

EFFECT OF THERMAL TREATMENT ON THE CHEMICAL COMPOSITION AND MECHANICAL PROPERTIES OF BIRCH AND ASPEN

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The high temperature treatment of wood is one of the alternatives to chemical treatment. During this process, the wood is heated to higher temperatures than those of conventional drying. The wood structure changes due to decomposition of hemicelluloses, ramification of lignin, and crystallization of cellulose. The wood becomes less hygroscopic. These changes improve the dimensional stability of wood, increase its resistance to micro-organisms, darken its color, and modify its hardness. However, wood also might lose some of its elasticity. Consequently, the heat treatment conditions have to be optimized. Therefore, it is important to understand the transformation of the chemical structure of wood caused by the treatment. In this study, the modification of the surface composition of the wood was followed with Fourier transform infrared spectroscopy (FTIR) and inverse gas chromatography (IGC) under different experimental conditions. The effect of maximum treatment temperatures on the chemical composition of Canadian birch and aspen as well as the correlations between their chemical transformation and different mechanical properties are presented. FTIR analysis results showed that the heat treatment affected the chemical composition of birch more compared to that of aspen. The results of IGC tests illustrated that the surfaces of the aspen and birch became more basic with heat treatment. The mechanical properties were affected by degradation of hemicellulose, ramification of lignin and cellulose crystallization.

Keywords: Heat treatment; Birch; Aspen; Chemical composition; FTIR; Mechanical properties

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INTRODUCTION

Solid wood is a versatile and renewable material that is widely used in different applications. However, due to the hygroscopic nature of wood it has some undesirable properties such as poor resistance against biological attack of fungi and insects, and swelling and shrinkage caused by water adsorption and desorption. These limit the outdoor applications of wood. Chemical treatment of wood is the most common preservation method (Hingston et al. 2001), which causes toxic emissions during production, service life and after use. Thermal treatment method can be an alternative to the preservation methods using chemical agents. In fact, various thermal treatment methods have been commercialized in Europe, such as Thermowood in Finland, Plato in

Holland, and Bois-Perdure in France (Vernois 2001; Syrjanen et al. 2001; Militz 2002; Chanrion and Schreiber 2002). It is also starting to gain importance in North America (Kocaefe et al. 2007; Poncsak et al. 2006).

Thermal treatment of wood is carried out at higher temperatures (150-240°C) than those of a conventional drying process. This treatment not only removes water from wood but also causes significant transformation in the chemical composition of wood. Chemical modification and degradation of wood components take place through dehydration, hydrolysis, oxidation, decarboxylation, and transglycosylation, and the wood becomes less hygroscopic. The possibility of the re-absorption of the water decreases, and the dimensional stability increases (Dirol and Guyonnet 1993; Alén et al. 2002; Pavlo and Niemz 2003). The hemicelluloses are the most reactive components of the cell wall. In fact, due to their relatively low molecular weight, they degrade at lower temperature (160-220°C) than the other components (Fengel and Wegener 1989). Ramification of lignin takes place (Burmester 1975; Bobleter and Binder 1980; Tjeerdsma et al. 1998; Sivonene et al. 2002; Weiland and Guyonnet 2003; Nuopponen et al. 2004; Repellin and Guyonnet 2005; Hakkou et al. 2005) and the relative amount of the crystalline cellulose increases due to the degradation of the amorphous components at this temperature range. This also affects the hardness of the wood. However, certain mechanical properties of the wood decrease during the heat treatment (Santos 2000; Chanrion and Schreiber 2002; Yildiz et al. 2002). The changes taking place in wood molecular structure due to decomposition of the long polymers can cause a decrease in the elasticity, and the wood becomes more fragile. The moisture content of wood and some water soluble products of the heat treatment (such as organic acids) promote the degradation of long chains by hydrolysis (Fengel and Wegener 1989; Chanrion and Schreiber 2002; Gosselink et al. 2004).

The objective of this study is to investigate the chemical modifications of Canadian white birch (*Betula papyrifera*) and quaking aspen (*Populus tremuloides*) during heat treatment. The chemical modifications of hemicelluloses, lignin and extractives in treated wood samples were examined with FTIR and IGC. The correlations between the chemical modifications, maximum heat treatment temperature and the mechanical properties of the wood were also investigated.

EXPERIMENTAL AND DATA ANALYSIS

Wood Samples

White birch (*Betula papyrifera*) and quaking aspen (*Populus tremuloides*) coming from a local saw mill were utilized in thermal treatment studies. The pre-dried wood samples contained 7–12 % of moisture before the thermal treatment. After the treatment, the moisture content decreased to 2-3 %. In all cases, the higher maximum heat treatment temperature resulted in lower final moisture content in wood.

Heat Treatment Process

Canadian birch and quaking aspen wood samples (35 x 35 mm in cross section and 20 cm in length) were heat-treated in a thermo-gravimetric furnace. The samples,

which were suspended from a balance into a furnace, were heated with hot inert gas, and the change of their weight with time was recorded during the tests. The gas contained 80% of nitrogen and 20% of carbon dioxide. Above 100 °C, 100 g/m³ water vapor was added to the gas mixture. Nitrogen assures an inert environment, while CO₂ and water vapor represent the combustion products of the industrial burners. During the heat treatment process, water vapor content of gas (humidity) facilitates the thermo-hydrolysis of hemicelluloses in wood and prevents the crack formation, which can occur if there is a large humidity gradient between a wood surface and gas. Water vapor also protects wood from oxidation.

During the tests, wood samples were heated using a constant heating rate of 20°C/h up to different maximum treatment temperatures, and then they were cooled down with water spray. At 120°C, the temperature was kept constant for 30 minutes to represent the industrial process. In the industrial process the quantity of wood treated is very large. Even if it is pre-dried, it contains a large quantity of moisture. This moisture is evaporated at the initial stage of the treatment. The heat coming from the gas is mostly spent for evaporation; consequently, the wood temperature stays constant until the moisture is eliminated. In a laboratory system the wood sample and its moisture content are small, and evaporation does not consume all the heat coming from the gas. Therefore, this constant temperature period is not observed. Thus, during experimentation the temperature was kept constant artificially at this temperature to simulate the industrial furnace.

Due to the relatively small dimensions of the specimen, the cooling down rate was relatively high (about 10 °C/minute). The heat-treated samples were used to investigate the effect of maximum heat treatment temperature on the wood surface chemistry and the mechanical properties. In one experiment, the wood sample was kept at the maximum temperature for 45 min before the cooling down period. The prescribed temperature increase was followed with a precision of ±2°C. The thermal treatment parameters used are shown in Table 1. In order to assure the uniform conditions in the experimental system, gas temperature and wood temperatures at the surface and the center of the sample were measured. The experimental set-up is presented more in detail by Poncsak et al. (2006) and by Kocafe et al. (2007).

