Comparison of weathering behavior of heat-treated jack pine during different artificial weathering conditions

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Abstract: - Heat treatment improves the dimensional stability (reduced hygroscopicity and wettabilty) of wood and its resistance to fungi, and results in darker color. However, wood loses its color when exposed to weathering (sunlight, rain etc.). In this study, the surface degradation and color loss of het-treated wood taking place during weathering were investigated under different conditions. Jack pine (*Pinus banksiana*) samples, heat-treated at 210°C, were exposed to artificial weathering with and without water spray for different times. Before and after exposure, their color and wettability by water were determined. Structural changes and chemical modifications at exposed surfaces were also investigated using florescent microscopy, SEM, FTIR spectroscopy, and XPS. The results revealed that the photo-degradation of lignin play important roles in color change and wetting behavior of heat-treated wood surfaces during weathering. Heat-treated wood was degraded more during weathering if exposed to water spray.

Key-Words: - heat-treated wood, weathering, water spray, SEM, FTIR, XPS

1 Introduction

Heat treatment in the range of 180 and 240°C modifies wood both chemically and physically. Consequently, heat-treated wood possesses new physical properties such as reduced hygroscopicity, improved dimensional stability, better resistance to degradation by insects and micro-organisms, and attractive darker color. Nevertheless, it might lose some of its elasticity. Therefore, the heat treatment requires optimisation of treatment conditions for each wood species. The new versatile and attractive properties make heat-treated wood popular for outdoor applications. However, similar to untreated wood, heat-treated wood is also susceptible to weathering degradation. Among the weathering factors, UV radiation which is a part of solar radiation is known to be mainly responsible for initiating a variety of chemical changes and discoloration of wood surfaces [1, 2]. The chemical and physical changes of heat-treated wood which take place due to artificial weathering in the presence of water which simulates rain were investigated [3-6].

Investigations reported in the literature the effect of artificial weathering on heat-treated wood are very limited, and there is no publication available in literature on the comparison of wettability changes, chemical changes and microscopic changes taking place under different weathering conditions for the heat-treated North American jack pine.

The objective of this work is to understand the effect of weathering on chemical and physical changes taking place on heat-treated jack pine surface. It is important to note that, in the artificial weathering tests without water spray, air had a relative humidity of 50%. The regional jack pine was chosen to investigate the different degradation mechanisms occurring due to weathering with and without water spray where water spray represents the rain. The modifications in microscopic and chemical structures of jack pine surfaces were analyzed using different analysis methods. Color measurement, contact angle test for wettability analysis, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) for chemical analysis, and scanning electron spectroscopy (SEM) for microscopic structural analysis were carried out.

2 Material and methods

2.1 Materials

The jack pine (*Pinus banksiana*), which is commonly used for outdoor applications in North America, was studied. The dimensions of wood boards were approximately 6500 × 200 × 30 mm in the radial, tangential and longitudinal directions, respectively.

2.2 Heat treatment

A new technology of wood treatment is developed which is adaptable to a given load. The furnace capacity and energy efficiency are higher compared to other technologies per unit volume of the chamber (Fig 1).The wood is placed vertically in the furnace which results in uniform flow, consequently, uniform temperature distribution. It consists of different chambers where the gas is conditioned and the wood is treated. In this furnace, propane was used as gaseous fuel and the wood was modified thermally in a non-oxidizing environment composed of hot combustion gases (CO_2 and H_2O). The wood samples were treated at different maximum temperatures, heating rate and holding times. Holding time refers to the period where wood boards are maintained at constant maximum treatment temperature. The conditions of heat treatment used during the optimization of treatment parameters are shown in Table 1.

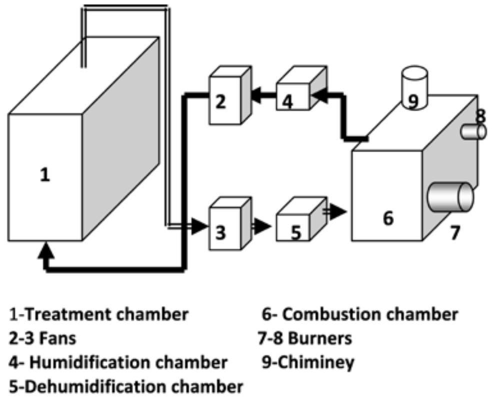

Fig. 1 Wood Heat-Treatment Furnace

Table 1 Conditions of heat treatment

N.	Surface	Temp. (°C)	Heating rate (°C/h)	Holding time (h)	Humidity (g water vapor/m3 dry gas)
1	LT	-	-	-	-
2	LT	190	15	1	100
3	LT	200	15	1	100
4	LT	210	15	1	100

