BEHAVIOR OF SCOTS PINE (*PINUS SYLVESTRIS*) AND SILVER BIRCH (*BETULA PENDULA*) AT 200–230°C

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ABSTRACT

Scots pine (*Pinus sylvestris*) and silver birch (*Betula pendula*) were heated for 4–8 h in a steam atmosphere at low temperatures (200–230°C). The birch feedstock decomposed slightly more extensively (6.4–10.2 and 13.5–15.2% of the initial DS at 200°C and 225°C, respectively) than the pine feedstock (5.7–7.0 and 11.1–15.2% at 205°C and 230°C, respectively). The results indicated that the differences in mass loss between these feedstocks were due to mainly the fact that carbohydrates (cellulose and hemicelluloses) were more amenable to various degradation reactions than lignin in intact wood. The degradation reactions were also monitored in both cases by determining changes in the elemental composition of the heat-treated products.

Keywords: Heat treatment, carbohydrates, lignin, extractives, *Pinus sylvestris*, *Betula pendula*.

INTRODUCTION

In our previous experiments (Alén et al. 2000), the thermal degradation of the structural constituents (lignin and polysaccharides, i.e., cellulose and hemicelluloses) of Norway spruce (*Picea abies*) was established under conditions (temperature range 180–225°C, heating time 4–8 h) relevant to the industrial process of stabilizing wood against fungal attack (Dirol and Guyonnet 1993; Viitaniemi and Jämsä 1996). However, the lignin and hemicelluloses present in softwood differ slightly chemically from those in hardwood (Fengel and Wegener 1989; Sjöström 1993). In addition, softwood generally contains more lignin (25–30% of dry solids (DS)) and lower

content of hemicelluloses (25–30% of DS) than hardwood (lignin and hemicelluloses are usually in the range 20–25 and 30–35% of DS, respectively). On the basis of these facts, the thermal behavior of softwood and hardwood can be expected to be different, even at low temperatures. Clearly, a better understanding of these differences will be of benefit to the development of heat-treatment processes.

The primary aim of this study was to find out what differences exist in the thermal behavior of Scots pine (*Pinus sylvestris*) and silver birch (*Betula pendula*) under conditions similar to those of our earlier experiments (Alén et al. 2000). The study focused on the changes occurring in the chemical composition of these feedstocks during heating at 200–230°C with particular emphasis on polysaccharide degradation.

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TABLE 1. Some characteristics of the wood feedstocks used (% of DS).

Relative composition of the main components	Pine (<i>Pinus sylvestris</i>)	Birch (<i>Betula pendula</i>)
Carbohydrates*	72.3	75.6
Lignin	24.5	21.8
Extractives	3.2	2.6
Elemental analysis		
Carbon	47.8	47.3
Hydrogen	6.7	6.4
Nitrogen	0.1	0.1
Oxygen*	45.4	46.2

* Calculated by difference.

EXPERIMENTAL

Wood material and the heat treatments

The wood feedstocks used were air-dried and bark-free Scots pine (*Pinus sylvestris*) and silver birch (*Betula pendula*). The basic characteristics of these wood samples are presented in Table 1.

The heat treatments were carried out at VTT (Technical Research Center of Finland), in the Section of Building Technology. The treatment system consisted of a temperature-controlled tube furnace in which pine and birch wood boards (22 mm × 100 mm × 1500 mm) were positioned so that each board had sufficient space around it and maintained in a steam atmosphere under the conditions shown in Table 2. Before the heat treatments commenced, the boards were stabilized at 65% RH and had a moisture content about 11%.

For the chemical analyses, the untreated and treated wood samples were ground in a Cyclotec 1093 sample mill (Tecator, Inc.) and sieved through a round-holed screen using the <1 mm fraction.