Table 1. Heat Treatment Parameters Used for Thermo-gravimetric Experiments

	A	B	C	D	E	F	G
Maximum temperature reached (°C)	non treated	120	160	200	220	220	230
Holding time at maximum temperature (min)	0	0	0	0	0	45	0

Mechanical Properties

The mechanical property tests were carried out using an MTS Alliance RT/100 testing machine. The three point static bending tests (MOE, MOR) and the hardness tests

were carried out according to ASTM D143-94 (2004) standards. The details of the tests are given elsewhere (Poncsak et al. 2006; Kocaefe et al. 2007).

Inverse Gas Chromatography (IGC)

Inverse gas chromatography (IGC) technique was used to study the effects of thermal treatment on wood surface chemistry. Theory and applications of IGC have been well established in the literature (Condar and Young 1979; Lloyd et al. 1989). Measurements were carried out using a Varian Gas Chromatograph with inert helium carrier gas and a Thermal Conductivity Detector (TCD). Wood samples were ground using a Wiley mill and they were passed through a 200 mesh sieve. The particles with sizes less than 0.074 μm were used for IGC tests. Approximately 2 grams of wood powder samples were packed into stainless chromatographic columns of 0.25 m length and 0.006 m diameter. Packed columns were preconditioned at 50°C for two hours before the measurements. The probe injector temperature was set at 150°C. Measurements were done at 50°C column temperature.

n-Hexane, n-Octane, and n-Decane were selected as saturated alkane probes in addition to tetrahydrofuran (THF), which was used as electron pair donor probe, and chloroform (CHCl_3), which was used as electron pair acceptor probe. 5 μl of selected probes were injected separately into the flow of carrier gas before the column packed with wood powder and passed through the column. The retention time of standard probes depend on the interactions between the organic probe molecule and stationary phase (wood powder in packed column). The physical properties including dispersive energy component and electron pair donor (DN) and acceptor (AN) numbers of probes are listed in Table 2 (Liu et al. 1998). All tests were repeated three times when reproducibility was good and five times in other cases. Retention volumes of probes were measured and used to determine the thermodynamic values representing the interaction of probe molecules with wood powder surfaces.

Table 2. Properties of Probe Molecules used in the Inverse Gas Chromatography Experiment

Probe	Probe Character	a_p (Å^2)	\square^d (mJ/m^2)	DN (kcal/mol)	AN (arb.unit)
n-Hexane	Neutral	51.5	18.4	0	0
n-Octane	Neutral	63	21.3	0	0
n-Decane	Neutral	75	23.4	0	0
THF	Base	45	22.5	20.1	8.0
CHCl_3	Acid	44	25.9	0	25.1

The specific retention volume per gram of wood sample was calculated from the measured retention time, as follows:

$$V_N = \frac{273.15}{T} \frac{1}{m} jF(t_r - t_i) \quad (1)$$

where T is the column temperature, m is the weight of wood powder packed in the column, j is the correction factor for gas compressibility, F is the helium carrier gas flow rate, and t_r and t_i are the retention time of probe and inert gas, respectively.

According to Schultze and Lavielle (1989), the specific retention volume, V_N is related to the free energy of adsorption (ΔG_A^0) of probe on the wood powder surfaces by:

$$\Delta G_A^0 = RT \ln V_N + c \quad (2)$$

where R is the gas constant, T is the column absolute temperature, and c is a constant. The constant, c , depends on chromatographic column and the reference state chosen.

The interaction between the probe molecule and wood powder surface can be expressed as the sum of dispersive and acid-base terms. The adsorption of n-alkanes is predominantly by the van der Waals dispersive forces. Therefore the dispersive component can be determined by using the relationship given by (Schreiber et al. 1982; Panzer and Schreiber 1992),

$$RT \ln V_N = 2N(\gamma_s^d)^{1/2} a_p (\gamma_L^d)^{1/2} + c \quad (3)$$

where N is the Avagadro number, a_p is the surface area of the probe molecule, γ_s^d is the dispersive components of total surface energy, and γ_L^d is the dispersive component of the surface energy of the probe molecule. The slope of $RT \ln V_N$ versus $2Na_p(\gamma_L^d)^{1/2}$ plot gives $(\gamma_s^d)^{1/2}$. The a_p and γ_L^d values of n-alkanes are given in Table 4.

The acid-base specific interaction potential of wood powder samples can be obtained by measuring V_N values for acidic and basic probes. CHCl_3 and THF were used as acidic and basic probes, respectively. There are several approaches to distinguish the acid-base specific interaction component from dispersive component by employing the retention volumes of polar probe molecules (Schreiber et.al. 1982; Saint-Flour and Papirer 1982; Lavielle et.al. 1991; Panzer and Schreiber 1992). Since the interest of this study is to monitor the relative changes due to heat treatment, the acid-base characteristics of wood samples were calculated by using the method proposed by Schreiber et al. (1982). The acid-base parameter (Ω) is not a thermodynamic value. It is obtained from the following empirical relation:

$$\Omega = \frac{(V_N)_{\text{CHCl}_3}}{(V_N)_{\text{THF}}} \quad (4)$$

Fourier Transform Infrared Spectroscopy (FTIR)

For these tests, KBr powder was mixed with powder of the wood samples using a weight ratio of 100:1. From this mixture, small discs of about 13mm diameter and 1mm thickness were prepared using a Beckman pellet apparatus under high pressure and vacuum. The IR spectra of every sample were analyzed with a Perkin Elmer Spectrum One FTIR spectrometer. Averaged curves from eight repeated scans were obtained between wave-numbers of 4000 and 600 cm^{-1} . This corresponds to the functional group

(4000-1300 cm^{-1}) and the finger print (1300-900 cm^{-1}) regions. Precision of the spectrometer was 4 cm^{-1} .

RESULTS AND DISCUSSION

Heat Treatment

The color characteristics of untreated wood samples depend on the chemical components that interact with light within the wavelength range of 380-780 nm. Typical molecules that have chromophore bindings in wood are lignin, below the wavelength of 500 nm, and phenolic extractives such as tannins, flavonoids, stilbenes, and quinones, above the wavelength of 500 nm (Hon and Minemura 2001). Cellulose and hemicelluloses in untreated wood don't absorb light in the visible region; therefore they don't contribute to color change. However, colored byproducts formed during the degradation of hemicelluloses might have a contribution to this change.