The samples heat-treated at a maximum temperature of 210 °C with a heating rate of 15 °C/h, and held for 1 h at this maximum temperature were chosen for study their weathering behavior. The gas humidity was controlled as 100 g water vapor/m^3 dry gas during all the heat treatment process. Specimens of 70 × 65 mm cross-section on longitudinal tangential (LT) surfaces and 20 mm in length were cut from sapwood of heat-treated wood and then planed to have smooth surfaces. All samples were arbitrarily selected for complete statistical randomization. They were stored in an environment-controlled chamber at 20°C and 40% relative humidity (RH) until they were exposed to the artificial weathering, and the characterization tests were carried out as described below.

2.2 Artificial weathering tests

Artificial weathering tests with and without water spray were conducted using Atlas Material Testing Technology LLC (USA) Ci65/Ci65A Xenon Weather-Ometer. The black panel temperature was set to 63±3˚C and the irradiance level was 0.35W/m^2 at 340 nm. . The relative humidity was set at 50±5% for these tests.

Tests with water spray were performed according to Cycle 1 of Standard ASTM G155: 102 min Xenon light, 18 min light and water spray to simulate rain in natural weathering

2.3 Surface characterization

The surface color of specimens was measured using a reflectance spectrophotometer (Datacolor, CHECK TM). The total color difference (ΔE) was calculated according to the equation given below.

$$\Delta E = \left[(L_t^* - L_0^*)^2 + (a_t^* - a_0^*)^2 + (b_t^* - b_0^*)^2) \right]^{\frac{1}{2}}$$

Transverse sections were examined and photographed with the Nikon eclipse E600 microscope.

The contact angles were determined using a sessile-drop system, First Ten Angstroms FTA200, equipped with CCD camera and image analysis software.

FTIR analysis was carried out using Jasco FT/IR 4200 equipped with a diamond micro-ATR crystal. All relative intensity ratios were normalized relative to the peak of the band at 2900 cm^{-1}.

A Jeol scanning electron microscope (JSM 6480LV) were used to analyze sample surface

The XPS measurements were performed on AXIS Ultra XPS spectrometer (Kratos Analytical) at University of Alberta.

3 Results and discussion

The heat treatment conditions were optimized with respect to the mechanical properties and dimensional stability of jack pine and this work was published elsewhere [7]. Here, the weathering of jack pine which is heat treated at the best conditions identified during the previous study.

Fig.2 compares the color and physical changes occurring on surfaces of heat-treated jack pine during artificial weathering with and without water spray. The visual inspection shows that the color of heat-treated jack pine becomes ligher with increasing weathering time during weathering when there is no water spray. On the other hand, color starts to become lighter at the initial weathering period and then appears darker on the surface of specimens after accelerated weathering exposure of 1008 h with water spray, and then becomes lighter again after 1500 h. These results indicate that the is more significant during weathering with water spray than then that of without water spray for heat-treated jack pine. This phenomenon is probably due to the effect of UV light combined with that of water spray. Color of heat-treated wood becomes lighter due to UV light and then changes back to darker due to the washing action of water spray on the surface layer. After long time of weathering, the colors become similar regardless of presence of water. This means the presence of humidity during artificial weathering without water spray plays a similar role to that of water spray, yielding similar results.

Fig.3 presents color changes of jack pine wood surfaces using the CIE L*a*b* system. Increase in a* and b*values indicates a tendency of wood surface to become redder and yellower while decrease points out to a tendency to become greener and bluer. During early times of weathering with water spray, a* value of wood increases significantly with artificial weathering exposure up to 72 h while those during weathering with water spray decreases significantly on both radial and tangential surfaces (see Fig 3.(a)). Then, the a* values of both heat-treated (radial and tangential surfaces) during two weathering tests decrease rapidly and reach almost the similar end value with weathering time up to 672 h. Subsequently, the a* values of heat-treated jack pine during weathering without water spray continue to decrease at a slower rate up to 1500 h. On the other hand, the values appear to increase to a maximum value at 1008 h and then decrease rapidly after weathering for 1500 h. As shown in Fig.3 (b), the trend observed for the b*value changes of heat-treated wood on both radial and tangential surfaces are similar to those of a*value.