Analytical determinations

The analysis of the untreated and treated wood samples was based on well-established methods in wood chemistry. The lignin content was determined as the sum of acid-insoluble Klason lignin (TAPPI T-249 cm-85) and acid-soluble lignin (TAPPI UM-250). The extractive content was determined by extracting

sample first with acetone (4 h) and then with dichloromethane (4 h) in a Soxhlet apparatus. The elemental analysis (carbon, hydrogen, and nitrogen) was performed using a micro-elemental analyzer (LECO CHN-600). The oxygen content was calculated by difference (100% - C% - H% - N%). The amount of DS was measured by drying a sample at 105°C for 12 h.

The composition of monosaccharides in the hydrolyzate obtained from the lignin determination was analyzed on the basis of their per(trimethylsilyl)ated derivatives by GC (Biermann and McGinnis 1989). A J & W DB-1701 fused silica capillary column (60 m × 0.32 mm with a film thickness of 0.17 μm) was employed. The temperature program was 2 min at 100°C, 2°C min⁻¹ to 185°C, 15 min at 185°C, 39°C min⁻¹ to 300°C, and 5 min at 300°C. Hydrogen as a carrier gas (1.6 ml min⁻¹) and xylitol as an internal standard were used. The temperature of both the injection port and the detector was 300°C. The relative retention times for the different anomers of the pyranoid and furanoid wood monosaccharides compared with the internal standard were determined by model compounds. For the quantitative calculations, the response factors between the internal standard (1.00) and the peaks derived from arabinose, xylose, galactose, glucose, and mannose were 1.25, 1.22, 1.19, 1.17, and 1.26, respectively.

RESULTS AND DISCUSSION

Table 1 shows the chemical composition of the softwood and hardwood feedstocks used. Although not analyzed in detailed here, it is well known (Fengel and Wegener 1989; Sjöström 1993) that pine contains more glucomannans (15–25% of DS) and less xylans (5–10% of DS) than birch, the average content of glucomannans and xylans in birch is 2–5% of DS and 15–30% of DS, respectively.

In contrast to the variation in hemicellulose content, it can be assumed that both feedstocks have an equal cellulose content (about 40% of DS). There are also some characteristic chem-

TABLE 2. Mass loss of the wood feedstocks during heat treatments (% of initial).

Pine (<i>Pinus sylvestris</i>)			Birch (<i>Betula pendula</i>)		
Heat treatment (°C/h)	Total mass loss	Total mass loss of carbohydrates	Heat treatment (°C/h)	Total mass loss	Total mass loss of carbohydrates
205/4	5.7	13.8	200/4	6.4	15.9
205/6	6.8	13.4	200/6	7.1	19.9
205/8	7.0	17.0	200/8	10.2	26.7
230/4	11.1	23.7	220/4	13.5	35.5
230/6	13.2	29.7	220/6	14.7	35.7
230/8	15.2	32.7	220/8	15.2	36.9

ical differences between softwood and hardwood hemicelluloses. Furthermore, softwood and hardwood lignins and the fractions of the extractives in softwood and hardwood differ typically from each other (Fengel and Wegener 1989; Sjöström 1993).

The total mass loss of the pine samples during heating at 205°C and 230°C varied in the range 5.7–7.0 and 11.1–15.2% of the initial DS (Table 2), respectively, revealing the clear bearing of temperature on overall mass loss. Furthermore, birch samples decomposed slightly more extensively than the pine samples; at 200°C and 225°C the corresponding mass losses in the birch samples were in the range 6.4–10.2 and 13.5–15.2% of the initial DS, respectively. This can be explained partly by the fact (Alén et al. 1995b) that carbohydrates are in general degraded to a greater extent during heating than lignin (cf. the higher content of carbohydrates in intact birch wood, see Table 1) (Fig. 1 and Table 2). However, it is also likely that differences in the chemical

structures of the hemicelluloses had an important influence on the thermochemical behavior of the feedstocks studied. For example, it has been shown (Radlein et al. 1991; Alén et al. 1995a) that xylans (rich in birch) degrade on heating more easily than glucomannans (rich in pine). In addition, the monosaccharide content of the heat-treated samples (Fig. 2) suggested, as expected, that under the conditions studied, cellulose (a linear homopolysaccharide of β -D-glucopyranose moieties) was thermally more stable than the hemicelluloses.