Figure 1 shows how the color changed with maximum thermal treatment temperatures for birch and aspen samples. The color of both species became significantly darker when heat treatment was carried out at temperatures higher than 160°C, compared to the color of untreated species. The color of birch was darker than that of the aspen. Although both white birch and quaking aspen have the same percentage of lignin, the density of the former is much higher. This means that the actual lignin content of birch is higher, which results in darker color in heat-treated white birch compared to heat-treated quaking aspen.

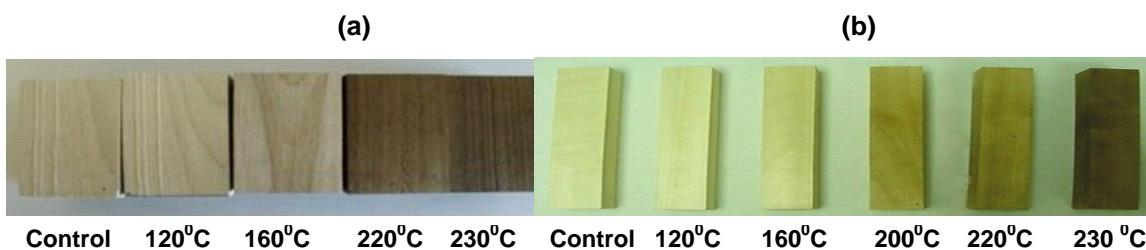


Fig. 1. Color change with maximum heat treatment temperatures for (a) Birch (b) Aspen

Figures 2 (a) and 2(b) show the temperature history of the gas phase (furnace), wood surface, and wood center as a function of dimensionless time, which is the ratio of any given time (t) to the total heat treatment time, excluding the cooling down period (t_{max}). The similar trends were observed for the both species studied. The temperature gradient between the gas phase and wood was very small up to about 100°C. Then, this gradient increased up to certain temperature. In fact, the moisture content of wood retards the increase in wood temperature, since the part of heat coming from the gas is used to evaporate water rather than to heat the wood. This phenomenon increases the difference between the temperature of the samples and the gas during the moisture evaporation period. When the moisture content of wood was removed, the temperature difference began to decrease. For both birch and aspen, the decrease in temperature gradient started around 140°C. At higher temperatures, initiation of the exothermic reactions may also contribute to the decrease of the temperature difference between gas and wood. The

wood temperature exceeded the temperature of the heating gas above 170°C for birch and 180°C for aspen. A steeper slope of the birch curve indicates that its transformation is more exothermic compared to that of aspen.

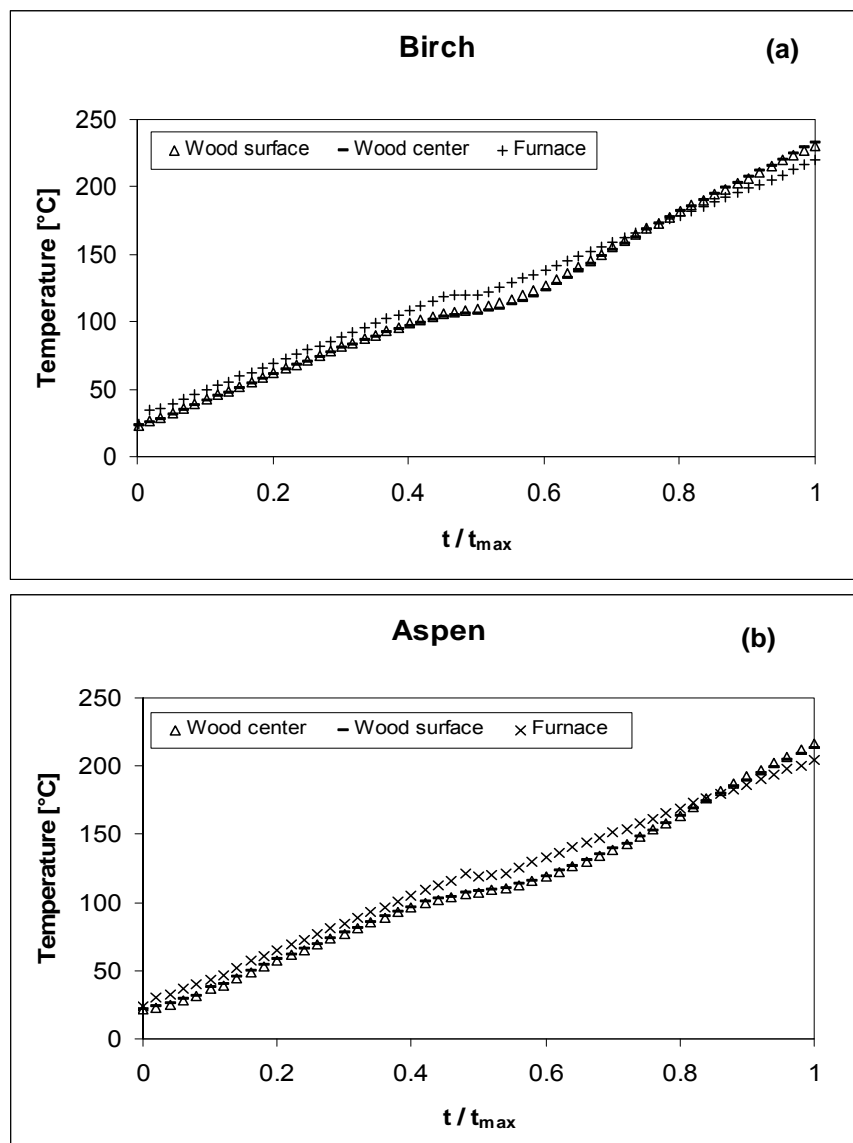


Fig. 2. Temperature history of the furnace (Gas) and the wood sample for (a) Birch (b) Aspen

The initial moisture content of the samples was similar (11.7% for birch and 11.5% for aspen), but the total amount of water in birch was higher due to its higher density. Water content might affect the reaction mechanism. As mentioned in the above paragraph, the initial moisture content of the wood plays an important role during the thermal treatment of wood. Figure 3 shows the evolution of the relative weight loss of wood samples, measured continuously with an analytical balance during the thermo-transformation for both birch and aspen. The relative weight loss is defined as the weight loss measured at any given time divided by the initial sample weight (including

humidity). This facilitates the comparison of the weight loss results obtained using samples with slightly different initial weights. The relative weight loss includes the evaporation of water as well as evaporation of extractives, degradation of wood components especially hemicelluloses and evaporation of degradation products.