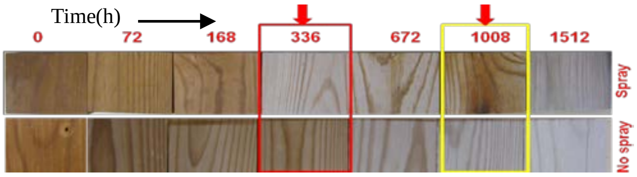

Fig. 2 Jack pine surfaces during artificial weathering

As shown by the changes in L* values, lightening and darkening of wood surface were evaluated. Fig.3 (c) shows L* plotted as a function of the weathering time for heat-treated jack pine. Similar to a*and b*value, L*displays different trends depending on whether the water spray is present or not. However, the trends observed for radial and tangential surfaces are found to be similar similar.

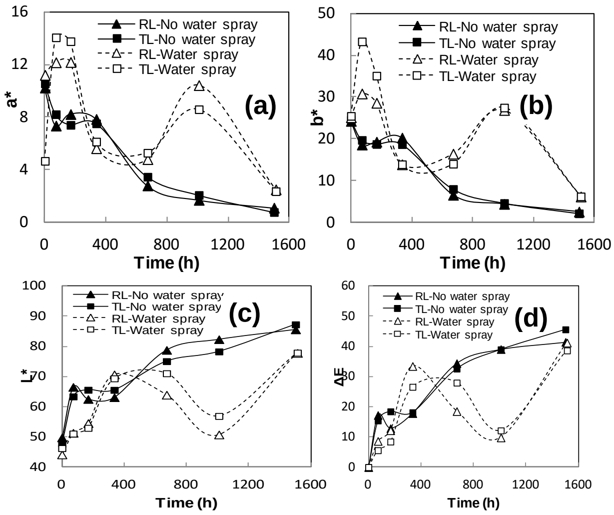

Fig. 3 Color changes of heat-treated jack pine during weathering using CIE-L*a*b* system: (a) red/green coordinate (a*), (b) yellow/blue coordinate (b*), (c) lightness coordinate (L*), (d) total color difference (ΔE)

L* increases at different rates at all times of weathering without water, implying that heat-treated wood surface become lighter as the weathering time increases. Changes in lightness of heat-treated wood with increasing time of artificial weathering are mainly due to the lignin photo-degradation. The lightening of heat-treated wood increases during the earlier weathering stage of 168 h with water spray, later stays more or less stable up to 672 h, and then decreases at 1008 h followed by an increase until the end of the test. This matches with the results obtained by visual observation. It is demonstrated that the darkening of samples during the artificial weathering with water spray is mainly due to the washing out of cellulose layer left on the surface caused by the photo-degradation of lignin. After a weathering of 1500 h, similar to the tendencies observed for redness (a*) and yellowness (b*), the lightness levels during weathering tests are mainly similar regardless of the presence of water spray.

Although the color change (ΔE) trends of samples on radial and tangential surfaces due to weathering have some similar features, samples have a uniquely different color change pattern (in terms of both the rapidness and extent of the weather effects) during artificial weathering depending on whether the water spray is present or not (see Fig3 (d)).

Fig.4 (a) and (b) presents the dynamic contact angle of wood/water system as a function of time for heat-treated jack pine during artificial weathering without and with water spray, respectively. As it can be seen from this figure, weathering both with and without water spray reduced the hydrophobic behavior of heat-treated wood; consequently, all dynamic contact angles of weathered wood were lower than those before weathering (0 h). Contact angles of heat-treated samples after weathering reduced with increasing exposure time to different extents depending on weathering time and weathering condition (presence of water spray). The contact angles after weathering with water spray for 72 h are lower considerably than those during weathering with water spray due to the washing effect of water spray on the degradation products. The contact angles during two tests do not seem to differ significantly after weathering for 1500 h, and water is absorbed by both woods within one second.

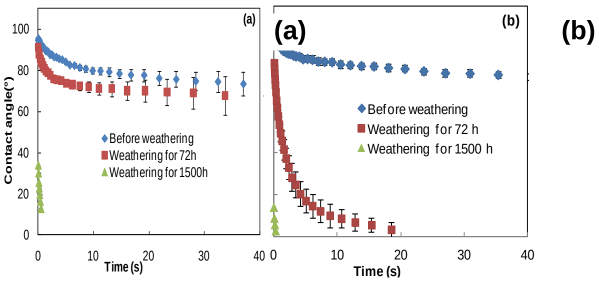

Fig. 4 Wettability of heat-treated jack pine surface during artificial weathering under different condition: (a) without and (b) with water spray

The difference in wood surface structure can cause wettability differences [8, 9]. Fig. 5 shows the fluorescence microscopy images of heat-treated jack pine during artificial weathering without and with water spray for 1500 h, respectively. Delamination and thinning of cells appear after 1500 h of both weathering tests of this study. The degree of damage to wood treated without water spray is less compared to that of weathering with water for the same weathering time. This indicates that water spray intensifies the degradation of heat-treated jack pine wood surface.