During heating, a multitude of chemical reactions on the part of the individual wood constituents take place (Antal 1983; Shafizadeh 1985; Elder 1991; Radlein et al. 1991; Boon et al. 1994; Emsley and Stevens 1994; Ponder and Richards 1994; Alén et al. 1995a). For example, it should be pointed out that lignin and carbohydrates are gradually converted into volatiles and “extractive-like material,” which in turn is partly degraded together with the orig-

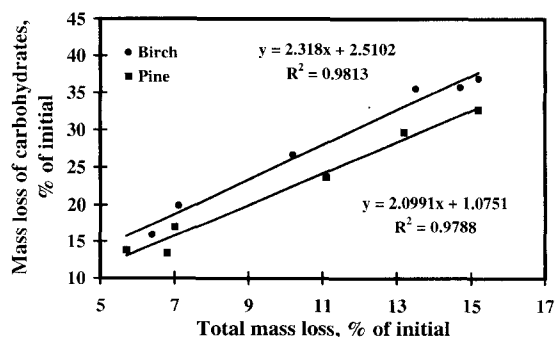


FIG. 1. Mass loss of carbohydrates vs. total mass loss in the treated pine and birch samples.

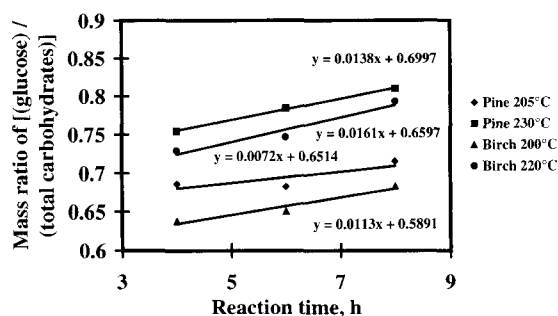


FIG. 2. Change in mass ratio of [(glucose)/(total carbohydrates)] in the wood feedstocks during the heat treatments. The mass ratio value for the untreated pine and birch samples was 0.64 and 0.55, respectively.

TABLE 3. Total amount of lignin, extractives, and carbohydrates in the heat-treated wood samples (% of DS).

Pine (<i>Pinus sylvestris</i>)				Birch (<i>Betula pendula</i>)			
Heat treatment (°C/h)	Lignin	Extractives	Carbohydrates*	Heat treatment (°C/h)	Lignin	Extractives	Carbohydrates*
No treatment	24.5	3.2	72.3	No treatment	21.8	2.6	75.6
205/4	30.1	3.8	66.1	200/4	26.3	5.7	68.0
205/6	30.5	2.7	66.8	200/6	28.1	6.7	65.2
205/8	32.3	3.2	64.5	200/8	30.6	7.8	61.6
230/4	35.0	3.0	62.0	220/4	35.4	8.3	56.3
230/6	37.1	4.4	58.5	220/6	35.1	8.0	56.9
230/8	38.7	3.8	57.5	220/8	35.8	8.0	56.2

* Calculated by difference.

inal extractives, into various volatile products (cf. Alén et al. 1996). In addition, the heating of carbohydrates probably led to some extent to the formation of unsaturated nonvolatile material (i.e., UV-detectable “lignin-like material”). For this reason, it was difficult to draw definite conclusions concerning the degradation of the individual wood components during the treatments, thus complicating the interpretation of the composition data in Table 3.

However, these data indicated that, as a general trend, the steady increase in relative mass proportion of lignin was accompanied by a simultaneous decrease in the relative mass proportion of carbohydrates during heating at all temperatures and in both feedstocks. It should also be pointed out that a relatively high mass proportion of “extractives” was formed in case of the birch experiments. This finding can best be explained by the assumption that birch lignin, as a lower-molecular-mass material compared to pine lignin, also degraded more

easily to low-molecular-mass conversion products (i.e., to different extractable compounds) than pine lignin.