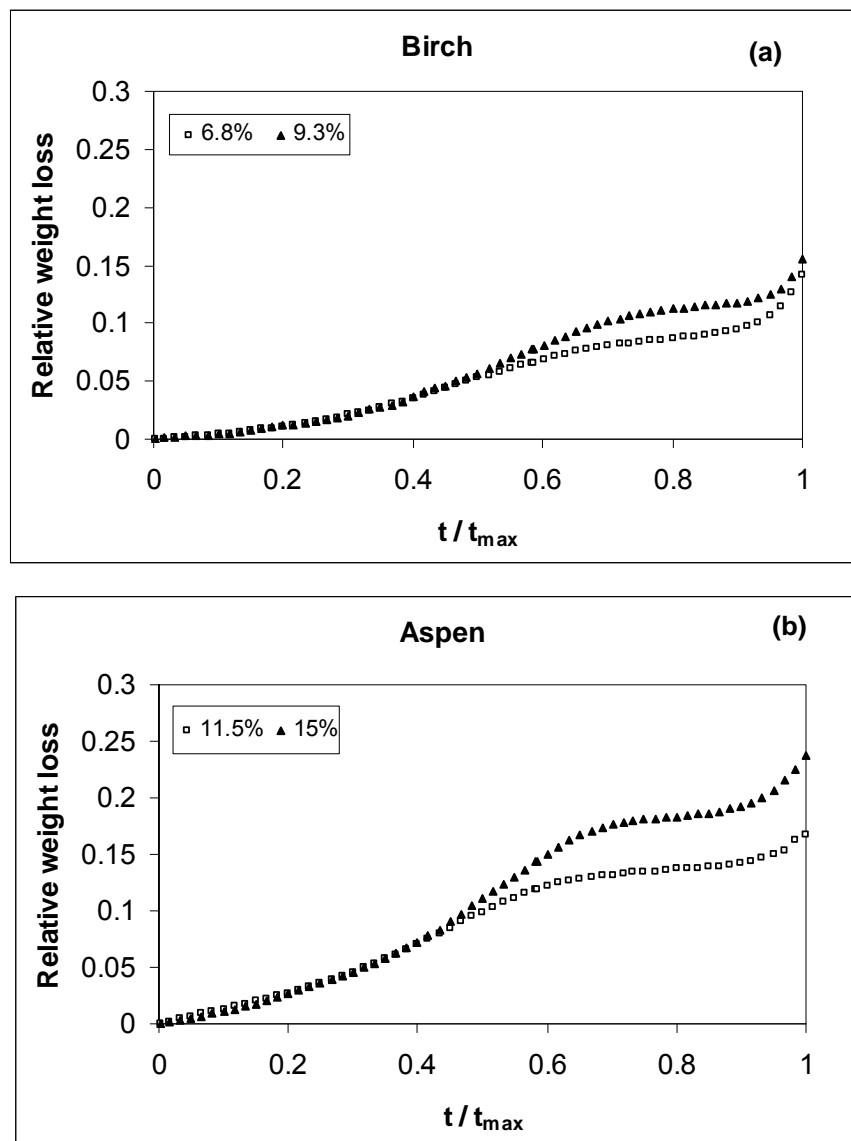


Fig. 3. Effect of initial moisture content of wood on relative weight loss of (a) Birch and (b) Aspen

Increase of the initial wood moisture resulted in a significantly higher weight loss above 100°C*. This is mainly due to increase in mass transfer rate because of larger moisture gradient between wood and gas. In addition, if the initial wood moisture content and the heating rates are high, wood may still have contained moisture when wood transformation reactions begin. Such residual water can promote the degradation of wood by hydrolysis (Fengel and Wegener 1989).

* $t/t_{max} = 0.4$ corresponds to approximately 100°C, see Figure 2

Figure 4 shows the effect of holding time on the relative weight loss of birch. A similar trend was observed for aspen. As it can be seen, the weight loss increased if the wood was kept at the maximum heat treatment temperature for a longer time. This is as expected, since increasing holding time increases the contact time between hot gas and wood at high temperature. Consequently, the thermo-transformation reactions continue to take place during this period.

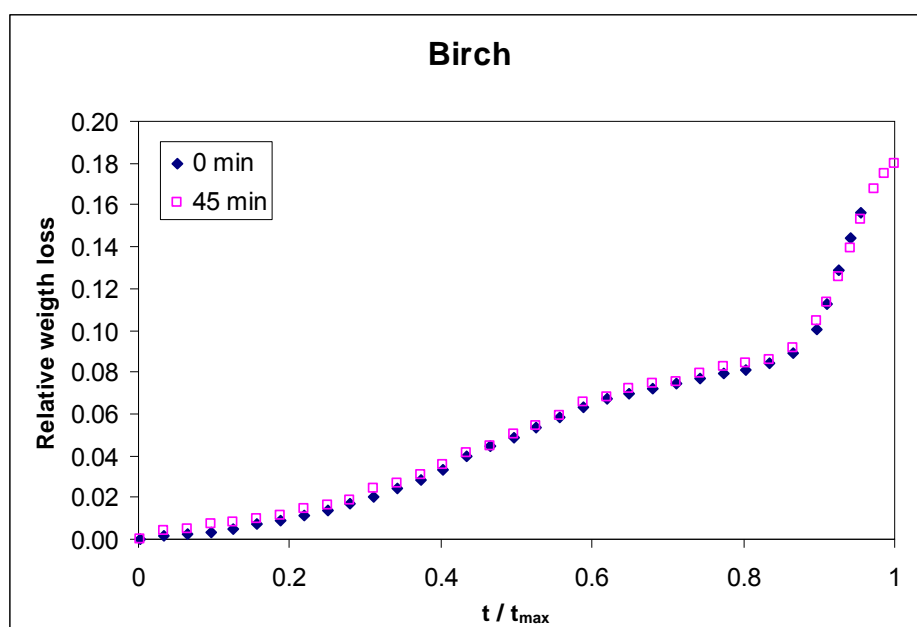


Fig. 4. Effect of holding time on the relative weight loss of birch during heat treatment

IGC Analysis

The dispersive component of surface free energy was determined from the retention volumes of alkane probes and using Equation 3. The acid-base specific interaction component was expressed by using $\Omega_{\text{Acid/Base}}$ parameter, which was defined by Equation 4.

Table 3. Determination of Dispersive Energy, γ^d , Acid/Base Parameters from IGC Data

Sample	γ^d (mJ/m ²)	$\Omega_{\text{Acid/Base}}$
Birch-untreated	40.1	1.0
Birch 120°C	18.9	1.0
Birch 200°C	18.9	4.4
Birch 220°C	5.3	3.5
Aspen-untreated	42.5	1.0
Aspen 220°C	23.2	5.10

Untreated aspen and birch samples had comparable dispersive surface energy. The surfaces of the polymers in those samples were amphoteric with balanced acid-base

characteristics before the heat treatment. These results are in agreement with Papirer et al. (2000) and Felix et al. (1993). The heat-treated samples showed a decrease in dispersive surface energy most likely due to the oxidation of non-polar groups in lignin. At higher temperatures both birch and aspen samples became basic due to oxidation of non-polar components in lignin (see Table 3). A similar tendency was observed by Gérardin et al. (2007) for pine and beech wood.