SEM micrographs of the heat-treated jack pine revealed the formation of different patterns of cell wall cracks due to artificial weathering under different conditions (see Fig. 6 (a,b)). Both weathering processes changed significantly heat-treated wood structural properties (see arrows in Fig. 6). SEM analysis indicated that the anatomical structure of samples was affected less during weathering if the water spray was not present. There were less checks (Fig.6 (a)) which is in agreement with confirms florescence microscopy results.

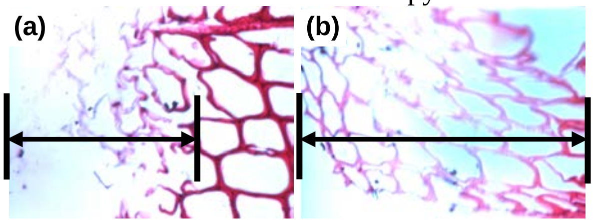

Fig. 5 Fluorescent microscope images (x50) of transverse surface of heat-treated jack pine after weathering for 1500 h: (a) without and (b) with water spray

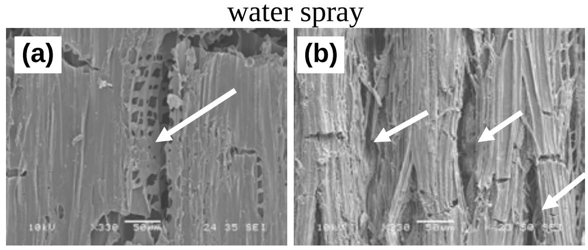

Fig. 6 SEM images of heat-treated jack pine on radial longitudinal surface after weathering for 1500h: (a) without and (b) with water spray

It seems that the binding of cellulose microfibrils by lignin in the various cell wall layers has been degraded by UV light. Consequently, separation between two adjacent cells occurs and cracks form. The water flow into wood cell lumena and diffusion within the cell wall is attributed to the wettability of wood surface by water [10]. Cracks present on heat-treated sample surfaces after weathering (shown in Fig.6) results in easier entrance of water into cell lumena and cell wall, which consequently decreases contact angles and increases wettability (see Fig.4). In addition, water spray in artificial weathering seems to promote the entrance of water into wood, which further accelerates the degradation process.

Weathering induces changes also in chemical properties of a wood surface, which contributes to color change and increase in wettability during weathering[11, 12]. Fig. 7 shows the FTIR spectra within the spectral region of 1800-750 cm^{-1} on heat-treated jack pine before and after artificial weathering for 1500 h with and without water spray. Differences due to weathering can be clearly seen in the infrared spectra in the band shapes.

The spectra in Fig.7 (b-e) show uniquely different trends for heat-treated samples after weathering for different times and conditions, respectively. The degradation of heat-treated wood samples in both weathering tests affected the absorption intensit as the shown in Fig.7. All the characteristic bands of lignin at 1600 cm^{-1}, 1510 cm^{-1},1483 cm^{-1} and 1263 cm^{-1} decreased to different extents as a result of artificial weathering depending on different weathering times and conditions. The peak at 1510 cm^{-1} is mainly the characteristic absorption of C=C in an aromatic ring that originated from lignin in wood. It can be seen that the peak at 1510 cm^{-1} disappeared after weathering for 72 h during both weathering tests. The loss of lignin made the surface more hydrophilic (see Fig.4). New bands at 1730 and 1650 cm^{-1} were detected for heat-treated wood surfaces after weathering with water spray for 72 h (see Fig.7 c). According to Erin et al. [13], this may be due to the formation of unconjugated free carbonyl groups and quinines and quinine methides which were generated and changed as a result of this significant photochemical degradation of lignin caused by weathering. However, these changes depend on different artificial weathering conditions.

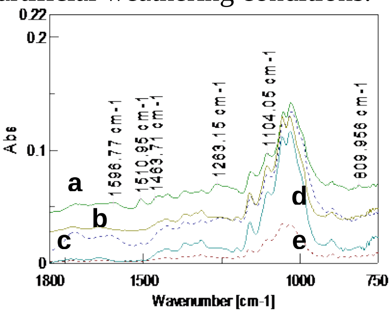

Fig. 7 FTIR spectra of heat-treated jack pine on radial longitudinal surface: (a) before weathering, (b-c) after weathering for 72 h without and with water spray, (d-e) after weathering for1500 h without and with water spray

As Fig. 7 shows, the new bands at 1730 and 1650 cm^{-1} were not detected for heat-treated wood surfaces after weathering without water spray for 72 h and after 1500 h for both weathering with and without water spray. In this study, the natural rain was simulated with water spray during the artificial weathering test, which might leach out the by-products of the degradation of lignin such as quinines and quinine methides after long term weathering. The leaching out of these by-products leaves white cellulose and hemicelluloses layer on wood surface, which is responsible for the lightening of heat-treated wood surface. As the weathering continues, the leaching of these exposes the polymers on wood surface, consequently, the color returns to darker tone (see data at 1008 h in Fig.3). The degradation processes continue repeatedly and sequentially, subsequently, the surface is degraded.