The relative mass proportion of carbon in the heat-treated samples increased in all experiments along with increasing temperature and duration of treatment and was accompanied by a corresponding decrease in the mass proportion of oxygen (Table 4). This finding was in good accordance with the earlier observation that “oxygen-rich” carbohydrates were more amenable to various degradation reactions than the “oxygen-poor” and mainly aromatic moiety-containing lignin fragments. This general trend can also easily be confirmed when either total mass loss of the heat-treated sample is depicted as a function of the change in oxygen content in the heat-treated product or the change in the mass ratio of carbon to oxygen as a function of total mass loss (Figs. 3 and 4).

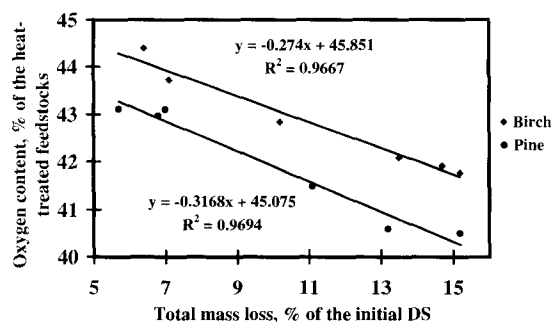


FIG. 3. Total mass loss vs. oxygen content in the heat-treated wood samples.

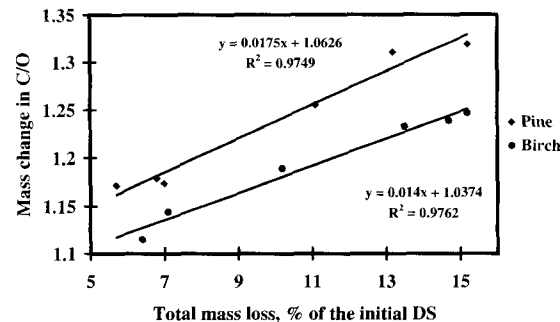


FIG. 4. Change in the carbon-to-oxygen mass ratio vs. total mass loss of the heat-treated samples.

TABLE 4. *Elemental analysis of the initial and the treated wood samples (% of DS).**

Pine (<i>Pinus sylvestris</i>)				Birch (<i>Betula pendula</i>)			
Heat treatment (°C/h)	Carbon	Hydrogen	Oxygen**	Heat treatment (°C/h)	Carbon	Hydrogen	Oxygen**
No treatment	47.7	6.5	45.7	No treatment	47.2	6.5	46.2
205/4	50.5	6.2	43.1	200/4	49.5	6.0	44.4
205/6	50.7	6.2	43.0	200/6	50.0	6.2	43.7
205/8	50.6	6.2	43.1	200/8	50.9	6.1	42.8
230/4	52.1	6.2	41.5	220/4	51.9	5.9	42.1
230/6	53.2	6.1	40.6	220/6	51.9	6.1	41.9
230/8	53.4	6.0	40.5	220/8	52.1	5.9	41.8

* Nitrogen content was < 0.2% in all samples.
 ** Calculated by difference.

CONCLUSIONS

In this study pine and birch feedstocks were heated at 200–230°C for 4–8 h in a steam atmosphere to stabilize these materials against fungal attack. The most important findings were:

The birch samples decomposed slightly more extensively than the pine samples

Both temperature and treatment time had a clear bearing on the overall mass loss in the case of both feedstocks

Carbohydrates (cellulose and hemicelluloses) were more amenable to various degradation reactions than lignin in intact wood material

Cellulose was thermally more stable than hemicelluloses (glucomannans and xylans)

The thermal decomposition of wood material can easily be monitored by elemental analysis.

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