In addition, a butanol probe was also used to investigate the change in the number of hydroxyl groups accessible to water in the wood. The formation of hydrogen-bonds between the hydroxyl groups increases the retention time of alcohols in wood. Table 4 presents the variation of the retention volume (V_g) of butanol with maximum heat treatment temperature for aspen and birch samples. The retention volume of butanol does not seem to change until 120 °C, but it decreases significantly and gradually at higher temperatures. This tendency indicates a significant decrease in number of hydroxyl groups at higher treatment temperatures.

Table 4. Variation of Retention Volume (V_g) of Butanol in Aspen and Birch Packed Column with the Maximum Heat Treatment Temperature

50 °C	Untreated	120 °C	200 °C	220 °C
Aspen,	398.8	-	-	347.5
Birch	275.5	275.6	215.93	208.15

FTIR Analysis

FTIR spectra of the untreated and heat-treated birch and aspen wood samples were taken between the wavelengths of 4000 and 600 cm^{-1} . Figures 5(a) and 5(b) show the FTIR spectra of these samples.

Since the quantity of the wood meal in KBr pellets was not controlled in high precision during the sample preparation, it was not easy to monitor the effects of heat treatment by comparing directly the spectra of untreated and treated samples. To overcome this problem, the C-H aliphatic stretching peak at 2910 cm^{-1} was chosen as a reference peak. The ratios of other peak areas to C-H aliphatic peak area were used to monitor the changes in the birch and aspen samples (Fig. 6) caused by the thermal treatment. It was assumed that the thermal treatment doesn't cause any change in C-H bonds. This chemical bond – whether it is on cellulose or hemicelluloses – is more stable than C-OH, C-O-C, R-COO-R or Ar-OCH₃ bonds and can be expected to stay almost unchanged. In reality, the number of C-H groups can decrease slightly because of the C-H presence in volatile components. Nevertheless those molecules represent only 4-6% of mass of hardwood. Furthermore, the volatiles, such as hydrocarbons, fatty acids, steroids, lactones, furans, terpenes (Fengel and Wegener 1989, Nishimura et al. 1983) etc., which leave the surface, can be partially replaced by those migrating toward the surface from the inside of the wood sample.

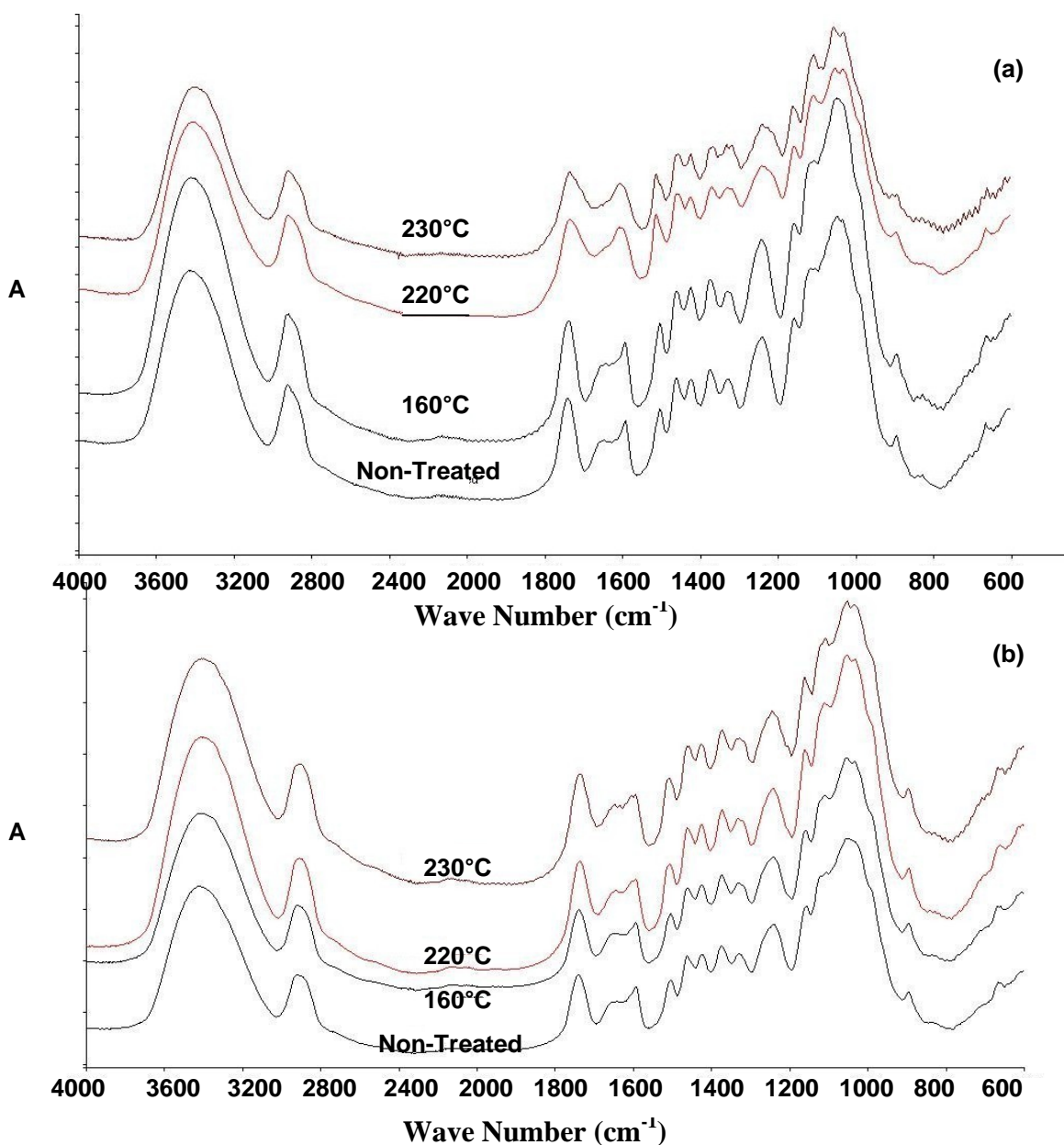


Fig. 5. FTIR Spectra of untreated and heat-treated (a) Birch (b) Aspen wood

First the untreated aspen and birch samples were compared. The adsorption peak at 3405 cm^{-1} is one order of magnitude higher than the other ones; this is the reason why it is shown separately. The only significant difference between the two species is the 60% higher adsorption of the birch sample at 1736 cm^{-1} . This peak corresponds to the C=O stretching in the carboxyl group (Colom et al. 2003; Hakkou et al. 2005) and shows that the hemicelluloses of birch contain more acetyl side groups than those of aspen.