In the XPS analysis, the focus is placed on the high-resolution of C 1s and O/C ratio. The high-resolution of C 1s was fitted with their decomposition into four components. The spectra of C1s of heat-treated sample surfaces before and after weathering (with and without water spray) for 1500 h are shown in Fig.8. The concentrations of contribution at C_1 and C_2 peaks are higher than C_3 and C_4 for all samples, and they are also modified by the weathering process even without water spray. The most important contributions for heat-treated jack pine surfaces before weathering come from the C_1 class which corresponds to C–C and C-H groups present in lignin, hemicelluloses and extractives. However, the contributions from the C_2 class, corresponds to OCH groups of lignin and C–O–C linkages of extractives and polysaccharides of wood [14], become more important for surfaces after weathering(see Fig.8 (b-c)). This indicates the weathering increases the contribution of hemicelluloses and celluloses for heat-treated jack pine. The weathering with water spray affects similarly the changes in component contributions.

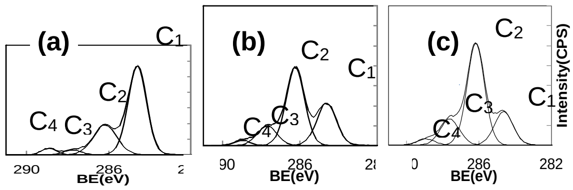

Fig. 8 C1s spectra of heat-treated jack pine (a) before weathering, (b) after weathering for 1500 h without water spray, (c) after weathering for 1500 h with water spray

The variations in peak area contributions of C_1 and C_2 components and O/C ratio as a function of weathering time for both weathering tests are shown in Fig.9. As stated previously, the C_1 is associated with the presence of lignin, and the C_2 mainly originates from cellulose and hemicelluloses on wood surface. The C_1 contribution decreases while the C_2 contribution increases with increasing weathering time during both tests (Fig. 9 (a)). This indicates that the lignin is more sensitive than cellulose to weathering and is degraded more; consequently, the lignin content becomes less important after weathering. The results show that the weathered heat-treated jack pine surface is rich in cellulose and poor in lignin. C_1 and C_2 contributions change less during weathering without water spray compared to that of with water spray, implying that water spray intensifies the influence on the C1s component change of heat-treated wood surface. The changes provoked in wood composition by weathering without water spray are less compared to those induced by weathering with water spray on wood surface. This is confirmed by the changes observed in O/C ratio as shown in Fig. 9 (b).

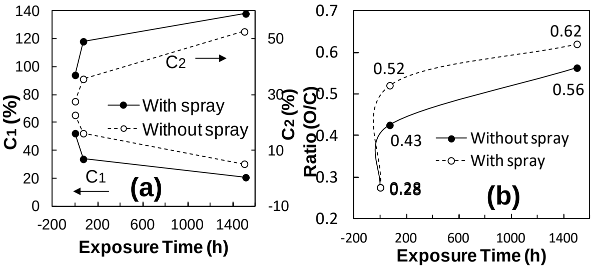

Fig. 9 (a) Effect of weathering on the C_1 and C_2 components; (b) O/C ratio of heat-treated jack pine wood surface during different artificial weathering

4 Conclusions

The developed wood heat treatment technology is used successfully in treating of North American jack pine. Since the darker color gained during this treatment is one of the most important modifications of wood species, the surface degradation and subsequent loss of this color during exposure to light is characterized during this study.

The combined action of sunlight and humidity results in lightening of the surface during the weathering of heat-treated wood surface and leads to the formation of macroscopic and microscopic cracks or checks. As weathering continues, humidity washes out degradation by-products present on the wood surface and the exposed surface goes through further degradation. Thus, a cyclic damage of heat-treated wood surface occurs during the weathering process. Discoloration and checking of heat-treated wood surfaces during different weathering tests differ in intensity. The formation of macro-cracks and micro-cracks during weathering results in easier entrance of water into cell, which consequently increases wood wettability. Lignin is more sensitive to irradiation compared to other wood components; therefore, the heat-treated wood surface becomes richer in cellulose and poorer in lignin after weathering.

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