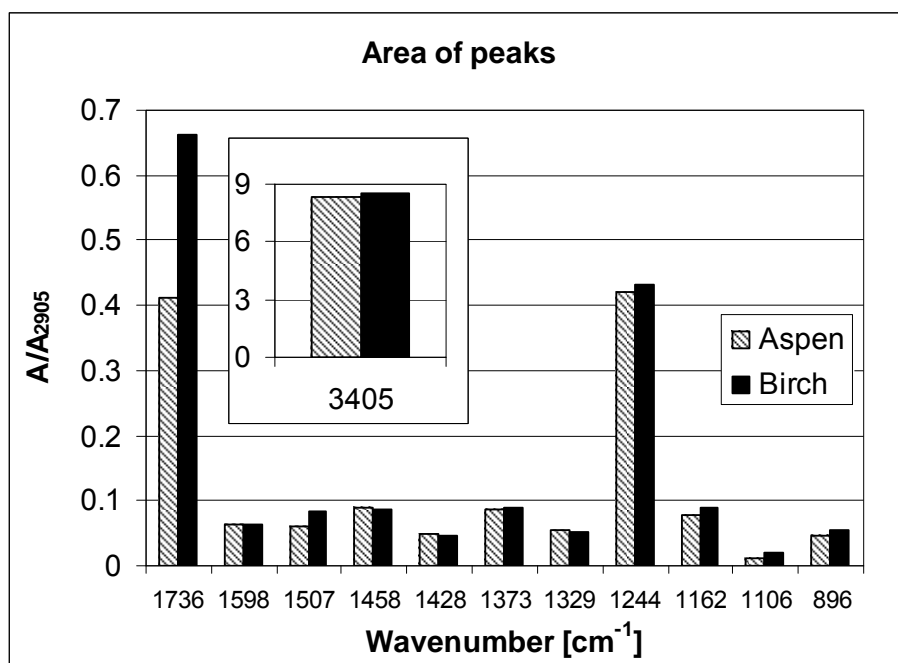


Fig. 6. Adsorption spectra of untreated birch and aspen between 800 and 4000 cm^{-1}

Secondly, the impact of the maximum treatment temperature and the prolongation of the heating at the maximum temperature on IR spectra were studied for both birch and aspen. Only the results for the cases when any significant change in the area of a given peak with maximum treatment temperature could be observed are shown in Table 5 (a) and (b) for birch and aspen, respectively.

Even if the wood samples were pre-dried and didn't contain more than 11% of water before the treatment, surprisingly no significant change with treatment could be observed relative to the peak at 3420cm^{-1} . This peak corresponds to the hydrogen bonded OH group that both water and all the three wood polymer components contain (Feipeng and Rial 1998; Chang and Chang 2000; Muller et al. 2003; Ercin and Yurum 2003; Pandey and Pitman 2003). This observation requires further investigation.

There are three significant changes in peak area of the infrared absorbance spectra that can be identified for both birch and aspen samples. They are situated at 1507, 1244, and 1106 cm^{-1} . Three other differences were found only in birch at 1736, 1373, and 895 cm^{-1} . Both 1507 cm^{-1} and 1106 cm^{-1} peak areas increased with maximum heat treatment temperature. The peak at 1507 cm^{-1} indicates splitting of the aliphatic side chains in lignin and cross-linking formation by condensation reactions of lignin (Colom et al. 2003; Muller et al. 2003; Ercin and Yurum 2003; Pandey and Pitman 2003). New cross-linking in the lignin network (Kollmann and Schneider 1963; Burmester 1975; Boonstra and Tjeerdsma 2006) can decrease the water absorption; consequently, it can reduce the shrinkage and swelling of the wood.

Table 5*. Evolution of the Normalised Area of Adsorption Peaks of Birch and Aspen Samples with Maximum Thermal Treatment Temperature and Holding Time

a) Birch

wave number, cm ⁻¹	25	120	160	200	220	230	220°C 45min
1736	0.772	0.712	0.603	0.594	0.494	0.442	0.459
1507	0.084	0.093	0.116	0.106	0.114	0.145	0.145
1373	0.090	0.083	0.088	0.080	0.082	0.066	0.064
1244	0.437	0.447	0.461	0.429	0.404	0.343	0.303
1106	0.020	0.037	0.061	0.052	0.088	0.182	0.119
895	0.056	0.055	0.057	0.047	0.045	0.039	0.025

b) Aspen

Wave number, cm ⁻¹	25	120	160	200	220	230	220 45min
1507	0.061	0.105	0.087	0.100	0.105	0.110	0.130
1244	0.419	0.438	0.373	0.371	0.324	0.321	0.311
1106	0.012	0.071	0.079	0.091	0.084	0.078	0.080

*The area of the peak of the C-H aliphatic stretching around 2910 cm⁻¹ was used for normalization (A/A_{2910})

The increase of the C-O peak at 1106 cm⁻¹ can be the result of a different reaction taking place in the wood during heat treatment. This might indicate the formation of new alcohols and esters. On the other hand, the formation of an ether linkage from the hydroxyl groups within hemicelluloses and lignin was reported by Colom et al. (2003). This coincides with the clear reduction of the peak at 1373 cm⁻¹ in comparison to the peak at 1320cm⁻¹ in birch. They correspond to the OH plane bending (Colom et al. 2003). The reduction of the number of the free hydroxyl groups, accessible to the water, makes the wood more hydrophobic (Pizzi et al.1994)

Contrary to the above described peaks at 1507 and 1106 cm⁻¹, the C-O carbonyl band at 1244 cm⁻¹ diminished during treatment for both birch and aspen. However, the decrease seemed to be more gradual for aspen while it only took place above 200°C for birch. This peak indicates the cleavage of acetyl groups in the hemicelluloses, which form carbon acids (Gerardin et al. 2007; Boonstra et al. 2007). In the case of the birch, the carbonyl absorption peak at 1736 cm⁻¹ decreased with maximum heat treatment temperature. The change of this peak confirms the cleavage of the acetyl side chains in hemicelluloses. The temporary increase can be related to the formation of degradation

byproducts, such as carboxyl acids, during the treatment (Colom et al. 2003; Chang and Chang 2000). These acids can decrease the degree of polymerization of the hemicelluloses by catalyzing the hydrolysis. Further investigation is necessary in order to explain the reason for the absence of a similar significant change of the C=O peak with maximum heat treatment temperature for aspen. Finally, also only for birch, the asymmetric ring stretching band of cellulose at 895 cm^{-1} (Colom et al. 2003) started to diminish above 200°C . This reduction of the peak can be caused by the thermo-degradation (depolymerization) of the hemicelluloses.

Correlation between the Chemical Structure and the Mechanical Properties

Previously, the impact of heat treatment on mechanical strength of different wood species was studied by other researchers (Kubojima et al. 2000; Bekhta and Niemz 2003; Boonstra et al. 2007). They found that MOR increases slightly in the beginning of the heat treatment at moderate temperature ($100\text{-}200^{\circ}\text{C}$) and then decreases significantly at higher temperature and / or after a longer heating period. Pavlo and Niemz (2003) reported an important decrease of MOR even between $100\text{-}200^{\circ}\text{C}$ for spruce wood, but they did not study higher temperature range. MOE is affected much less by heat treatment compared to MOR. It can decrease or even increase very slightly depending on the treatment conditions. Kubojima et al. (2000) observed a very significant deterioration in air compared to nitrogen gas. Oxidation makes the wood more brittle.

Sundqvist et al. (2006) studied the heat treatment of Swedish birch in a closed reactor. He explained the decrease of the bending strength with the formation of carbonic acids which promote the hydrolysis of carbohydrate polymers (Theander and Nelson 1988). The impact of thermal treatment on mechanical properties of Canadian birch and aspen were studied also by Poncsak et al. (2006) and Kocaefe et al. (2007), respectively. They used a thermogravimetric analyser where inert humid gas was continuously passing through the system. These experiments were conducted in an environment similar to that of an industrial furnace. Contrary to the closed reactor of Sundqvist, the circulating water vapor can remove the acid formed in the wood and thus reduce the accumulation of the acetic and formic acids in the system.

Figure 7 shows the effect of maximum heat treatment temperature on the modulus of elasticity (MOE) and the modulus of rupture (MOR), and Fig. 8 presents its effect on hardness both for aspen and birch. In these figures, the mechanical properties presented at 25°C (room temperature) are those of untreated wood. For birch, the MOE, MOR, and hardness decreased after 200°C . This is in agreement with the dispersive energy results shown in Table 5. This energy decreased sharply after 200°C , indicating a significant change in chemical composition, which affects the mechanical properties. For aspen, MOR decreased after 200°C , similar to the behavior of birch. Pavlo and Niemz (2003) reported an important decrease of MOR even between $100\text{-}200^{\circ}\text{C}$ for spruce wood, but they did not study higher temperature range. However, the MOE of aspen increased with maximum heat treatment temperature. The hardness of aspen is much lower than that of birch. It showed a slight decrease in radial direction, whereas in the tangential direction, the hardness values passed through a maximum around 160°C . These results are also in agreement with the previously reported weight loss results (Poncsak et al. 2006; Kocaefe et al. 2007). They show that the significant weight loss was observed at the same

temperatures where the mechanical properties were affected. The significant increase in hardness of the birch and the slight and temporary increase of the MOR of both species at relatively low temperature range (160-200 °C) is probably related to ramification of the lignin, as mentioned previously (Burmester 1975; Bobleter and Binder 1980; Tjeerdma et al. 1998; Sionene et al. 2002; Weiland and Guyonnet 2003; Nuopponen et al. 2004; Repellin and Guyonnet 2005; Hakkou et al. 2005). The increase in crystallization of cellulose due to the degradation of the amorphous hemicelluloses content (Bhuiyan et al. 2000; Dwianto et al. 1996; Kubojima et al. 2001; Sinoven et al. 2002) can also slightly increase the hardness under 200 °C.

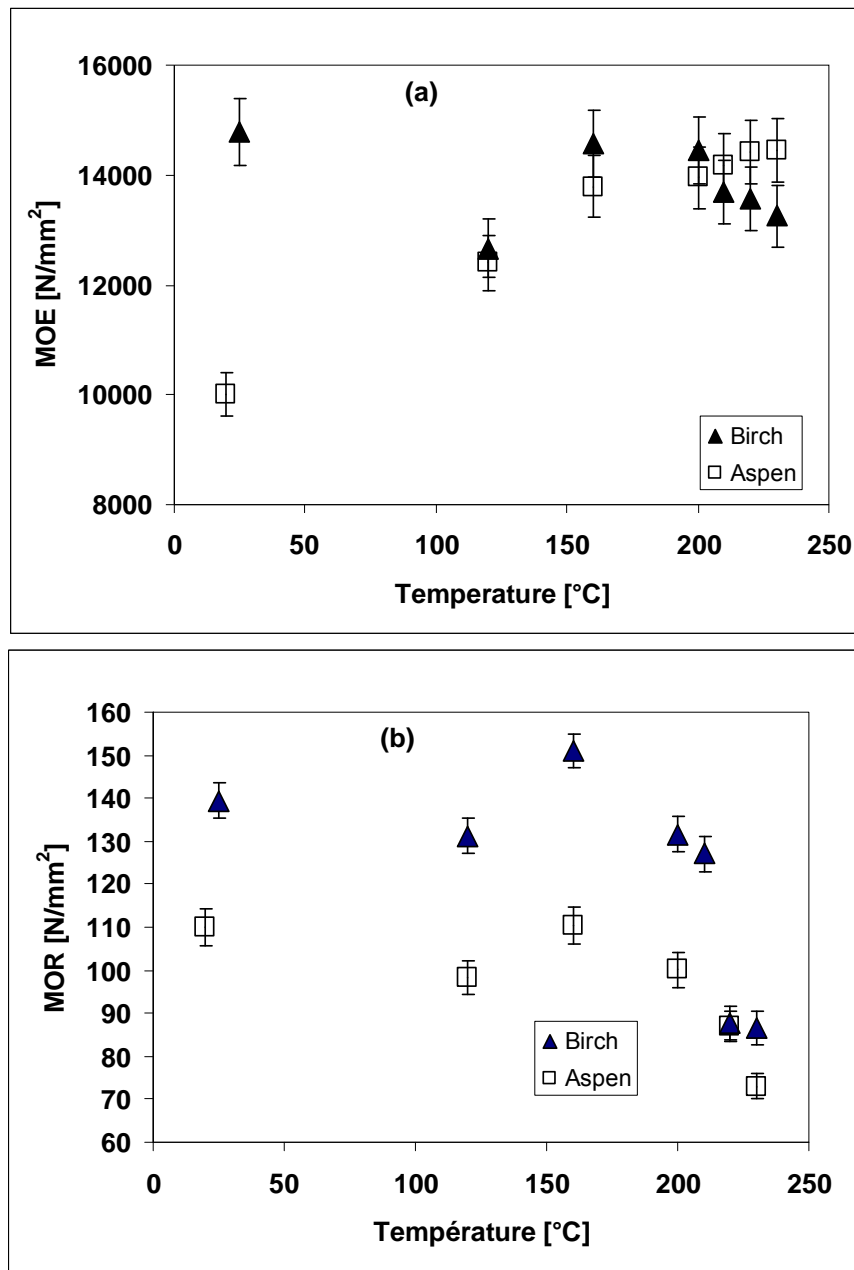


Fig. 7. Effect of heat treatment on MOE and MOR of (a) Birch and (b) Aspen

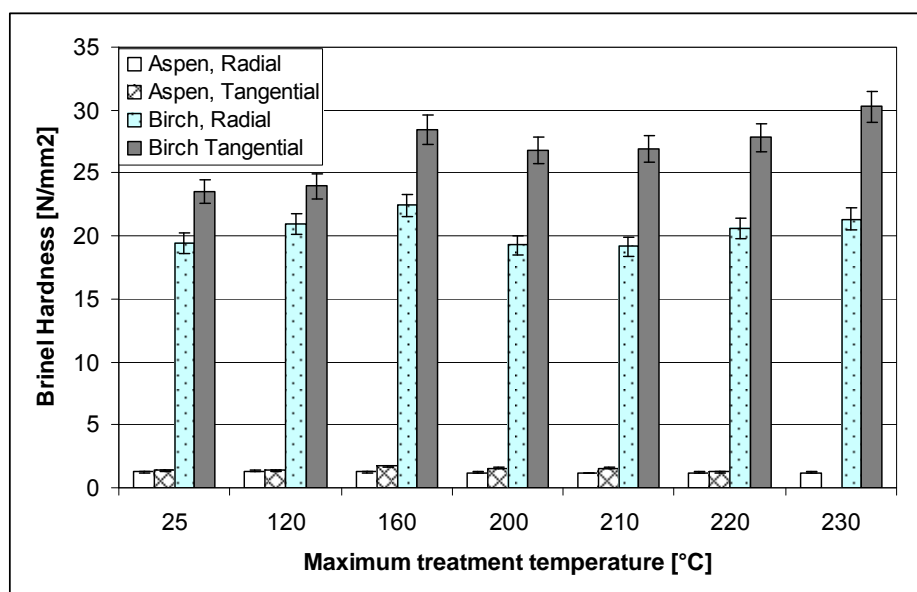


Fig. 8. Effect of Maximum Heat Treatment Temperature on Hardness of Birch and Aspen

The loss of mechanical strength of wood fibers was studied earlier (Spiegelberg 1966), and the decrease of hemicellulose was identified as the main reason for this loss. In brief, cellulose, which is the main component of wood, is formed by a linear, high molecular weight, crystalline homopolymer of β -(1 \rightarrow 4)-D- glucopyranose units. The noncrystalline, heterogenous and low molecular weight polysaccharide hemicellulose coexists with cellulose in the cell wall. Cellulose and hemicellulose are intimately linked among themselves and lignin. Lignin acts as an adhesive, holding microfibrils that are formed by cellulose chains and covered by hemicellulose. Because of the amorphous structure, hydroxyl groups in hemicellulose are much more accessible to water than those of cellulose. This means that hemicellulose is a major contributor to the hygroscopicity of plant fibers (Sørensen 1997). Removal of hemicelluloses decreases hygroscopicity. It also increases the crystalline part in wood material due to relative increase of cellulose component. When the relatively flexible hemicellulose-cellulose-hemicellulose bond is replaced by a more rigid cellulose-cellulose bond, the flexibility of the material decreases. Letourneau (2006) arrived at a similar conclusion for heat-treated jack pine. The decrease of hemicelluloses content was clearly observed for the heat-treated birch and aspen during this study (see FTIR results). It was also observed that the ramification of lignin and crystallization of cellulose also had some effect on the mechanical properties.

As mentioned above, the MOE of birch decreased, whereas the MOE of aspen increased with maximum heat treatment temperature. The cellulose content of aspen is higher than that of birch, as shown in Table 6, which presents the compositional analysis of these wood species compiled by Pettersen (1984). Consequently, birch has more hemicelluloses than aspen, and their lignin contents are comparable. During the heat treatment there is decomposition of hemicelluloses and decomposition of binding between hemicelluloses and lignin. Since hemicelluloses content of birch is higher compared to that of aspen, birch is affected by heat treatment more than aspen is affected.

This can be seen from the FTIR Spectra (see Table 5). Birch has an additional peak corresponding to the hemicelluloses decomposition (1373 cm^{-1}). This might explain the decrease in MOE. On the other hand, for aspen, there is degradation of amorphous cellulose content and increase in relative crystallinity with heat maximum treatment temperature (Bhuiyan et al. 2000; Dwianto et al. 1996; Kubojima et al. 2001; Sinoven et al. 2002) and this might explain the slight increase in MOE. The IR results showed that the birch goes through more significant chemical change than aspen (changes in six IR peaks in aspen compared to in three peaks for birch, see Section 3). Also the IGC results show that the structures of these two hardwood species are different. This also might explain the difference in MOE results between birch and aspen.

Table 6. Chemical Compositions of Wood Species

Wood	Holo cellulose (%)	Alpha Cellulose (%)	Pentosan (%)	Klason Lignin (%)	1% NaOH Extract (%)	EtOH/ C_6H_6 extract (%)	Hot-water extract (%)	Ash (%)
White birch	78	45	23	18	17	3	2	0.3
Quaking aspen	78	49	19	19	18	3	3	0.4

For aspen, the MOR decreased slightly, whereas MOE did not change significantly with increasing holding time. Also increasing holding time increased the tangential hardness slightly for aspen. MOE, MOR and overall hardness decreased with holding time for birch. These results show that the chemical changes continue if the wood samples is held at constant heat treatment temperature.

Previously, the dimensional stability of aspen as well as jack pine were investigated (Shi et al. 2007), and it was found that this property was improved by heat treatment. This is in agreement with the chemical changes observed in this study taking place due to the heat treatment (hydroxyl group transformation at 1106 cm^{-1} , see FTIR results).

CONCLUSIONS

1. The heat treatment of wood is becoming more popular in North America as a wood preservation method. However, this treatment causes chemical changes in wood. Consequently, it affects its properties. In order to optimize characteristics of heat-treated wood, the changes taking place for different species should be carefully studied.
2. During this study, the chemical changes taking place during heat treatment of birch and aspen were studied. It was seen that the chemical structure of birch was affected more compared to that of aspen.

3. The results of IGC study suggest that the surface of the Aspen and Birch particles becomes more basic.
4. It was observed that mostly hemicelluloses degradation and to lesser extent ramification of lignin and crystallization of cellulose affected the mechanical properties.

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